

Electrodeposition and Corrosive Properties of Environmental ZnFe/Polyaniline on Low Carbon Steel

İ.H. KARAHAN* AND F. TILTI

Mustafa Kemal University, Faculty of Art and Science, Department of Physics, 31040 Hatay, Turkey

Zinc-iron alloy plating (ZnFe) was successfully deposited on AISI 4140 steel applying cyclic voltammetry technique. Polyaniline (PANI) film was synthesized with cyclic voltammetry technique from 0.10 M aniline containing 0.30 M oxalic acid solution on zinc-iron plated carbon steel (AISI4140/ZnFe) electrode. ZnFe film was characterized by scanning electron microscopy and X-ray diffraction technique. The corrosion behaviour of zinc-iron deposited carbon steel electrodes with and without PANI film in 3.5% NaCl solution was investigated with polarization curves. Effect of pH and current density on the synthesis of the aniline was also examined. The results showed that PANI coating led to decrease of the permeability of metallic plating. The PANI homopolymer film provided an effective barrier property on zinc-iron coating and a remarkable anodic protection to substrate. ZnFe particles had more homogeneous, smooth prismatic structure. It is suggested that ZnFe/PANI deposits produced in the bath applying 0.1 mA/cm² current density probably offer bigger protection to the steel substrate.

DOI: [10.12693/APhysPolA.130.282](https://doi.org/10.12693/APhysPolA.130.282)

PACS/topics: 81.05.Bx, 82.35.Gh, 81.65.Kn

1. Introduction

The plating of mild steel and iron by metals such as zinc, chrome, and nickel has been widely used to protect them against corrosion for many years [1–6]. Thin top coat phosphatation and chromatisation on electrodeposited metal coatings have improved the corrosion resistance of the substrates [7]. But such top coat treatments are undesired due to their highly toxic and carcinogenic feature [8].

Electroconductive polymers have recently attracted a great deal of attention mainly due to their potential applications in a variety of new technologies [9] such as in electronic devices [10], electrochromic displays [11], rechargeable batteries [12], polymer-modified electrodes and biosensors [13, 14]. Polyaniline family has been the most widely studied on account of ease of synthesis, environmental stability [15] and especially corrosion protection [16–18]. On the other hand, a number of reports on the synthesis and characterization of PANI have appeared in the literature during the past decade. However, the synthesis of conductive polymer onto the surface of metal alloy coating being the first of this kind, no such proceedings have been reported in the literature so far.

This study aims to synthesize electrochemically PANI films on thin zinc-iron plated carbon steel in sodium oxalate (NaO_x) medium, which would enable the passivation of the carbon steel surface. The corrosion performance of zinc-iron plated AISI 4140 steel substrate with and without PANI coating was investigated in 3.5% NaCl and compared with the Tafel diagrams.

2. Experimental

Zn_{1-x}Fe_x alloys were prepared by electrodeposition under cyclic voltammetry technique on CS disk substrates from a sulphate plating bath at room temperature (Table I). The electrolytes were prepared using (18 MΩ cm) twice distilled water. The dimensions of the deposits were about 1.5 cm × 1.5 cm. Before the deposition, the substrates are prepared in the standard industrial way and then dried in air. Thus, the wettability and therefore the reactivity of the substrate surface are increased. After these preparation steps, the substrates were ready to be electrodeposited. Counter electrode was a platinum electrode. The reference electrode used in all experiments was a saturated calomel electrode (SCE). The surface of this electrode was carefully polished with abrasive paper (1200 grid), degreased with 1/1 ethanol/acetone mixture, washed with distilled water and dried.

TABLE I

Solutions compositions for the ZnFe alloy electrodeposition.

Solutions compositions	ZnFe
FeSO ₄ [gl ⁻¹]	20
ZnSO ₄ [gl ⁻¹]	41.25
C ₆ H ₅ Na ₃ O ₇ · 2H ₂ O [gl ⁻¹]	25
H ₃ BO ₃ [gl ⁻¹]	16
solution pH	4
temperature [°C]	40
deposition time [min]	10
voltage [V]	-0.9 to -2

Polyaniline film was synthesized galvanostatically at room temperature. Currents for deposition selected as 0.1, 0.2, 0.3 mA/cm² and effect of current was investigated.

*corresponding author; e-mail: ihkarahan@gmail.com

The surface structure analysis of the electrodeposits were examined by using JEOL 6400 scanning electron microscope (SEM) working at 15–30 kV. The preferred orientations of the deposits were determined by X-ray diffraction (XRD) analysis, using a Siemens D500 X-ray diffractometer with Cu K_{α} radiation. The 2θ range of 0–90° was recorded at a rate of 0.02° 2θ /0.5 s. The crystal phases were identified by comparing the 2θ values and intensities and the thickness of the deposits was determined by an X-ray fluorescence spectrometer as $\approx 2 \mu\text{m}$.

