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Original scientific paper

Studies on electrodeposited Zn-Fe alloy coating on mild steel and its characterization

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Abstract

Chloride bath containing $ZnCl_2 \cdot 7H_2O$, $FeCl_2 \cdot H_2O$ and a combination of sulphamic acid and citric acid (SA+CA) were optimized for electrodeposition of bright Zn-Fe alloy coating on the mild steel. Bath constituents and operating parameters were optimized by the Hull cell method for highest performance of the coating against corrosion. The effect of current density and temperature on deposit characteristics such as corrosion resistance, hardness, thickness, cathode current efficiency and glossiness, were studied. Potentiodynamic polarization and electrochemical impedance spectroscopic (EIS) methods were used to assess corrosion behaviour. Surface morphology of coatings was examined using scanning electron microscopy (SEM). The Zn-Fe alloy with intense peaks corresponding to Zn (100) and Zn (101) phases, evidenced by X-ray diffraction (XRD) study, showed the highest corrosion resistance. A new and economical chloride bath for electrodeposition of bright Zn-Fe alloy coating on mild steel was proposed and discussed.

Keywords

Zn-Fe alloy; chloride bath; sulphamic/citric acid; corrosion; XRD study

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Introduction

Electrodeposition of metals and alloys has become extensively used in many industries, showing distinctive advantages compared to most of other finishing technologies [1]. Implementation of Zn and Zn alloy coatings appears to be one of most original and simplest methods for attainment of high protection against corrosion [2]. The most commonly used metals for Zn alloying are of the Fe group [3-5]. Zn-Fe alloy coatings are characterized by excellent corrosion resistance and good weldability, formability and paint ability. They have numerous important applications such as in chemical and galvanic processes within automobile and aerospace industries [6]. Behaviour of Zn, Fe and Zn-Fe alloy deposited onto copper from acid chloride solutions containing EDTA and boric acid was investigated by cyclic voltammetry and steady state polarization techniques [7]. Electrodeposition of Zn-Fe alloys from a chloride-based electrolyte has already been studied using electrochemical polarization techniques and other instrumental methods [8]. It was found that the coating of Zn-Fe alloy is formed following the mechanism of nucleation and subsequent growth. The Zn^{2+} ions in the electrolyte were found to inhibit deposition of Fe, while Fe^{2+} ions promote deposition of Zn. It was also found that co-deposition of Zn and Fe behaves anomalously [9]. Sulphate containing bath was developed for the preparation of Zn-Fe alloy coatings by Yang *et al.* [10]. The effects of citric acid and sodium citrate used respectively as a buffer and complexing agent were studied by Diaz *et al.* [11]. It was found that the kinetics of deposition is governed by the interfacial pH. Hegde *et al.* [12] showed that transition of metal alloys shows anomalous co-deposition, occurring as a result of changes in the applied current density during electrodeposition of zinc–nickel, zinc-iron and zinc-nickel alloys in the acidic medium. Eliaz *et al.* [13] concluded that deposition of iron group metals shows good corrosion resistance compared to the single metal deposition.

Electrodeposition of Zn-Fe alloys is generally classified as anomalous co-deposition process due to the preferential deposition of Zn as less noble metal [2]. Several hypotheses have been proposed to explain this anomalous co-deposition [2,14]. Many extensive research works have been reported on deposition mechanism of Zn-Fe group metal alloys, concentrating on anomalous co-deposition and dependency of deposit characteristics on the bath constitution and operating parameters. Not any work, however, has been reported on optimization of Zn-Fe alloy bath containing sulphamic acid (SA) in conjunction with citric acid (CA) for obtaining bright Zn-Fe alloy coatings. In the present study, the role of SA and CA used in a combination, on electrodeposition of Zn–Fe alloy and its corrosion protection performance are investigated. The main focus of this work is related to optimization of the bath composition, operating parameters and characterization of the coatings. Techniques such as scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used to characterize the coatings.

Experimental

Plating solutions were prepared from laboratory grade chemicals and distilled water. Standard Hull cell of 267 ml capacity was used to optimize bath constituents. All depositions were carried out at 303 K and pH 3.0 (except during its deviation). Polished mild steel plates were used as cathode (surface area 7. 5 cm^2) and a pure zinc plate with the same exposed surface area was used as anode. A PVC cell of 250 cm^3 in capacity was used with the cathode-anode space of about 5 cm. All depositions were carried out galvanostatically under constant temperature and pH for duration of 10 minutes using power source (N6705C, Keysight Technologies). A combination of sulphamic acid and citric acid, (SA+CA), was used as an additive for improving the brightness and homogeneity of the coating. The constituents and deposition parameters were optimized on the basis of coating appearance and corrosion resistance.

