

MARCH 2023

Ph.D. in Engineering Physics

CEMİL AKDOĞAN

**REPUBLIC OF TÜRKİYE
GAZİANTEP UNIVERSITY
GRADUATE SCHOOL OF NATURAL & APPLIED SCIENCES**

**ANALYSIS OF THE MICROSTRUCTURE AND CORROSION
BEHAVIOUR OF ELECTRODEPOSITED FE AND FE ALLOYS**

**Ph.D. THESIS
IN
ENGINEERING PHYSICS**

**by
CEMİL AKDOĞAN
MARCH 2023**

**ANALYSIS OF THE MICROSTRUCTURE AND CORROSION
BEHAVIOUR OF ELECTRODEPOSITED FE AND FE ALLOYS**

**Ph.D. Thesis
in
Engineering Physics
Gaziantep University**

**Supervisor
Prof. Dr. Ömer F. BAKKALOĞLU**

**Co-Supervisor
Prof. Dr. Mustafa ÖZTAŞ**

**by
Cemil AKDOĞAN
March 2023**



©2023[Cemil AKDOĞAN]

**ANALYSIS OF THE MICROSTRUCTURE AND CORROSION
BEHAVIOUR OF ELECTRODEPOSITED FE AND FE ALLOYS**

submitted by **Cemil AKDOĞAN** in partial fulfilment of the requirements for the degree of Doctor of Philosophy in **Engineering Physics, Gaziantep University** is approved by,

Prof. Dr. Mehmet İshak YÜCE
Director of the Graduate School of Natural and Applied Sciences.....

Prof. Dr. Ramazan KOÇ
Head of the Department of Engineering Physics

Prof. Dr. Ömer F. BAKKALOĞLU
Supervisor, Engineering Physics
Gaziantep University

Prof. Dr. Mustafa ÖZTAŞ
Electrical and Electronics Engineering
Yalova University

Exam Date: 09 March 2023

Examining Committee Members:

Prof. Dr. Ömer F. BAKKALOĞLU
Thesis Supervisor, Engineering Physics
Gaziantep University

Prof. Dr. Metin BEDİR
Engineering Physics
Gaziantep University

Prof. Dr. İsmail H. KARAHAN
Physics
Mustafa Kemal University

Prof. Dr. Hüseyin TOKTAMIŞ
Engineering Physics
Gaziantep University

Assoc. Prof. Dr. Rasim ÖZDEMİR
Electrical and Energy Engineering
Kilis 7 Aralık University

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Cemil AKDOĞAN

ABSTRACT

ANALYSIS OF THE MICROSTRUCTURE AND CORROSION BEHAVIOUR OF ELECTRODEPOSITED FE AND FE ALLOYS

AKDOĞAN, Cemil

Ph.D. in Engineering Physics

Supervisor: Prof. Dr. Ömer F. BAKKALOĞLU

Co-Supervisor: Prof. Dr. Mustafa ÖZTAŞ

March 2023

135 pages

Corrosion is material deterioration owing to materials' interaction with their surroundings. When the surface of metals/alloys is converted to a stable form having its oxide, hydroxide or sulphide state, corrosion progression (the deterioration of the material) could be ceased. This process is called passivation which is the main point of this thesis. This thesis aimed to obtain an iron-based alloy coating that can be passive. As Zn is a passivable element, it was used with Fe for alloy coating in this research. Fe and Fe alloys (Fe-Zn, Fe-Mn, Fe-Mn-Zn) have been electrodeposited potentiostatically on AISI 4140 steel in aqueous and ionic liquid media for corrosion resistivity. Ionic liquids containing solely anions and cations (without solvent) have been employed as metals and alloys electrodeposition baths. The corrosion behavior of resulting films obtained in ionic liquid media was compared with that of the films electrodeposited from aqueous solutions. A scanning electron microscope, an energy dispersive spectrometer, X-Ray Diffraction and a Fourier Transform Infrared Spectrometer were used to characterize the surface morphologies, compositions, and structures of the synthesized coatings. The corrosion behavior of the alloy coatings was determined in NaCl solution by linear sweep voltammetry. Bulk steel material itself is oxidized at the potential window in which metals/alloys fabricated in this work oxidize in NaCl solution. Therefore, inert substrate (graphite and platinum) was coated by the metals/alloys and analyzed in terms of corrosion behavior. It was found that growth conditions have a considerable effect on the corrosion properties of coatings. Fe, Mn and Fe-Mn obtained from ionic liquid deposition bath could have pitting-like corrosion. Zn based coatings (pure Zn, Zn-Fe, Zn-Mn or Zn-Fe-Mn) electrodeposited from ionic liquid could have passivation behavior. Fe-Zn modified electrode obtained from aqueous solution has passivation. However, ternary Zn-Fe-Mn alloy electrodeposited from an aqueous solution cannot show passivation behavior.

Key Words: Electrodeposition, Ionic Liquid, Corrosion, Passivation.

ÖZET

FE VE FE ALAŞIMLI ELEKTROKAPLAMALARIN MİKRO YAPI VE KOROZYON DAVRANIŞLARININ ANALİZİ

AKDOĞAN, Cemil

Doktora Tezi, Fizik Mühendisliği

Danışman: Prof. Dr. Ömer F. BAKKALOĞLU

İkinci Danışman: Prof. Dr. Mustafa ÖZTAŞ

Mart 2023

135 sayfa

Korozyon, malzemelerin çevreleriyle etkileşimi nedeniyle malzemenin bozulmasıdır. Metallerin/alaşımların yüzeyi oksit, hidroksit veya sülfid durumuna sahip kararlı bir forma dönüştürüldüğünde, korozyon ilerlemesi (malzemenin bozulması) durdurulabilir. Bu işleme, bu tezin ana noktası olan pasivasyon denir. Bu tez, pasif olabilen demir bazlı bir alaşım kaplama elde etmeyi amaçlamıştır. Zn pasif bir element olduğundan bu araştırmada alaşım kaplama için Fe ile birlikte kullanılmıştır. Fe ve Fe alaşımları (Fe-Zn, Fe-Mn, Fe-Mn-Zn), korozyon direnci için sulu ve iyonik sıvı ortamda AISI 4140 çeliği üzerinde potansiyostatik olarak elektro-çökeltiştir. Çözücü olmadan, yalnızca anyon ve katyon içeren iyonik sıvılar, metallerin ve alaşımların elektrokaplama sıvıları olarak kullanılmıştır. İyonik sıvı ortamında elde edilen filmlerin korozyon davranışı, sulu çözeltilerde elde edilen filmlerinki ile karşılaştırıldı. Sentezlenen kaplamaların yüzey morfolojilerini, bileşimlerini ve yapılarını karakterize etmek için taramalı elektron mikroskobu, enerji dağılımlı spektrometre, X-Işını Kırınımı ve Fourier Dönüşümlü Kızılötesi Spektrometre kullanıldı. Alaşım kaplamaların korozyon davranışı, NaCl çözeltisinde doğrusal tarama voltametri ile belirlendi. Dökme çelik malzemenin kendisi, bu çalışmada üretilen metallerin/alaşımların NaCl çözeltisinde oksitlendiği potansiyel pencerede oksitlenir. Bu yüzden inert substrat (grafit ve platin) metallerle/alaşımlarla kaplandı ve korozyon davranışı açısından analiz edildi. Büyüme koşullarının kaplamaların korozyon özellikleri üzerinde önemli bir etkiye sahip olduğu bulundu. İyonik sıvı elektrolitinde elde edilen Fe, Mn ve Fe-Mn malzemelerin korozyonu çukurlaşma korozyonuna benzedi. İyonik sıvıdan elektrokaplanmış Zn bazlı kaplamalar (saf Zn, Zn-Fe, Zn-Mn veya Zn-Fe-Mn) pasivasyon davranışına sahipti. Sulu çözeltiden elde edilen Fe-Zn modifiye elektrot pasivasyona sahipti. Ancak, sulu çözeltiden elektrokaplanmış üçlü Zn-Fe-Mn alaşım pasivasyon davranışı gösteremez.

Anahtar Kelimeler: Elektro Biriktirme, İyonik Sıvı, Korozyon, Pasivasyon.



"Dedicated to my family"

ACKNOWLEDGEMENTS

I would like to thank my supervisor, Prof. Dr. Ömer F. BAKKALOĞLU for his guidance and support throughout the study. I am thankful for his encouragement and motivation.

I would like to thank, Prof. Dr. Mustafa ÖZTAŞ who is my co-supervisor from Yalova University, Prof. Dr. Metin BEDİR from Gaziantep University, Prof. Dr. İsmail H. KARAHAN from Mustafa Kemal University. their guidance and supports throughout the study. I am thankful for their encouragements and motivations.

I would like to thank Prof. Dr. Hüseyin TOKTAMIŞ who was very successful one during bachelor's level student from Gaziantep University and Assoc. Prof. Dr Rasim ÖZDEMİR (from 7 Aralık Kilis University) who did not offend me and kindly participating in my PHD thesis speech.

Moreover, I would like to thank Perihan Yılmaz Erdoğan in Gaziantep University, for her guidance, advice and suggestions. I also would like to thank to Metallurgical and Materials Engineering Department for providing me with all the laboratory opportunities to carry out a part of experimental studies.

