Journal of Metals, Materials and Minerals, Vol.20 No.2 pp.43-51, 2010

Development of Layered Zn-Fe Coatings for Better Corrosion Protection

Ramesh S. BHAT[1], Rajendra UDUPA K[2] and A. Chitharanjan HEGDE[1]

[1] *Electrochemistry Research Laboratory, Department of Chemistry*
[2] *Department of Metallurgical and Materials Engineering*
National Institute of Technology Karnataka, Srinivasnagar- 575 025, India.

Abstract

In this research, the Zn-Fe coating having successive layers of alloys of two different compositions were developed alternatively on mild steel for better corrosion protection. The multilayer coatings, or alternatively, composition modulated alloy (CMA) coatings of different configurations have been developed, and their corrosion behaviors were evaluated by electrochemical DC and AC methods. The cyclic cathode current densities and numbers of layers have been optimised for peak corrosion stability of the coatings. Under optimal condition, the CMA coating having 300 layers, having about 67 nm average thickness was found to be approximately six times higher corrosion resistant than monolayer coating of same thickness. The better corrosion resistance was attributed to the changed dielectric property, consequent to difference in phase structure of alloys in alternate layers, evidenced by dielectric spectroscopy and X-ray diffraction (XRD) study, respectively. Layers formation and corrosion mechanisms were examined using Scanning Electron Microscopy (SEM).

Key words: Layered Zn-Fe coating, Corrosion study, Dielectric spectroscopy, XRD, SEM.

Introduction

Layered, or alternatively, composition modulated alloy (CMA) coatings are those in which alloy composition can be varied either as a step function to produce multilayer coatings of sharp change or gradual change.(1) The term multilayer is taken to mean a sequence of two or more metals/ alloys, alternately deposited one above the other. The number of such layers, which can consist of a metal or an alloy, is in theory unlimited. In multilayer coatings, the deposition process can be modulated (usually by a complex pulse sequence) to create successive layers of alternating composition. Such multilayers exhibit electrical, magnetic, optical, chemical and mechanical properties quite distinct from their parent metals or alloys. They are, in effect, new materials and that they are difficult to form other than by electrodeposition, promise an exciting extension to the range of surface coatings and associated applications made possible by electroplating. Those multilayers can be produced by means of two main techniques, known as the dual bath technique (DBT) and single bath technique (SBT).(2)

Basically the electroplated coatings are metallurgical materials and their properties are closely related to their equilibrium phase diagram and one can explain the microstructure logically using a metallurgical concept.(3) The physical properties, such as the surface morphology, grain size and texture, can also be controlled independently by controlling the deposition conditions. Thus it may be concluded that all the physical properties of electroplated films must originate from their microstructure. If such films are developed in multilayers, the deposited coatings exhibit extraordinary properties, not attainable by any of the metallurgical process.

CMA coating are of commercial interest, because these layered coatings possess improved properties or novel phenomenon such as increased mechanical strength, micro-hardness, giant magneto-resistance and corrosion resistance.(4-9) The attractiveness of electroplating for the synthesis of many advanced materials is linked to the large selection of plating conditions, which allows tailoring of the characteristics of electrodeposited materials, in terms of cathode current/voltage,

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

temperature and agitation. Taking this as tool, recently electrodeposition of CMA coatings of Zn-M (where M = Fe group metal alloys such as Ni, Co, Fe and less commonly Mn) has been tried, and received more attention in surface engineering; because of their enhanced corrosion resistance, increased mechanical strength, micro hardness etc.(10-12)

DBT involves the deposition of constituents from two separate plating baths. In SBT, the metal ions required to form both deposit layers are contained in the single electrolyte and the alloy deposition is made possible, by alternately changing the plating current/potential, possibly in combination with a modulation of the mass transport towards the cathode. Both techniques are known to have their own advantages and disadvantages. In most cases, the drawbacks of the DBT have been deemed to outweigh the benefits, so that the SBT approach is used instead. Kalantary et al.(1998) obtained Zn-Ni CMA coatings with an overall thickness of 8µm by electrodepositing alternate layers of zinc and nickel from the zinc sulphate and nickel sulphate electrolytes. Chawa et al.(1998) reported the corrosion resistance of Zn-Ni CMA coatings from zinc sulphate and nickel sulphamate baths have better corrosion resistance compared to monolayer Zn-Ni coatings of similar thickness.

