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ABSTRACT

Zn–Fe alloys were electrodeposited on mild steel plates and their morphology were evaluated. Electrodeposition was carried out using electrolytic sulphate bath with glycine as an additive. The composition of the electrolytic bath, experimental parameters and current density was optimized using Hull cell. The corrosion properties of developed coatings were evaluated in 3.5% NaCl solution using potentio-dynamic polarization and electrochemical impedance spectroscopic techniques. Zn-Fe alloy coatings at 4 A dm^{-2} presented a remarkable corrosion resistance performance due to morphology changes in the alloy.

Keywords: Zn-Fe alloy, SEM, Corrosion resistance.

1. INTRODUCTION :

Zn coatings have been the useful protection layer on steel, mainly in the automobile and aerospace industries [1]. Investigations have shown that by co-deposition of Fe group metals with Zn like Zn-Fe, Zn-Co, Zn-Ni, less corrosion rate was achieved [2-5]. These alloy coatings were more corrosion resistant than pure Zn coatings due to their improved mechanical properties [6, 7]. Zn–Fe alloys have been used a lot recently due to their excellent corrosion resistance because of the natureof the zinc–iron phase and good paintability, weldability and ease of formation of the coating [8, 9].

Moreover, the studies on the Nanostructured materials were reported by several researches as a great emphasis due to their attractive properties [10,11]. Therefore, the nanostructured Zn-Fe coatings on mild steel would provide upgraded corrosion resistance to the substrate. Various techniques like ball milling, electrochemical deposition, sputtering was employed for the preparation of nanostructured materials [12-17]. Among these, electrodeposition method was known as a suitable technique. With this understanding, the present work deals with the development of nanostructured Zn-Fe alloy coatings with glycine as additive and evaluation of their corrosion resistance properties.

2. OBJECTIVES :

1. Optimization of Sulphate Electrolytic bath using glycine as additive for development ofZn-Fe alloy coatings.
2. Electrodeposition of Zn-Fe alloy coatings on mild steel at various current densities (c.d.).
3. To establish the corrosion resistance properties of nanostructured Zn-Fe alloy coatings by Potentiodynamic polarisation and EIS technique.
4. Surface morphology characterization by SEM.

3. MATERIALS AND METHODS :

Electrodeposition of Zn-Fe Alloys were prepared on mild steel panel substrates from a sulphate plating bath. The area of the substrates was 7.5 cm^2 (3 cm × 2.5 cm). Before the deposition, the substrates were polished mechanically using emery papers of various grit size (from 100 to 2500) and then cleaned electrochemically, the wettability and therefore the reactivity of the substrate surface are increased. After the preparation of substrate, Zn-Fe alloys were deposited from a sulphate plating bath

which consisted of 95 gL^{-1} $ZnSO_4 \cdot 7H_2O$, 35gL^{-1} $FeSO_4 \cdot 7H_2O$, 15gL^{-1} $Na_3C_6H_5O_7$, and 32 gL^{-1} H_3BO_3. The pH value was 4.5 and Temperature maintained was 300K (room temperature). The bath composition, parameter and the experimental condition for the development of bright Zn-Fe alloy coatings was carried out by the conventional Hull cell method.

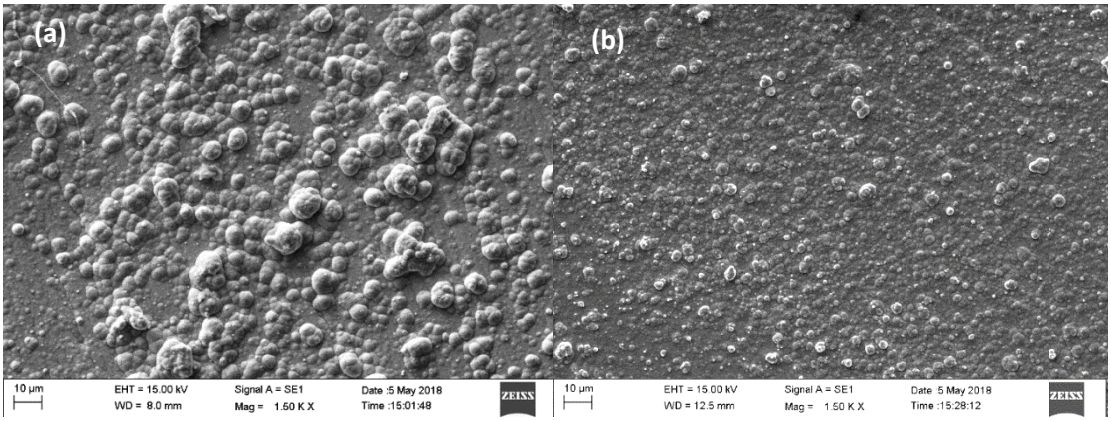
All the depositions were carried out for c.d. of 1A dm^{-2} to 8 A dm^{-2} using direct current power source, N6705B, Keysight Technologies for 10 minutes. The resultant coatings were then cleaned with distilled water and air dried. The surface was examined by using scanning electron microscope (SEM) working at 15kV. Corrosion Measurements of the developed coatings for the electrochemical behaviour of the electrodeposited Zn-Fe alloys were analysed in 3.5% NaCl aqueous solution at room temperature. The corrosion behaviour of the samples was investigated by a Potentiodynamic polarization technique and by Electrochemical Impedance Spectroscopy (EIS) measurements performed with an electrochemical analyzer/workstation (Model CHI608D, CH Instruments, USA) with Ag/AgCl as reference electrode and platinum wire as a counter electrode.