TABLE OF CONTENTS

	Page
ABSTRACT	v
ÖZET	vi
ACKNOWLEDGEMENTS	viii
TABLE OF CONTENTS	ix
LIST OF TABLES	xii
LIST OF FIGURES	xiv
LIST OF SYMBOLS	xx
LIST OF ABBREVIATIONS	xxii
CHAPTER I: INTRODUCTION	1
CHAPTER II: THEORY	8
2.1. Corrosion	8
2.1.1. Factors Causing Corrosion	8
2.1.1.1. Electrochemical Factors	8
2.1.1.2. Physical Factors	9
2.1.1.3. Environmental Factors	9
2.1.2. Types of Corrosion	10
2.1.2.1.1. Uniform Corrosion	10
2.1.2.2. Galvanic (Electrochemical) Corrosion	10
2.1.2.3. Pitting Corrosion	11
2.1.2.4. Intergranular Corrosion	12
2.1.2.5. Filiform Corrosion	12
2.1.2.6. Exfoliation Corrosion	13
2.1.2.7. Stress Corrosion	15
2.1.2.8. Fatigue Corrosion	15
2.1.2.9. Fretting Corrosion	16
2.1.3. Corrosion Prevention Methods	17
2.1.4. Passivation	18

2.2	Electrodeposition Systems	19
2.2.1.	Electrolytes.....	21
2.2.1.1	Ionic Liquids	22
2.2.1.2	Deep Eutectic Solvent.....	23
2.2.2.	Electrodes	24
2.3.	Characterizations of Electrodes	25
2.3.1.	Cyclic Voltammetry (CV).....	25
2.3.2.	Scanning Electron Microscope (SEM).....	25
2.3.3.	Energy Dispersive X-Ray (EDX) Analysis.....	25
2.3.4.	X-Ray Diffraction (XRD)	26
2.3.5.	FTIR Spectra	28
2.3.6.	Polarization	29
CHAPTER III: EXPERIMENTAL STUDIES		30
3.1.	Materials	30
3.1.1.	Growth of Metals/Alloys from Aqueous Solutions	30
3.1.2.	Growth of Metals/Alloys from Ionic Liquid.....	32
3.2.	Procedure	32
3.2.1.	Growth of Metals/Alloys from Aqueous Solution with Pyrophosphate Ligands	32
3.2.2.	Growth of Coating on AISI 4140 Substrate with Different Ligands ...	33
3.2.2.1.	Growth of Fe-Zn Alloy	34
3.2.2.2.	Growth of Fe-Mn Alloy	35
3.2.2.3.	Growth of Fe-Zn-Mn Alloy	36
3.2.3.	Preparation of Coating Electrodes for the Electrodeposition of Steel in Ionic Liquid	37
3.3.	Characterization of the Electrodes.....	37
3.3.1.	Metals/Alloys from Aqueous Solution with Pyrophosphate Ligands..	37
3.3.2.	Characterization of the Electrodes for the Electrodeposition of Steel in Ionic Liquid	38
CHAPTER IV: RESULTS AND DISCUSSION		39
4.1.	Electrodepositions of Fe and Fe Alloys (Fe-Zn, Fe-Mn and Fe-Zn-Mn) from Aqueous Electrolyte with Pyrophosphate Ligand.....	39
4.2.	Electrodepositions of Fe and Fe Alloys (Fe-Zn, Mn-Fe and Zn-Fe-Mn) from	

Aqueous Electrolyte with Different Ligands	50
4.2.1. Analysis of Fe-Zn Alloy	50
4.2.1.1. Cyclic Voltammetry of Fe-Zn Alloy	50
4.2.1.2. Scanning Electron Microscope (SEM) Pictures of Fe-Zn Alloy ..	55
4.2.1.3. Energy Dispersive X-Ray (EDX) Analysis of Fe-Zn Alloy	58
4.2.1.4. X- Ray Diffraction (XRD) of Fe-Zn Alloy.....	64
4.2.1.5. Polarization Curve Analysis of Fe-Zn	68
4.2.2. Analysis of Fe-Mn Alloys.....	74
4.2.2.1. Scanning Electron Microscope (SEM) Pictures of Fe-Mn Alloy .	74
4.2.2.2. Energy Dispersive X-Ray (EDX) Analysis of Fe-Mn Alloy.....	77
4.2.2.3. X-Ray Diffraction (XRD) of Fe-Mn Alloy.....	83
4.2.2.4. Polarization curve analysis of Fe-Mn	85
4.2.3. Studies on Fe-Zn-Mn Alloy	89
4.2.3.1. Cyclic Voltammetry of Fe-Zn-Mn Alloy.....	89
4.2.3.2. Scanning Electron Microscope (SEM) Pictures of Fe-Zn-Mn Alloy.....	93
4.2.3.3. Energy Dispersive X-Ray (EDX) Analysis of Fe-Zn-Mn Alloy ..	95
4.2.3.4. X-Ray Diffraction (XRD) of Fe-Zn-Mn Alloy	100
4.2.3.5. Polarization Curve Analysis of Fe-Zn-Mn	100
4.3. Electrodepositions of Fe and Fe Alloys (Fe-Zn, Fe-Mn and Fe-Zn-Mn) from Ionic Liquid Electrolyte	104
4.3.1. Growth of Fe-Zn, Fe-Mn and Fe-Zn-Mn Alloy Films in Ionic Liquid....	104
4.3.2. Characterization of the Electrodes	106
4.3.3. Corrosion Study of the Electrodes	110
CHAPTER V: CONCLUSION.....	114
REFERENCES.....	125
CURRICULUM VITAE (CV)	135

LIST OF TABLES

	Page
Table 3.1 Contents of the liquids.....	34
Table 3.2 Sample used for the experiment and their data during the preparation of Fe-Zn samples.	35
Table 3.3 Sample used for the experiment and their data during the preparation of Fe-Mn samples.....	35
Table 3.4 Insides of the solutions for Fe-Mn alloys.	36
Table 3.5 Sample used for the experiment and their data during the preparation of Fe- Zn-Mn samples.	36
Table 3.6 Contents of the solutions for the Fe-Zn-Mn alloys.....	36
Table 3.7 EDX Results Fe-Zn with 10 g/L Fe concentration.	59
Table 3.8 EDX Results Fe-Zn with 20 g/L Fe concentration.	60
Table 3.9 EDX Results Fe-Zn with 30 g/L Fe concentration.	61
Table 3.10 EDX Results Fe-Zn with 40 g/L Fe concentration.	62
Table 3.11 EDX Results Fe-Zn with 50 g/L Fe concentration.	63
Table 3. 12 Diffraction indices of the peaks of AISI 4140 iron substrate with respect to Miller indices	64
Table 3.13 Peak numbers, planes (hkl), diffraction angles and diffracted elements for the measured XRD of five samples in different Fe concentration of Fe-Zn alloys.....	67
Table 3.14 The definition of samples in Figure 4.38.....	72
Table 3.15 The corrosion potential E_{corr} and corrosion current I_{corr} of AISI 4140 steel substrate and Fe-Zn obtained in different concentrations of Fe^{2+}	73
Table 3.16 The manganese content as 16.308 at % weight in the coatings measured via EDS analyses.....	78
Table 3.17 The manganese content as 78.029 at % weight in the coatings measured via EDS analyses.....	79

Table 3.18	The manganese contents as 13.769 at % weight in the coatings measured via EDS analyses.....	80
Table 3.19	The manganese content as 10.640 at % weight in the coatings measured via EDS analyses.....	81
Table 3.20	The manganese content as 5.614 at % weight in the coatings measured via EDS analyses.....	82
Table 3.21	The corrosion potential E_{corr} , corrosion current I_{corr} and carried charge Ah of AISI 4140 steel substrate and Fe-Mn samples for different concentrations of Mn.	88
Table 3.22	Mn with 10 g/L Zn concentration.....	95
Table 3.23	Mn with 20 g/L Zn concentration.....	96
Table 3.24	Mn with 30 g/L Zn concentration.....	97
Table 3.25	Mn with 40 g/L Zn concentration.....	98
Table 3.26	Amounts of Zn, Fe, Mn before and after the electrodeposition.	99
Table 3.27	The corrosion potential E_{corr} and corrosion current I_{corr} AISI 4140 steel substrate and Fe-Zn-Mn for different concentrations of Zn...	102
Table 3.28	Elemental ratio in Fe-Zn, Fe-Mn and Fe-Zn-Mn alloys electrodeposited on steel.....	108
Table 3.29	Electrochemical parameters of Fe-Zn, Fe-Mn, and Fe-Zn-Mn alloys synthesized electrochemically on steel and platinum electrode and shifted into 3.5% NaCl solution. The data given in Figure 4.83a were used for I_{corr} and E_{corr} of the electrodes.	112

LIST OF FIGURES

	Page
Figure 2.1 Top of a ship.	10
Figure 2.2 A hanger screwed to the wall.	11
Figure 2.3 Ground to which the engine of a fishing boat is connected.....	12
Figure 2.4 Bonnet of a ship (guide to inter-granular corrosion).	12
Figure 2.5 A car bodywork.	13
Figure 2.6 A boat engine apparatus.	14
Figure 2.7 Load-bearings chain links.....	15
Figure 2.8 A seat next to a water-tank with a fountain.	16
Figure 2.9 Garden door hinge.	17
Figure 2.10 Ternary Electrodes Setup; Working Electrode (sample), Counter electrode (Substrate) and reference electrode [69].	21
Figure 2.11 The condition for reflection- The Bragg's Law.....	27
Figure 2.12 An illustration of a sine wave's plot with three pairs of related locations where the wavelength (λ) may be measured [100]..	28
 Figure 3.1 a)Weighting salts; b) electrolyte for metal growth and; c) all growth solutions. Metals/alloys written in panel c were fabricated from electrolytes.	 31
Figure 3.2 a) Graphite and tape to prepare graphite substrate. b) Graphite coated tape. c) Graphite (1 cm^2) for immersing in growth electrolyte.	32
Figure 3.3 a) Experimental setup (potentiostat). b) Photo of the electrodes used in this research. WE, CE and RE refer to counter electrode, working electrode and reference electrode. c) Photo of three-cell electrodeposition system. d) Photo of the modified electrodes after electrodeposition process explained in the main text.	33