CMA coatings consist of alternate layers of two or more metals/alloys having different composition and each layer plays its own distinctive role in achieving preferred corrosion performances. Ivanov et al.(2002) studied the corrosion performance of CMA Zn-Ni coatings with total thickness of 12µm obtained by successive deposition of individual metals using DBT. Later, attempts were made for electrodeposition of CMA coatings using SBT i.e. from the bath having ions of both metals.(13-14) Recently, Thangaraj et al.(2008) reported optimization of an acid chloride bath for production of CMA Zn–Co alloy, showing the highest corrosion stability, compared to monolayer alloy of constituting metals.(15) No much work is reported in relation to optimization of deposition conditions and number of layers, for synthesis of multilayer coatings of Zn-Fe alloy for better corrosion resistance. In the present work, a stable Zn-Fe bath using thiamine hydrochloride (THC), as additive has been optimised for development of high corrosion resistant monolayer coatings of Zn-Fe alloy on mild steel (MS), using direct current. The corrosion stability of the coatings were attempted to enhance further by CMA technique using the same bath. The results of investigations are reported, concentrating on its application as protective coatings for MS, for industrial purpose.

Materials and Experimental Procedures

The plating solutions were freshly prepared from distilled water and analytical grade reagents. Electroplating of MS plates was carried out at different current densities using optimal bath, composed of $ZnSO_4.7H_2O$ ($50gL^{-1}$), Fe_2 $(SO_4)_3.H_2O$ ($20gL^{-1}$), CH_3COONa ($60gL^{-1}$), THC, (0.5 gL^{-1}) and CA (4.0 gL^{-1}) at pH 3.0 ± 0.05 and temperature 30 ± 2°C. THC [$C_{12}H_{17}N_4OSCl.HCl$] is a water-soluble B-complex vitamin, freely soluble in water and is reportedly compatible with many metal ions, acting as a primary additive. CA [$C_6H_8O_7.H_2O$] is a colorless crystalline organic compound, used as secondary additive impart brightness to the deposit. The polished MS plates (0.063% C, 0.23% Mn, 0.03% S, 0.011% P, 99.6% Fe) having exposed surface area of 7.5 cm^2 served as a cathode. The anode was pure Zn with the same exposed area. All depositions were carried in a rectangular PVC cell, containing 250 cm^3 electrolytes at constant condition of stirring, without purging any gas in order to maintain a steady-state of mass transport. All coatings, viz. monolayer and CMA were carried out using sophisticated power source (N6705A, Agilent Technologies) for 10 minutes, of about ~20 µm thickness, for comparison purpose. While thicknesses of the coatings were estimated by Faraday's law, it was verified by measurements, using a Digital Thickness Meter (Coatmeasure model M & C). The composition of the coatings was determined colorimetrically using standard analytical method.(16) All electrochemical studies were made using Potentiostat/Galvanostat (VersaSTAT^3, Princeton Applied Research) in a three-electrode configuration cell using $Ag/AgCl/Cl^-_{sat,}$ as reference electrode. The corrosion behaviors of the coatings were evaluated, in 5% NaCl solution by potentiodynamic polarization and Electrochemical Impedance spectroscopy (EIS) method. Polarization study was made in the potential limit of ± 250 mV from open circuit potential (OCP), at scan rate of $1mVs^{-1}$. EIS study was carried out in the frequency range, from 100 KHz to 20 mHz with perturbing signal of 10 mV. Scanning Electron Microscopy (SEM), Model JSM-6380 LA from JEOL, Japan, was used to examine the layers, formed during coating and its deterioration, after corrosion tests. The phase structure of the alloys, corresponding to different current densities were analysed using X-ray Diffractometer (Bruker AXS), using Cu Kα-radiation, ($\lambda = 1.5405$ A^0, 30kV).

