coatings

Article

Structural Properties of Zn-Fe Alloy Coatings and Their Corrosion Resistance

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Abstract: Single-layer and multilayer alloy deposits were coated onto a mild steel substrate by a single-bath electroplating process. The developed coating consists of Zn and Fe alloys having different compositions with different layers. The anticorrosion behavior of single-layer and multilayer deposits was evaluated by the potentiodynamic polarization method. The surface morphology of the deposits was studied with a scanning electron microscope. The crystal structure of the deposits was analyzed with the X-ray diffraction technique. The Fe content in the deposit was analyzed by a colorimeter and verified with energy-dispersive X-ray spectroscopy. The micro-hardness tester with a Vickers indenter was used to evaluate the microhardness of the developed single-layer and multilayer coatings. It was found that the microhardness increased with applied current densities. The Zn-Fe multilayer coatings with 300 layers deposited with square and triangular pulses at the applied current density of 2.0/3.0 A dm^{-2} were five and four times more corrosion-resistant, respectively, than the single-layer coating of the same thickness. The development of Zn-Fe coatings that are resistant to corrosion is particularly important for the automotive industry and steel-based vehicle parts.

Keywords: electrodeposition; corrosion; surface morphology

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Citation: Bhat, R.S.; Balakrishna, M.K.; Parthasarathy, P.; Hegde, A.C. Structural Properties of Zn-Fe Alloy Coatings and Their Corrosion Resistance. *Coatings* **2023**, *13*, 772. https://doi.org/10.3390/coatings13040772

Academic Editors: Alina Vladescu and Ludmila B. Boinovich

Received: 28 February 2023
Revised: 3 April 2023
Accepted: 10 April 2023
Published: 15 April 2023

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1. Introduction

Electroplating is one of the low-cost and widely used techniques for the preparation of alloy coatings. The electroplating technique is relatively easy, simple, fast, and productive compared to other techniques. For certain systems, electroplating is the only method of preparation. Electroplating improves surface properties by enhancing the hardness and resistance to corrosive environments [1,2]. This method is largely used for industrial applications such as automobiles, electronics, aerospace, defense, decorative, etc.

In the past fifteen years, a number of researchers have given multilayer coatings a great deal of attention, generally because of their electrochemical, physical, and/or improved mechanical properties. Additionally, the ability to modify the structures of the materials to meet the requirements of specific mechanical, optical, and electrochemical applications has expanded the design flexibility of materials. Multilayer coatings, on the other hand, normally require a large number of parameters, viz., structural, chemical periodicity, morphology, and roughness, to be determined in order to characterize their structure in detail [2–4]. Zinc alloys with nickel, cobalt, and other deposits exhibited superior corrosion protection compared to zinc plating [4–7]. An electroplated zinc–nickel alloy in an acidic bath with a Ni concentration of 12% to 16% exhibited the maximum corrosion resistance [8].

Nanostructured materials are one of the potential materials for modern technologies because of their superior properties compared to their bulk counterpart and have applications in aerospace, machining, automotive industries, etc. Compositionally modulated multilayer alloys are included in this category of materials. These multilayer alloy deposits comprise very thin sub-layers of various metals or alloys with an ultrafine microstructure organized in an alternating pattern, with a thickness of a few micro-meters. Nanostructured multilayer coatings can have exceptional and unique characteristics not found in regular metallurgical alloys. The formation of thin films by the sputtering technique yields good mechanical properties [9,10]. The synthesis of thin film coatings by an electrochemical method delivers better structural, strength, and corrosion properties [11,12].

Multilayer coatings (MLCs) have recently attracted the interest of numerous researchers, owing to their increased mechanical, electrochemical, and physical properties [3,13–15]. Additionally, the ability to alter the edifice of supplies to meet specific mechanical and electrochemical applications has expanded the design of materials. For a thorough assessment of the structure of multilayer coatings, however, a number of characteristics, such as the structural, surface, and interface roughness, as well as the sub-layer coherency, must normally be determined [16]. These multilayer alloy coatings are prepared by a new technique, the single bath technique (SBT), which is gaining much interest because it exhibits superior corrosion properties [17–21]. From the literature, it is indicated that there is not much work that has been reported concerning the deposition optimization of multilayer deposits to produce nanostructured multilayer deposits for superior corrosion resistance (CR). The current work reports the optimization of the cyclic cathode current densities (CCCDs) and the number of layers of Zn-Fe multilayer alloy plating applying different current pulses for better corrosion resistance using the single bath technique (SBT). The enhanced anti-corrosion characteristics of the multilayer deposits were deliberated in terms of the hardness, roughness, and surface topography of the deposit.

2. Experimental

2.1. Materials

Analytical-grade chemicals, namely zinc sulphate, ferric sulphate, sodium chloride, citric acid, sodium acetate, and thiamine hydrochloride, were purchased from Merck (Sri Durga Laboratory chemicals Supplies, Mangalore, (Karnataka), India).

2.2. Materials' Preparation and Characterization

A commercial-grade mild steel (MS, Hi-Tech Agencies Mangalore, (Karnataka), India) sample 3 cm × 2 cm in size was used as a cathode and the same area of zinc was used as an anode. Surface polishing of the sample was performed with fine-grade sandpaper of grit sizes 100, 400, 800, and 1200, followed by cleaning with double-distilled water and organic solvent trichloroethylene and then drying. The bath or electrolytic solutions were prepared using analytical-grade chemicals and deionized water. The pH of the electrolyte was maintained at 4 by using dilute sulfuric acid, and the temperature of the electrolyte was maintained at 30 °C. Using a typical Hull cell allowed for the optimization of the bath constituents. The single-layer (SL) and multilayer electrodeposition used a polyvinyl chloride cell of a capacity of 100 mL with a cathode and anode distance of 5 cm. A pure Zn plate (Hi-Tech Agencies Mangalore, (Karnataka), India) 6 cm^2 in size was used as an anode and a mild steel substrate of the same surface area was used as a cathode. All the depositions were carried out by the galvanostatic method using a DC power source (Keysight Technologies India Private Limited, Bangalore, (Karnataka), India). The surface brightness of the electrodeposition was improved by using thiamine hydrochloride. The bath pH was maintained with a buffer solution (Citric acid), and the conductivity of the bath was increased with sodium acetate. The chemical configuration of the electroplating baths and the electroplating conditions are given in Table 1.

