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Fabrication of Multi-Layered Zn-Fe Alloy Coatings for Better Corrosion Performance

Ramesh S. Bhat

Abstract

Zn-Fe compositionally modulated multilayer alloy (CMMA) coatings were developed onto low carbon steel from acid sulphate bath; and their corrosion resistance was calculated using Tafel polarization and impedance methods. The deposit layers were formed galvanostatically by single bath technique (SBT), using square current pulses. An optimal configuration for the growth of most corrosion resistant Zn-Fe coating was proposed and discussed. At maximum switching cathode current density (SCCD) ($2.0\text{--}5.0\text{ A dm}^{-2}$), the deposit with 300 layers showed ~ 43 times superior corrosion resistance than the same thickness of monolayer coating. The improved corrosion resistance of multilayered coatings is due to small change in iron content, leading to change the phase structure of the alternate-layers of the alloy coatings. The surface morphology and structure of film and roughness of the deposit were assessed using Scanning Electron Microscopy and Atomic Force Microscopy. Thus, superior corrosion resistance of Zn-Fe multilayer coatings was used for industrial applications including defense, machinery and automobile etc.

Keywords: corrosion, electroplating, single bath technique, thickness, additives

1. Introduction

Electroplating, also known as electrodeposition, is the process of creating solid films from dissolved substances by changing their oxidation states with electricity. The electroplating technique is a flexible tool for improving the characteristics of a metal, alloy, or composite on the surface of a substrate. It has a wide range of uses in electronics, protective coatings, and a variety of other sectors of surface engineering. Many books are available that cover a wide range of issues, including surface preparation prior to deposition, atomistic reactions, electrodeposition thermodynamics and kinetics, crystal growth mechanisms, bath chemistry, and so on [1, 2]. Electrochemical polarization techniques and other instrumental approaches were used to investigate the electrodeposition of Zn-Fe alloys from a chloride-based electrolyte [3–6]. Using cyclic voltammeter (CV) and the steady state polarization approach, the behavior of Zn, Fe, and Zn-Fe alloy onto copper from acid chloride solutions containing EDTA and boric acid was examined [7]. The Zn^{+2} ions in the electrolyte prevent Fe from forming, while Fe^{+2} ions stimulate Zn formation. The codeposition of Zn and Fe was discovered to behave peculiarly [8–10]. Yang et al. [11] created a sulphate bath for the preparation of Zn-Fe alloy coatings. As a buffer

and a complexing agent, citric acid and sodium citrate were utilized [12]. The interfacial pH was discovered to control the kinetics of metal deposition.

Materials with ultra-fine microstructures hold promise as new generation materials, and one such group of materials is compositionally modulated multilayer alloy (CMMA) coatings. It is made up of metal or alloy layers that alternate in thickness (a few nanometers). Multilayered deposits may have extraordinary and, unique functional qualities that are not possible to obtain in conventional metallurgical alloys. The corrosion resistance of CMMA coatings will be improved [13–17], such as giant magneto-resistance, increased hardness, wear and corrosion resistance, optical x-ray characteristics etc. The thickness of each layer in a CMMA coating, which should be as thin as feasible, is the most essential condition for displaying these qualities. Periodic modifications in the deposition circumstances can be used to provide a periodic change in the composition/structure of every layer [18]. Dry or wet techniques are used to create multilayered alloy coatings. There are several methods used for the production of CMMA coatings in dry process, including physical vapor deposition, chemical vapor deposition [19], and electrodeposition (wet process) [20]. Single-bath and dual-bath electroplating are the two procedures utilized in the CMMA electroplating process. A single solution comprising all the elements of the metal salts required for deposition in a single bath. Plating current density is varied alternately throughout deposition, with or without variation in mass transfer towards the cathode. In a dual-bath, the substrate is manually or mechanically transported between the two plating solutions, resulting in higher electrolyte consumption as well as the possibility of an oxide layer forming on the cathode surface [19–24].

The current study documents the production of Zn-Fe CMMA coatings on MS employing square pulses from an acidic sulphate bath. The SA was used as a brightener or complexing agent. The corrosion resistance of the coating is compared to that of a single layer coating. The impact of current pulses on coating characteristics and corrosion behavior is examined. The fluctuation of wt. % Fe in the alloy coating is the primary reason for Zn-Fe CMMA coatings with improved corrosion resistance.