Results and Discussion

Development of Monolayer Zn-Fe Coating

To begin with, the bath constituents and operating parameters for deposition of monolithic, or monolayer coatings of Zn-Fe were optimised; using direct current (DC), following the standard Hull cell procedure.(2) The effects of current density (c.d.), on wt% Fe, deposit thickness, corrosion rate of the coatings were reported in Table 1. The coating at 3.0 A dm^{-2}, represented as $(Zn\text{-}Fe)_{3.0,}$ was found to be more corrosion resistant (2.26×10^{-2} mm y^{-1}), than at other current densities. Hence, it has been taken as optimal the c.d. for monolayer deposition, and is represented by notation, $(Zn\text{-}Fe)_{3.0}$.

Table 1. Effect of current density on the deposit characters of monolayer Zn-Fe alloy, developed from optimized bath.

Current density (A dm^{-2})	wt% Fe	thickness (μm)	$-E_{corr}$ V vs.Ag /AgCl/Cl_{sat}	$i_{corr.}$ (μA cm^{-2})	Corrosion rate ($\times 10^{-2}$ mm y^{-1})
1.0	2.12	7.9	1.259	12.26	18.20
2.0	2.71	9.6	1.240	6.063	8.82
3.0	3.62	12.5	1.233	1.556	2.26
4.0	4.93	16.7	1.234	3.972	5.78
5.0	6.86	18.9	1.259	8.023	11.68

CMA Coatings

Development of CMA Zn-Fe Alloy Coating

Generally, the electroplating using the direct current or constant current results in coating of constant composition, called monolayer, or alternatively monolithic coatings. But periodic change in the c.d. allows the growth of layers on substrate, with periodic change in the chemical compositions.(1) i. e. Pulses of low c.d. results in layers of low Fe content, and pulses of high c.d. results in layers of high Fe content. The instrument can be set to cycle between two different cathode current densities, called cyclic cathode current densities (CCCD's) in a repetitive way. While the thickness of the each layer can be controlled by the number of Coulombs passed, and the composition of the alloy in each c.d. (in turn, in each layer) can be determined by standard methods. The total numbers of layers can be fixed appropriately, by adjusting the time for each cycle. Accordingly, in the present study, the multilayered deposition was accomplished electrolytically, from single bath containing Zn^{+2} and Fe^{+2} ions by galvanodynamic cycling of the cathode current between two pre-set values. Such multilayer coatings are hereafter represented as $(Zn\text{-}Fe)_{1/2/n,}$ where (Zn-Fe) represents alloy of Zn and Fe**,** and 1 and 2 represent, respectively the cathode c.d. that is made to cycle, and 'n' represents the total number of layers formed during total deposition time (10 minutes).

Optimization of CCCD's

The electrochemical deposition of CMA coatings with different coating matrices were developed on MS from aqueous solution containing metal ions. As mentioned earlier, even a small change in the concentration of the Zn-Fe alloy may result in significant properties change, due to change in the phase structure of alloys. Initially, multilayer alloy coatings having 10 layers were developed at different sets of CCCD's to increase their corrosion resistance. Among the various sets of cathode current densities tried, the less corrosion rate was measured in the coatings produced at difference of 3.0 and 2.0 A dm^{-2}, i.e. at 2.0-5.0 A dm^{-2} and 3.0-5.0 A dm^{-2} respectively, as shown in Table 2. These coatings were found to be bright and uniform. These combinations of CCCD's have been selected for studying the effect of layering, as described in the following subsection.

Optimization of Overall Number of Layers

The properties of CMA electrodeposits, including their corrosion resistance, may often to be improved by increasing the total number of layers (usually, up to an optimal number), as long as there is no interlayer diffusion. Therefore, at the optimal current density sets, namely, 2.0-5.0 A dm^{-2} and 3.0-5.0 A dm^{-2}), CMA coatings with 10, 20, 60, 120, 300, 400 and 600 layers were produced. As observed in Table 2, the corrosion rate decreased drastically as the number of layers increased, in both set of current densities, up to 300 layers only and then increased. The lowest corrosion rate (0.37×10^{-2} mm y^{-1}) was observed, in case of $(Zn\text{-}Fe)_{3.0/5.0/300.}$ Therefore, $(Zn\text{-}Fe)_{3.0/5.0/300}$ has been proposed as the optimal configuration, and is found to be specific to that bath chemistry, and to that coating conditions like pH and temperature. From the total thickness (about 20μm), the average thickness of each layer in $(Zn–Fe)_{3.0/5.0/300}$ coating can be calculated, the average thickness of each layer is found to be ~ 67 nm.