4. RESULTS AND DISCUSSION :

Zn-Fe alloys were deposited on mild steel panels at various c.d.'s from 1 A dm^{-2} to 8 A dm^{-2} from the Hull cell optimized electrolytic sulphate bath given in table 1. The pH variation in the bath during electrodeposition due to the liberation of hydrogen by consumption of electric current would disrupt the electrodeposition process. This was controlled by the addition of boric acid as buffer to the electrolytic bath which maintains the pH throughout the electrodeposition process. In the present work Glycine was used as an additive for the electrodeposition of Zn-Fe alloy coatings. The investigation made by Esmail Hakki Karahan et al has proved glycine as a levelling agent for Zn-Fe co-deposition. Addition of glycine results in good coating with finer grain size [18].

Table 1 : Bath composition and parameters

Bath Components	**Composition (gL^{-1})**
$ZnSO_4 .7H_2O$	95
$FeSO_4.7H_2O$	35
H_3BO_3	32
Glycine	15
Electrodeposition Parameters	
c.d.	4 Adm^{-2}
pH	4.5
Temperature	300K



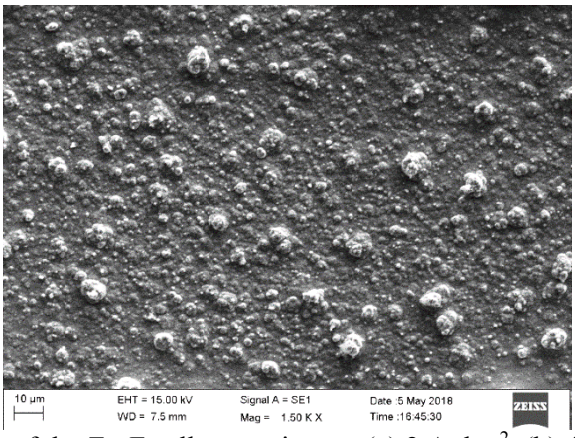


Fig. 1: SEM micrographs of the Zn-Fe alloy coatings at (a) 2 A dm^{-2}, (b) 4 A dm^{-2} and (c) 6 A dm^{-2}

The surface morphology of the nanostructured Zn-Fe alloy coatings obtained by electrodeposition was evaluated using SEM. SEM micrographs of the coatings developed at 2 A dm^{-2}, 4 A dm^{-2} and 6 A dm^{-2} is given in Fig 1(a), (b) and (c). From the figures it was observed that the Zn-Fe alloys are deposited on mild steel in the form of grains or nodules. It is worth notice that the deposition at 2 A dm^{-2} are rough and are composed of large unequal sized nodules. With the increase in c.d., the size of the nodules was observed to decrease and finer deposits with almost equal sized grains are witnessed in 4 A dm^{-2}. This indicates the improvement in the coating surface with increase in applied c.d. This decrease in size and the resulting finer grains may direct towards the increase in Fe content in the coatings [19]. However, with further increase in c.d., at 6 A dm^{-2}, the aggregation of grains was observed which consequence in its coarse surface morphology. Hence coatings developed above 4 A dm^{-2} may result in poor corrosion resistance due to its rough surface. From the surface analysis of the developed Zn-Fe alloy coatings, the electrodeposits developed at 4 A dm^{-2} was expected to have good corrosion resistance ability.

The potentiodynamic polarization technique was carried out to determine the corrosion rate (CR) of the developed Zn-Fe coatings at c.d.'s from 1 A dm^{-2} to 8 A dm^{-2}. During corrosion testing, the electrodes were immersed in the corrosive electrolyte 3.5% NaCl solution and left at open circuit potential for 10 minutes. This stabilizes the corrosion potential E_{corr} and yields reproducible polarization curves. The resulting polarization curves are shown in Fig.2 and the corresponding electrochemical parameters are listed in table 2.

