

Optimization of deposition conditions for development of high corrosion resistant Zn–Fe multilayer coatings

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ABSTRACT

Composition modulated multilayer alloy (CMMA) coating of Zn–Fe was developed galvanostatically on mild steel through single bath technique (SBT), using thiamine hydrochloride as additive. Electrodeposits with different coating matrices were developed, using square current pulses. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods were used to assess the corrosion performance of the coatings. The cyclic cathode current densities (CCCDs) and number of layers were optimized, for highest corrosion resistance. Experimental results showed that CMMA Zn–Fe coating, developed at 2.0–4.0 A/dm², having 300 layers is ~30 times higher corrosion resistant than corresponding monolithic alloy of same thickness. The corrosion resistance increased with number of layers up to a certain number of layers; and then decreased. The better corrosion resistance was attributed to the dielectric barrier at the interface, evidenced by dielectric spectroscopy. The formation of multilayer and corrosion mechanism was analyzed using scanning electron microscopy (SEM).

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1. Introduction

Corrosion is a destructive phenomenon which affects almost all metals and alloys. Iron is most widely used metal for many industrial applications, on which serious corrosion problems were encountered. Electroplating is one of the cheapest approaches to combat it. In this regard, the development of Zn–M (where M = Ni, Co, Fe and less commonly Mn) alloy coatings is the most volume consuming, due to its commercial interest (Short et al., 1984; Roventi and Fratesi, 2000; Fei and Wilcox, 2005; Heydarzadeh Sohi and Jalali, 2003; Panagopoulos et al., 2005). Amongst them, Zn–Ni alloy has been studied extensively and put into practical use in the mass production of steel sheets for automobile bodies, and also for small components such as nuts and bolts (Wilcox and Gabe, 1993; Roventi and Fratesi, 2000).

Despite the fact that the development of Zn–Ni alloy coatings has produced a larger improvement in the corrosion resistance than pure zinc coatings, further development for getting even better protective properties is of distinct commercial interest (Fei et al., 2006). Possibly, a relatively new electrodeposition coating technique called, composition modulated multilayer alloy (CMMA) coating is a possible route to enhance the efficacy of simple monolithic Zn–Ni alloy coatings (Gabe, 1994). CMMA coatings consist of a large number of thin alternate layers of metals/alloys, and each

layer plays its own distinctive role in achieving preferred performances. Further, these multilayer coatings have attracted attention in the field of engineering, because such structures have a considerable number of practical applications, and fundamental interesting properties (Leisner et al., 1996; Strafford and Subramanian, 1995; Garcia et al., 2003).

There are different approaches for producing CMMA coatings, viz. physical vapor deposition (PVD), chemical vapor deposition (CVD) methods (Dobrzanski et al., 2007), and electrodeposition method. Electrolytically such alloys can be obtained, by either a single bath technique (SBT), where deposition takes place in a plating solution, containing ions of the alloy components or a double-bath technique (DBT), where deposition is carried out from separate plating baths by manual/automated transfer of the substrate from one bath to another. Recently, electrolytic methods have been employed for fabricating multilayers, because of its low cost and ease of operation. A large number of researchers have investigated the development and characterization of binary multilayer system. Kalantary et al. (1998) obtained Zn–Ni CMMA coatings with an average thickness of 8 μm by electrodepositing alternate layers of zinc and nickel from zinc sulphate electrolyte and nickel sulphate electrolyte. Chawa et al. (1998) reported the corrosion resistance of Zn–Ni CMMA coatings, deposited from zinc sulphate and nickel sulfamate baths, and was found to be better than zinc or nickel monolithic coatings, of similar thickness. Electrodeposited Zn–Fe alloys have found considerable use as sacrificial coatings for ferrous metal surfaces. To this end, Liao et al. (1998a, 1998b, 1998c) applied both SBT and DBT for deposition of Zn/Zn–Fe and Zn–Fe coatings.