Figure 4.1	Chronoamperometric responses of potentiostatic growth of the films. Electrodeposited metals and alloys are indicated in the graphs.....	40
Figure 4.2	a) Linear sweep polarization of metals (obtained in aqueous solutions) in NaCl. b) linear sweep voltammetry responses of Mn..	42
Figure 4.3	Tafel plot of Zn, Mn and Fe coating in NaCl. The data was retrieved from Figure 4.2.....	43
Figure 4.4	Tafel plot responses of a) Zn; b) Mn and; c) Fe coating in NaCl....	44
Figure 4.5	Linear sweep polarization of alloys (Zn-Mn, Zn-Fe and Mn-Fe obtained in aqueous solutions) in NaCl.....	45
Figure 4.6	Tafel plot responses of Zn-Mn, Zn-Fe and Mn-Fe coating in NaCl.	46
Figure 4.7	Tafel plot responses of a) Zn-Mn, b) Zn-Fe and c) Mn-Fe coating in NaCl.....	47
Figure 4.8	a) Linear sweep polarization and b) Tafel plot responses of metal alloys (Zn-Fe-Mn obtained in aqueous solutions) cycling in NaCl electrolyte.	49
Figure 4.9	The cyclic voltammogram of Fe-Zn sample in solution containing (10g/L) of Fe concentration.....	50
Figure 4.10	The cyclic voltammogram of Fe-Zn sample in solution containing (20g/L) of Fe concentration.....	51
Figure 4.11	The cyclic voltammogram of Fe-Zn sample in solution containing (30g/L) of Fe concentration.....	52
Figure 4.12	The cyclic voltammogram of Fe-Zn sample in solution containing (40g/L) of Fe concentration.....	53
Figure 4.13	The cyclic voltammogram of Fe-Zn sample in solution containing (50g/L) of Fe concentration.....	54
Figure 4.14	The overlapped cyclic voltammogram of Fe-Zn sample containing (10-50 g/L) of Fe concentration.....	55
Figure 4.15	The SEM images of Fe-Zn containing 10g/L of Fe concentration...	56
Figure 4.16	The SEM image of Fe-Zn containing 20g/L of Fe concentration. ...	56
Figure 4.17	The SEM image of Fe-Zn containing 30g/L of Fe concentration. ...	57
Figure 4.18	The SEM image of Fe-Zn containing 40g/L of Fe concentration. ...	57

Figure 4.19	The SEM image of Fe-Zn containing 50g/L of Fe concentration. ...	58
Figure 4.20	EDX image of Fe-Zn with 10 g/L Fe concentration.....	59
Figure 4.21	EDX image of Fe-Zn with 20 g/L Fe concentration.....	60
Figure 4.22	EDX image of Fe-Zn with 30 g/L Fe concentration.....	61
Figure 4.23	EDX image of Fe-Zn with 40 g/L Fe concentration.....	62
Figure 4.24	EDX image of Fe-Zn with 50 g/L Fe concentration.....	63
Figure 4.25	XRD patterns of AISI 4140 iron substrate	64
Figure 4.26	XRD patterns of Fe-Zn alloy containing (10g/L) of Fe concentration.	65
Figure 4.27	XRD patterns of Fe-Zn alloy containing (20g/L) of Fe concentration.	65
Figure 4.28	XRD patterns of Fe-Zn alloy containing (30g/L) of Fe concentration.	65
Figure 4.29	XRD patterns of Fe-Zn alloy containing (40g/L) of Fe concentration.	66
Figure 4.30	XRD patterns of Fe-Zn alloy containing (50g/L) of Fe concentration.	66
Figure 4.31	Overlap XRD patterns of Fe-Zn alloy containing (from 10 to 50 g/L) of Fe concentration.	66
Figure 4.32	Polarization curve of the AISI 4140 corrosion potential and corrosion current of the substrate have been obtained -1.148 V, and $10^{-3.2}$ A respectively.....	68
Figure 4.33	Polarization curve of the Fe-Zn including 10.889 wt. % of Fe.	68
Figure 4.34	Polarization curve of the Fe-Zn for 6.765 wt. % concentration of Fe	69
Figure 4.35	Polarization curve of the Fe-Zn for 6.255 wt. % concentration of Fe	70
Figure 4.36	Polarization curve of the Fe-Zn for 7.194 wt. % concentration of Fe	71
Figure 4.37	Polarization curve of the Fe-Zn for 7.656 wt. % concentration of Fe.	71
Figure 4.38	Potentiodynamic polarization curve of electrodeposited Fe-Zn alloys for all concentrations of Fe on AISI 4140 substrate [57].....	72

Figure 4.39	Corrosion potential of the Fe-Zn alloy coatings.....	74
Figure 4.40	The SEM image of Fe-Mn containing 83.692 % of Fe and 16.308 wt. % of Mn weight concentration with pH=3.2.	75
Figure 4.41	The SEM image of Fe-Mn containing 21.971% of Fe and 78.029 wt. % of Mn weight concentration.	75
Figure 4.42	The SEM image of Fe-Mn containing 86.231% of Fe and 13.769 wt. % of Mn weight concentration.	76
Figure 4.43	The SEM image of Fe-Mn containing 89.360 of Fe and 10.640 of Mn weight % concentration.....	76
Figure 4.44	The SEM image of Fe-Mn containing 94.386 of Fe and 5.614 of Mn weight % concentration.....	77
Figure 4.45	EDS spectra [113] of Fe-Mn alloy contains 16.308 Mn at % weight	78
Figure 4.46	EDS spectra of Fe-Mn alloy contains 78.029 Mn at % weight	79
Figure 4.47	EDS spectra of Fe-Mn alloy contains 13.769 Mn at % weight	80
Figure 4.48	EDS spectra of Fe-Mn alloy contains 10.640 Mn at % weight	81
Figure 4.49	EDS spectra of Fe-Mn alloy contains 5.614 Mn at % weight	82
Figure 4.50	XRD images of a Fe-Mn alloy with a content of 83.692% Fe.	83
Figure 4.51	XRD images of a Fe-Mn alloy with a content of 21.971% Fe.	83
Figure 4.52	XRD images of a Fe-Mn alloy with a content of 86.231 Fe.	83
Figure 4.53	XRD images of a Fe-Mn alloy with a content of 89.360 % Fe.	84
Figure 4.54	XRD images of a Fe-Mn alloy with a content of 94.386 Fe.	84
Figure 4.55	Polarization curve of the Fe-Mn sample for 16.308 wt.% concentration of Mn.....	85
Figure 4.56	Polarization curve of the Fe-Mn sample for 13,769 wt. % concentration of Mn.....	86
Figure 4.57	Polarization curve of the Fe-Mn sample for 10,640 % concentration of Mn.....	86
Figure 4.58	Polarization curve of the Fe-Mn sample for 5,614 % concentration of Mn.	87
Figure 4.59	Corrosion potential of the Fe-Mn alloy coatings.....	88
Figure 4.60	The cyclic voltammogram of Fe-Zn-Mn sample containing (10g/L) of Zn concentration.	89

Figure 4.61	The cyclic voltammogram of Fe-Zn-Mn sample containing (20g/L) of Zn concentration.	90
Figure 4.62	The cyclic voltammogram of Fe-Zn-Mn sample containing (30g/L) of Zn concentration.	91
Figure 4.63	The cyclic voltammogram of Fe-Zn-Mn sample containing (40g/L) of Zn concentration.	92
Figure 4.64	The overlapped cyclic voltammogram of Fe-Zn-Mn sample containing (10,20,30, and 40g/L) of Zn concentration.....	92
Figure 4.65	The SEM picture of Fe-Zn-Mn containing (10g/L) of Zn concentration	93
Figure 4.66	The SEM picture of Fe-Zn-Mn containing (20g/L) of Zn concentration.	93
Figure 4.67	The SEM picture of Fe-Zn-Mn containing (30g/L) of Zn concentration	94
Figure 4.68	The SEM picture of Fe-Zn-Mn containing (40g/L) of Zn concentration	94
Figure 4.69	EDX image of Fe-Zn-Mn with 10 g/L Zn concentration.	95
Figure 4.70	EDX image of Fe-Zn-Mn with 20 g/L Zn concentration.	96
Figure 4.71	EDX image of Fe-Zn-Mn with 30 g/L Zn concentration.	97
Figure 4.72	EDX image of Fe-Zn-Mn with 40 g/L Zn concentration.	98
Figure 4.73	Zn amounts before electrodeposition versus Zn, Fe and Mn concentrations after electrodeposition.	99
Figure 4.74	Polarization curve of the Fe-Zn-Mn for 30.785 % concentration of Zn.....	100
Figure 4.75	Polarization curve of the Fe-Zn-Mn for 82.212 % concentration of Zn.....	100
Figure 4.76	Polarization curve of the Fe-Zn-Mn for 80.116 % concentration of Zn.....	101
Figure 4.77	Polarization curve of the Fe-Zn-Mn for 47.856 % concentration of Zn.....	101
Figure 4.78	Linear sweep voltammogram [116] of electrodeposited of electro - deposited Fe-Zn- Mn alloys for all concentrations of Zn on AISI 4140 substrate.	102