The increase of corrosion rate at higher degree of layering, like 400 and 600 layers, is attributed to less relaxation time for redistribution of solutes in the diffusion layer, during plating.(11). As the number of layers increased, the time of deposition for each layer, say, $(Zn\text{-}Fe)_1$ is small (as the total time for deposition remains same). At high degree of layering, there is no sufficient time for metal ions to relax (against diffusion under given c.d.) and to get deposit on cathode, with modulation in composition. In other words, the cathode c.d. is cycling so fast that the ions near the cathode can not be redistributed, and bring modulation in composition of alloys. As a result, at high degree of layering modulation in composition is not likely to take place. In other words, CMA deposit is tending to become monolayer.

Corrosion Study

Potentiodynamic Polarization Study

The CMA $(Zn\text{-}Fe)_{2.0/5.0}$ and $(Zn\text{-}Fe)_{3.0/5.0}$ coatings, having different degree of layering were developed, and their corrosion behaviors were studied, and corresponding data is given in Table 2. In both cases, a progressive decrease of corrosion potential, E_{corr} corrosion current density, i_{corr} and hence, corrosion rate may be observed up to 300 layers, and then (i.e. > 300 layers) they increased, as shown in Table 2. The polarization behaviors of CMA coating pertaining to $(Zn\text{–}Fe)_{3.0/5.0,}$ with different number of layers are shown in Figure 1 (only representative curves).

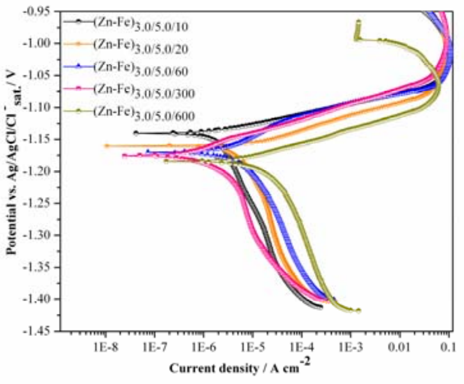

Figure 1. Potentiodynamic polarization curves of CMA $(Zn\text{-}Fe)_{3.0/5.0}$ coatings with different number of layers at scan rate: 1mV s^{-1}.

EIS Study

Electrochemical reactions consist of electron transfer at the electrode surface. These reactions mainly involve electrolyte resistance, adsorption of electro active species, charge transfer at the electrode surface, and mass transfer from the bulk solution to the electrode surface. The better corrosion resistance of CMA coating, in relation to monolithic alloy may reasoned by the electrochemical process taking place at the interface of the substrate. i.e. between MS and corrosion medium. The process taking at the interface may be represented by an electric circuit composed of resistance R, capacitance C , Inductance I and constant phase elements (CPE), combined in parallel or in series. In EIS technique, it is common to plot the data as imaginary impedance versus real impedance with provision to distinguish the polarization resistance contribution, R_p from the solution resistance, R_s. These plots are often called Nyquist diagrams. Accordingly, the Nyquist plots of $(Zn\text{-}Fe)_{3.0/5.0}$ coatings, having different number of layers are shown in Figure 2. Impedance responses indicates that the polarization resistance of the coatings increased progressively with the number of layers up to only 300 layers, and then decreased (i.e.>300 layers).

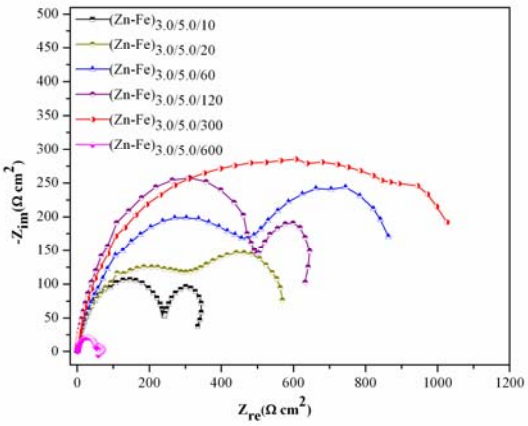

Figure 2. Nyquist plots of CMA $(Zn\text{-}Fe)_{3.0/5.0}$ coatings having different number of layers.