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Kirilova and Ivanov (1998) obtained CMA coatings of Zn–Co by means of both the SBT and the DBT. The coatings obtained from a single bath dissolved at more positive potentials, as compared with pure Zn coatings, but much more negative than the dissolution potentials of pure Co coatings. As the number of layers was increased, regardless of their thickness and sequence, the dissolution potentials were shifted in the positive direction. The corrosion potentials of the CMMA coatings deposited from a single bath were significantly more positive than those deposited from a dual bath. Further, Kirilova and Ivanov (1999) studied the corrosion behavior of Zn–Co CMMA coatings, using corrosion potential measurement and the neutral salt spray (NSS) method. The best corrosion resistance was found for multilayer consisting of four layers, each $3.0\ \mu\text{m}$ thick, deposited both from a dual bath and from a single bath. No red rust appeared on the surface of CMMA with an outer layer of Zn, Co or Zn–1% Co, even after 1584 h in a salt spray corrosion test.

The experimental results, pertaining to corrosion behavior of CMMA coatings, reported by above workers are based on either anodic dissolution potentials or E_{corr} values without determining corrosion rates. In this direction, Thangaraj et al. (2008) have recently studied the corrosion behavior CMMA Zn–Fe alloy through SBT, using glycine as additive. The corrosion rates were calculated from Tafel's extrapolation method, supported by EIS study. It was reported that CMMA Zn–Fe coating, with 600 layers is ~ 45 times better corrosion resistant than corresponding monolithic alloy of same thickness. The present work is concerned with development and optimization of Zn–Fe alloy bath, using thiamine hydrochloride (THC) as additive. The coating configuration has been optimized for highest corrosion resistance. The corrosion performance of monolayer and multilayer coatings developed using, respectively; direct current (DC) and square current pulses, from same bath for same time was compared and discussed. The methods employed for optimization, and effect of layer thickness (or number of layers) on deposit characters were discussed. Factors responsible for increased corrosion rates at higher layer thickness were analyzed, and results were discussed.

2. Experimental

The plating solutions were freshly prepared from distilled water using analytical grade reagents. Electroplating was carried out on mild steel plates, at pH, 3.5 ± 0.05 and temperature, $30 \pm 2\ ^\circ\text{C}$. The polished mild steel plates (0.063% C, 0.23% Mn, 0.03% S, 0.011% P, 99.6% Fe) with an exposed surface area of $7.5\ \text{cm}^2$ served as a cathode. The anode was pure Zn with the same exposed area. A rectangular PVC cell containing $250\ \text{cm}^3$ electrolyte was used. Depositions were carried out at constant condition of stirring without purging, to maintain a steady-state of mass transport.

All coatings, viz. monolithic and CMMA were accomplished using DC power analyzer, having output speeds of up to 160 microseconds per step voltage/current change (N6705A, Agilent Technologies) for 10 min ($\sim 15\ \mu\text{m}$ thickness), for comparison purpose. While the thickness of the coating was 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 method (Vogel, 1951). The hardness of the deposited alloys was measured using a computer-controlled micro-hardness tester (CLEMEX, Model: MMT-X7). All electrochemical studies were made using Potentiostat/Galvanostat (VersaSTAT³, Princeton Applied Research) in a three-electrode configuration cell using Ag/AgCl/KCl_{sat} as reference electrode. The 5% NaCl solution was used as corrosion medium. Potentiodynamic polarization study was carried out in a potential ramp of $\pm 250\ \text{mV}$ around open circuit potential (OCP), at scan rate of $1\ \text{mV s}^{-1}$. EIS study was made using AC signal of $10\ \text{mV}$, at

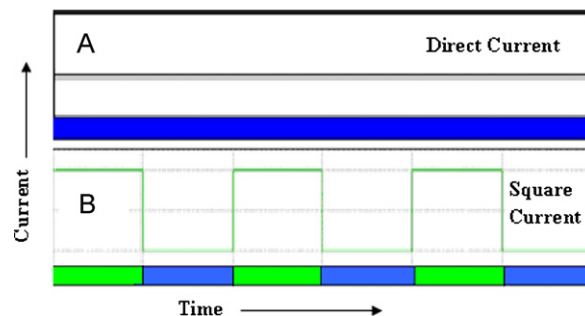


Fig. 1. Schematic representation of resulting monolayer and multilayer Zn–Fe alloy due to direct current (A) and square current pulses (B), respectively.

frequency range, from 100 kHz to 10 mHz. The formation of multilayers and corrosion mechanism were examined using scanning electron microscopy (SEM, Model JSM-6380 LA from JEOL, Japan).