Table 1. The deposition parameters of the single-layer and multilayer coatings.

Bath Configuration	Concentration (g L^{-1})	Working Parameters
$ZnSO_4 \cdot 7H_2O$	50	pH: 4.0 Temperature: 30 °C Anode: Zinc Current density (CD): 3.0 A dm^{-2}
$Fe_2 (SO_4)_3 \cdot H_2O$	20	
$CH_3COONa \cdot 3H_2O$	60	
$C_{12}H_{17}N_4OSCl \cdot HCl$	0.5	
$C_6H_8O_7 \cdot H_2O$	4.0	

The electrochemical characteristics of the electrodeposition were studied by an electrochemical impedance spectroscopy (CH Instruments, Inc., Austin, TX, USA) and potentiodynamic polarization processes (CH Instruments, Inc., Austin, TX, USA). The potentiostat consists of a three-electrode cell used to carry out the electrochemical test. Electroplated mild steel, platinum, and calomel were used as working, counter, and reference electrodes, respectively. As a corrosive environment, a solution of 3.5% sodium chloride was utilized. The potentiodynamic polarization investigations were performed at a scan rate of 0.1 mVs^{-1}, and the open circuit potential (OCP) varied between −0.200 mV and +0.200 mV. The corrosion data were obtained with the potentiodynamic polarization technique [2]. While measuring impedance, sinewaves with 10 mV voltage and a 1 h exposure duration were used with a frequency range between 100 kHz and 20 MHz. The surface and cross-sectional analysis of the deposit after the corrosion test were performed with the scanning electron microscopy (SEM, JEOL JSM-6380 LA, Akishima, Tokyo, Japan) technique. The surface roughness of the Zn-Fe alloy coatings was evaluated with atomic force microscopy (AFM, Nanosurf Flex AFM, Liestal, Switzerland). The hardness of single-layer and multilayer electroplating was determined using a Vickers microhardness tester (Clemex Tech USA Corp., Fenton, MI, USA). The compositions of the deposits were evaluated with a colorimetric technique (Digital-Photoelectric-Colorimete, Systronics, Ahmedabad, (Gujarat), India). Knowing the mass and composition of the deposit allowed for the percentage of cathode current efficiency (%CCE) of the electroplating to be computed [22].

The electrodeposition of Zn-Fe single-layer and multilayer was done with the same deposition conditions except for the current densities. Further, single-layer and multilayer coatings were developed with square and triangular current pulses (Figure 1). The compositions of the single-layer and multilayer deposits can be determined as $(Zn\text{-}Fe)_{1\_2\_n}$, where 1 and 2 denote two changed CDs of the cathode, and n corresponds to the number of layers deposited during the deposition process of 10 min duration.

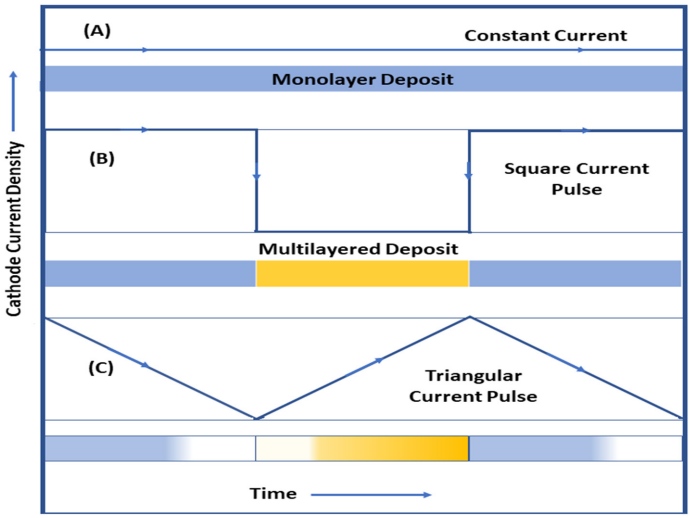

Figure 1. Graphical depiction of waveforms of single-layer (**A**) multilayer using square (**B**) and triangular current pulses (**C**).

3. Result and Discussion

3.1. X-ray Diffraction (XRD) Analysis

The XRD method (Bruker, AXS), using Cu Kα-radiation, (λ = 1.5405 Å, 30 kV, (JDX-8P JEOL, Rigaku, Tokyo, Japan) was used to examine the phase structure of single-layer Zn-Fe alloy coatings. The resulting X-ray diffractogram is displayed in Figure 2. The position of the intensity peaks remained constant for all coatings regardless of the CD at which they were deposited, while the intensity peak increased with CD. XRD patterns of all alloy coatings have constant diffraction angles, which suggests that the coatings are the solid solution of the component metals [23]. The CR of Zn-Fe alloy depends practically on the wt. % Fe in the deposit, and consequently, its phase structure depends on the CDs employed for its electroplating [24]. Hence, an actual modulation of composition can be achieved by the successive layering of alloys having distinct phase differences by proper selection of CCCDs. This was confirmed by taking the XRD patterns of a Zn-Fe alloy (single-layer) developed from the same bath at two different current densities (2.0 A dm^{-2} and 5.0 A dm^{-2}). Therefore, the structural properties of the alloys plated at various CDs can be used as a tool for modulation of composition. The XRD patterns of the Zn-Fe alloy, shown in Figure 2, evidence that the phase structures of the alloy at two different CDs are different. It can be observed that depending on the CDs at which they are plated, the relative intensity corresponding to Zn (100), (101), and (110) greatly varies among the deposited coatings [3].