2. Experimental method

A flat Mild steel specimen of approximately $3\text{ cm} \times 2\text{ cm} = 6\text{ cm}^2$ area of the substrate was taken as cathode and a zinc plate of the same area as anode. Sand paper of fine grade was used for surface polishing. Then the polished substrate was rinsing with distilled water and finally cleaned with trichloroethylene at room temperature (30°C). The electrolytic bath was formulated using research grade chemicals and distilled water. Electroplating was dependent on pH and time. The pH increases, the formation of metal hydroxide deposited on the substrate resulting increase in thickness and it is mainly depends on the time for deposition. Other factors like temperature, concentrations of electrolyte, applied potential/current are also influence the morphology, electrochemical behavior, thickness and hardness of the coating. The pH of the plating solution was adjusted to 3.0 by adding required quantity of sulfuric acid. The experiments were carried out under room temperature (30°C) and at a manually stirring with time of 10 minutes for deposition. The coated substrates were cleaned with water after electroplating followed by drying. The electroplating bath compositions and functioning parameters for Zn-Fe monolayer and multilayer coatings were optimized with the normal Hull cell system [1]. Sulphanilic acid (SA) is a colorless, water-soluble compound and also complexing agent with metal ions. Citric acid (CA) serves as a buffer to maintain the pH of the bath and sodium acetate is

Bath components	Amount (g/L)
Zinc sulphate	100.0
Ferrous sulphate	20.0
Sulphanilic acid	1.0
Citric acid	4.0
Sodium acetate	50.0
Functional parameters	
Anode	Pure zinc
pH	3.0
Temperature (°C)	30
Current density (A dm ⁻²)	3.0

Table 1.
 Solution compositions and functional parameters.

conducting agent. The solution compositions and functional parameters for the electroplating were given in **Table 1** for achieving smooth deposit on the cathode.

An electroplating cell, of 200 ml capacity was used. The monolayer and multilayer coatings were carried out using DC power analyzer for 10 minutes (comparison purpose). Potentiostat (CH-Instruments) with standard three-electrode arrangement was used to carry out electrochemical studies. The calomel (SCE), platinum and MS were used as reference, auxiliary and working electrodes respectively. The corrosion characteristics of the coatings were conducted, in 3.5% Sodium chloride (NaCl) solution by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. A potential limit of ± 200 mV from open circuit potential (OCP) was used for polarization study, at a scan rate of 1 mV s^{-1} . The frequency range, from 100 KHz to 10 mHz was used for EIS study with perturbing signal of 10 mV. The thickness of the coating was evaluated by faradays law and cross checked using digital thickness tester. Scanning Electron Microscopy (SEM), Model JSM-6380 LA from JEOL, Japan, in the magnification of 1000X was used to observe the surface morphology, cross-sectional view of multilayer formation and to check the layers formed after corrosion test. The hardness of the coating was measured using a micro hardness meter. The composition of metal contents in the coatings was calculated by using colorimetric method [25]. Zn-Fe CMMA coating with alternatively different compositions was defined as: $(\text{Zn-Fe})_{1/2/n}$ (where 1 and 2 signify the two different switched cathode current densities, and 'n' is the

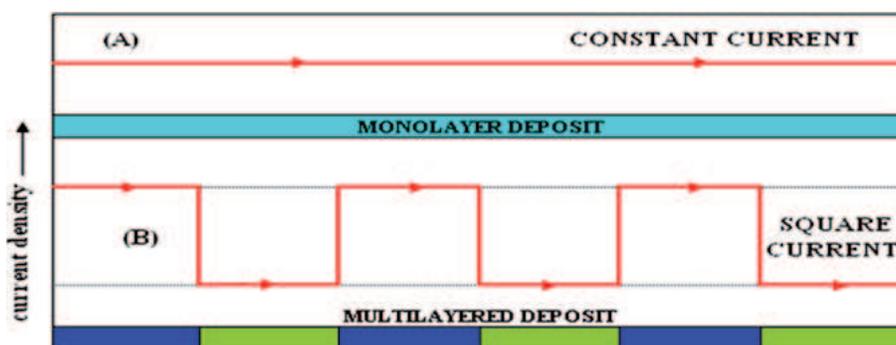


Figure 1.
 Schematic representation of direct current pulses (A), and square current pulses (B), respectively used for production of monolayer and multilayer Zn-Fe coating from the optimal bath.

number of layers formed during the total plating period, i.e. 10 min). The Zn-Fe CMMA depositions were produced and characterized with different configurations. All conditions of coatings were kept constant, except current density. Alternatively, programmed cathode current densities were applied by accurate power source set-up. Monolayer and multilayered composition-graded deposits were produced using DC, and square current pulses, as shown schematically in **Figure 1**.

3. Results and discussion

3.1 Effect of current density

The monolayer Zn-Fe coatings have been developed onto MS using direct current from the optimized bath shown in **Table 1**. In the alloy electroplating, the current density (CD) has significant effect on the coating composition, structure, and properties. The effects of CD on metal content, CCE, hardness, thickness, and corrosion resistance of the coatings were reported in **Table 2**. It was found that the iron content in the deposit have been increased with CD (**Table 2**). It is due to the fact that at high CD, more content of Zn deposited on cathode, as observed in Zn-Fe group metal alloys. However, at low CD, the wt. % Fe in the deposit was increase (**Table 2**), may be due to the tendency of bath to follow the normal co-deposition [1]. It could be due to lower hydrogen liberation, which results in lower alkalization at the cathode film, as explained by the hydroxide suppression process [26]. The cathode current efficiency (CCE) is increased with increase in CD's.