In order to study the electrochemical properties of coatings, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements were performed. All electrochemical tests were carried out using a potentiostat/galvanostat (CH instruments) and a three-electrode cell. The working electrode was the coated metal specimen. The counter electrode was a platinum electrode with the same surface area as the working electrode. All electrochemical potentials in this work are referred to the Ag/AgCl electrode. The 5 % NaCl solution was used as a corrosion medium throughout the study. Potentiodynamic polarization study was carried out in a potential ramp of -

0.250 V to +0.250 V around the open circuit potential (OCP), at the scan rate of 1 mV s^{-1}. Corrosion rates were determined by the Tafel's extrapolation method. Impedance measurements were carried out over the frequency range of 100 kHz to 20 mHz, using sine waves of 10 mV amplitude. The microstructure of deposits was examined using SEM (JSM-6380 LA from JEOL, Japan). X-ray diffraction (XRD) patterns were collected by JDX-8P JEOL, Japan, with CuKα radiation (k = 1.5418 Å) as the X-ray source. While the thickness of the coatings was calculated from Faradays law, it was verified using digital thickness tester (Coat measure M&C, ISO-17025). The Fe content in the coating was estimated by spectrophotometer method [14]. The hardness of the deposits (~19 µm thickness) was measured by Vickers method, using micro hardness tester (CLEMEX). The cathode current efficiency (CCE) of the deposition was determined by knowing the mass and composition of the deposit [2]. The brightness of deposit was measured using Gloss Meter (Nova-Elite, 600).

Results and discussion

Hull cell study

The bath composition and operating parameters of Zn-Fe bath have been optimized by usual Hull cell method [2] at 1.0 A cell current and temperature 30 °C. Varieties of deposits having greyish white/bright/porous bright appearance were obtained over the wide range of current density of 1.0-5.0 A dm^{-2}. Effect of each bath constituent on Hull cell panels were examined in terms of their appearance and surface morphology. The composition and operating parameters of the optimal bath are collected in Table 1.

Table 1. *Composition and operating parameters of optimized bath for electroplating Zn-Fe alloy on mild steel*

Bath composition	Amount, g L^{-1}	Operating parameters
Zinc chloride	70	pH 3.0 Temperature: 303 K Anode: Pure zinc Current density: 3.0 A dm^{-2}
Ferric chloride	20	
Sodium acetate	60	
Sulphamic acid	1.0	
Citric acid	4.0	

Effect of current density

The current density over wide range (1.0-5.0 A dm^{-2}) was found to have a predominant influence on many characteristics of plated deposits. Appearance and corrosion performance of deposit formed at each current density are described with data listed in Table 2. At low current density, the bath produced greyish white coating with ~2.64 wt.% Fe and a porous bright deposit with ~9.81 wt.% Fe at high current density. A sound bright deposit with ~5.87 wt.% Fe was found at 3.0 A dm^{-2}. Increase in Fe content with current density is attributed to the rapid depletion of more readily depositable Zn^{2+} ions at the cathode coating [2]. As shown in Table 2, the hardness of Zn-Fe alloy deposit increased together with Fe content in the deposit, hardness may ascribed to higher current density of iron compared to zinc (d_{Fe}= 7.90 g cm^{-3} and d_{Zn}= 7.14 g cm^{-3}). At high current density, the coating was very thick with increased hardness. Thick and porous bright deposit formed at very high current density is due to the metal hydroxide formation caused by rapid evolution of hydrogen during plating. The reflectance of Zn-Fe alloy coatings at different current densities were also tested and it was found that the deposit formed at very low current density showed lower glossiness, whereas at the optimal current density the glossiness was found to be maximum. At higher current density, glossiness decreased due to increased porosity and thickness. The thickness of deposits was found to increase substantially with current density, thickness may be due to the adsorbed metal hydroxide at the cathode, caused by the steady increase of pH due to cathodic evolution of hydrogen gas. Under all conditions of deposition, cathodic current efficiency (CCE) of the bath is found high. *i.e.* >85 %. A slight decrease in CCE with increasing current density as observed in Table 2, may be due to the excessive hydrogen evolution during plating.