3. Results and discussion

3.1. Development of monolithic Zn–Fe alloy coating

The optimization of a stable zinc chloride bath was carried out by standard Hull cell method (Nasser Kanani, 2006). Deposition was carried out at different current densities using electrolytic bath (optimized) consisting of 10 g/L ZnO, 10 g/L $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 200 g/L NH_4Cl , 20 g/L boric acid, 10 g/L citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) and 3 g/L THC ($\text{C}_{12}\text{H}_{17}\text{N}_4\text{OSCl} \cdot \text{HCl}$). The effects of current density (c.d.) on wt.% Fe, deposit thickness, Vickers hardness, corrosion rate and appearance of the coatings are reported in Table 1.

The Zn–Fe alloy deposited at $3.0\ \text{A/dm}^2$, represented as $(\text{Zn–Fe})_{3.0}$, was found to be more corrosion resistant ($25.08 \times 10^{-2}\ \text{mm y}^{-1}$), compared to all at other current densities, as shown in Table 1. Hence $3.0\ \text{A/dm}^2$ has been taken as optimal c.d. for monolithic Zn–Fe alloy deposition. Further, it was observed that, both thickness and hardness of the deposit increased with c.d., due to significant effect of cathodic current density on physico-mechanical properties of the coatings. High wt.% Fe observed at low c.d. (at $1.0\ \text{A/dm}^2$) may be due to tendency of the bath to follow normal codeposition (against anomalous codeposition), as a characteristic of Zn–Fe group metal alloys.

3.2. Development of Zn–Fe CMMA coatings

CMMA coatings, having layers of different compositions were developed using square current pulses of two different current density, by setting the power source conveniently i.e. sharp change in current density brings a sharp change in composition. The power pattern generated for monolithic and CMMA coating systems is shown schematically in Fig. 1.

In the present study, the multilayered deposition is carried out from single bath containing Zn^{2+} and Fe^{2+} ions by galvanodynamic cycling of the cathode current density between two pre-set values. These multilayer coatings are hereafter represented as $(\text{Zn–Fe})_{1/2/n}$, where (Zn–Fe) represents alloy of Zn and Fe, and 1 and 2 represent, respectively the low and high cathode current density, which are set to cycle in between, and 'n' represents the total number of layers formed during total deposition time (10 min).

3.3. Optimization of CCCDs

In the case of alloys of Zn–M (where M = Ni, Co and Fe), it is well known that, even a small change in the concentration of the alloying element may result in significant change in properties, due to change in the phase structure. In electrodeposition of CMMA Zn–Ni

Table 1
Corrosion data and deposit characters of Zn–Fe alloy coatings under different conditions of c.d.

C.d. (A/dm ²)	Wt.% Fe	Thickness (μm)	Vickers hardness V ₁₀₀	E _{corr} (V) vs. Ag,AgCl/KCl _{sat}	i _{corr} (μA/cm ²)	CR (10 ⁻² mm y ⁻¹)	Nature of the deposit
1.0	8.0	6.5	135	-1.012	32.26	40.77	Blackish
2.0	2.23	7.0	153	-1.017	21.87	31.9	Bright
3.0	2.88	11.3	158	-1.013	16.90	25.08	Bright
4.0	3.50	12.5	165	-0.993	18.36	27.24	Bright
5.0	4.60	15.0	181	-1.121	19.74	29.29	Bright
6.0	5.30	17.0	195	-1.189	23.30	34.56	Bright
7.0	5.0	17.6	205	-1.022	24.60	36.50	Semi bright

coating by potentiostatic method, reported by Prabhu Ganeshan et al. (2007), it was found that Ni content varied as a function of varying potential. It was concluded that at higher potentials γ -phase corresponding to (6 0 0) planes were preferentially deposited while lower potentials lead to the deposition of other crystal planes of γ -phases (2 2 2), (3 3 0) and (4 4 4). With this incentive, it has been attempted to bring modulation in Zn–Fe coatings, using square current pulses.