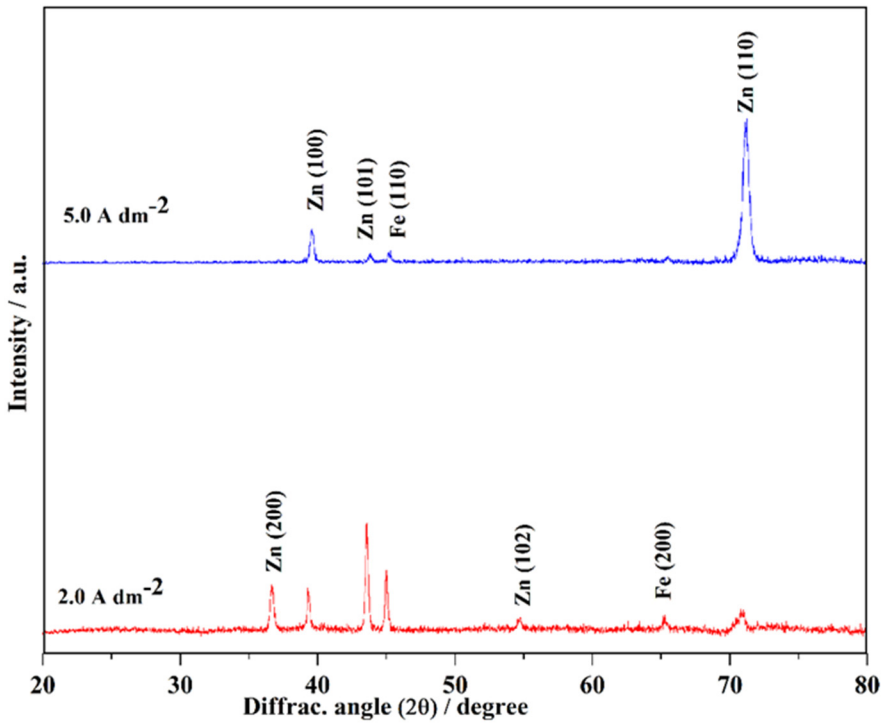

Figure 2. X-ray diffraction profiles of Zn-Fe alloy electroplate on MS developed from the optimized bath at i = 3.0 and 5.0 A dm^{-2}.

Moreover, as illustrated in Figure 2, the Zn-Fe alloy exhibits three significant peaks at 2.0 A dm^{-2}, which correspond to Zn (200), Zn (100), and Zn (101), but only two major peaks at 5.0 A dm^{-2}, which correspond to Zn (110) and Zn (100). This implies that the improved corrosion resistance of lamellar coatings is due to Zn-Fe alloy layers deposited at 2.0 and 5.0 A dm^{-2}, which validate different phase configurations.

3.2. Zn-Fe Single-Layer Coating

The deposition of the Zn-Fe alloy on the MS samples was carried out with a galvanostatic mode electrodeposition process with different current densities. The Fe contents

and anti-corrosion properties of the deposits were determined and are shown in Table 2. Table 2 indicates that Fe content increases with applied current densities. The deterioration resistance of the deposits rises with the Fe content of the coatings up to a particular current density, and at higher current densities, deterioration resistance declines; this may be due to the highly porous deposition. The bath follows anomalous co-deposition for the range of CDs (1.0 A dm^{-2} to 5.0 A dm^{-2}) [25,26]. At the optimal current density, i.e., 3 A dm^{-2}, the coating had a bright and uniform deposition and showed the minimum corrosion rate (2.30×10^{-2} mm y^{-1}). The thickness (x) and hardness of the electroplating increased with applied current densities (Table 2). The increased thickness with CD may be due to the metal hydroxide deposited at the cathode due to the evolution of hydrogen (increase in pH). This is because a higher current density has a higher rate of deposition [27,28]. The hardness of the deposit increased with Fe content (Table 2); this may be due to the high density of Fe in comparison to Zn content. However, at high CD, the deposit was dense, hard, and porous because of the metal hydroxide deposition brought on by the release of hydrogen during the electroplating [29]. This can be attributed to the Zn and Fe in the coating by inherent high density (d_{Zn} = 7.14 g cm^3 and d_{Fe} = 7.87 g cm^3). However, the coating became thick and porous and lost hardness at very high CD. At high CD, a thick and porous deposit was obtained, which is due to the development of metal hydroxide because of the fast release of hydrogen during the coating. The cathodic current efficiency (%CCE) of the bath was determined to be high, or >85%, for all deposition conditions. Table 2 shows that the %CCE somewhat decreased with the increased current density; this may be because of the high evolution of hydrogen during plating [5].

Table 2. Effect of current density on wt. % Fe, hardness, thickness, and corrosion resistance of the coating.

i (A dm^{-2})	Wt. % Fe	%CCE	x (μm)	HV_{500}	i_{corr} (μA cm^{-2})	$-E_{corr}$ (V) vs. SCE	CR × 10^{-2} (mm y^{-1})
1.0	2.13	86.1	7.3	142	12.26	1.259	12.40
2.0	2.75	89.3	10.5	165	6.063	1.240	8.51
3.0	3.67	93.5	15.9	177	1.556	1.233	2.30
4.0	4.99	89.5	17.7	191	3.972	1.237	5.80
5.0	7.86	87.3	22.1	207	8.023	1.259	11.70

3.3. Multilayer Zn-Fe Alloy Coatings

Zn-M (M = Ni, Co, and Fe) multilayer coatings can undergo significant modifications in response to even slight variations in the concentration of metallic ions. Prabhu Ganesan et al. deposited Zn-Fe alloy by galvanostatic approach from SBT [2], where the Fe content varied by applying a change in CD as function of the thickness of the deposit. With this opportunity, the modulation of Zn-Fe multilayer deposits was tried by means of different +9current pulses, such as triangular and square, was performed. Precise control of cyclic cathode current densities (CCCDs) has allowed to develop a Zn-Fe multilayer coatings with various compositions and, therefore, various properties. The main prerequisite for better characteristics in multilayer materials is clear layer demarcation without interlayer diffusion. Different sets of CCCDs were tested to determine the right combinations of barrier and sacrificial protection in alternate layers to give extended protection to the base material (MS) against corrosion. When choosing a larger number of layers, CCCDs should be carefully chosen. To begin with, both square and triangular current pulses were used to build the coating with only 10 layers. Among the various sets tried, the lowest corrosion rate was measured in the coatings formed at the difference of 2.0 A dm^{-2} and 3.0 A dm^{-2} between CCCD, and the corrosion rates are shown in Table 3. These coatings, which have been chosen to evaluate the effect of stacking between the CCCD of 2.0 and 5.0 A dm^{-2},

were revealed to be consistent, smooth, and more corrosion-resistant. Table 4 indicates that the multilayer (square and triangular) coatings having 60, 120, and 300 layers exhibit improved corrosion resistance behavior compared to the single-layer (Table 2) coating. The weight % of Fe content in the depost at 3.0 and 5.0 A dm^{-2} was found to be 3.67 and 7.86, and at 2.0 and 5.0 A dm^{-2} was found to be 2.75 and 7.86, respectively. Thus, the same values were taken as optimal CCCDs to produce Zn-Fe multilayer coatings. The fact that the $(Zn\text{-}Fe)_{2.0\_5.0\_10}$ arrangement has the highest corrosion resistance (CR) shows that its layers have the best composition.