The electrochemical behaviours of the electrodeposited Zn–Fe alloys were analysed in 3 wt% NaCl aqueous solution at room temperature in a Pyrex glass cell. The corrosion behaviours of the samples were investigated by a potentiodynamic polarization technique. Polarization measurements were performed with an electrochemical analyser/workstation (PARSTAT 2273) with a three-electrode configuration. The exposed areas of the specimens were about 1 cm². The specimens were embedded in a cold setting resin and immersed into the solution until a steady open circuit potential (ocp) was reached. After equilibration (45 min later), polarization was started at a rate of 1 mV/s. Composition of the AISI 4140 substrates is given in Table II.

TABLE II

Chemical composition of AISI 4140 low alloy steel [%].

Elem.	C	Mn	Si	Cr	Ni	Mo	V	S	Cu	P
wt%	0.36	0.80	0.005	0.914	0.30	0.85	0.075	0.07	0.143	0.034

3. Results and discussion

To determine the main characteristics of the zinc–iron alloy deposition process, the cyclic voltammetry technique was used. Figure 1 shows voltammetric diagrams of ZnFe deposition from coating bath. The scans were performed near open circuit potentials of the baths. The scans were initiated at near open circuit potentials. In solutions, during the forward scan towards the negative direction, as it is can be seen, there is a sharp increase at the cathodic current when the deposition starts. Without borax, deposition started at -1.18 V because of the dominance of the Zn deposition. In the anodic scan the broad peak at about -0.5 V can attribute to dissolution of pure Zn and/or Zn from the η phase (a solid solution of Fe in Zn with an hcp structure).

Cyclic voltammetry was used to define the major characteristics of the zinc deposition process. Figure 1 shows typical voltammograms for ZnFe alloy electrodeposition. The scans were initiated at $E = -400 \text{ mV}$. In solution without additive, during the forward scan towards the negative direction, the cathodic current increased sharply once Zn–Fe deposition began. The sign of a nucleation and growth process as current crossover is observed [19].

Figure 2 shows the XRD patterns of the electrodeposited $\text{Zn}_{1-x}\text{Fe}_x$ alloys, from electrolytic bath. The XRD analysis showed that electrodeposited samples have different crystal orientations among them because of

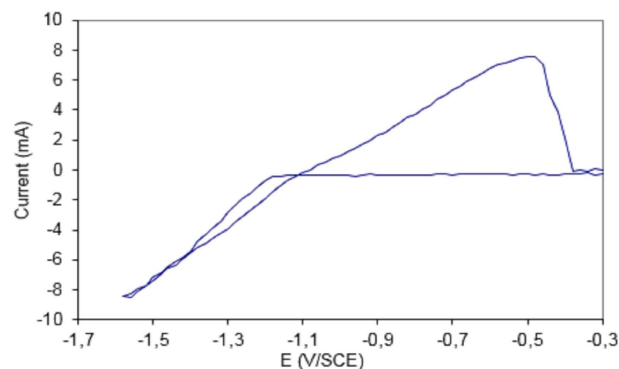


Fig. 1. Cyclic voltammogram for ZnFe alloy deposition.

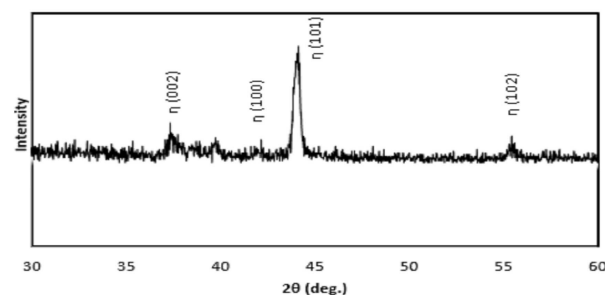


Fig. 2. XRD pattern obtained from Zn–Fe coating.

their polycrystalline structure. XRD peaks exhibit a preferred orientation along the (002), (100), (101), and (102) planes. The preferred crystal orientation of zinc electrodeposits depends on the experimental conditions such as current density, pH, and temperature. The Zn–Fe alloy coatings have the same structure as zinc [20], but with different crystallographic orientation, which is the consequence of the small iron amount. The phases of the electrodeposited Zn–Fe alloy are very complicated depending on the chemical compositions [21, 22]. The reflections of zinc-rich phase (JCP: 4-0831) [23] and a ζ phase are present in all investigated deposits. The electrodeposited Zn–Fe alloys have metastable structures and many phases coexist over a wide range of composition. Adaniya et al. reported that the phases of electrodeposited Zn–Fe alloys include: η phase (100–81% Zn), δ_1/γ phase (89–70% Zn), γ phase (87–48% Zn) and α phase (62–0% Zn) [24]. Only relative intensities of the two phases change among the deposited layers with different compositions. As the Zn content in the deposits increases the signals belonging to the η phase become more intense.