By precise control of cathode current densities (CCCDs), the coatings with layers, having different compositions and, consequently, different corrosion behaviors were developed. Table 2 demonstrates the effect of the CCCDs on corrosion behavior of CMMA coatings. In order to increase the corrosion resistance, CMMA coatings having 10 layers (arbitrarily chosen) were developed at different sets of CCCDs. Amongst the various sets tried, the less corrosion rate was measured in the coatings produced, at difference of 2.0 and 4.0 A/dm² as shown in Table 2. These coatings were found to be bright and uniform. These sets of CCCDs have been selected for studying the effect of layering, as described in the following subsection.

3.4. Optimization of number of layers

The physico-mechanical properties, including corrosion resistances of CMMA coatings may often be increased substantially by increasing the number of layers (usually up to an optimal limit), without sacrificing the demarcation between each layers. Therefore, 2.0/4.0 A/dm² and 2.0/6.0 A/dm² were selected for layering. Zn–Fe CMMA coatings having 10, 20, 60, 120, 300 and 600 layers were developed and their corrosion rates were measured by Tafel's extrapolation method. It was observed that the corrosion rates were decreased as the number of layers increased up to 300 layers only, and then increased, in both sets of CCCDs as shown in Table 3.

However, at 2.0/4.0 A/dm², corrosion rate reached saturation (beyond which no decrease of corrosion rate with layering was observed) value at 300 layers with minimum corrosion rate ($0.81 \times 10^{-2} \text{ mm y}^{-1}$ relative to $25.08 \times 10^{-2} \text{ mm y}^{-1}$ of monolithic). Though there is substantial decrease of corrosion rate (CR) at 2.0/6.0 A/dm², as shown in Table 3, but the results pertaining to 2.0/4.0 A/dm² are more encouraging, due to less CR. However, an effort of increasing the corrosion resistance further, by increasing number of layers (i.e. 600 layers) in each set of CCCDs has resulted in increase of CR, as shown in Table 3.

The increase of CR at high degree of layering (like 600 layers) is attributed to less relaxation time for redistribution of ions (Zn²⁺ and Fe²⁺) in the diffusion layer, during plating or due to higher probability of defects being present in the layers (Nasser Kanani, 2006). As the number of layers increased, the time for the deposition of each layer, say (Zn–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.

As a result, at high degree of layering modulation in composition is not likely to take place. In other words, CMMA deposit

is tending to become monolithic. Therefore (Zn–Fe)_{2.0/4.0/300} has been proposed as the optimal configuration of CMMA coating, with individual layer thickness $\sim 50 \text{ nm}$; for peak performance against corrosion.

3.5. Corrosion study

3.5.1. Potentiodynamic polarization method

Potentiodynamic polarization curves of CMMA (Zn–Fe)_{2.0/4.0} coating system with different number of layers are shown in Fig. 2. Tafel's extrapolation on such curves resulted in determination of the corrosion potential, corrosion current density and CR, as listed in Table 3. A progressive decrease of corrosion current, i_{corr} and hence, the CR was observed up to 300 layers, after which CR started increasing drastically.

3.5.2. Electrochemical impedance spectroscopy (EIS) study

EIS, also referred to as AC impedance spectroscopy is a suitable technique to gain valuable information about the interface (between substrate and medium); responsible for improved corrosion resistance, on the basis of electrical double layer (EDL) capacitance (Craig, 1991). Information about the interaction of coating with corrosion medium was obtained from Nyquist plots (Yuan et al., 2010). It was observed that in (Zn–Fe)_{2.0/4.0} coating systems, the radius of the semi-circle increased with number of layers, up to 300 layers as shown in Fig. 3.

It may be noted that the solution resistance R_s is nearly identical in all cases, as the same bath chemistry and cell configuration were used. But polarization resistance, R_p increased as the number of layers increased. But, in case of deposit with 600 layers (magnified image shown in inset), the radius of the semi-circle decreased substantially; indicating its poor corrosion resistance, as shown in Fig. 3.