In all CD's of the coatings, the CCE is high (>79). But at higher CD, a small decrease in CCE was observed. This may be due to large evolution of hydrogen (**Table 2**). The hardness of the coatings depends on the applied CD used for deposition. It may be observed that at small CD, less amount iron content in the deposit and showed less hardness. The hardness of the deposit is found to increase with CD, and decreased at higher CD. This may be due to porous metal hydroxide into the crystal structure, caused by much liberation of hydrogen during electroplating. The thickness of the deposit is increased with CD (**Table 2**). It may be due to the adsorbed metal hydroxide, caused by stable increase of pH during plating. The Zn-Fe alloy deposited at the optimal CD (3.0 A dm^{-2}), the deposit shows smooth and uniform coating with lowest corrosion rate compared with other CDs shown in **Table 2**.

3.2 Optimization of CCCD's

The production and characterization of 3D nanostructured crystallites has received the most attention among nanostructure materials, followed by those of

i (A dm^{-2})	pH of bath	Wt. % Fe	CCE (%)	Hardness (VH)	t (μm)	$-E_{\text{corr}}$ (V vs. Calomel)	$\text{CR} \times 10^{-2}$ (mm y^{-1})
1.0	3.0	1.95	79.1	121	9.5	1.013	35.71
2.0		2.37	83.2	138	10.1	1.019	29.09
3.0		3.89	90.8	155	11.3	0.994	20.17
4.0		4.13	87.2	151	12.5	1.015	30.78
5.0		4.95	85.1	147	15.0	1.125	40.29

Table 2. Effect of current density on deposit characters of monolayer Zn-Fe coating, deposited from optimized bath at 30°C .

SCCD's (A dm ⁻²)	-E _{corr} (V vs. Calomel)	i _{corr} (μA cm ⁻²)	CR × 10 ⁻² (mm y ⁻¹)
Multilayered Zn-Fe coatings produced at the difference of 3.0 A dm ⁻² between SCCD's			
(Zn-Fe) _{2,0/5,0/10}	1.182	9.99	15.29
CMMA Zn-Fe coatings produced at the difference of 2.0 A dm ⁻² between CCCD's			
(Zn-Fe) _{3,0/5,0/10}	1.177	12.56	18.37

Table 3.

Corrosion rates of multilayer Zn-Fe coatings developed from the optimized bath at different set of SCCD's with 10 layers each.

2D layered nanostructures. The former will be employed in applications requiring high strength, better formability, and soft magnetic characteristics, while the latter will be used in electrical and corrosion applications [27]. Multilayer deposits were formed using the square current pulse approach, which has been demonstrated to improve corrosion resistance in a variety of metals and alloy systems. As a result, multilayer coatings with alternate layers of alloys of varying compositions have been produced. Using the potentiodynamic polarization approach, the corrosion behavior of monolayer and multilayered Zn-Fe alloy coatings with varying numbers of layers is described, and the associated corrosion results are provided in **Table 3**. **Table 3** shows that the coatings produced at a difference of 2.0 and 5.0 A dm⁻² had the lowest corrosion rate among the various sets tested. These SCCDs were chosen for additional research into the effect of layering, as indicated in the sections below.

3.3 Optimization of number of layers

To achieve a well-defined differentiation between Zn-Fe layers of different composition, Multilayer coating have been produced at 2.0/5.0 A dm⁻² and 3.0/5.0 A dm⁻². The Zn-Fe CMMA coatings having 10, 20, 60, 120, 300 and 600 layers, including 10 layers were developed and their corrosion rates were measured by potentiodynamic polarization method.

Corrosion rates in both sets of SCCDs were shown to decrease as the number of layers increased up to 300 layers, then increase, as shown in **Table 4**. At 2.0/5.0 A dm⁻², the corrosion rate reached saturation (beyond which there was no further decline in corrosion rate with layering) at 300 layers with the lowest corrosion rate (0.41×10⁻² mm y⁻¹), compared to 20.17×10⁻² mm y⁻¹ of monolayer Zn-Fe coatings. Though there is a significant decrease in corrosion rate at 3.0/5.0 A dm⁻², as shown in **Table 4**, the data for 2.0/5.0 A dm⁻² have been considered. However, an attempt to improve corrosion resistance by increasing the number of layers (i.e. 600 layers) in each set of SCCDs resulted in an increase in CR (**Table 4**).

The increased corrosion rate at higher degree of layering (such as 600 layers) is due to a shorter relaxation period for the ion redistribution (Zn⁺² and Fe⁺²) in the diffusion layer [2]. Because the overall time for deposition remains constant, the time for deposition of each layer, such as (Zn-Fe)₁, decreases as the number of layers increases. With a high degree of layering, there is not enough time for metal ions to relax and deposit on the cathode, resulting in composition modulation. As a result, compositional modulation at a high level of layering is unlikely to occur. To put it another way, the CMMA deposit is becoming monolayer. Therefore, (Zn-Fe)_{2,0/5,0/300} has been proposed as the optimal configuration of multilayer coating, with individual layer thickness ~ 50 nm; for peak protection against corrosion.