Figure 4.79	(a) Cyclic voltammogram curve of bare steel working electrode in pure Ethaline solution (black line) and in Ethaline liquid comprising Fe^{2+} , Zn^{2+} and Mn^{2+} ions (red line); (b) Cyclic voltammogram curve of bare steel working electrode in Ethaline liquid comprising Fe^{2+} and Zn^{2+} (black line) and Fe^{2+} and Mn^{2+} (red line). $v = 20 \text{ mV s}^{-1}$	105
Figure 4.80	SEM pictures of a) bare steel, b) electrodeposited Fe-Zn based alloy on steel; c) electrodeposited Fe-Mn based alloy on steel and; d) electrodeposited Fe-Zn-Mn basis alloy on steel. The films were fabricated potentiostatically from Ethaline ionic solution.....	107
Figure 4.81	The patterns of X-ray diffraction (XRD) of a) bare steel; b) Fe-Mn; c) Fe-Zn and; d) Fe-Zn-Mn coated steel.	108
Figure 4.82	FTIR spectra of a) bare steel electrode (black line); b) Fe-Mn (red line); c) Fe-Zn (green line); and d) Fe-Zn-Mn (blue line) alloy deposited on steel electrode.....	109
Figure 4.83	a) Potentiodynamic polarization responses of bare steel (black line) electrode, iron manganese alloy (red line), iron zinc alloy (green line), and iron, zinc and manganese alloy (blue line) electrodes coated on steel substrate electrochemically in 3.5% NaCl solution at 25 °C. b) Potentiodynamic polarization responses behavior of bare platinum (blue line) electrode, iron manganese alloy (black line), iron zinc alloy (red line), and iron, zinc and manganese alloy (green line) alloy electrodes electrochemically coated on platinum substrate in 3.5% NaCl solution at 25 °C.	111

LIST OF SYMBOLS

I	Current
V	Potential (Volt)
Cm²	Centimeter square
μA	Microampere
mA	Milliampere
E(V)	Electrical Potential (volt)
Log I	Logarithmic Current
g/L	gram per liter
θ	theta
λ	Lambda (Wave length)
d	distance
x	Horizontal axis
y	Vertical axis
keV	kilo electron volt
I_{corr}	Corrosion current
E_{corr}	Corrosion potential
mA	Milli ampere
mV	Milli volt
°C	Santi grate degree Celsius
hkl	Miller indices
NaCl	Sodium chloride
Fe	Iron
Zn	Zinc
Mn	Manganese
Na	Sodium
K	Potassium
Li	Lithium

Au	Gold
Pt	Platinum
Ag	Silver
KH₂PO₄	Potassium-dihydrogen-phosphate
K₄P₂O₇	Potassium pyrophosphate
FeSO₄	Iron Sulphate
ZnSO₄	Zinc Sulphate
ZnCl₂	Zinc Chloride
MnCl₂	Manganese chloride
C₂H₆O₂	Ethylene glycol
MnCl₂·4H₂O	Manganese dichloride tetrahydrate
MnSO₄H₂O	Manganese sulphate monohydrate
(NH₄)₂SO₄	Ammonium Sulphate
AgCl	Silver chloride

LIST OF ABBREVIATIONS

CV	Cyclic Voltammetry
SEM	Scanning Electron Microscope
EDX	Energy Dispersive X-Ray
EDS	Energy Dispersive Spectroscopy
XRD	X-Ray Diffraction
FTIR	Fourier transform infrared
WE	Working Electrode
CE	Counter Electrode
RE	Reference Electrode
CMMA	Composition modulated multilayer alloy
EDTA	Etylenediamminetetraacetate
DESS	Deep Eutectic Solvents
SHE	Standard Hydrogen Electrodes
NHE	Normal Hydrogen Electrodes
SCE	Saturated Calomel Electrodes
DC	Direct Current
IR	Infrared

CHAPTER I

INTRODUCTION

Iron is one of the oldest known metal and its pure form was used around 3000 BC. It comprises more than 5% of the earth's crust and found in earth's core. Iron objects were fabricated in ancient Egypt. The Iron Age was an era started from 1200 B.C. to 600 B.C. [1] when the Hittites smelt iron-based ore to make iron tools. Low cost and high strength properties of iron make it indispensable as structural components for buildings, automotive, construction of ship's body [2]. But corrosion which is typically defined as the degradation of metals as a result of an electrochemical reaction [3]. It is an oxidation reaction that happens mostly on the surface of metal-based materials. However, oxidation of metals or alloys may act as a barrier to further oxidation [4].

A passive layer is formed when oxidation of materials results in a layer that prevents further oxidation of the bulk material. When corrosion occurs on the surface of bronze and aluminum, it appears as a thin greenish layer known as patina and alumina, respectively [5], [6]. In stainless steel, the creation of a Cr_2O_3 layer can be detected, and this layer is also a passive layer. Zinc has a passive layer, and the coating of metals/alloys with zinc, referred to as galvanization [7], is a regular occurrence in daily life. Corrosion on the surface of these four very recognizable metals eliminates interaction with the external environment and protects the lower surfaces. However, rust in iron, which is the most common engineering metal, exfoliates from the surface of the metal [8]. Keeping this layer on the surface of the iron (or steel) can help prevent additional rusting. This spongy structure, however, was unable to prevent the metal from coming into contact with the air or the surrounding environment [9]. Due to the fact that rust is poured from the iron surface, the remaining lower portions of the iron metal chemically react with the environment and oxidize anew; this process continues until the iron metal is fully consumed [10].

The motivation of this work is to have a stable Fe-based alloy on steel surface. As Zn based coating cause a passive layer, it was added to Fe in this study for preventing corrosion of steel. Corrosion with wear exists as material deterioration and these two phenomena could also cause energy losses with mechanical and chemical processes [11]. Iron is the most widely utilized metal, accounting for more than half of all metals produced globally [12].

Today, the widespread usage of iron-based metals, particularly in the automotive, ship, and aircraft industries, has spawned research into corrosion prevention [13]. The most straightforward method is to protect metal objects from moisture, so delaying corrosion. However, after a period of time, when this procedure is no longer sufficient, methods such as painting are applied. While these procedures appear to be effective in the short term, they may soon be overtaken by electrodeposition methods that delay metal corrosion [14]. When corrosion of metals is postponed; the labor, time, and economic losses associated with corrosion could be minimized [15]. Corrosion occurs when the microstructure of metals/alloys reacts with oxygen and water. As a result of the absence of water-containing moisture, areas with arid climates are less prone to corrosion. Because of the oxygen in humid environments, metals are more susceptible to rust [16].

In light of current economic conditions, it has been determined that the losses caused by rust exceed the expense of working on corrosion-prevention technologies. In corrosion-resistance investigations, electrodeposition of a single element or alloys of two or more elements was utilized on the surfaces of materials subjected to adverse environmental conditions such as moisture or chemical particles. To investigate corrosion change, iron alloys (Zn-Fe, Mn-Fe, and Mn-Fe-Zn) were electrochemically coated on steel, in this study. Because of the corrosion, iron was needed to protect by using some methods like painting, coating surface by oily product (such as grease) and coating by some non-corrosive alloys including Cr, Cu, Al, Ti and Zn based alloys by electroplating. Electrolysis have been used recently to produce multilayered coatings of iron and iron-based alloys for surface treatment in order to protect metals from the corrosion. The composite coatings can be included in the large system of composite materials, which are defined as systems formed from two or more materials for

improving the properties relative to the pure components.

Electrodeposition from a metal/alloy coating media, containing generally metal salts could cause metal deposition on a conductive surface and this could prevent metals/alloys from corrosion. Composite coatings such as metal-matrix composites could also obtain through electrodeposition. One of the most significant areas in corrosion science has been the features and function of passive coatings on Fe basic metal and alloys. The chemical makeup and microstructure of passive films, which have been studied in terms of their layer of protection, have received a lot of attention. [17].

Prior research has unequivocally shown that the existence of intermetallic particles containing iron reduces corrosion resistance [18]–[21]. About 0.1wt% iron is commonly found in primary aluminum, which is a significant amount more than the solid solubility of iron in alloys at ambient temperature. Additionally, very few goods are fabricated entirely of primary aluminum; instead, a sizable amount of reused aluminum is included, which raises the quantity of iron in alloys. Iron is therefore expected to play a substantial role in alloy corrosion. In order to protect the iron metal used in various applications, which are easy to find in nature, against corrosion, researchers have studied the coating of metal surface with alloys by electrodeposition method. Zinc has found widespread use as the basis of a whole range of sacrificial coatings for ferrous substrates Zinc is frequently used as the basement for a variety of target coatings for ferric substrates. [22].

Lodhi et. al. used a range of complimentary analytical techniques to study Zn-Co-Fe alloy coatings. One has a low cobalt level (around 6 wt%), whereas the other has a greater cobalt content (15-35 wt%). Zn-Fe-Co alloys having a cobalt concentration of at least 32 weight percent Co exhibit a homogenous structure that is thought to be nanocrystalline in origin. [23]. Zn-Fe-Co coatings with 30 wt% Co+1 wt% were discovered by Lodhi et al. iron exhibits higher corrosion resistance compared to Zn, Zn-Co-Fe coatings with inadequate Co content, and Cd coatings because they are nano-crystalline in nature [24]. Using the potentiodynamic polarization approach, Chansena and Sutthiruangwong studied the corrosion of electrodeposited iron-cobalt alloys from cyclic galvanodynamic polarization. In both aerated acidic solutions and

aerated deionized water, it was discovered that the corrosion rate of iron-cobalt alloys increased with increasing iron concentration. The alloy with the uppermost Fe concentration, at about 79%, still shown the highest corrosion rate in aerated deionized water, at 59×10^{-4} mm per year, while the alloy with the lowest Fe content, at around 20 %, displayed the lowest corrosion rate, at 45×10^{-4} mm per year. [25]. Ullal and Hegde searched Ni-Fe alloy coating deposited on copper which was found to be the most corrosion resistant [26]. Karahan found that with varied chloride-sulphate baths, Fe-Zn-Ni coatings have the maximum corrosion resistance [27]. From light acid chloride solutions, Yang et al. produced decorative and protective Zn-Fe coatings. They also achieved optimum scientific parameters for Zn-Fe coating and smooth Zn-Fe electroplating with strong corrosion resistances [28].