Table 3. Corrosion rates of multilayer coatings, having 10 layers each, developed using square and triangular current pulses at different sets of CCCDs.

CCCDs (A dm^{-2})	$-E_{corr}$ (V) vs. SCE	i_{corr} (μA cm^{-2})	CR × 10^{-2} (mm y^{-1})
Multilayer films developed at the change of 2.0 A·dm^{-2} among CCCDs			
$(Zn\text{-}Fe)_{3.0\_5.0\_10\_square}$	1.160	4.49	6.63
$(Zn\text{-}Fe)_{3.0\_5.0\_10\_triangular}$	1.157	4.95	7.21
$(Zn\text{-}Fe)_{2.0\_4.0\_10\_square}$	1.159	5.04	7.32
$(Zn\text{-}Fe)_{2.0\_4.0\_10\_triangular}$	1.610	5.24	7.63
Multilayer films developed at the change of 3.0 A·dm^{-2} among CCCDs			
$(Zn\text{-}Fe)_{2.0\_5.0\_10\_square}$	1.167	4.33	6.36
$(Zn\text{-}Fe)_{2.0\_5.0\_10\_triangular}$	1.147	3.70	5.39
$(Zn\text{-}Fe)_{1.0\_4.0\_10\_square}$	1.151	4.52	6.64
$(Zn\text{-}Fe)_{1.0\_4.0\_10\_triangular}$	1.710	5.01	7.36

Table 4. Corrosion properties of multilayer coatings with square and triangular current pulses.

(CCCDs) (A dm^{-2})	Layers	VH_{500}	$-E_{corr}$ (V) vs. SCE	i_{corr} (μA cm^{-2})	CR × 10^{-2} (mm y^{-1})
$(Zn\text{-}Fe)_{2.0\_5.0\_square}$	10	117	1.166	5.333	7.34
	20	122	1.185	3.126	4.51
	60	135	1.035	1.285	1.93
	120	141	1.217	0.670	0.95
	300	155	1.225	0.331	0.46
	600	161	1.167	1.558	2.35
$(Zn\text{-}Fe)_{2.0\_5.0\_triangular}$	10	116	1.156	3.72	5.35
	20	124	1.157	2.41	3.53
	60	132	1.156	1.13	1.60
	120	140	1.131	0.75	1.05
	300	149	1.212	0.37	0.53
	600	157	1.116	1.86	2.68

The multilayer coatings formed at a combination of 2.0 and 5.0 A dm^{-2} were determined to be the best (Table 3) and exhibited the lowest i_{corr} values among the various sets of CCCDs tested. This combination of CDs was chosen to produce multilayer alloy coatings with 10, 20, 60, 120, 300, and 600 layers, and their corrosion properties were investigated. Table 4 reports the corrosion properties of multilayer alloy deposition with several layers. It was found that the corrosion rates of the coating films decreased up to 300 layers and then increased (Table 4). The multilayer coatings were developed at the CDs of 2.0, and

5.0 A dm^{-2} with a square current pulse (SCP) and triangular current pulse (TCP) exhibited the lowest corrosion rate of 0.46 × 10^{-2} mm y^{-1}, and 0.53 × 10^{-2} mm y^{-1}, respectively, relative to that of the single-layer coating (2.30 × 10^{-2} mm y^{-1}).

Further, an attempt to improve the corrosion rate increased the coating layers up to 600 layers in each combination of CCCDs, leading to an increase in the corrosion rate of the multilayer deposit, as shown in Table 4. The rise in the corrosion rate with a higher number of layers (e.g., 600 layers) of the multilayer coating is due to the shorter reduction time for the redistribution of ions (Zn^{2+} and Fe^{2+}) in the diffusion layer (tends to become a single-layer coating) [1,2]. Therefore, the modulation in the composition is not likely to happen at higher step of layering. In other words, multilayer coatings tend to become single-layer coatings showing less corrosion resistance. Because of interlayer diffusion, a multilayer coating having 600 layers and a Zn-Fe single-layer alloy coating at 3.0 A dm^{-2} both have almost the same CR. The corrosion properties of the single-layer, multilayer square, and triangular current pulses are given in Table 5.

Table 5. The corrosion rate of the single-layer and multilayer alloy coatings.

Coating Configuration	E_{corr} (V) vs. SCE	i_{corr} (μA cm^{-2})	CR × 10^{-2} (mm y^{-1})
Single-layer $(Zn\text{-}Fe)_{3.0}$	−1.2335	1.556	2.30
MLC $(Zn\text{-}Fe)_{2.0\_5.0\_300\_square}$	−1.2132	0.331	0.46
MLC $(Zn\text{-}Fe)_{2.0\_5.0\_300\_triangular}$	−1.1756	0.370	0.53

The potentiodynamic polarization behavior of multilayer coatings of $(Zn\text{-}Fe)_{2.0\_5.0\_300\_square}$ and $(Zn\text{-}Fe)_{2.0\_5.0\_300\_triangular}$ in comparison with that of the single-layer coating $(Zn\text{-}Fe)_{3.0}$ is shown in Figure 3. Consequently, the $(Zn\text{-}Fe)_{2.0\_5.0\_300\_square}$ was obtained as best multilayer coating for the highest corrosion efficacy.