SCCD's (A dm ⁻²)	No. of layers	-E _{corr} (V vs. Calomel)	i _{corr} (μA cm ⁻²)	CR (×10 ⁻² mm y ⁻¹)
Optimization of layer thickness at SCCD's of 2.0–5.0 A dm ⁻²				
(Zn-Fe) _{2.0/5.0}	10	1.215	10.01	15.89
(Zn-Fe) _{2.0/5.0}	20	1.220	9.56	14.26
(Zn-Fe) _{2.0/5.0}	60	1.233	6.57	8.93
(Zn-Fe) _{2.0/5.0}	120	1.235	3.16	4.34
(Zn-Fe) _{2.0/5.0}	300	1.261	0.39	0.46
(Zn-Fe) _{2.0/5.0}	600	1.247	8.11	11.98
Optimization of layer thickness at SCCD's of 3.0–5.0 A dm ⁻²				
(Zn-Fe) _{3.0/5.0}	10	1.191	9.54	13.18
(Zn-Fe) _{3.0/5.0}	20	1.195	8.30	12.29
(Zn-Fe) _{3.0/5.0}	60	1.215	5.08	7.87
(Zn-Fe) _{3.0/5.0}	120	1.213	3.43	5.10
(Zn-Fe) _{3.0/5.0}	300	1.181	0.67	0.99
(Zn-Fe) _{3.0/5.0}	600	1.217	8.61	12.78

Table 4.

Decrease of corrosion rate with increase in number of layers of Zn-Fe alloy coatings, produced from the optimal bath.

4. Corrosion study

4.1 Potentiodynamic polarization method

The electrochemical corrosion behaviors of monolayer and multilayer Zn-Fe coatings, having different number of layers are characterized using potentiodynamic polarization method, and results are reported in **Table 4**.

A progressive decrease of corrosion current, i_{corr} and hence, the CR was observed up to 300 layers, after which CR started increasing significantly. The potentiodynamic polarization curves with increase in number of layers as shown in **Figure 2**. From the **Table 4**, it is clear that as increase in the corrosion potential, with decrease of corrosion current density, corrosion rate up to 300 layers and the increased the corrosion rate as explained in 3.3.

The resistance, R , is defined by Ohm's equation, $V = IR$, as the ratio of voltage V to current I . Its application is confined to the optimal resistor for a DC system that is frequency agnostic. Real electrochemical systems, on the other hand, exhibit far more complex behavior. They are not simply resistive. The capacitive term is added by the electrochemical double layer. Diffusion, for example, is a time and/or frequency dependent electrode process. As a result, impedance is employed instead of resistance in an actual electrochemical system. The AC response of an electrochemical system, denoted as $Z(\omega)$, is the AC response of the system under investigation to the introduction of an AC signal (e.g., a sinusoidal wave) [28]. On the basis of electrical double layer capacitance, EIS is a useful approach for gaining vital information about the interface (between substrate and medium), which is responsible for better corrosion resistance [29]. Nyquist plots were used to gain information on the interaction of the coating with the corrosive medium. It was observed that in (Zn-Fe)_{2.0/5.0} coatings, the radius of the semi-circle increased with number of layers, up to 300 layers as shown in **Figure 2** indicating that corrosion rates had decreased with layering. Because the same bath chemistry and cell

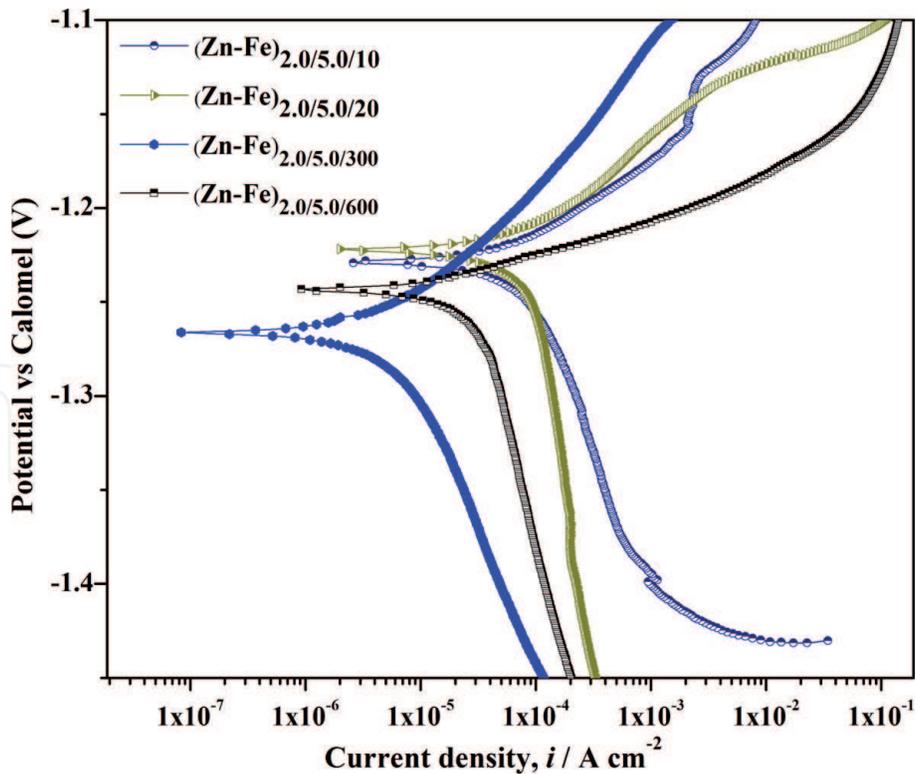


Figure 2.
 Potentiodynamic polarization curves of multilayer $(\text{Zn-Fe})_{2.0/5.0}$ coatings, produced from optimized bath at 30°C with increased number of layers.