The electrodeposition of trinity Zn- Co-Fe alloy on Cu (concentration almost 100%), AISI 4340 steel, 9021I steel bar (iron nearly 100%), and 304-stainless steel substrata was examined by Abou-Krishna et al. They discovered in comparison to steel bar, steel, and Cu substrates, Zn-Co-Fe alloy placed on stainless steel had superior corrosion resistance among steel bar, steel, and Cu substrates [29]. Winiarski investigated the electrodeposition of ternary Zn-Fe-Mo alloy coatings with pH ranges of 4, 8 to 6, 0, 1.5 to 7.9 weight percent Fe, and 0.8 to 2.7 weight percent Mo. However, Zinc-iron (7.9 wt%)- molybdenum (2.7 wt%) alloy coating shown the strongest resistance of charge transfer response over 24 hours of exposure to NaCl solution. Fe-Zn-Mo coating exhibits lower corrosion value at pH 5.7 and 6.0 [30].

In order to analyze Zn-Fe-Mo alloy coatings, Winiarski et al. varied the amounts of 0.4 -2.7% molybdenum and 2.8 - 7.6% iron in the alloy. After a day of exposure to a NaCl liquid mixture, their testing results showed that trinity Fe-Zn-Mo alloy coatings (7.6% at iron and 2.4% at Molybdenum) show higher corrosion resistance than Fe-Zn (1.7% at) bimetal coatings and unalloyed Zn coatings. [31]. By using anomalous deposit, Kanagasabapathy et al. studied the textural, morphological, and phase structural properties of Fe-Zn alloys. They found that these electrodeposits have industrial importance because they outperform unalloyed Zn coatings in terms of corrosion resistance and mechanical properties [32]. When Ordine et al. investigated the corrosion manner of a Fe-Zn-P alloy, they discovered that it had the same

characteristics as Zn-Fe. Though, the quickest corrosion rate was demonstrated by crystalline Fe-Zn-P. They discovered that P can significantly enhance the anticorrosive characteristics of zinc alloys [33]. Abou-Krishna et al. examined the corrosion resistance of the electrodeposited alloys on the steel substrate as well as the electrodeposited coating operating parameters for Fe-Zn-Ni alloys from sulphate baths. They contrasted Zn-Ni and Fe-Zn-Ni alloys in an effort to determine Fe^{2+} . They discovered that raising the amount of iron in an alloy enhances corrosion resistance [34]. Hegde et al. electro-deposited Fe-Zn, Ni-Zn, and Fe-Zn-Ni coatings on steel using galvanostatic methods in acidic baths (pH 3.5) containing zinc chloride, Nickel chloride, iron chloride, gelatine, sulphanilic (p-amino benzene sulphonic) acid, and ascorbic acid. After doing study, they discovered that Fe-Zn-Ni coatings had the smoothest surfaces, the most distinctive facet morphology, and contained ZnO throughout, not just on the surface. When comparing to bilateral alloys, electrodeposition of trinity alloys in this study shows superior corrosion resistance [35].

Nayana et al. investigated the corrosion performance of electrodeposits made from veratraldehyde and valine condensation products that were both bright and dull. The Fe-Zn alloy deposit's rigidity, adhesion, ductileness, and corrosion resistance were all increased by the additional appearing. Hardly ever corrosion was seen on the brightly deposited material at the conclusion of the studies and after twelve days of weight loss monitoring [36]. Yogesha and Hegde used thiamine hydrochloride as an additive while performing multi-layer alloy (CMMA) coating of Fe-Zn that was created galvanostatically on meek steel utilizing the sole bath technique. When compared to an equivalent monolithic alloy of the same thickness, the CMMA Fe-Zn coating, created at 2-4 A/dm², has three hundred layers and is about thirty times more corrosion resistant [37]. Adelkhania et al. looked into the structure and corrosion resistance of trinity Ni-Fe-Cr alloy coatings in NaCl liquid mixture by applying direct and pulse current. They came to conclusion that pulse current, which exhibits higher corrosion resistance than direct current coating, can reduce the microcracks of alloy coating [38].

A search on electro-deposited Zn-Cu alloy thin films was conducted by Özdemir et. al. They looked at how the current density affected the behavior of nanocrystalline Zn-

Cu alloys electrodeposited on aluminum substrata using a citrate electrolyte free of cyanide in terms of micro strain, grain size, phase structure, and direct current electric resistivity. Cyclic voltammetry tests were used to study the electrolyte's electrochemical properties. The deposits' morphologies were examined using a SEM. XRD and EDX were used to analyze the deposited alloys [39]. Zn, Ni-Zn, Fe-Zn, and Fe-Zn-Ni films were electrochemically deposited onto steel sheet substrates by Karahan et al. Their studies aimed to describe the corrosion characteristics of these alloys in salty solution for use as novel, environmentally acceptable immolated coatings for steel structural protection. Using X-Ray Diffraction and Scanning Electron Microscope systems, the morphological and structural characteristics of the alloys were methodically investigated. To better comprehend the electroplating procedure for the films, CV of the different metals was carried out [40].

Karahan looked into how the electrolyte's pH level and the addition of glycine affected the creation and characteristics of electrodeposited Fe-Zn coatings. He performed electrochemical studies in a liquid mixture containing 3.5% NaCl with glycine present or absent in order to study the corrosion performance of electrodeposits of Fe-Zn alloys in an ecofriendly and non-cyanide sulphate bath under nonstop current. SEM was utilized to analyze the deposit morphology, and XRD was employed to ascertain the preferred crystallographic orientations of the deposits. It was discovered that the pH of the coating electrolyte had a strong relationship with the homogeneity and corrosion resistance of Fe-Zn coated films [41].

Numerous research on the electrodeposition of iron and iron alloys in aqueous solution have been conducted, according to literature searches [42]. To mitigate the detrimental effects of aqueous solutions (for example, hydrogen evolution during cathodic electrodeposition), the thin films using ionic liquid were grown [43].

In this thesis, to see the protection effect of the metal from the corrosion, Fe and Fe alloys (for example, Fe-Zn, Fe-Mn, Fe-Mn-Zn) films have been applied to AISI 4140 carbon steel substrates by using the electrodeposition approach. The growth conditions of metals/alloys were aqueous electrolyte and ionic liquid electrolyte. Utilizing XRD and SEM methods, the morphological and structural characteristics of the alloys have

been thoroughly investigated. Although numerous studies mentioned some of them above have carried out, this study may supply small contribution for the big area which consist of corrosion protection of the metal but it is significant to notice impact to the metal surface plated by Zn-Fe, Mn-Fe, Zn-Fe-Mn alloys utilizing electrodeposition method. Another technique in this study was using of ionic liquid formed by combining one unit of ethylene glycol and couple units of choline chloride called Ethaline. Electro-deposited coatings of alloys (Zn-Fe, Mn-Fe, Zn-Fe-Mn) was accomplished by applying a constant potential to an ionic liquid containing salts of Zn-Fe, Mn-Fe, Zn-Fe-Mn, respectively. The electrochemical, morphological, steric and compositional characteristics of thin films (iron-basic alloys) grown on steel were determined using a cyclic voltammogram, a SEM an EDX, an XRD and a FTIR.

CHAPTER II

THEORY

2.1. Corrosion

Materials are impaired by corrosion [44] by reacts electrochemically with the media which they are in. Metals are present in compound in nature. Metals that are purified for use in industry want to return to their stable state when the conditions are favorable. Precisely in this case corrosion occurs. Not only metals but also non-metallic objects are exposed to the corrosive effect. However, this event is more pronounced in metals.

2.1.1. Factors Causing Corrosion

There are electrochemical, physical and environmental factors that cause corrosion. Environment in which materials are in contact and materials themselves are the most critical parameters for corrosion phenomena. Therefore, these two parameters must be considered firstly.

2.1.1.1. Electrochemical Factors

In order for electrochemical corrosion to occur, there must be moisture in contact with metals, there must be a difference between the electro potentials of metals, and the current formed must complete the circuit. An electro-corrosion cell has four elements [45]. These elements are anode, cathode, metal path and electrolyte. Without one of these elements, corrosion does not occur. The carbon-zinc dry cell is an example of corrosion cell. The outer of the dry cell is zinc one of the two electrodes, forms the cathode. The carbon rod in the center is the anode. The moist paste between the two electrodes forms the electrolyte. In the corrosion cell, the same elements are necessary for the initiation and maintenance of corrosion. When two metals are immersed in the electrolyte, they have electrical potential that directs the solubility in solution. When

metals dissolve in solution, the metal atoms leave one or more electrons on the surface, leaving the metal as ions with a positive charge. The electrons left on the surface reach the cathode through the metal (via the conductor). Corrosion occurs in the anode, soluble in anodic metal electrolyte. It is an electron cathode which is less active than the anode and does not corrode.

2.1.1.2. Physical Factors

Materials can corrode more easily under conditions of high pressure and temperature. Corrosion is inevitable if a load is subjected to a greater amount of resistance than a part or under the influence of multiple forces. The friction of the protective surfaces of the materials may lead to corrosion. For example, corrosion occurs easily in an environment of extreme temperature differences during the day.