SEM Study

Formation of alternate layers of alloys having distinct properties was confirmed by Scanning Electron Microscopy (SEM) study. Cross sectional view of $(Zn\text{-}Fe)_{3.0/5.0/10}$ is shown in Figure 3(A) and demonstrates the layered structure of the coatings. Inspection of the microscopic appearance of surface, after corrosion tests was used to understand the reason for improved corrosion resistance, shown in Figure 3(B). By subjecting the coating to dissolve by corrosion test, and a region displaying the layers, with distinction was observed. This was accomplished by the anodic polarization up to +250mV vs. OCP in 5% NaCl. The corroded specimens were washed with distilled water, dried and was examined under SEM. Figure 3(B) shows SEM image of the coating, represented by CMA $(Zn\text{-}Fe)_{3.0/5.0/10}$ after corrosion test. The deposit with alternate layers of alloys, were found to be breached to different extent (due to the phase difference) was observed, shown in Figure 3(B).

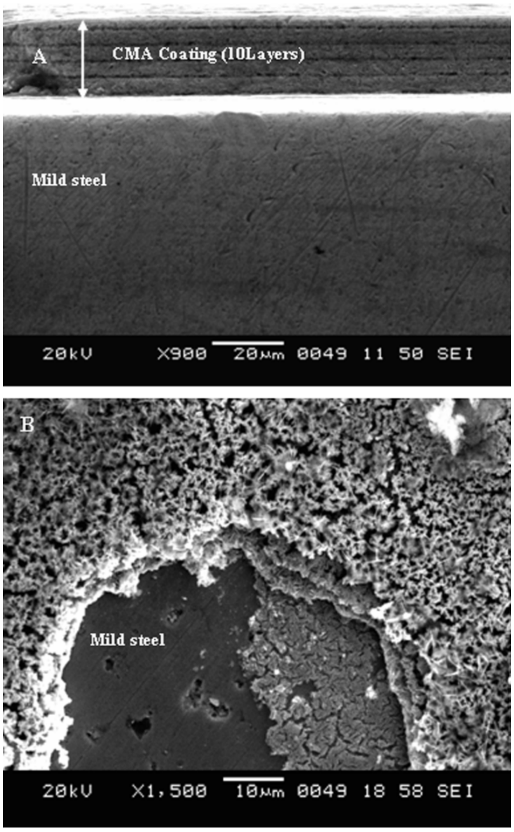

Figure 3. Cross-sectional view of Zn-Fe CMA coating with 10 layers (A), surface morphology of CMA Zn-Fe 10 layers after corrosion test (B).

Hence it may inferred that the improved corrosion resistance afforded by CMA coating is due to formation of alternate layers of alloys with low and high wt% of Fe, in the deposit. In other words, defects and failures, occurring in a single layer in the deposition process are covered by the successively deposited coating layers.(17-18) Hence, the corrosive agent path is extended or blocked. The improved corrosion resistance of CMA Zn-Ni coatings was explained by Prabhu Ganesal et al.(2007) by treating the difference in phase structures of alloys in alternate layers.(19) It was concluded that at higher potentials γ-phase corresponding to (600) planes are preferentially deposited while lower potentials leads to the deposition of other crystal planes of γ-phases (222), (330) and (444). The modulation in composition, due to modulation in deposition condition is an established fact responsible for improved corrosion resistance of many CMA Zn-M alloy depositions, and same explanation of difference in phase structures may be extended for present CMA Zn-Fe alloys, as evidenced by XRD peaks.

X-ray Diffraction (XRD) Analysis

The phases of the electrodeposited Zn-Fe alloy are very complicated depending on the deposition c.d., and consequently, their chemical composition.(20) XRD patterns of the Zn-Fe alloys in Figure 4, shows that the phase structures alloys varies with c.d. employed for their deposition. The XRD peak reveals that Zn-Fe alloys developed at different current densities, having a range of compositions and can exist in different phases. It may be noted that, the relative intensity corresponding to Zn (100), (101), (200) and (103) changes significantly among the deposited coatings, depending on current densities at which they are deposited.(21) Further, it may be observed that Zn-Fe alloy, at 3.0 A dm^{-2} exhibits two major peaks at Zn (100) and (101), and Zn-Fe alloy at 5.0 A dm^{-2} shows only one major peak at Zn (103), as shown in Figure 4. This implies that Zn-Fe alloy layers, deposited at 3.0 and 5.0 A dm^{-2} demonstrates different phases structures, and is responsible for enhanced corrosion resistance of layered coatings.