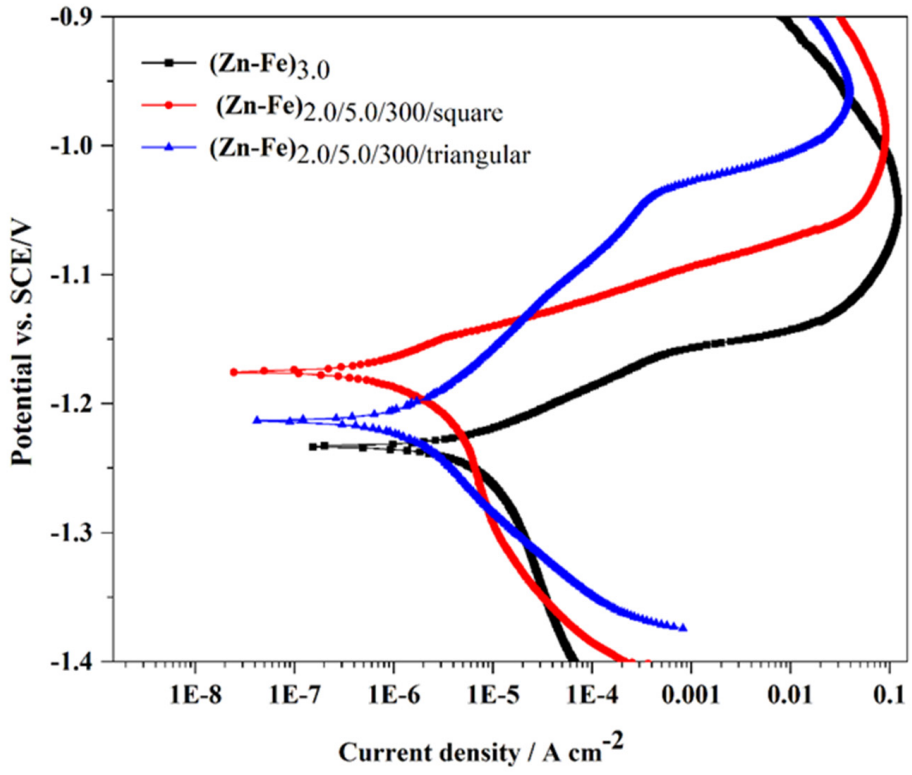

Figure 3. Potentiodynamic polarization curves of SL and ML alloy deposits.

3.4. Corrosion Analysis

3.4.1. Potentiodynamic Polarization Analysis

The corrosion properties of the single-layer and multilayer square and triangular current pulses are given in Table 5 and show that multilayer Zn-Fe coatings have higher corrosion resistance than single-layer Zn-Fe coatings made in the same optimum bath. This is because nanostructured multilayer coatings with micron-sized grain formations have enhanced material characteristics. The corrosion rate in square and triangular current pulses reduces as the overall number of layers increases. The number of contacts between two different compositions thus becomes important for the increased corrosion resistance. The potentiodynamic polarization behavior of multilayer coatings of $(Zn\text{-}Fe)_{2.0\_5.0\_300\_square}$ and $(Zn\text{-}Fe)_{2.0\_5.0\_300\_triangular}$ in comparison with that of the single-layer coating $(Zn\text{-}Fe)_{3.0}$ is shown in Figure 2. The corrosion potential (E_{corr}) values shift towards the anodic side (a potential with less negative value) when comparing a single-layer coating to a multilayer coating, indicating that the multilayer coating has a passivated or nobler behavior [30].

Table 5 indicates that multilayer coatings exhibit superior corrosion-resistant characteristics than single-layer coatings. Further, the corrosion resistance of the multilayer $(Zn\text{-}Fe)_{2.0\_5.0\_300\_square}$ and multilayer $(Zn\text{-}Fe)_{2.0\_5.0\_300\_triangular}$ coatings exhibit about five and four times more CR than the SL $(Zn\text{-}Fe)_{3.0}$ alloy coating, respectively. It must be noted that compared to single-layer coatings, both multilayer coatings are more corrosion-resistant. With both types of current pulses, the protective capacity rises with the number of layers.

No significant variation in the corrosion rates of multilayer coatings was found, whether the modulation of the composition was sharp or gradual. A comparative account of the protective efficacy of multilayer coatings deposited with square and triangular current pulses in comparison with that of a single-layer coating of the same thickness is given by the histogram shown in Figure 4.

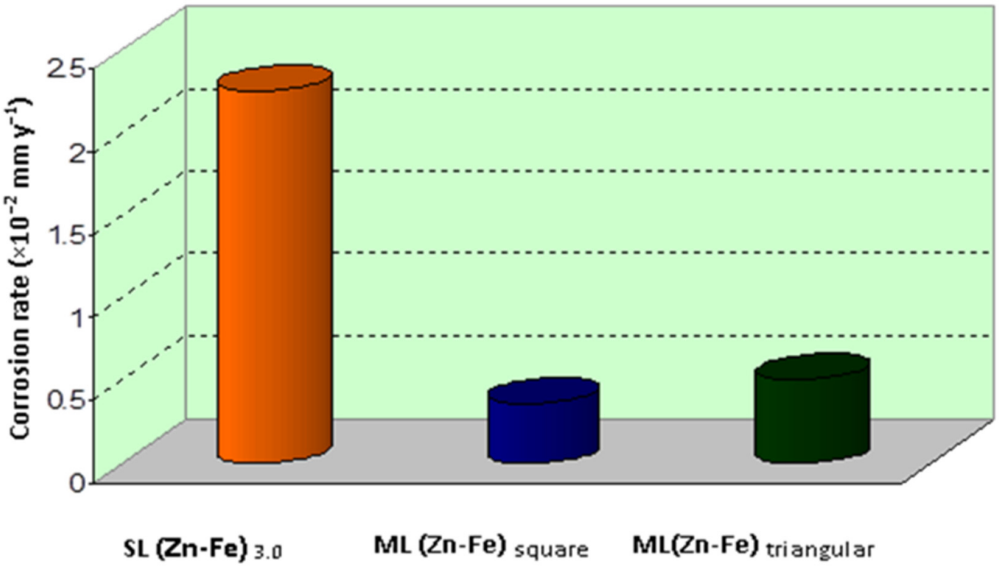

Figure 4. Relative analysis of corrosion rate of single-layer and ML alloy films.