Table 2. *Effect of current density on pH, Fe content, CCE, thickness, hardness, glossiness and appearance of Zn-Fe electrodeposited from optimized bath at 303 K*

j / A dm^{-2}	pH	Fe content, wt.%	CCE, %	Thickness, µm	Vickers hardness (HV$_{200}$)	Glossiness	Appearance of deposit
1.0	3.0	2.64	87.6	7.2	135	109.0	Greyish white
2.0	3.0	4.71	90.5	10.6	158	117.0	Bright
3.0	3.0	5.87	93.6	15.8	181	156.1	Bright
4.0	3.0	8.19	87.0	17.9	195	138.6	Bright
5.0	3.0	9.81	85.8	21.5	199	146.8	Porous bright

Effect of temperature

Temperature is also found to play outstanding role on the composition and appearance of the deposit, as is the case of Zn-Fe alloys. As shown in Table 3, the deposit was found greyish white (due to high Fe content) at low temperature, and silver bright (due to low Fe content) at high temperature, respectively. This may be ascribed by the fact that at elevated temperature, more readily depositable metal (zinc) are favoured to be replenished at the cathode film.

Table 3. *Effect of temperature on Fe content in the deposit plated at 3.0 A dm^{-2} from bath having optimal composition*

T / K	Fe content in deposit, wt.%	Appearance of deposit
283	6.02	Greyish
293	6.08	Bright
303	5.87	Bright
313	3.78	Bright
323	2.14	Porous bright

Corrosion study

Potentiodynamic polarization study

Electroplated specimens were subjected to corrosion study and corrosion data of Zn-Fe coatings corresponding to different current densities are given in Table 4. The increase of corrosion rate (CR) with current density is due to the changed phase structure caused by high Fe content in the deposit. High CR observed at very low current density is due to increased Fe content. This may be due to the tendency of bath to transit from anomalous to normal co-deposition [15].

Table 4. *Corrosion parameters of Zn-Fe alloy coatings plated at different current density in potential ramp of -0.250 V to +0.250 V from OCP at scan rate of 1 mV s^{-1} in 5 % NaCl*

j / A dm^{-2}	i_{corr} / µA cm^{-2}	E_{corr} / V *vs.* Ag/AgCl	β_c / mV dec^{-1}	β_a / mV dec^{-1}	Corrosion rate x10^{-2}, mm year^{-1}
1.0	12.36	-1.259	41.0	20.4	13.2
2.0	6.083	-1.240	54.6	37.8	9.42
3.0	1.666	-1.233	22.7	16.6	3.36
4.0	4.072	-1.239	29.3	20.1	6.38
5.0	9.011	-1.259	145.4	50.3	12.13

Large variation in the Tafel's slope of cathodic polarization shown in Figure 1, indicates that the corrosion rate is controlled more by the cathodic reaction. It was observed that the deposit formed at 3.0 A dm^{-2} with ~5.87 wt.% Fe showed the lowest corrosion rate (3.36×10^{-2} mm $year^{-1}$). Hence it is inferred that at 3.0 A dm^{-2}, the added (SA+CA) combination has reduced the availability of free Fe^{2+} ions in the solution by proper complexation, improving thus homogeneity of coatings and reducing the corrosion rate.

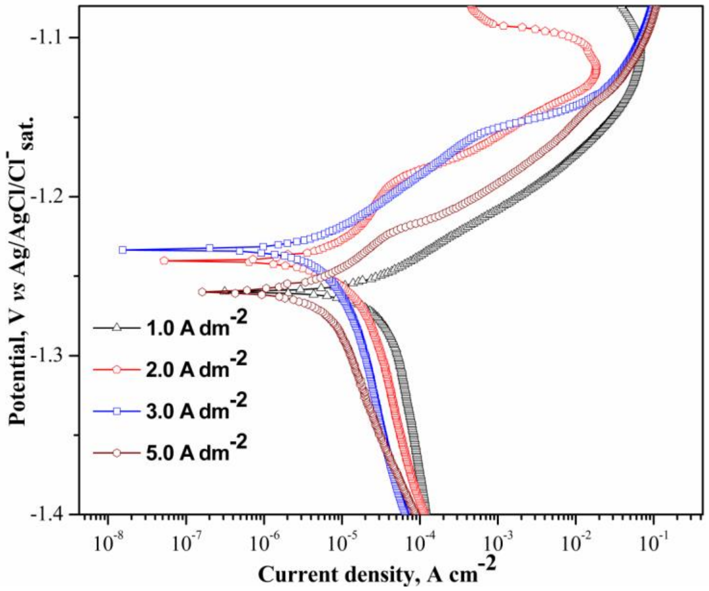

Figure 1. *Tafel plots for Zn-Fe alloy coatings formed at different current densities from the optimal bath at scan rate of 1 mV* s^{-1}