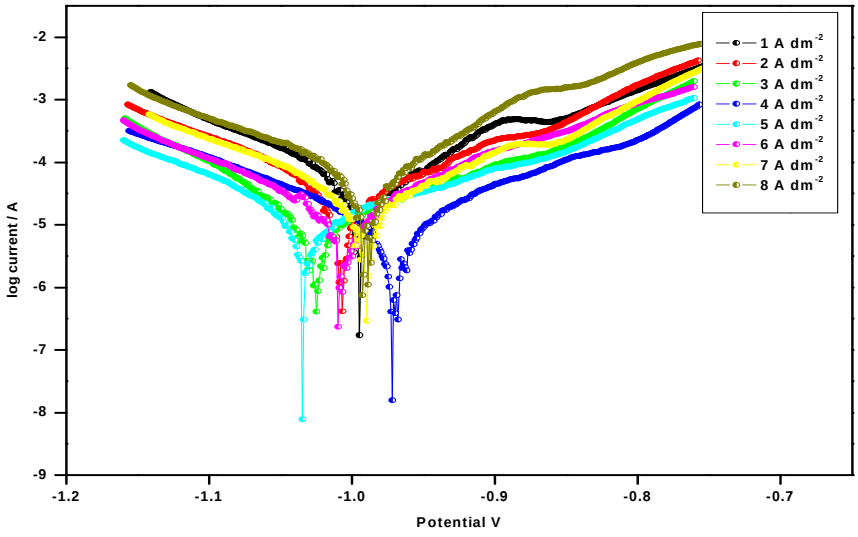


Fig. 2 : Potentiodynamic polarization curves of the developed Zn-Fe alloy coatings

Table 2 : Corrosion data obtained from potentiodynamic polarisation method

c.d. (Adm^{-2})	$-E_{corr}$ (V vs SCE)	i_{corr} ($\mu A\ cm^{-2}$)	β_a (V/dec)	β_c (V/dec)	C.R. (mpy)
1.0	0.995	49.13	10.539	8.836	25.56
2.0	1.007	32.41	10.411	8.234	16.87
3.0	1.025	13.90	7.457	11.031	7.234
4.0	0.972	10.12	7.690	8.624	5.265
5.0	1.035	22.04	6.256	8.555	11.47
6.0	1.010	20.78	10.087	8.833	10.81
7.0	0.990	29.30	8.713	8.143	15.25
8.0	0.993	43.50	14.254	7.726	22.64

From the Fig.2 it was observed that all the curves are having similar behavior with different values of their electrochemical parameters. Taking a note on the corrosion parameters given in table 2, it was observed that the corrosion potential of the coatings at 4 A $dm^{-2}$was more positive (-0.972V)and thus has more protection characteristics than other coatings. Corrosion current (i_{corr}) decreases with c.d. and least value was observed for 4 A dm^{-2} (10.12 µA cm^{-2}).Moreover, it's evident that the CR also decreases with increase in c.d. and was least at 4 A dm^{-2}(5.265mpy). This result is attributed to the surface analysis of the coatings where Zn-Fe alloy coatings at 4 A dm^{-2}has finer and almost uniform morphology, which contributes towards the high corrosion resistance. Above 4 A dm^{-2}, due to the aggregation of the grains, the surface was rough and thus the rise in the corrosion rate of the coatings was observed as listed in table 2.