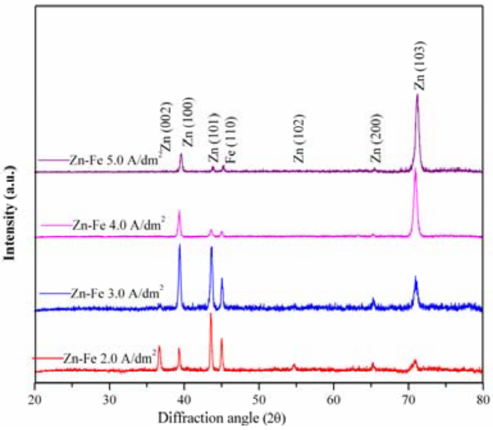

Figure 4. X-ray diffraction patterns of Zn-Fe electrodeposits at different current densities from optimised bath.

Dielectric Spectroscopy

The improved corrosion resistance of CMA coating may be attributed to the increased number of interfaces (between layers of two distinct composition), due to multilayer coating using pulsed current of different densities. This may be demonstrated using EIS data points, in terms of dielectric properties of materials, and the technique is called dielectric spectroscopy.(22) It is based on the interaction of an external field with the electric dipole moment of the sample, often expressed by permittivity. This technique measures the relative dielectric constant, ε_r of a system over a range of frequencies, and the frequency response of the system, including the energy storage and dissipation properties can be identified. The capacitance is inversely proportional to the electric field between the plates, and the presence of the dielectric reduces the effective electric field. The capacitance C may expressed as,

$$C = \frac{k\varepsilon_0 A}{d} = \frac{\varepsilon_r A}{d} \tag{1}$$

Where k is dielectric constant of the medium, ε_0 is permittivity of vacuum, A is surface area of parallel plates and d is the spacing distance. When coating having definite *dielectrics i*s placed between charged plates having electric field E, the polarization of the medium produces an electric field opposing the field of the charges on the plate. The relative dielectric constant is a characteristic of space between plates, and is a way to characterize the reduction of electric field due to polarization, represented as $E_{\text{polarization}}$. Then the effective electric field, $E_{\text{effective}}$ is given by relation,

$$E_{effective} = \mathrm{E} - \mathrm{E}_{polarization} = \frac{\sigma}{k\varepsilon_0} = \frac{\sigma}{\varepsilon_r} \tag{2}$$

Here σ is the surface charge density; or quantity of charge per unit area of capacitor plate (C/m^2). Then decrease of effective electric field between the plates will increase the capacitance of the parallel plate structure. Therefore dielectric must be a good electric insulator to minimize any DC leakage current through a capacitor.(23)

The variation of ε_r vs. frequency (from 100 kHz to 20 mHz) for different coating systems is shown Figure 5. It may be observed that at high frequency limit, ε_r is independent of number of layers. It is due to the fact that, at high frequencies, there is no charging of the capacitor and the capacitance is effectively like that of an open circuit (vacuum). Therefore, ε_r is almost same for all coatings, irrespective of the number of layers. At low frequency side, the frequency response of the capacitor was found to dependent of ε_r, as shown in Figure 5. This is due to the fact that at low frequency; AC becomes equivalent to DC. Hence, the increase of ε_r with number of layers indicates the increased polarizing ability of the corresponding Electrical Double Layer (EDL) capacitor.(24) Therefore less ε_r of CMA (Zn-Fe)$_{3.0/4.5/300}$ compared to other coating systems indicates that coating behaves as good dielectric barrier for passage of current through the capacitor, with less corrosion tendency.