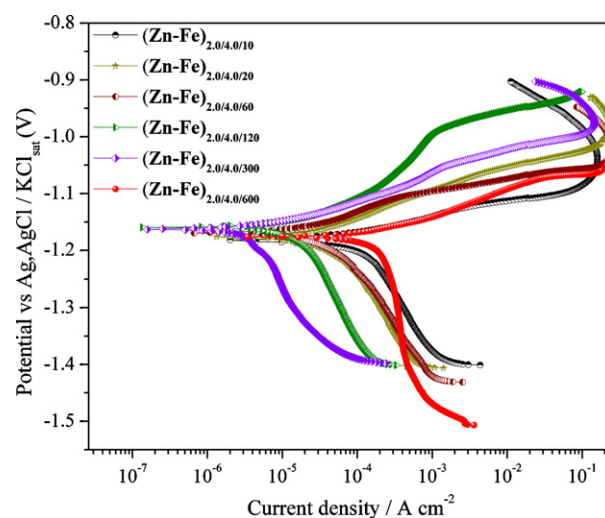


Fig. 2. Potentiodynamic polarization curves of CMMA (Zn–Fe)_{2.0/4.0} coatings having different number of layers.

Table 2
Corrosion rates of CMMA Zn–Fe coatings at different sets of CCCDs (with 10 layers each).

CMMA Zn–Fe coatings developed at difference of 2.0 A/dm ² between CCCDs			
CCCDs (A/dm ²)	E_{corr} (V) vs. Ag,AgCl/KCl _{sat}	i_{corr} ($\mu\text{A}/\text{cm}^2$)	CR (10^{-2} mm y ⁻¹)
(Zn–Fe) _{2.0/4.0/10}	–1.182	11.944	17.72
CMMA Zn–Fe coatings developed at difference of 4.0 A/dm ² between CCCDs			
CCCDs (A/dm ²)	E_{corr} (V) vs. Ag,AgCl/KCl _{sat}	i_{corr} ($\mu\text{A}/\text{cm}^2$)	CR (10^{-2} mm y ⁻¹)
(Zn–Fe) _{2.0/6.0/10}	–1.177	13.214	19.605

Table 3
Decrease of corrosion rate with increase in number of layers of CMMA (Zn–Fe) coating system.

Coating configuration	No. of Layers	E_{corr} (V) vs. Ag,AgCl/KCl _{sat}	i_{corr} ($\mu\text{A}/\text{cm}^2$)	CR (10^{-2} mm y ⁻¹)
<i>Effect of number of layers at 2.0–4.0 A/dm²</i>				
(Zn–Fe) _{2.0/4.0}	10	–1.182	11.944	17.72
(Zn–Fe) _{2.0/4.0}	20	–1.177	10.129	15.02
(Zn–Fe) _{2.0/4.0}	60	–1.169	8.602	12.76
(Zn–Fe) _{2.0/4.0}	120	–1.159	2.418	3.58
(Zn–Fe) _{2.0/4.0}	300	–1.162	1.148	0.81
(Zn–Fe) _{2.0/4.0}	600	–1.174	19.53	28.97
<i>Effect of number of layers at 2.0–6.0 A/dm²</i>				
(Zn–Fe) _{2.0/6.0}	10	–1.177	13.214	19.65
(Zn–Fe) _{2.0/6.0}	20	–1.167	5.302	16.86
(Zn–Fe) _{2.0/6.0}	60	–1.167	5.120	7.86
(Zn–Fe) _{2.0/6.0}	120	–1.162	3.565	5.29
(Zn–Fe) _{2.0/6.0}	300	–1.154	1.251	1.85
(Zn–Fe) _{2.0/6.0}	600	–1.176	23.11	34.29

3.6. Dielectric study of CMMA coating

EIS data points can also be used to study the dielectric properties of materials, and the technique is called dielectric spectroscopy (Gellings and Bouwmeester, 1997). 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 surface charge density D , or quantity of charge per unit area of capacitor plate (C/m^2), is proportional to the electric field, and in the pres-

ence of dielectric it is reduced due to polarization (William, 2000). The capacitance C may be expressed as,

$$C = \frac{k\epsilon_0 A}{d} = \frac{\epsilon_r A}{d} \quad (1)$$

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 is 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,

$$E_{\text{effective}} = E - E_{\text{polarization}} = \frac{\sigma}{k\epsilon_0} = \frac{\sigma}{\epsilon_r} \quad (2)$$

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 (Conway, 1999). The variation of ϵ_r vs. frequency (from 10 mHz to 100 kHz) for different coating systems is shown Fig. 4.