2.1.1.3. Environmental Factors

Climatic conditions also play an important role in terms of causing corrosion. This corrosion can be called atmospheric corrosion. It affects many sectors of the economy like infrastructure (bridges, highways, roads), transportation (ships, automobile, buses, aircrafts), communication (electronics, information technology), buildings and cultural heritage [46]. Climates are divided into four according to geographical location in causing corrosion. The tropical marine environment is the most corrosive one in which high temperature and humidity influence. In this environment, corrosion increases rapidly with temperature. Industrial pollution is the industrial environment that carries residues such as pollution, smoke and fog. Rising gases from industrial establishments combine with the moisture of the air to condense in acid form and accelerate corrosion. Since the poles are at very low temperatures, electrochemical reactions are rare. Although the electro chemicals are very low in this environment, when the metal in the cold state heats up, moisture accumulates. This causes corrosion in metal. On the other hand, desert is the only environment where humidity is very low and there is no corrosion. Due to there is no moisture in this environment, the temperature has no effect.

2.1.2. Types of Corrosion

Some of important corrosion types have been mentioned here among various kind of corrosions.

2.1.2.1.1. Uniform Corrosion

It is the most basic type of corrosion in atmospheric conditions due to a chemical effect on liquids or contaminated metal surfaces. Internally, corrosion does not reach very far. The most well-known illustration is the rusting of steel in air [47]. It causes a color change on the surface of the metal. It usually manifests itself as dulling on metal surfaces. Corrosion of iron, dulling of the color of copper, fogging of nickel surface, darkening of silver is examples of this type of corrosion.



Figure 2.1 Top of a ship.

2.1.2.2. Galvanic (Electrochemical) Corrosion

Different metals with various electrochemical potentials can exposure galvanic corrosion [47] come into contact with each other in heat and moisture environments. They act as electrolyte and cause galvanic corrosion cell. One of the connected two metals is noble and has lower standard electrode potential, behaves as anode and more exposed to corrosion than the other metal which is less noble, has higher standard electrode potential and behaves as cathode. For example, if stainless steel or titanium

material is mounted on an aluminum alloy material without using any insulation material in between, corrosion will occur on the aluminum material over time. In Figure 2.2 screws represent anode or sacrifice side. This situation can be used for protecting some metal products like large lampposts, underground fuel tanks, metal water and fuel pipes which have important mission. To protect these metal products, less noble sacrifice metals are chosen and connected to them so that corrosion will occur these sacrifice metals. Thus, the important metal product is protected. To change rusty sacrifice metal will be easy and cheap.

In fact, corrosion is not a desired condition even for protection purposes, but here is a profit from loss.



Figure 2.2 A hanger screwed to the wall.

2.1.2.3. Pitting Corrosion

It is formed by the presence of anodic and cathodic parts on the surface of the alloy in contact with moisture. This type of corrosion is more common in metals like aluminum and steel that create passive films [48]. The metal alloy forms the metal path for the transport of electrons. Aluminum and magnesium alloys frequently exposure the corrosion known as "pitting corrosion.". The first sign is white and grey powdery heaps collected and swollen on the surface. Small cavities may be visible after cleaning these piles. Yet the cavities are small from the beginning, they grow over time.



Figure 2.3 Ground to which the engine of a fishing boat is connected.

2.1.2.4. Intergranular Corrosion

Corrosion that occurs more often at grain boundaries is referred to as intergranular corrosion [48]. This corrosion occurs along the grain boundaries. The metal composition between the beads is different according to the grain. Alloy elements, sediments settle in grain boundaries. Improper heat treatment damages the grain boundaries and makes them more anodic than the grain. The most hazardous kind of corrosion is intergranular corrosion, which cannot be seen with the naked eye.



Figure 2.4 Bonnet of a ship (guide to inter-granular corrosion).

2.1.2.5. Filiform Corrosion

A painted metal surface may experience filiform corrosion, which is a type of corrosion that develops underneath the paint in wormlike veins that run in different

directions [49]. This corrosion occurs when humidity is high in the air and the surface is slightly acidic. This type of corrosion starts from scratches around the binders where the paint layer is interrupted. Oxygen in water and air penetrates from these lines under the paint.



Figure 2.5 A car bodywork.

2.1.2.6. Exfoliation Corrosion

One kind of corrosion that affects aluminum alloys is exfoliation corrosion [50]. It is characterized by the flaking or raising of the metal's surface, caused by a combination of mechanical and corrosion processes. The corrosion process occurs along the grain boundaries of the alloy, causing the surface layers to separate and lift away from the underlying metal[51]. This can lead to a loss of strength and integrity in the affected material, and can ultimately lead to failure.

The exfoliation corrosion mechanism in detail is not completely comprehended, but it is believed to be caused by a combination of factors, including stress, alloy composition, and environmental conditions. Some of the key factors that are thought to contribute to exfoliation corrosion include:

Stress: Exfoliation corrosion is more likely to occur in materials that are under stress [52], as the stress can cause the grain boundaries to become more vulnerable to attack by corrosive agents.

Alloy composition: Different aluminum alloys have different levels of

susceptibility to exfoliation corrosion. For example, some alloys, such as 7075 and 6061 [53], are more resistant to exfoliation corrosion than others, such as 6063 [54].

Environmental conditions: Exfoliation corrosion is more likely to occur in environments with high humidity, high temperatures, and high levels of chloride ions[55].

Exfoliation corrosion can be prevented by using aluminum alloys that are more resistant to the corrosion, and by controlling the environmental conditions to minimize the chances of corrosion. It can also be mitigated by using surface treatments, such as anodizing or painting, to provide a defense mechanism between the metal and its corrosive surroundings. The most sophisticated type of intergranular corrosion is this. Intergranular attack known as exfoliation corrosion affects rolled and pressed items made of aluminum alloys [56]. Overall, exfoliation corrosion is a serious problem that can lead to failure in aluminum structures. Therefore, it is important for engineers and designers to be aware of the potential for exfoliation corrosion and to take steps to prevent or mitigate it in their designs.



Figure 2.6 A boat engine apparatus.

2.1.2.7. Stress Corrosion

Stress corrosion is a form of corrosion that develops in a material when mechanical stress and a particular corrosive environment work together [57]. It is a form of accelerated corrosion that occurs under conditions of tensile stress and specific corrosive environments, such as high-temperature water or certain types of acids. Stress corrosion can cause the material's surface to develop tiny fissures, which can ultimately cause the material to collapse. Stress corrosion is a special kind of intergranular corrosion. However, stress corrosion, which happens when stress acts constantly or cyclically in a corrosive environment, produces fractures that mostly follow intergranular routes, is less hazardous than intergranular corrosion [48]. This corrosion occurs in a corrosive environment when it meets the tensile stress of the metal. Stress corrosion occurs when the binders are improperly cooled with water after heat treatment or press operations. Stress corrosion is the result of tensile stresses only.



Figure 2.7 Load-bearings chain links.

2.1.2.8. Fatigue Corrosion

Fatigue corrosion, also known as stress corrosion fatigue, is a form of corrosion that develops in metal materials as a result of the interaction between corrosion and mechanical stress [58]. It is a specific type of corrosion that is caused by cyclic loading and unloading of a material. The most common forms of fatigue corrosion are found in metals that are exposed to a corrosive environment[59], such as saltwater or acidic solutions. The corrosion process can lead to the formation of small cracks on the

surface of the metal, which can eventually cause the material to fail. The phenomenon of fatigue corrosion has been extensively studied in the field of materials science, and various methods have been developed to prevent or mitigate its effects, such as the use of corrosion-resistant coatings and alloying elements. Corrosion fatigue is the result of repetitive dynamic straining in a corrosive environment [60].



Figure 2.8 A seat next to a water-tank with a fountain.

2.1.2.9.Fretting Corrosion

A kind of corrosion known as fretting corrosion develops at the junction of two surfaces that are in contact with each other and are subjected to relative motion. It is a form of mechanical corrosion that occurs as a result of small amplitude oscillatory motion between two surfaces in contact. This motion causes the formation of wear debris, which can then promote corrosion of the surfaces. Fretting corrosion can occur in a variety of applications, including mechanical joints, bearings, and fasteners. It can also occur in biomedical implants, such as joint replacements and dental implants. Corrosion can cause mechanical qualities to deteriorate, which can lead to component failure. Research in the field of fretting corrosion has focused on understanding the mechanisms of fretting corrosion, developing methods or the purpose of measuring and detecting fretting corrosion, and the strategic development for preventing and mitigating fretting corrosion [61].



Figure 2.9 Garden door hinge.

2.1.3. Corrosion Prevention Methods

The application of these materials in industrial practice is governed by the physical properties of a material, such as strength, toughness, ductility, hardness, corrosion resistance, high/low temperature behavior, wear resistance, and so on, which are strongly influenced by the microstructure of the material. Microstructure is the structure of a prepared surface as it appears under a microscope with a magnification of more than twenty-five times. Microstructure could also effect corrosion behavior of materials. If the surface of materials is changed, its microstructure could be hidden. The most common corrosion prevention method is coating. Common coating techniques are painting, hot-dip coating, Sol-gel, physical and chemical vapor depositions, thermal spraying and electrodeposition.