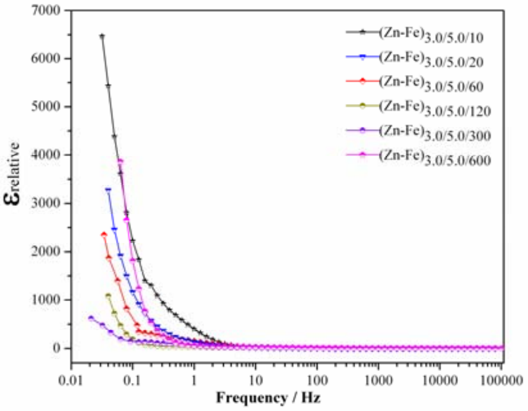

Figure 5. Relative permittivity of CMA (Zn-Fe) $_{3.0/\,5.0}$ coatings with different number of layers as function of frequency.

Comparison between Monolayer and CMA Zn-Fe Coatings

The comparison of corrosion rates of CMA (Zn-Fe)$_{3.0/5.0/300,}$ given in Table 2, and monolayer Zn-Fe alloy at 3.0 A dm^{-2}, shown in Table 1 (both under optimal conditions), it was found that CMA coating is about six times higher corrosion resistant than monolayer alloy, and corresponding polarization behaviors is shown in Figure 6. It may be observed that, a substantial decrease of corrosion current, i_{corr} was observed when the coating pattern was changed from monolayer to multilayer type. The improved corrosion resistance afforded by CMA coating can also explained in terms of the formation of alternate layers of alloys with different phase structures, caused by low (3.62) and high (6.86) wt% of Fe, shown in Table 1. It was found that the CMA (Zn-Fe) coating, having 300 layers, deposited at 3.0 and 5.0 A dm^{-2} found to show the least corrosion rate (0.34×10^{-2} mm y^{-1}) compared to other CMA and monolayer alloy (2.26×10^{-2} mm y^{-1}) of same thickness. The decrease of corrosion rate at higher degree of layering indicates that the protection efficacy of coatings does not bear upon only the composition, but also the thickness of individual layers. A synergism between the phase difference and thickness of individual layers was found to be key point for improved corrosion stability of the layered coatings.

Table 2. Effect of overall number of layering on corrosion properties of Zn-Fe CMA coatings obtained with 2.0-5.0 A cm^{-2} and 3.0-5.0 A cm^{-2} CCCD's.

Cyclic cathode current densities (CCCD's)	Number of layers	Deposition time for each layer /sec	Average thickness of layer(nm)	-E_{corr} V vs. Ag/AgCl /Cl_{sat}	i_{corr} / µA cm^{-2}	Corrosion rate (×10^{-2} mm y^{-1})
(Zn-Fe)$_{2.0/5.0}$	10	60	2000	1.167	4.336	6.36
	20	30	1000	1.186	3.125	4.55
	60	10	334	1.037	0.988	1.44
	120	5	167	1.219	0.672	0.97
	300	2	67	1.228	0.332	0.48
	400	1.5	50	1.224	2.322	3.56
	600	1	33	1.165	3.456	5.07
(Zn-Fe)$_{3.0/5.0}$	10	60	2000	1.160	2.493	3.63
	20	30	1000	1.171	1.339	1.94
	60	10	334	1.184	0.746	1.08
	120	5	167	1.198	0.567	0.83
	300	2	67	1.175	0.256	0.37
	400	1.5	50	1.224	2.322	4.76
	600	1	33	1.184	5.513	8.09

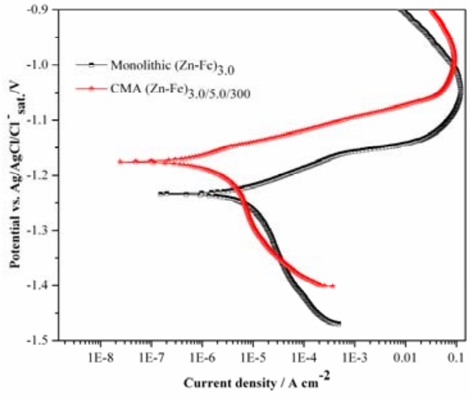

Figure 6. Comparison of polarization behaviors of monolayer and CMA (Zn-Fe)$_{3.0/5.0}$ coatings of same thickness.