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 on ϵ_r , as shown in Fig. 4. This is due to the fact that, at low frequency, AC becomes equivalent to DC, and is more responsive to ϵ_r . Hence, the decrease of ϵ_r with number of layers indicates, that the polarizing ability of the electrical double layer (EDL) capacitor decreases with layering (Ravinder and

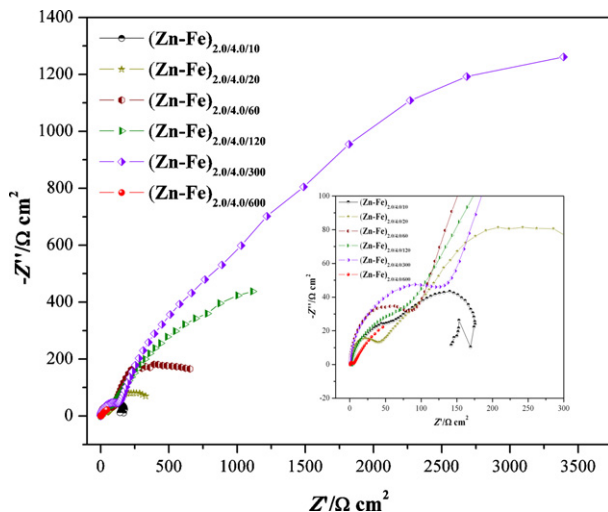


Fig. 3. Electrochemical impedance response of CMMA (Zn–Fe)_{2.0/4.0} coating systems measured at frequency range of 100 kHz to 10 mHz, and perturbing voltage of 10 mV (high frequency range is shown in inset).

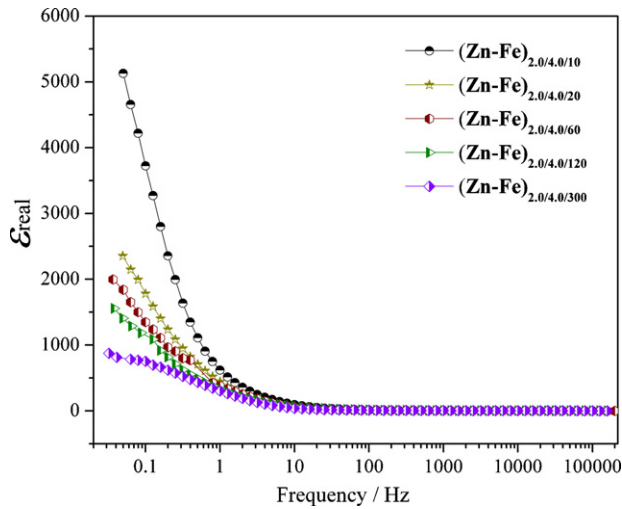


Fig. 4. Frequency response of relative dielectric constant of CMMA (Zn-Fe)_{2.0/4.0} coatings having different number of layers.

Latha, 1999). Therefore less ϵ_r of CMMA (Zn-Fe)_{2.0/4.0/300} compared to other coating systems, indicates that coating behaves as good dielectric barrier for passage of current through the capacitor, causing the less corrosion.

3.7. Comparison between monolithic and CMMA coatings

A substantial change in corrosion rate was observed when coatings is changed from monolithic to multilayer type, and is supported by the corrosion data, reported in Table 4.

It may be observed that both i_{corr} and E_{corr} value of CMMA coating has decreased considerably compared to that of monolithic alloy. It was found that corrosion protection of coatings with (Zn-Fe)_{2.0/4.0/300} configuration is ~30 times better ($0.81 \times 10^{-2} \text{ mm y}^{-1}$) than monolithic (Zn-Fe)_{3.0} alloy ($25.08 \times 10^{-2} \text{ mm y}^{-1}$) alloy, obtained from same bath during same time.