A substance corrodes when chemical interactions with its environment cause it to break down into its component atoms [62]. This indicates that metals interacting with oxygen and water lose electrons. Corrosion can spread over a large region to cause overall degradation or it can be localized to form a pit or fracture [63]. Most structural alloys erode simply from exposure to airborne moisture, but specific compounds can have a significant impact on the process [64]. Therefore, environments can be changed to reduce corrosion for example less oxygen and moisture could cause less corrosion. Inhibition is a technique to reduce corrosion significantly when a small amount of chemicals is added into the material. While some attempts at corrosion management just reroute the damage into less obvious, less predictable forms, regulated corrosion

treatments like passivation and chromate-conversion will strengthen a material's resistance to corrosion [65].

2.1.4. Passivation

A substance can become less reactive to its surroundings through[66] a process called passivation. This can be done a variety of methods, such as by creating a surface that is less conductive to chemical reactions, forming an oxide layer on the material's surface, or adhering a protective coating. The particular passivation mechanism will vary depending on the substance and the environmental circumstances. For instance, passivation of stainless steel can be accomplished by the development of a protective oxide. The aerospace, biomedical, and electronics sectors, among others, all depend on passivation because it may shield materials from corrosion, oxidation, and other types of degradation. Metals that rapidly interact with other substances or elements are said to be chemically active. During these reactions, electrons are frequently lost. These metals have relatively low ionization energies and are typically located in the lower rows inside the periodic table. Examples of chemically active metals are lithium, potassium, and sodium (Na, K) (Li).

Additionally, noble metals have a strong resistance to chemical reactions and are typically found in the upper rows of the periodic table. These metals are also known as chemically inert metals. They are less likely to lose electrons because they have relatively high ionization energies. Gold (Au), platinum (Pt), and silver are a few examples of chemically inactive metals (Ag). The energy necessary to eject an electron from a neutral atom or ion is known as the ionization energy. The number of protons inside nucleus and the separation between the outermost electron and the nucleus both affect how strong the metallic connection is in a metal atom. A metal is more prone to lose electrons and become ionized the lower its ionization energy. As a result, these metals are more likely to take part in chemical processes, increasing their chemical activity.

On the other hand, metals with high ionization energies have a strong metallic link, causing it to be challenging to extract an electron from the metal atom without

expending a lot of energy. They become more resistant to chemicals as a result of having a lower propensity to participate in chemical interactions. Metallic property is connected to chemical reactivity as well as ionization energy. Metals having a strong metallic character are frequently more reactive than those with a low metallic character. The lower a metal's ionization energy, the greater the likelihood that it will lose electrons and ionize. These metals consequently have a higher propensity to engage in chemical reactions, enhancing their chemical activity.

The strong metallic bond present in metals with high ionization energies, on the other hand, makes it challenging to remove an electron from the metal atom without using a significant amount of energy. They are less likely to engage in chemical interactions, which makes them more resistant to chemicals. Ionization energy and chemical reactivity are related to metallic properties. Strongly metallic metals are frequently more reactive than metals with weakly metallic properties. The metal's electron configuration affects its metallic character because metals with more electrons in the outermost shell have a higher tendency to be metallic and more reactive. Metals with low ionization energy are more reactive chemically and are more likely to take part in chemical processes. On the other hand, metals with high ionization energy have a greater propensity to be resistant to chemical reactions and are less chemically active. Chemical reactivity and a metal's metallic character are related; metals with more electrons in the outermost shell typically have higher metallic characters and are more reactive.

2.2 Electrodeposition Systems

A well-known traditional surface modification technique called electrodeposition is used to enhance the aesthetic and functional surface properties of a wide range of materials [67]. By using the abbreviation electrodeposition instead of electrolytic deposition [68] or electroplating which is the technique of applying a thin coating of another metal or one of its alloys on an item manufactured of one kind of metal. In actuality, electrodeposition may be thought of as the process through which electroplating takes place. In other words, it is a method for coating a conductive substrate surface with a thin layer of a chosen material by removing its cations from a

solution. Electrochemical reactions involving a conductor (a metal or a semiconductor) and an ionic conductor (the electrolyte) entail the transport of electrons between the electrode and the electrolyte or species in solution. Sometimes, a cheap metal is plated with expensive one sometimes a metal or an alloy is plated on the surfaces of metals that are rustproof by electrodeposition. For whatever reason, it is said that the feature like value and durability of plated metals increases by electrodeposition.

Oxidation/reduction (redox) reactions are chemical processes that involve the exchange of electrons between molecules. Redox, short for reduction-oxidation, are electrochemical reactions in which an electron is transferred to or from a molecule or ion, causing the latter to change its oxidation state. Either the release of chemical energy or the introduction of an external voltage can cause this reaction.



The substance that takes the electrons is referred to as the oxidizing agent, or oxidant, while the atom or molecule that loses electrons is known as the reducing agent, or reductant. In a reaction, the reducing agent always undergoes reduction, whereas the oxidizing agent always undergoes oxidation. Although not the sole oxidizing agent, oxygen is a frequent one. Since electrodeposition does not require a vacuum or ambient temperature, it is relatively simple to scale and cost-effective. Additionally, substrates of different sizes can be employed.

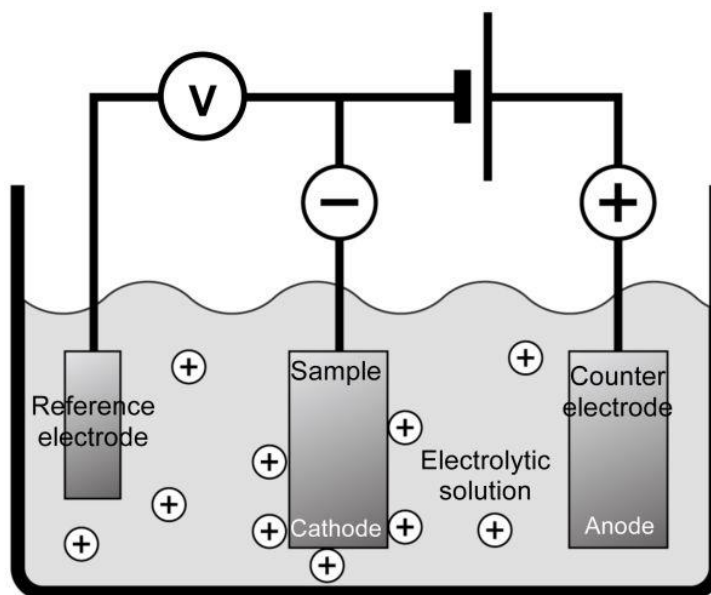


Figure 2.10 Ternary Electrodes Setup; Working Electrode (sample), Counter electrode (Substrate) and reference electrode [69].

A reaction vessel, two or three electrodes, and an electrochemical cell are used for the deposition (shown in Figure 2.10). The current flowing between a working electrode (the sample) and a counter electrode (the auxiliary electrode) in a two-electrode cell regulates the reactions. A reference electrode is utilized in the three-electrode cell to regulate or assess the voltage of the working electrode.

2.2.1. Electrolytes

It is known that applications based on electrochemistry consist of two main components. These are electrolyte and electrode (anode and cathode). Applications regarding electrochemical reactions (for example batteries [70], fuel cells [71], biosensors [72] and supercapacitors [73] have electrolytes and electrodes. Electrolysis (either anodization [74] and electropolishing [75]) can occur by using electrodes and electrolytes. Electrodeposition which is the coating process in this study requires electrolytes as well. Aqueous solutions (alkaline, acidic and neutral) and organic solvents have been commonly used as electrolyte in electrodeposition. However, aqueous and organic solvents have some problems for example hydrogen evolution during metals and alloys growth could cause metal hydroxide [76]. Therefore, it could be problematic to have a pure metal/alloy on a substrate. A method to avoid hydrogen

evolution reaction is to change electrolyte. Various types of ligands [77] such as acetate [78], cyanides [79], formate glycinate[80], ethylenediaminetetraacetate (EDTA) [81], pyrophosphate[82] and citrate[83] could be added to the electrolyte to obtain pure metal and alloy coatings. Electrolytes without ligand could be possibly used as electrodeposition media. As an electrolyte, ionic liquids with solely anions and cations have been researched [84].

2.2.1.1 Ionic Liquids

A class of substances known as ionic liquids are made completely of ions and have melting temperatures lower than 100 °C [85]. These distinctive materials have several distinctive qualities that make them appealing for a variety of industrial and research applications.

Ionic liquids' low volatility, which makes them excellent for use as solvents in chemical reactions and in the purification of gases, is one of their important characteristics. They are also non-flammable, making them safer to handle than many conventional organic solvents [86], and they have good thermal stability, allowing them to be employed in high-temperature operations.

Another important property of ionic liquids is their tunable ionic strength and hydrophobicity, which allows them to be used as electrolytes in batteries and other electrochemical devices. They are also being investigated as lubricants, catalysts, and in the separation of different metals and gases.

In addition to their industrial applications, ionic liquids are also being studied for their potential environmental benefits. They are biodegradable and non-toxic, which makes them an attractive alternative to traditional organic solvents. They have also been shown to be effective in the recovery of valuable metals from waste streams.

Despite their many advantages, there are still some challenges associated by using ionic solutions, including their high viscosity and tendency to form gels. Additionally, the lack of comprehensive data on the properties of these materials makes it difficult to predict their behavior in different applications.

Ionic solutions are a promising group of substances with several potential uses in business and science, in general. Further research is needed to fully understand their properties and to develop new methods for their synthesis and purification.

2.2.1.2 Deep Eutectic Solvent

Due to their distinctive characteristics, including low toxicity, excellent thermal stability, and low vapor pressure, deep eutectic solvents (DESs) are a type of ionic liquids that have gained interest recently. They often consist of two or more components mixed together to create a eutectic combination having a melting point lower than any of the constituent parts, such as a low melting point salt and a hydrogen bond donor.