Electrochemical Impedance study

EIS is useful technique for ranking coatings, assessing interfacial reactions, quantifying coating breakdown, and predicting the lifetime of coating/metal systems. Advantages of this AC technique over DC techniques include the absence of any significant perturbation of the system, applicability to the assessment of low conductivity media and existence of frequency components that may provide mechanistic information. The EIS responses of Zn-Fe alloy coatings, deposited from the optimal bath at different current densities, are shown in Figure 2.

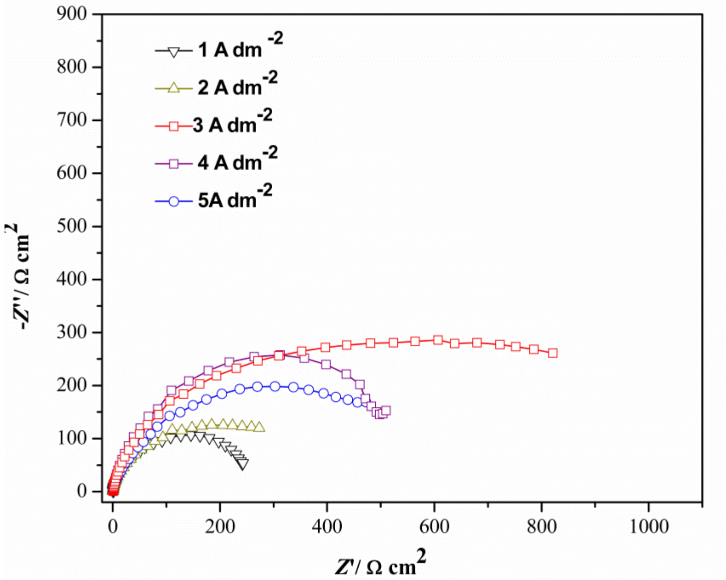

Figure 2. *Electrochemical impedance spectra (100 kHz–20 mHz) of Zn-Fe coatings electrodeposited at different current densities.*

Usual semicircle response due to corrosion can be noticed for each curve. The same origins of all curves are due to the solution resistance that is nearly identical in all cases, as the same bath chemistry and cell configuration were used. Since diameters of semicircles are related to the corrosion resistance, it may be noted that the highest corrosion resistance is exhibited by the coating deposited at the optimal current density, *i.e*. at 3.0 A dm^{-2}.

Cyclic polarization study

The cyclic polarization behavior shown in Figure 3 confirmed the formation of both air formed oxide layer and corrosion product layer. In the potential range of -0.3 V to -0.7 V, the current density of backward scanning was higher than that of the forward scanning, indicating the breakdown of the air formed oxide layer, while in the potential range from -0.7 V to -1.0 V it was lower than that of forward scanning, is due to formation of corrosion product initiated by pitting.