configuration were utilized, the solution resistance R_s is essentially comparable in all possible layers. However, as the number of layers increased, polarization resistance, or R_p , increased. The radius of the semi-circle reduced significantly in the case of a deposit with 600 layers (magnified image shown in inset), suggesting poor corrosion resistance as shown in **Figure 3**.

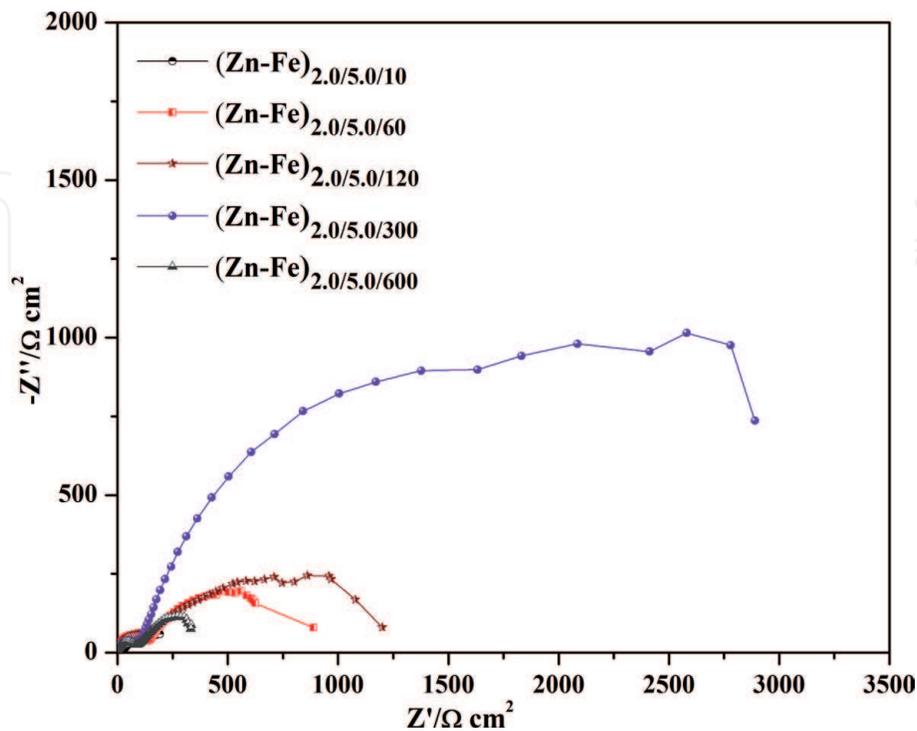


Figure 3.
 Electrochemical impedance response of multilayer $(\text{Zn-Fe})_{2.0/5.0}$ coating produced from optimized bath at 30°C with increased number of layers.