3.4.2. Electrochemical Impedance Spectroscopic (EIS) Analysis

One of the effective methods for researching the electrochemical characteristics of materials is the EIS approach. With this method, a small-amplitude AC signal is used to study the impedance behavior [31,32]. The transfer of electrons occurs at the electrode surface during electrochemical processes. These reactions generally involve mass transfer from the bulk solution to the electrode surface, charge transfer at the electrode surface, electrolyte resistance, and adsorption of electroactive species. The electrochemical mechanism occurring at the substrate–coating interface may explain why multilayer coatings exhibit

superior corrosion resistance than single-layer alloys, i.e., between MS and the corrosive media [24]. The double-layer capacitance behavior of the coatings plays a major role in the enhanced corrosion resistance of single-layer and multilayer coatings. Figure 5 displays the impedance behavior of single-layer and multilayer coatings deposited with square and triangular pulses. The multilayer coatings are associated with larger semicircle capacitive loops likened to SL deposits, which indicates the better CR of the coatings. With many layers, corrosion is prevented by the subsequent layers sealing the pores of the first layer. Alternating layers of alloys with low and high wt% Fe in multilayer coatings also contribute to increased corrosion resistance [33,34].

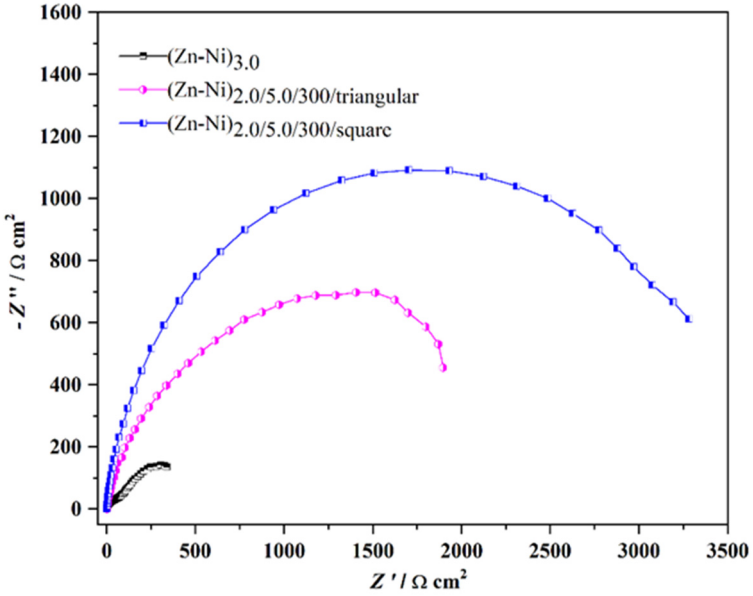

Figure 5. Electrochemical impedance spectra of single-layer and multilayer coatings.

3.4.3. Surface Analysis

Figure 6a shows the surface topography of Zn-Fe single-layer electroplating, which is bright, homogeneous, and has larger grain sizes. The electroplating was subjected to a corrosion investigation at ±200 mV vs. OCP in 3.5% NaCl solution to investigate the corrosion mechanism.

The corroded sample was then cleaned with deionized water and observed using scanning electron microscopy (SEM). The surface morphology of the Zn-Fe coating deposited at the CD 3 A dm^{-2}, exhibiting the surface enclosed with the deterioration product, is given in Figure 6b. Pits must have been caused by an area of the oxidation products that was separated from the coated surface during corrosion. This indicates that the corrosion followed the selective dissolution of low wt. % of Fe in the alloy coating. The surface structure of multilayer deposits (square and triangular) is given in Figure 6a,b, and is found to have uniform, crack-free, and bright surfaces compared with single-layer (Figure 6a) deposits. In square current pulse, the surface is found to be uniform, smaller grain size, and without any pores (Figure 7a), but in triangular current pulses, the surface is found to be uniform with a larger grain size of the deposit (Figure 7b).

The surface morphology of multilayer coating by square pulse is better than that of triangular pulse coatings due to the smoothness (based on the grain size) of the coating films. The development of sequential layers with different properties was confirmed by the cross-sectional image of multilayer coatings $(Zn\text{-}Fe)_{2.0/5.0/20/square}$ and $(Zn\text{-}Fe)_{2.0\_5.0\_20\_triangular}$, as shown in Figure 8a,b, respectively.

The lack of disparity in the cross-sectional images of multilayer coatings may be caused by the small change in Fe content in the different layers [35,36]. The white layer shown in Figure 8a,b at the intersection of the metal and multilayer coating is attributed to

the scattering of electrons due to the alumina-based suspension used while polishing the SEM specimen. Figure 9 shows the surface topography of a five-layer corroded multilayer, expressed as $(Zn\text{-}Fe)_{2.0\_5.0\_5.0\_square}$ and $(Zn\text{-}Fe)_{2.0\_5.0\_5.0\_triangular}$ (for better differentiation). By analyzing the surface microscopic structure, it is possible to comprehend the mechanism of corrosion and potential reasons for greater corrosion resistance. The possibility of high corrosion efficacy is due to the fact that the alloy film with one form of failure (such as pores or fissures) from electroplating at one CD is covered sequentially by an alloy film with a different type of failure, and thus, corrosion prevention is high (due to the electroplating at the other CD) [23,36].