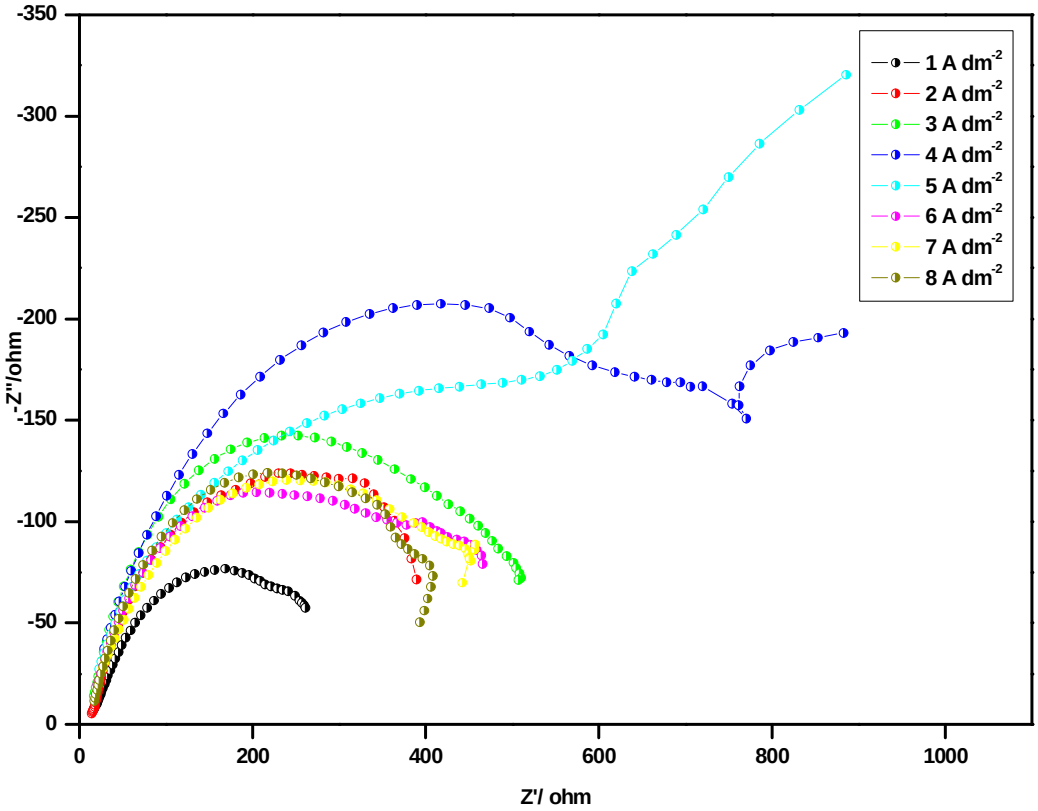


Fig.3: Nyquist graphs for the Zn-Fe alloy coatings

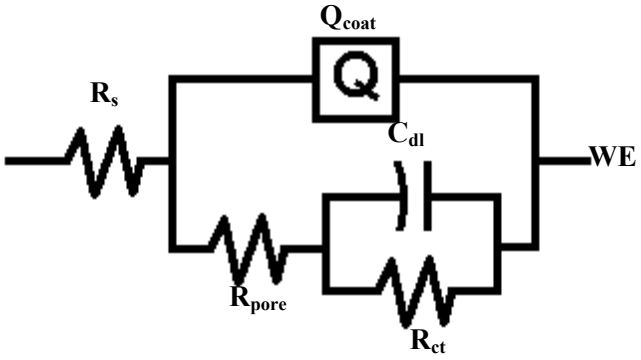


Fig. 4 : Equivalent circuit fit for the Nyquist graphs of Zn-Fe alloy coatings

Table 3 : Corrosion data obtained from Electrochemical impedance Spectroscopy

c.d. ($A\ dm^{-2}$)	R_S ($\Omega\ cm^2$)	R_{pore} ($\Omega\ cm^2$)	R_{ct} ($\Omega\ cm^2$)	C_{dl} ($\mu F cm^{-2}$)	Q_{coat}-Y_0 ($\mu F cm^{-2}$) CPE	n_{coat}
1.0	11.81	294.10	320.2	35550	765.9	0.5959
2.0	6.83	32.27	438.9	38.18	728.2	0.5488
3.0	9.68	98.80	453.2	2826	113.2	0.7413
4.0	17.80	4326	1034.0	4.003	261	0.4156
5.0	4.06	493.60	682.8	2201	162.5	0.5909
6.0	5.97	118.70	493.0	5559	153.6	0.6476
7.0	0.65	511.70	422.7	16910	174.0	0.5783
8.0	9.56	9.74	417.8	25020	206.9	0.6836

Electrochemical Impedance Spectroscopy (EIS) is a useful technique for the evaluation of corrosion process at electrode and electrolyte interface. The plots having higher impedance and the semicircle having larger diameter reflects the higher corrosion resistance ability. Fig.3 Shows Nyquist impedance plots of Zn-Fe alloy coatings at various c.d.'s. The proposed equivalent circuit is given in Fig. 4 and the corresponding corrosion data is given in table 3.

From the table 3, the R_{ct} value increases with c.d. and was maximum at 4 A dm^{-2} (1034 $\Omega\ cm^2$). This signifies the decrease in corrosion current which was witnessed in Potentiondynamic polarisation analysis. This highest pore resistance (R_{pore}) was observed for coatings at 4 A dm^{-2}, this direct towards the good coating surface at this c.d. This result agrees with the Surface morphology analysis (Fig.1). Moreover, the double layer capacitance (C_{dl}) decreased with c.d. and least C_{dl} was witnessed at 4 A dm^{-2} which further increased at higher c.d. Hence Zn-Fe coating obtained at 4 A dm^{-2} exhibits excellent corrosion resistance.

5. CONCLUSION :

- New stable electrolytic bath was optimized and employed for the galvanostatic electrodeposition of corrosion resistant Zn-Fe alloy coatings on mild steel using glycine as additive.
- The electrochemical corrosion analysis of the developed coatings confirms that coatings at 4 A dm^{-2} has excellent corrosion resistance ability. This result was supported by surface morphology of the coatings.

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