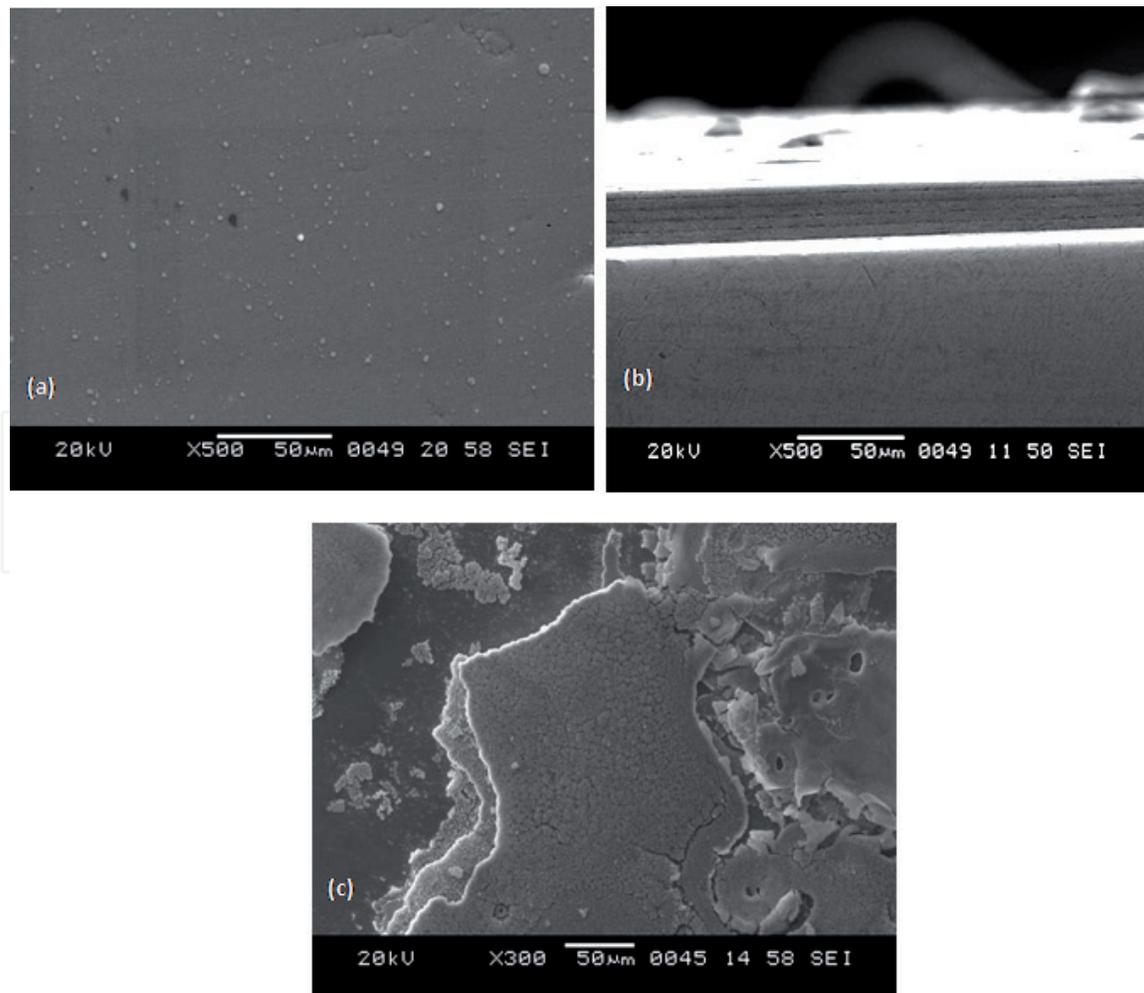
Coating configuration	$-E_{\text{corr}}$ (V vs. Calomel)	i_{corr} ($\mu\text{A cm}^{-2}$)	$\text{CR} \times 10^{-2}$ (mm y^{-1})
$(\text{Zn-Fe})_{3.0/\text{monolayer}}$	0.994	14.71	20.17
Multilayer $(\text{Zn-Fe})_{2.0/5.0/300/\text{square}}$	1.261	0.39	0.46

Table 5.

Comparison of corrosion rates of monolayer and multilayer Zn-Fe alloy coating of same thickness.

4.2 Comparison between monolayer and multilayer Zn-Fe coatings

It may be noticed that i_{corr} value of $(\text{Zn-Fe})_{3.0/\text{monolayer}}$ is much less compared to $(\text{Zn-Fe})_{2.0/5.0/300/\text{square}}$ coatings. The improved corrosion resistance afforded by multilayer coating can be explained in terms of the formation of alternate layers with different phase structures, caused by low and high metal (Fe) content in the deposit. The CR of multilayer $(\text{Zn-Fe})_{2.0/5.0/300}$ coating configuration is found to be ~ 43 times less ($0.46 \times 10^{-2} \text{ mm y}^{-1}$) than compared to monolayer Zn-Fe coating at optimal current density (3.0 A dm^{-2}) ($20.17 \times 10^{-2} \text{ mm y}^{-1}$), obtained from same bath, for same time (10 min). A large change in corrosion rate was observed when coatings was changed from monolayer to multilayer, and is supported by the corrosion data reported in **Table 5**.

**Figure 4.**

The surface morphology of $(\text{Zn-Fe})_{3.0}$ (a), CMMA $(\text{Zn-Fe})_{2.5/10}$ (b) and $(\text{Zn-Fe})_{2.5/10}$ after corrosion test.

5. SEM study

SEM images of Zn-Fe alloy having different coating configurations; deposited using direct and square current pulse is shown in **Figure 4a–c**. The surface topography of monolayer Zn-Fe coating at optimized current density (3.0 A dm^{-2}) as shown in **Figure 4a** displayed a smooth and uniform morphology. **Figure 4b** shows the cross-sectional view of multilayer $(\text{Zn-Fe})_{2.0/5.0/10}$.

The inspection of the microscopic appearance of the surface allows understanding the mechanism of corrosion; with possible reasons for improved corrosion resistance. The high corrosion prevention is due to fact that one layer of alloy having one type of failures (like pores, crevices, due to deposition at one current density) will be covered consecutively by the another layer, having another type of failures (due to deposition at other current density). Thus the coating possesses alternate layers, having different degree of failures, and consequently the corrosion agent's path is longer or blocked. That is why in multilayer coating the corrosive agent needs more time to penetrate through than in case of monolayer coating. As a whole, the protection efficacy of multilayer $(\text{Zn-Fe})_{2.0/5.0/300}$ coatings may be explained by the barrier effect of Zn-Fe layer, with high wt. % Fe and the sacrificial effect of Zn-Fe layer, with less wt. % Fe (**Table 2**) A small change in wt. % noble metal in the alloys layer is good enough to bring large change in the phase structures of the alloys and thereby their properties [23]. The examination of the acid treated surface under SEM confirmed the formation of layers as shown in **Figure 4c**. To understand the reason for the improved corrosion resistance, the multilayer coatings were examined under SEM after corrosion test.