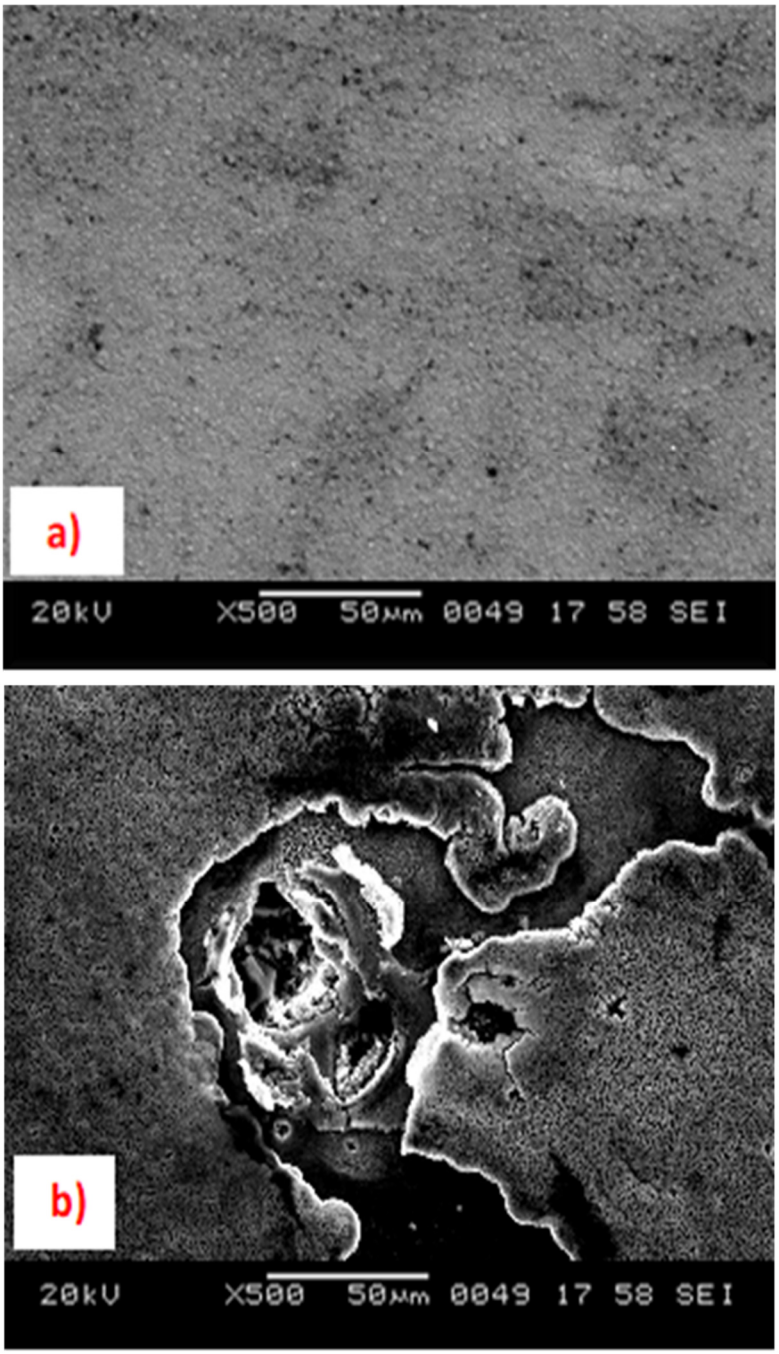

Figure 6. Surface topography of single-layer Zn-Fe alloy electroplating (**a**); the surface after corrosion test (**b**).

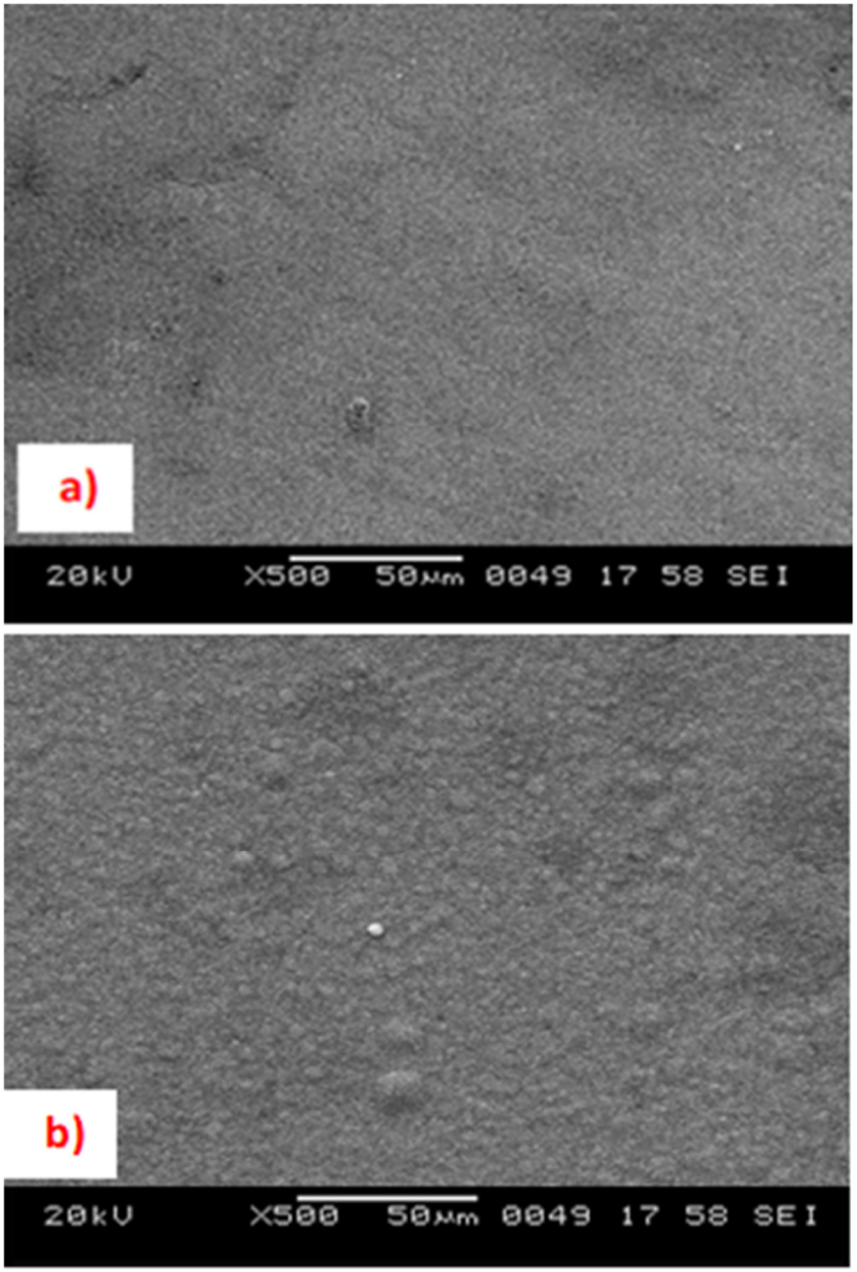

Figure 7. Surface topography of Zn-Fe multilayer coatings by the square (**a**) and triangular (**b**) current pulses.