The surface morphology of the films was examined by SEM. The SEM micrograph is shown in Fig. 3. The Zn–Fe deposits obtained from the solution is well adherent to the steel substrate. It is observed that the deposits are generally composed of fine grains. The metallic luster and brightness of the deposit is related with presence of iron in alloy [25].

The infrared spectrum of polyaniline film synthesized on AISI 4140/ZnFe electrode is given in Fig. 4. The fundamental bands of polyaniline were found as follows:

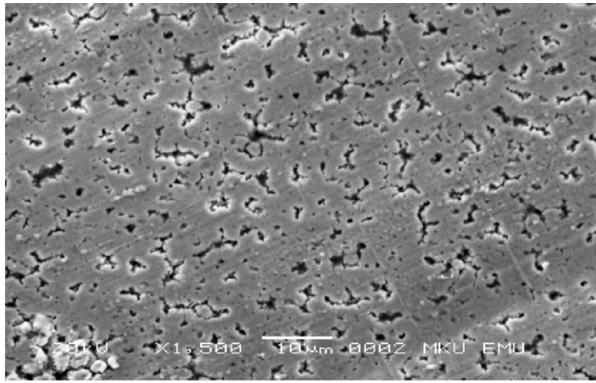


Fig. 3. SEM images of the Zn-Fe film.

the band located at 3354.4 cm^{-1} , which was the formation of PANI film corresponding to the characteristic NH stretching vibration. The presence of CH stretching in aromatic structure was demonstrated by the peaks at 3030.2 cm^{-1} . The band at 1597.6 cm^{-1} was related to quinoid ring unit while the presence of benzenoid ring was indicated by a band at 1495 cm^{-1} . The peaks at 1301.2 and 1237.4 cm^{-1} was due to CN stretching vibration. The band at 1071 cm^{-1} was represented as 1.4 branching of benzenoid ring.

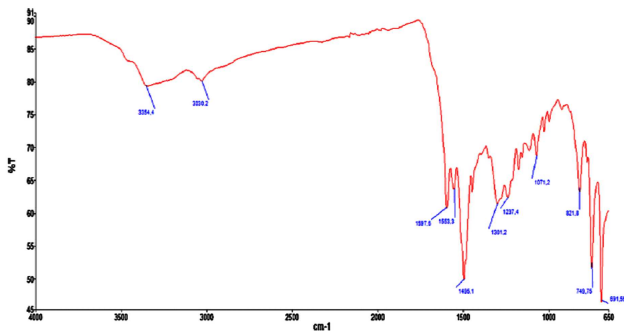


Fig. 4. The FTIR spectra for the PANI film.

Table III shows the corrosion performances obtained from the Tafel plots for all the used samples. It can be seen from the table that polyaniline film obtained from the current density of 0.1 mA/cm^2 is the most effective corrosion inhibition performance.

The corrosion velocity (mpy), corrosion potential (E_{CORR}) and corrosion current density (I_{CORR}) values calculated based on the Tafel extrapolation method are given in Table III. The E_{CORR} and I_{CORR} values of uncoated mild steel in 3.5% sodium chloride solution were found to be -802 mV and $17.8\text{ }\mu\text{A/cm}^2$, respectively. However, when the mild steel substrate was coated with ZnFe alloy the E_{CORR} and I_{CORR} values increased from -802 to -1161 mV and from $17.8\text{ }\mu\text{A/cm}^2$ to $87\text{ }\mu\text{A/cm}^2$. A coating of ZnFe/PANI decreased the E_{CORR} from -1161 to -1107 mV and the I_{CORR} from $87.1\text{ }\mu\text{A/cm}^2$. However, in the same coating system, when the current density of deposition was changed from 0.1 to 0.3 mA/cm^2 ,

TABLE III

Corrosion behaviour of uncoated 4140 steel and steel/ZnFe, steel/ZnFe/PANI coated mild steels in 3.5% sodium chloride solution evaluated by potentiodynamic polarization studies.

Sample	Current [mA/cm ²]	E ($I=0$) [mV]	I_{CORR} [μA]	β_{C} [mV]	β_{A} [mV]	Corrosion velocity [(mpy) $\times 1000$]
4140 steel	–	-802	17.8	59.5	167	5.3
steel/ZnFe	–	-1161	87.1	107	190	25.9
steel/ZnFe/aniline	0.1	-1107	77.0	53.3	63.4	22.9
steel/ZnFe/aniline	0.2	-1104	77.6	57.8	60.0	23.1
steel/ZnFe/aniline	0.3	-1056	78.38	93.2	34.2	23.3

E_{CORR} was observed (from -1107 to -1056 mV) and I_{CORR} values from 77 to $78.38\text{ }\mu\text{A/cm}^2$, respectively. When the metallic layer was coated with ZnFe alloy first and PANI layer was deposited over the metal layer, the corrosion resistance was found to be more protective (Table III). The observed behavior may be explained on the basis of the corrosion resistance offered by PANI layer deposited on mild steel substrate by a barrier layer mechanism.