The 2D and 3D surface images of Zn-Fe monolayer and multilayer alloy coated samples, obtained by AFM measurement are shown in **Figure 5a,b**. The mean roughness (R_a) and root mean square roughness Z_{rms} of the coatings are calculated from AFM images. In monolayer coating at optimal current density (3 A dm^{-2}), the deposit was uniform, and has a huge peak with bigger grains shown in **Figure 5a** and the R_a and Z_{rms} values are 56.8 and 69 nm. Where us in

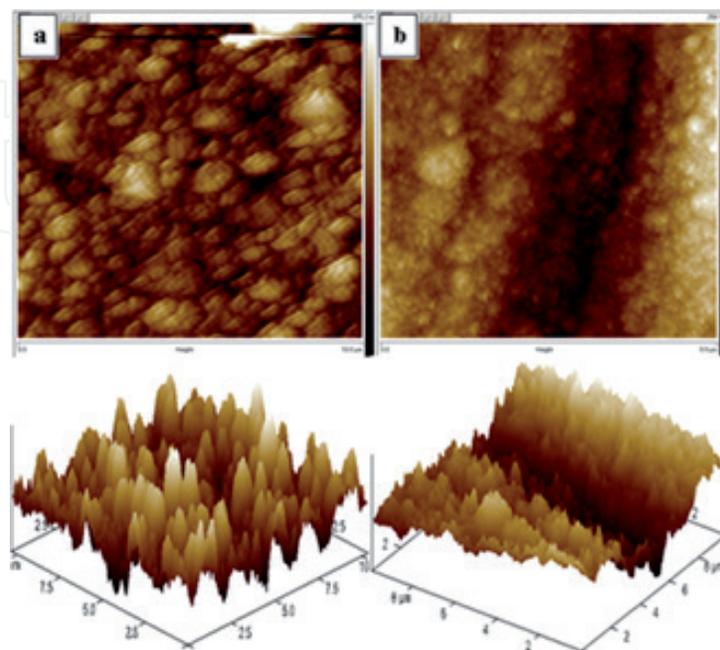


Figure 5. AFM images of Zn-Fe monolayer ($CD, i = 3.0 \text{ A dm}^{-2}$) (a) and multilayer alloy coatings $(\text{Zn-Fe})_{2/5/10}$.

case of multilayer coating at optimal number of layers (Zn-Fe_{3/5/300}), the deposit was uniform in texture, homogeneous, and exhibited small peaks with regular grain size as shown in **Figure 5b**, and R_a and Z_{rms} values are 28.5 and 30 nm and hence multilayer coatings shows better corrosion resistance compared to monolayer coating.

6. Conclusions

The following conclusions were drawn from the above study

- Under optimal condition, multilayered Zn-Fe coatings, developed using square current pulse is about ~ 43 times more corrosion resistance than corresponding monolayer alloy coating.
- The thickness of individual layers play important role in imparting better corrosion resistance. The corrosion rate decreased with number of layers only up to 300 (optimal) layers, and then increased. The increase of corrosion rate at high degree of layering was attributed to less relaxation time for redistribution of metal ions in the diffusion layer.
- The protection efficacy of multilayer coatings is attributed to the difference in phase structure of the alloys in consecutive layers, deposited at various current densities.
- The SEM and AFM study have demonstrated the surface chemistry and topography of alloy coating, with reasons responsible for better corrosion resistance of Zn-Fe alloy coating.
- The corrosion stability of the multilayer coatings is related to the defects and failures occurring in a single layer in the deposition process, can be neutralized or masked, by the sequentially deposited layers. Therefore, the corrosive agent path is extended or blocked.

Acknowledgements

I thankful to the NMAM Institute of Technology, Nitte, Karnataka, India for providing the instrumental facilities.

Conflict of interest

There is no conflict of interest declared by the authors.

Acronyms and abbreviations

CD	current density
AFM	atomic force microscopy
SEM	scanning electron microscopy
SCCD	switched cathode current density
SA	sulfamic acid

CA	citric acid
CMMA	compositional modulated multilayer alloy
CCE	cathode current efficiency
SBT	single bath technique