The experimental impedance data of monolithic and multilayered Zn-Fe coatings were fitted to an appropriate equivalent circuit using *ZSimpWin 3.21* software, interfaced with potentiostat/ galvanostat. A close agreement was found between measured and calculated values of circuit elements, as shown in Figure 7. It may be observed that monolayer alloy; (Zn-Fe)$_{3.0}$ exhibited two capacitive loops, corresponding to two CPE's, with less R_p, and high C values. The simulated circuit can be represented is as: LR(CR(QR)(LR)(CR)).On the other hand, CMA (Zn-Fe)$_{3.0/5.0/300}$ exhibited the corrosion circuit, consisting of only C and R, represented as: (CR(CR)(CR)(CR)(CR)), without CPE. It implies that increased corrosion resistance of the CMA coatings is due distortion of the capacitance, caused by the electrode surface roughness or distribution/accumulation of charge carriers.

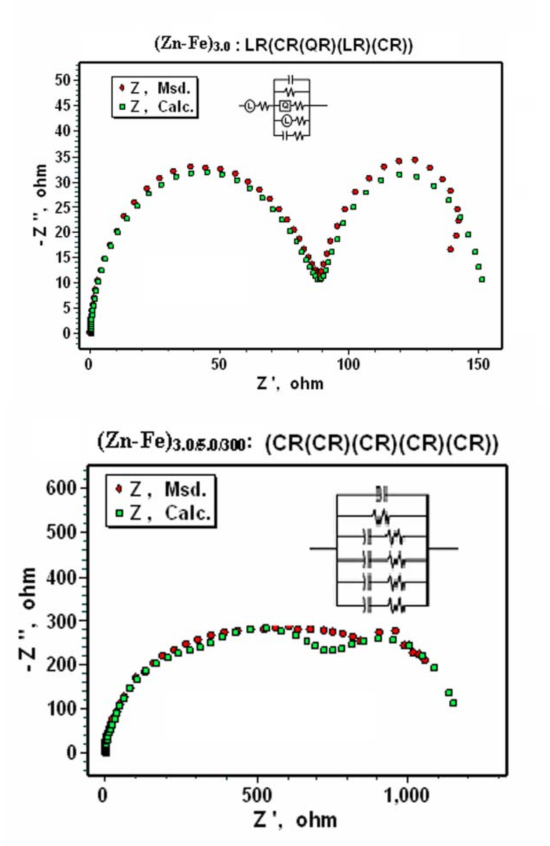

Figure 7. Equivalent circuit fitment for corrosion circuit, corresponding to monolayer and multilayer Zn-Fe coatings, under optimal current densities

Conclusions

The following conclusions were drawn from the present study

1. CMA Zn-Fe coating with successive layers of alloys of two different compositions were developed in layered fashion, from single bath technique on mild steel for better corrosion protection.

2. The CMA (Zn-Fe) coating, having 300 layers, deposited at 3.0 and 5.0 A dm^{-2} found to show the least corrosion rate (0.37×10^{-2} mm y^{-1}) compared to that of monolayer alloy at 3.0 A dm^{-2} (2.26×10^{-2} mm y^{-1}) of same thickness, from same bath.

3. Under optimal condition, the corrosion resistance of CMA Zn-Fe coatings was found to be about six times higher than the corresponding monolayer coating.

4. Corrosion resistance of CMA coating increased with number of layers only up to a certain optimal level (300 layers) and then decreased. Increase of corrosion rate at higher number of layers is attributed to less relaxation time for redistribution of metal ions (Zn^{+2} and Fe^{+2}) at the diffusion layer. In other words, at higher layering, the CMA coating tends to become monolayer.

5. SEM analysis confirmed the formation of multilayer during deposition, and the extended protection of base metal is due to development of layers of alloys, having different degree of pits and pores.

6. The XRD study revealed that the improved corrosion resistance afforded by CMA coating is due to the alternate layers of alloys, having different composition, and consequently different phase structures.

7. The dielectric spectroscopy study revealed that the high corrosion resistance of CMA coatings is due to the barrier effect of alloy layers, having distinct dielectric properties.

8. A synergism between the phase difference and thickness of individual layers was realized, and is key point responsible, for enhanced corrosion stability of layered coatings.

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