Because the coatings have multiple layers with varying degrees of failure, the corrosion agent's path is obstructed. This is why multilayer coating takes longer than single-layer coating for the corrosive chemical to pass through coating flaws and into the substrate material. So, the path of the corrosive chemical is either lengthened or blocked. In the multilayer coatings formed during corrosion, the Zn-Fe alloy film with a lower wt. % of Fe underneath a top layer with a higher wt. % of Fe dissolves through pores and microcracks. The blockade effect of the Zn-Fe film, which has a high wt. % of Fe, and the sacrificial effect of the Zn-Fe film, which has a lower wt. % of Fe, can both be used to explain the protection effectiveness of multilayer coatings [36].

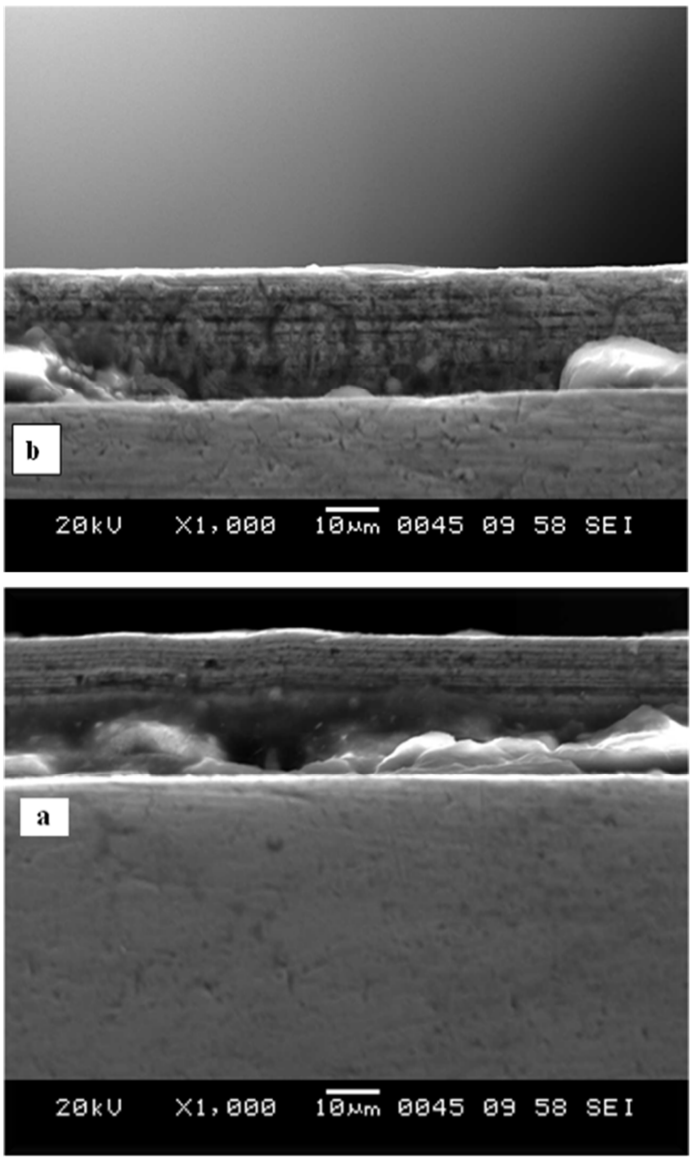

Figure 8. Cross-sectional images of multilayer Zn-Fe deposits with square (**a**) and triangular (**b**), pulses.

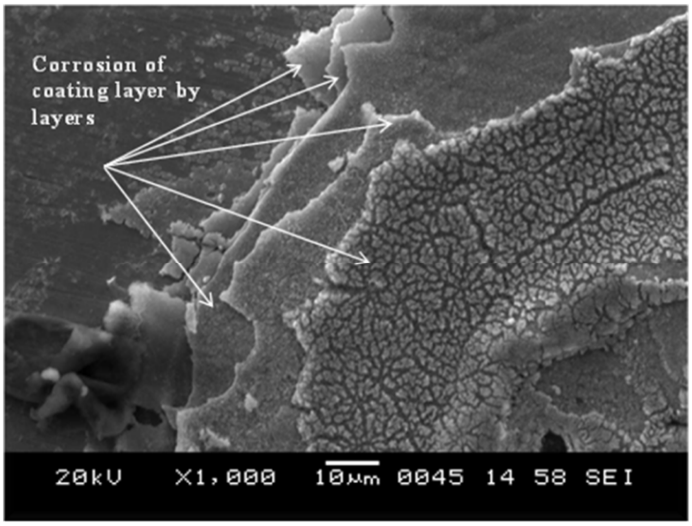

Figure 9. SEM image of multilayer electroplating after the corrosion analysis: $(Zn\text{-}Fe)_{3/5/4/square}$.

4. Conclusions

The multilayer Zn-Fe coatings were formed using single bath technique (SBT) with different current pulses namely square and triangular, and their corrosion behaviors were examined. With all types of current pulses, the corrosion resistance of multilayer coatings increased with an increase in the layers up to 300 and then decreased. The significant progress in the resistance towards corrosion of Zn-Fe multilayer coatings are attributed to sharp changes in the composition of alternate layers due to sharp changes in current densities observed in square current pulses, and gradual changes in the composition of different layers due to gradual changes in current densities observed in triangular current pulses during deposition. In ideal conditions, the multilayer coatings formed using square and triangular current pulses were found to be five and four times more corrosion-resistant than single-layer coatings of the same thickness. The formation of multilayer coatings was confirmed by SEM images. The enhanced protection of the multilayer is due to the blockage of pores by the successive layers.

Author Contributions: R.S.B.: Conceptualization, methodology, formal analysis, investigation, writing—original draft preparation, funding acquisition, M.K.B.: resources, data curation, software, validation, visualization. P.P.: Writing—review and editing, project administration. A.C.H.: Supervision, writing—review & editing, visualization. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: As per the request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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