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References

- [1] Brenner A. *Electrodeposition of Alloys-Principles and Practice*, N.Y. Academic Press. 1963; 1: 2.
- [2] Nasser Kanani. *Electroplating: Basic Principles, Processes and Practice*. Elsevier Ltd, Berlin, Germany, 2006.
- [3] Jensen JD, Gabe DR and Wilcox GD, The practical realization of zinc-iron CMA coatings. *Surf. Coat. Technol.* 1998; 105: 240-250.
- [4] Hegde AC, Venkatakrishna K, Eliaz N, Electrodeposition of Zn-Ni, Zn-Fe and Zn-Ni-Fe alloys. *Surf. Coat. Technol.* 2010; 205: 2031-2041.
- [5] Bhat RS, Bhat KU, and Hegde AC, Optimization of deposition conditions for bright Zn-Fe coatings and its characterization. *Prot. Met. Phys. Chem. Surf.* 2011; 47: 645-653.
- [6] Bhat RS, and Hegde AC, Studies on electrodeposited Zn-Fe alloy coating on mild steel and its characterization. *J. Electrochem. Sci. Eng.* 2019;9: 9-16
- [7] Zhang Z, Leng WH, Shao HB, Zhang JQ, Wang JM, and Cao CN, Study on the behavior of Zn-Fe alloy electroplating. *J. Electroanal. Chem.* 2001; 516: 127-130.
- [8] Lan CJ, Liu WY, Ke ST, and Chin TS, Potassium salt based alkaline bath for deposition of Zn-Fe alloys. *Surf. Coat. Tech.* 2006; 201:3103-3108.
- [9] Narasimhamurthy V, and Sheshadri BS, Electrodeposition of Zn-Fe alloy from an acid sulfate bath containing triethanolamine. *Plat. Surf. Finish.* 1996; 83:75-79.
- [10] Panagopoulos CN, Agathocleous PE, Papachristos VD, and Michaelides A, Sliding wear behavior of zinc-iron alloy electrodeposits. *Surf. Coat. Technol.* 2000; 123:62-71.
- [11] Yang CQ, Long ZL, and Zhou YC, A sulphate bath for the preparation of Zn-Fe alloy coatings. *Trans. IMF.* 2002; 80:161-163.
- [12] Diaz SL, Mattos OR, Barcia OE, and Fabri Miranda FJ, Zn-Fe anomalous electrodeposition stationeries and local pH measurements. *Electrochim. Acta.* 2002; 47:4091-4100.
- [13] Thangaraj V, Eliaz N, and Hegde AC, Corrosion behavior of composition modulated multilayer Zn-Co electrodeposits produced using a single-bath technique. *J. Appl. Electrochem.* 2009;39: 339
- [14] Wilcox GD, and Gabe DR, Electrodeposited zinc alloy coatings. *Corros. Sci.* 1993; 35(5-8):1251-1258.
- [15] Bhat RS, and Hegde AC, Production of layer by layer Zn-Fe compositional multilayer alloy coatings using triangular current pulses for better corrosion, protection, *Transactions of the IMF*, 2015;93(3):157-163
- [16] Rahsepar M, and Bahrololoom ME, Corrosion study of Ni/Zn compositionally modulated multilayer coatings using electrochemical impedance spectroscopy, *Corros. Sci.* 2009; 51: 2537-2543.
- [17] Fei J, Wilcox G, Electrodeposition of zinc-nickel compositionally modulated multilayer coatings and their corrosion Behaviors, *Surf. Coat. Technol.* 2006; 200:3533-3539.
- [18] Nabiyouni G, Schwarzacher W, Rolik Z, Bakonyi I. Giant magneto resistance and magnetic properties of electrodeposited Ni-Co-Cu/Cu multilayers, *J. Magn. Magn. Mater.* 2002; 253:77-85.
- [19] Dobrzanski LA, Lukaszewicz K, Pakula D, and Mikula J, Corrosion

resistance of multilayer and gradient coatings deposited by PVD and CVD techniques. *Arch. Mater. Sci. Eng.* 2007; 28:12-18.

[29] Craig BD, *Fundamental Aspects of Corrosion Films in Corrosion Science*. Plenum Press, New York. 1991.

[20] Leisner P, Nielsen CB, Tang PT, Dorge TC, and Muller P, Methods for electrodeposition composition-modulated alloys, *J. Mater. Process. Technol.* 1996; 58:39-44.

[21] Jensen JD, Gabe DR, and Wilcox GD, The practical realization of zinc-Iron CMA coatings, *Surf. Coat. Technol.* 1998; 105:240-250.

[22] Ivanov I, and Kirilova I, Corrosion resistance of compositionally modulated multilayered Zn-Ni alloys deposited from single bath. *J. Appl. Electrochem.* 2003; 33:239-244.

[23] Prabhu Ganeshan, Swaminatha PK, and Branko NP, Development of compositionally modulated Zn-Ni multilayer deposits as replacement for cadmium. *Surf. Coat. Technol.* 2007; 201:7896-7904.

[24] Bhat RS, KU, and Hegde AC, layered coating of Zn-Co alloys on mild steel using triangular current pulses for better corrosion protection. *T. Indian. I. Metals.* 2013; 66:193-199.

[25] Vogel AI, *Quantitative Inorganic Analysis* (Longmans Green and Co, London), 1951.

[26] Horans J, Effect of plating parameters on electrodeposited NiFe. *J. Electrochem. Soc.* 1981; 128: 45-49.

[27] Gurrappa I, and Leo B, Electrodeposition of Nano-structured coatings and their characterization-a review. *Sci. Technol. Adv. Mater.* 2008;9: 043001

[28] Yuan X, Song C, Wang H, and Zhang J, *Electrochemical Impedance Spectroscopy in PEM Fuel Cells – Fundamentals and Applications*. Springer Publications, London, 2010.