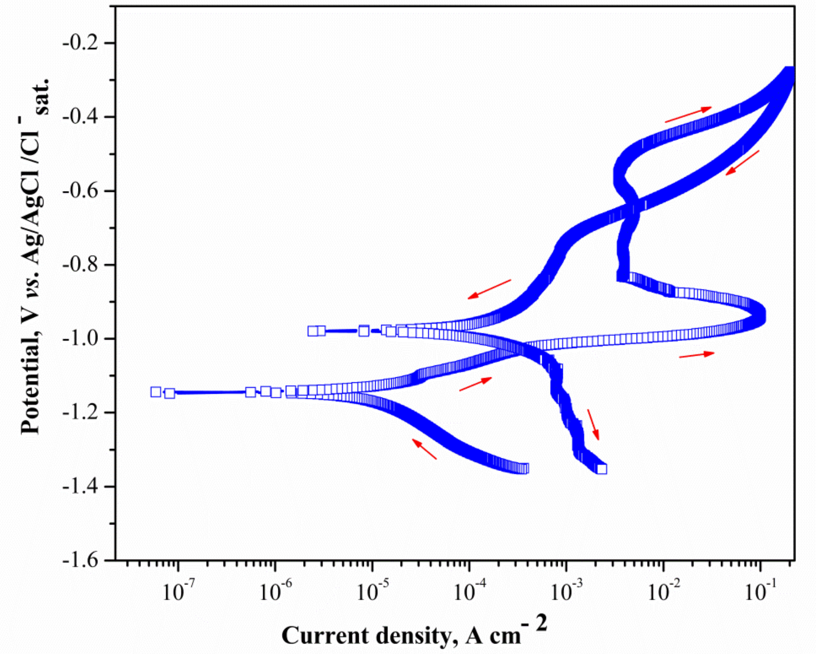

Figure 3. *Cyclic polarization curve of Zn-Fe alloy electrodeposited at 3.0 A dm^{-2} at scan rate of 1 mV s^{-1} in 5 % NaCl*

X-ray diffraction analysis (XRD)

The phases of the electrodeposited Zn-Fe alloy are very complicated, depending on their chemical compositions [9]. XRD patterns of Zn-Fe alloys presented in Figure 4 shows the formation of coatings having different phase structures, depending on the current density at which they were deposited. The XRD peaks reveal that Zn-Fe alloys having range of compositions is formed and many phases coexist. It may be noticed that only relative intensities of few phases of zinc like (100), (101), (200) and (110) change among coatings deposited at different current densities, and hence different compositions were generated [9]. It was found that Zn-Fe alloy deposited at 3.0 A dm^{-2} (with the lowest CR) exhibits two intense peaks corresponding to Zn with (100) and (101) phases.

SEM Analysis

SEM analysis showed that current density plays a significant role on the surface morphology and homogeneity of the deposit. Variation in the surface morphology with current density is shown in Figure 5. The coating was found to be very thin at 2.0 A dm^{-2} (Figure. 5a) and bright at optimal current density 3.0 A dm^{-2} (Figure 5b). At high current density, however, the deposit was found to be porous as shown in Figure 5c.

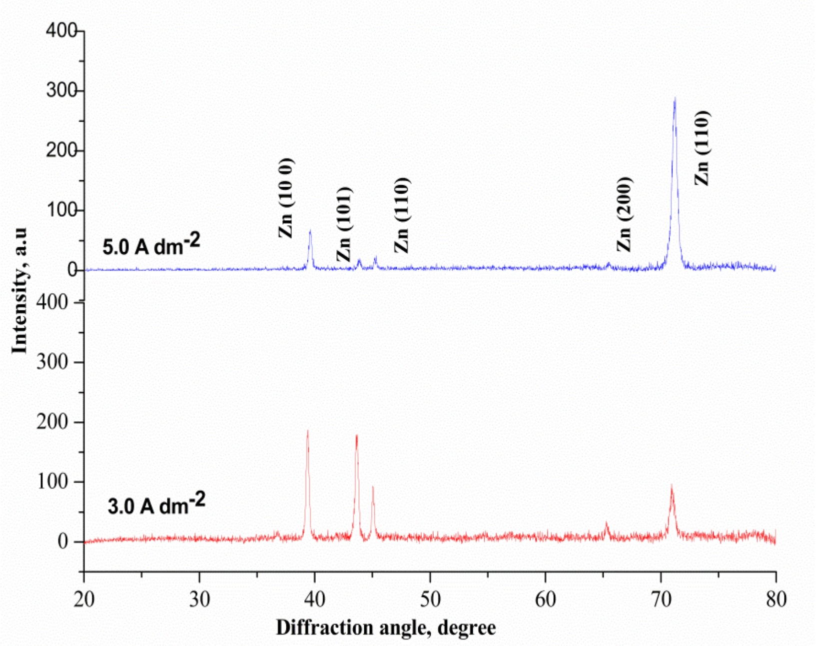

Figure 4. *X-ray diffraction profiles of Zn-Fe coating electrodeposited on mild steel from optimized bath at different current densities*