4. Conclusion

In this study, polyaniline coating was successfully obtained by galvanostatic deposition on AISI4140/ZnFe electrode, applying cyclic voltammetry technique. Homogeneous and adherent polyaniline film was produced from 0.10 M aniline containing 0.30 M sodium oxalate solution. It was found that the passivation of ZnFe alloy surface was necessary for homogeneous polymer film synthesis prior to monomer oxidation and film growth. The single ZnFe alloy plating exhibited significant physical barrier behaviour on carbon steel. PANI coating provided an increase in corrosion resistance of CS/ZnFe electrode. The corrosion performance of AISI4140/ZnFe/PANI electrode improved the formation of ZnFe oxide layers and the reduction of PANI coating, by the catalytic behaviour of PANI film.

Acknowledgments

Financial support of this research by the Mustafa Kemal University Scientific Research Projects is gratefully acknowledged (MKU-BAP-52).

References

- [1] A. Brenner, *Electrodeposition of Alloys. Principle and Practice*, Academic Press, New York 1963, p. 152.
- [2] İ.H. Karahan, H.A. Çetinkara, H.S. Güder, *Trans. Inst. Met. Finish.* **86**, 157 (2008).
- [3] İ.H. Karahan, H.A. Cetinkara, *Trans. Inst. Met. Finish.* **89**, 99 (2011).
- [4] I.H. Karahan, *J. Mater. Sci.* **42**, 10160 (2007).

- [5] N. Kup Aylikci, V. Aylikci, A. Kahoul, E. Tirasoglu, I.H. Karahan, E. Cengiz, *Phys. Rev.* **84**, 042509 (2011).
- [6] I.H. Karahan, O. Karabulut, U. Alver, *Phys. Scr.* **79**, 055801 (2009).
- [7] A.T. Ozyilmaz, G. Kardas, M. Erbil, B. Yazıcı, *Appl. Surf. Sci.* **242**, 97 (2005).
- [8] R. Rajagopalan, J.O. Iroh, *Appl. Surf. Sci.* **218**, 58 (2003).
- [9] B. Sari, A. Gok, D. Sahin, *J. Appl. Polym. Sci.* **101**, 241 (2006).
- [10] X.G. Li, M.R. Huang, W. Duan, Y.L. Yang, *Chem. Rev.* **102**, 2925 (2002).
- [11] M. Morita, *Makromol. Chem.* **194**, 2361 (1993).
- [12] J. Heinze, *Synth. Met.* **41–43**, 2805 (1991).
- [13] J. Ochmanska, P.G. Pichup, *J. Electroanal. Chem.* **297**, 197 (1991).
- [14] T.E. Campbell, A.J. Hodgson, G. Wallace, *Electroanalysis* **11**, 215 (1999).
- [15] C.K. Tan, D.J. Blackwood, *Corros. Sci.* **45**, 545 (2003).
- [16] A. Yagan, N.O. Pekmez, A. Yildiz, *Electrochim. Acta* **51**, 2949 (2006).
- [17] M.A. Malik, M.T. Galkowski, H. Bala, B. Grzybowska, P.J. Kulesza, *Electrochim. Acta* **44**, 2157 (1999).
- [18] T. Kobayashi, H. Yoneyama, H. Tamura, *J. Electroanal. Chem.* **177**, 293 (1984).
- [19] S. Fletcher, *Electrochim. Acta* **28**, 917 (1983).
- [20] R. Fratesi, G. Lunazzi, G. Roventi, in: *Organic and Inorganic Coatings for Corrosion Prevention*, Vol. 20, Eds. L. Fedrizzi, P.L. Bonora, The Institute of Materials, London 1997, p. 130.
- [21] V.B. Miskovic-Stankovic, J.B. Zotovic, Z. Kacarevic-Popovic, M.D. Maksimovic, *Electrochim. Acta* **44**, 4269 (1999).
- [22] J.B. Bajat, Z. Kacarevic-Popovic, V.B. Miskovic-Stankovic, M.D. Maksimovic, *Prog. Org. Coat.* **39**, 127 (2000).
- [23] *Powder Diffraction File*, Inorganic Volume PD/S 5iRB, Sets 1–5, American Society for Testing and Materials, Philadelphia, PA 1969.
- [24] T. Adaniya, T. Hara, M. Sagiyama, T. Homa, T. Watanabe, *Plat. Surf. Finish.* **72**, 52 (1985).
- [25] I.H. Karahan, *Chin. J. Phys.* **46**, 105 (2008).