Potentiodynamic polarization behaviors of both monolithic and CMMA coatings (both under optimal conditions) are shown in Fig. 5. Relative response for EIS study of monolithic (Zn-Fe)_{3.0} and CMMA

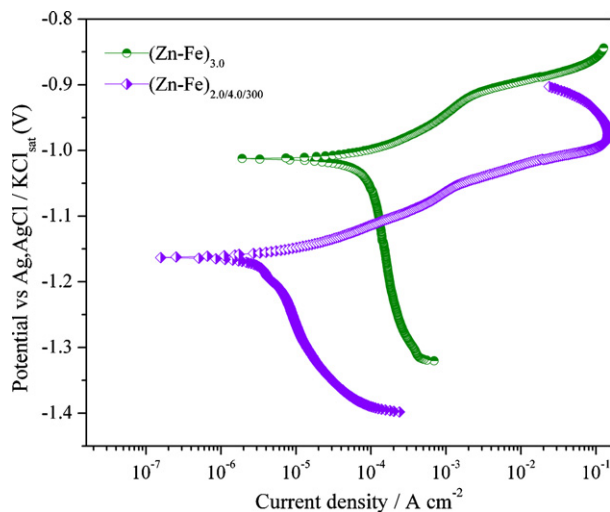


Fig. 5. Comparison of potentiodynamic polarization curves for monolithic (Zn-Fe)_{3.0} and CMMA (Zn-Fe)_{2.0/4.0/300} coating systems of same thickness.

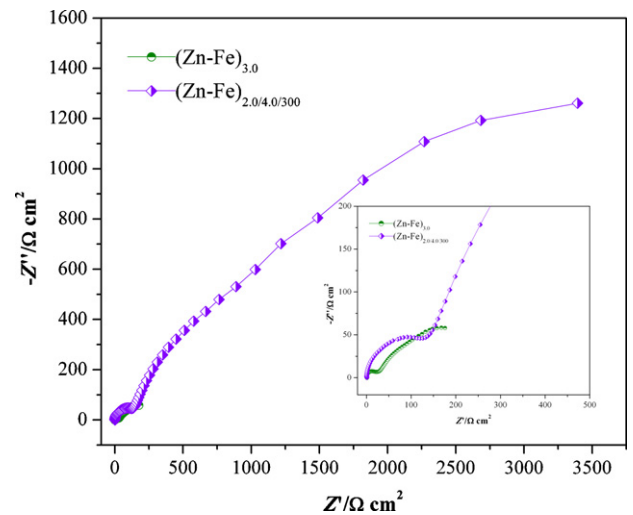


Fig. 6. Comparison of electrochemical impedance response of monolithic (Zn-Fe)_{3.0} and CMMA (Zn-Fe)_{2.0/4.0/300} coatings of same thickness.

(Zn-Fe)_{2.0/4.0/300} coating system is shown in Fig. 6. The less polarization resistance R_p (shown in inset) corresponding to (Zn-Fe)_{3.0} attests its less corrosion resistance compared to CMMA coating of same thickness.

3.8. SEM study

Surface morphology of (Zn-Fe)_{2.0/4.0/20} coating without corrosion marked as 7(A) displayed a uniform and crack-free morphology. Cross-sectional view of CMMA (Zn-Fe)_{2.0/4.0/20} (for better distinction) is shown in Fig. 7(B). The poor contrast may be due to marginal difference in chemical composition of layers.

Formation of layers was again confirmed, by acid test. CMMA (Zn-Fe)_{2.0/4.0/10} coating system was treated with a drop of 2N HCl for 30 s, and then washed and dried. The inspection of the treated surface under SEM confirmed the formation of layers as shown in Fig. 7(C). To understand the reason for the improved corrosion resistance, the CMMA coatings were examined under SEM after corrosion test. The coatings having (Zn-Fe)_{2.0/4.0/4} configuration was subjected to anodic polarization at +250 mV vs. OCP in 5% NaCl solution. The corroded specimen was washed with distilled water and examined. Formation of four layers, corresponding to CMMA (Zn-Fe)_{2.0/4.0/4} was confirmed, as shown in Fig. 7(D). The possibility of high corrosion prevention is due to fact that, the failures like pores, crevices or columnar structure occurring in case of the single layer put down in the deposition process may be neutralized by the successively deposited coating layers and thus the corrosion agents path is longer or blocked (Dobrzanski et al., 2005).