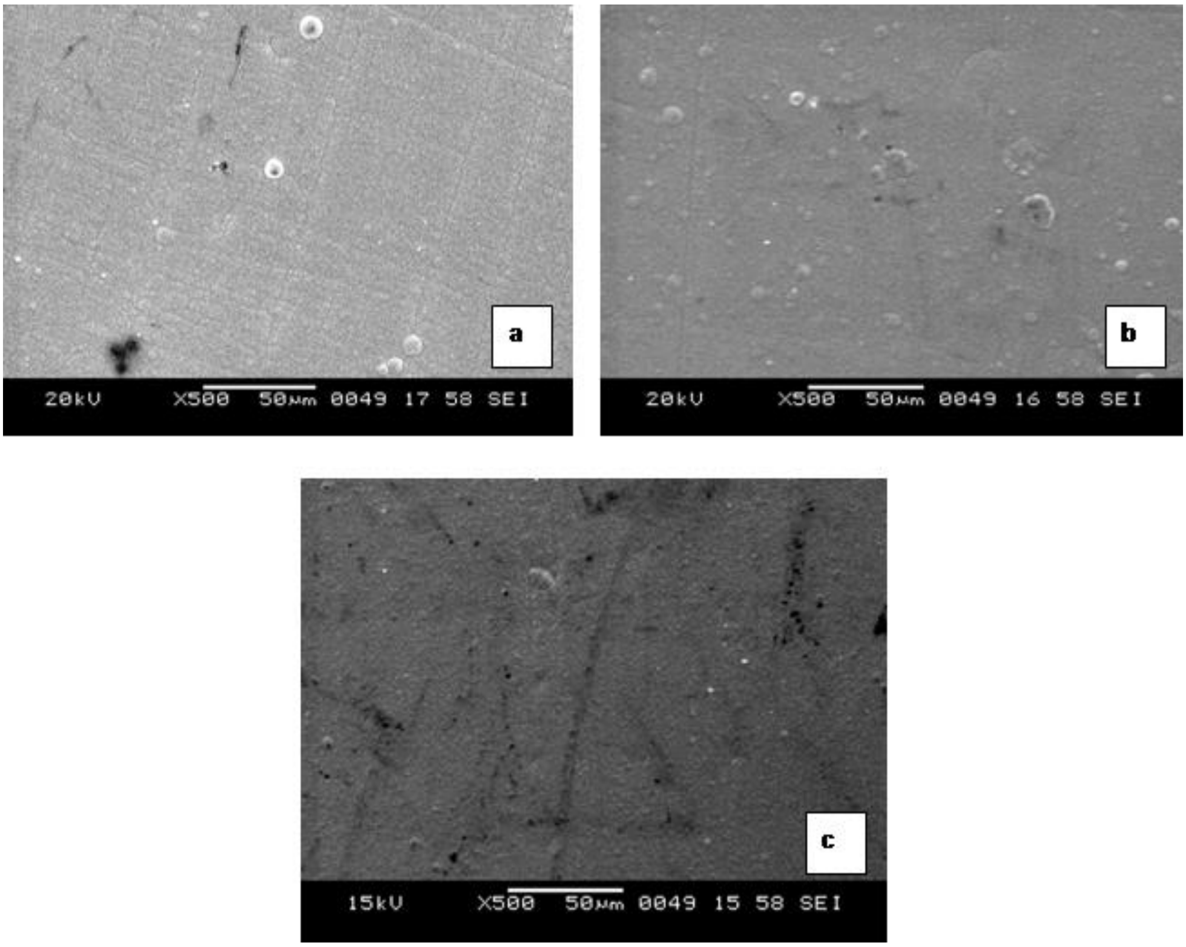

Figure 5. *Scanning electron microscopy (SEM) images of Zn-Fe alloys deposited at (a) 2.0; (b) 3.0 and (c) 4.0 A dm^{-2}*

Conclusions

- An electrolytic bath has been proposed for deposition of bright and corrosion resistive Zn-Fe alloy coatings on mild steel using SA and CA as additives. At all conditions, the electroplating process followed the anomalous co-deposition with preferential deposition of zinc. The effect of temperature on the deposition process showed that the co-deposition of metals is diffusion controlled. The optimum condition for electroplating of Zn-Fe alloy is found at the cathode current density 3.0 A dm^{-2}, bath temperature 30 °C and pH 3.0.

- At the optimum bath composition and processing parameters, the Zn-Fe alloy coating showed maximal corrosion resistance and minimal corrosion rate (3.36 ×10^{-2} mm year^{-1}).
- The current density was found to play an important role on the production and properties of the deposit. No transition current density at which the co-deposition behaviour changed from the anomalous to normal type was observed over the wide range of current densities (1.0-5.0 A dm^{-2}).
- Increase of Fe (less readily depositable metal) content in the deposit with temperature confirmed the diffusion controlled deposition process.
- The cyclic polarization study showed that improved corrosion resistance is due to barrier effect of oxide layer and corrosion products.
- XRD study revealed that Zn-Fe alloy coating with the highest corrosion resistance corresponds to Zn with (100) and (101) phases.

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