That is why with multilayer coating the corrosive agent needs more time to penetrate through coating defects into the substrate material, than in case of monolayer coating. In other words, the corrosive agent path is extended or blocked. Zn-Fe alloy layer, with less wt.% Fe beneath the high wt.% Fe top layer dissolves through the pores and micro-cracks existing in the CMMA coatings existing during corrosion (Fei et al., 2006). As a whole, the protection efficacy of CMMA (Zn-Fe)_{2.0/4.0/300} coatings may be explained by the barrier effect of Zn-Fe layer, with high wt.% Fe (3.50) and the sacrificial effect of Zn-Fe layer, with less wt.% Fe (2.23). A small change in wt.% noble metal in the alloys layer is good enough to bring large change in the phase structure of the alloys and thereby their properties (Prabhu Ganeshan et al., 2007).

Table 4
Comparison of corrosion rates of monolithic (Zn–Fe)_{3,0} and CMMA (Zn–Fe)_{3,0/4,0/300} coating systems of same thickness.

Coating configuration	E_{corr} (V) vs. Ag,AgCl/KCl _{sat}	i_{corr} ($\mu\text{A}/\text{cm}^2$)	CR ($10^{-2} \text{mm} \cdot \text{y}^{-1}$)
(Zn–Fe) _{3,0} (monolithic)	–1.013	16.90	25.08
CMMA (Zn–Fe) _{2,0/4,0/300}	–1.162	1.148	0.81

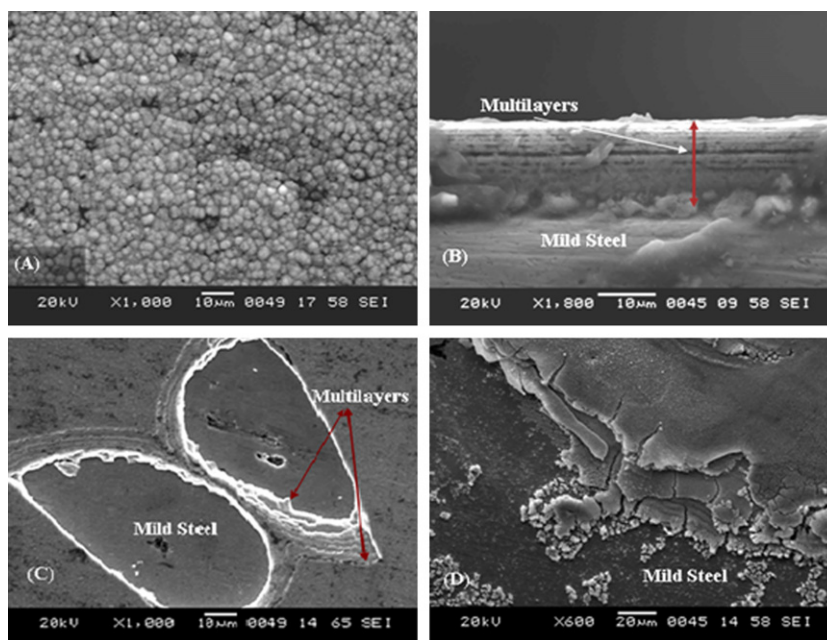


Fig. 7. SEM images of CMMA (Zn–Fe) coatings. (A) Surface morphology of (Zn–Fe)_{2,0/4,0/20} coatings, (B) cross-sectional view showing 20 layers, (C) surface morphology of (Zn–Fe)_{2,0/4,0/10} coating after acid test, (D) CMMA (Zn–Fe)_{2,0/4,0/4} after corrosion test.

4. Conclusions

A stable electrolytic bath has been proposed for deposition of bright and uniform coating of Zn–Fe alloy on mild steel using THC, as brightener.

- Under optimal condition, the corrosion resistance of CMMA Zn–Fe coatings was found to be about 30 times higher than corresponding monolithic coating of same thickness.
- The thickness of individual layers of CMMA coatings, plays important role in imparting better corrosion protection. The corrosion rate decreased with number of layers only up to certain (optimal) number 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 (Zn²⁺ and Fe²⁺ ions) in the diffusion layer, during plating. In other words, at higher layer thickness, the multilayer coating is tending to become monolithic.
- The protection efficacy of the CMMA coatings is related to the defects and failures occurring in a single layer in the deposition process may be neutralized or masked, by the successively deposited layers. Therefore, the corrosive agent path is extended or blocked.
- The dielectric spectroscopy study revealed that the high corrosion resistance of CMMA (Zn–Fe)_{2,0/4,0/300} is due to barrier effect of coatings, with distinct dielectric properties.

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