DESs have been found to be effective solvents for many different uses, including organic synthesis, biocatalysts, and the separation of biomolecules. In organic synthesis, DESs have been used as reaction media for a variety of reactions, including oxidation, reduction, and condensation reactions, due to their ability to dissolve both polar and nonpolar compounds.

In biocatalysts, DESs have been used as alternative to traditional solvents in enzyme-catalyzed reactions. The high stability and low toxicity of DESs make them well-suited for use in these reactions, and they have been found to improve enzyme activity and stability.

In addition, DESs have also been found to be effective for the separation of biomolecules such as proteins and nucleic acids, due to their ability to selectively interact with specific groups on the biomolecule surface. Overall, the DES is a promising group of solvents with several potential uses in chemistry, biology, and material science, among other disciplines.

2.2.2. Electrodes

2.2.2.1. Working Electrode (Sample)

In an electrochemical system, the electrode on which the reaction is occurring is known as the working electrode. The working electrode is an important component of the procedure since it controls the direction of the electrochemical reaction based on its material, adsorbent surface, etc. [86]. In a three-electrode system, the working electrode is frequently used in combination with a counter electrode and a reference electrode. Depending on whether the reaction taking place on the electrode is an oxidation or reduction, the working electrode can either be cathodic or anodic. Gold, silver, or platinum are common inert metals used to make functioning electrodes.

2.2.2.2. Reference Electrode

The important reactions in all electrochemical experiments take place on the working electrode's surface. Controlling the potential drop at the point where the working electrode's surface and the solution's surface meet is crucial. It offers a steady voltage to regulate the working electrode (WE) potential under control [87]. The most popular method of employing reference electrodes is to construct electrochemical cells using the reference electrode as a half cell. This makes it possible to determine the other half cell's potential. Standard hydrogen electrodes (SHE), normal hydrogen electrodes (NHE), saturated calomel electrodes (SCE), copper-copper (II) sulphate electrodes, and others are common reference electrodes.

2.2.2.3. Auxiliary (Counter) Electrode

An electrode utilized in a three-electrode electrochemical cell for voltametric analysis or other processes where an electrical current is anticipated to flow is known as the auxiliary, sometimes known as the counter electrode. The counter electrode is distinct from the working electrode, where the cell is located, and the reference electrode, which sets the electrical potential against which other potentials may be measured. To apply input potential to the working electrode, the counter or auxiliary electrode serves as a mechanism of doing so [88].

2.3. Characterizations of Electrodes

For analyzing of electrodeposited Mn-Fe, Zn-Fe and Zn-Fe-Mn alloys onto AISI 4140 stainless steel, measurement methods like Cyclic voltammetry, SEM, EDX, XRD and Polarization have been used.

2.3.1. Cyclic Voltammetry (CV)

When a potential scan is applied to the working electrode at a consistent scan rate in both the forward and backward directions, once or many times, the response in a current is recorded using the direct current (DC) electrochemical technique known as cyclic voltammetry [89]. It is a type of potentiodynamic electrochemical measurement. The most efficient and adaptable electroanalytical method for the mechanistic analysis of redox systems is cyclic voltammetry (CV). It enables quick scanning of the electrode potential to look for redox couples. In an electrochemical investigation, the first experiment is frequently the CV. During the potential scan, the current at the working electrode is monitored to produce a cyclic voltammogram.

2.3.2. Scanning Electron Microscope (SEM)

SEM is frequently used to examine the chemistry and microstructure of a variety of materials [90]. The Scanning Electron Microscope (SEM) is a microscope that creates images via the use of electrons as opposed to light. When compared to a light microscope, the SEM has numerous benefits. A sizable portion of the sample may be under focus at once thanks to the SEM's deep field. High magnification examinations of closely spaced features are possible thanks to the SEM's high resolution picture output.

2.3.3. Energy Dispersive X-Ray (EDX) Analysis

The elemental makeup of solid surfaces is examined using energy-dispersive X-ray spectroscopy (EDX) [91]. SEM is used in combination with the chemical microanalysis method known as energy dispersive X-ray spectroscopy (EDS or EDX)

(SEM). In order to characterize the elemental composition of the studied volume, the EDS technique uses the detection of x-rays released from the sample during bombardment by an electron beam. Analysis of features or phases as tiny as 1 μm or less is possible [92].

Electrons are expelled from the surface-containing atoms of the sample when it is blasted by the SEM's electron beam. In order to balance the energy disparity between the two electrons' states, an x-ray is released when the ensuing electron vacancies are filled by electrons from a higher state. The element from which the x-ray radiation was released is what makes it up. The relative quantity of emitted x-rays vs their energy is measured by the EDS x-ray detector. Typically, the detector is a solid-state silicon device with lithium drift. A charge pulse corresponding to the incoming x-energy ray's is produced when it hits the detector. A charge-sensitive preamplifier transforms the charge pulse into a voltage pulse that is still proportional to the X-ray energy. The pulses are then sorted by voltage in a multichannel analyzer once the signal has been transferred there. Each incident x-ray as calculated by the voltage measurement, is transferred to a computer for display and additional data analysis. The elemental makeup of the measured volume is ascertained by analyzing the spectrum of x-ray energy versus counts.

2.3.4. X-Ray Diffraction (XRD)

A potent non-destructive method for characterizing crystalline materials is X-ray diffraction (XRD). It offers details on crystal textures, optimum orientations for crystals, and other structural factors including average grain size, crystallinity, strain, and crystal defects. It also offers details on structures and phases. By constructively interfering with a monochromatic beam of X-rays dispersed at particular angles from each set of lattice planes in a sample, one may create X-ray diffraction peaks. The atomic locations inside the lattice planes determine the peak intensities. As a result, the X-ray diffraction pattern represents a material's unique signature of periodic atomic groupings [93].

It is a technique that entails passing X-Rays with a specified wavelength through a sample in order to determine the crystal structure. Similar to how light may be

diffracted by a grating of appropriately spaced lines, the wave structure of X-Rays causes them to be diffracted by the crystal's lattice to produce a distinctive pattern of peaks of reflection at different angles and of varied intensities. Without being in phase, the diffracted beams from atoms on succeeding planes cancel. The Bragg's relationship specifies the prerequisite for this.

The straightforward prerequisite for observing a diffracted beam is provided by Bragg's law. Figure 2.11. The condition for reflection- The Bragg's Law. depicts a parallel X-ray beam piercing a series of parallel lattice surfaces with indices h, k, and l, separated by d, and at an incidence angle of θ . The lattice planes are shown acting like mirrors.

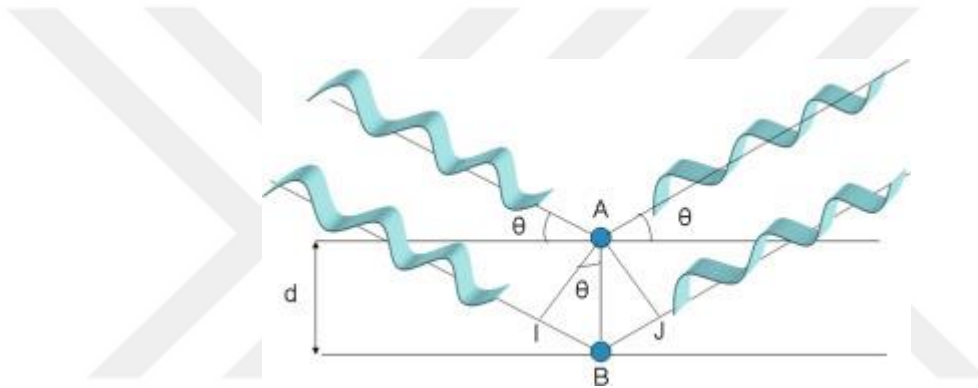


Figure 2.11. The condition for reflection- The Bragg's Law.

The waves spread in A and B have different paths that are equivalent to

$$BJ + IB = 2d \sin \theta \quad (4.1)$$

The 'reflected' waves integrate to fabricate a scattered beam (maximum interference that is beneficial, often known as "reflection") if the path disparity is a multiple of the wavelength λ .

$$2d \sin \theta = n\lambda \quad (4.2)$$

Equation (4.2) is the Bragg's equation [94]. Where d is the distance between atoms in a crystal lattice plane, λ is the X-ray wavelength, and θ is the angle of diffraction. The strength and location of these peaks are measured by the X-Ray detector as it travels around the sample (diffraction angle 2θ).

2.3.5. FTIR Spectra

The most popular kind of infrared spectroscopy is called "Fourier transform infrared," or FTIR. Infrared spectroscopy using Fourier transforms (FTIR) [95] is a method for obtaining an infrared spectrum of a solid, liquid, or gas's absorption or emission.

Infrared (IR) radiation is categorized as having wavelengths between 0.78 and 1000 μm in the electromagnetic spectrum [96]. By sending infrared rays in the range of wavelengths between 0.78 μm – 1000 μm to the atoms that form a dipole moment bond between them, these rays are expected to be absorbed by these atoms. The Fourier transformation spectra based on this basis provide information on material recognition. Infrared rays in this wave range are called near (0.78 μm - 2.5 μm), intermediate (2.5 μm -25 μm), and far (25 μm - 1000 μm). While calculating, the number of waves corresponding to $1/\lambda$ (cm^{-1}) is used instead of wavelength. Since $1/\lambda$ (cm^{-1}) is frequently employed in spectroscopy, it is also known as the spectroscopic wavenumber. [97]. A periodic wave's wavelength is its spatial period, or the length over which its form repeats [98], [99].

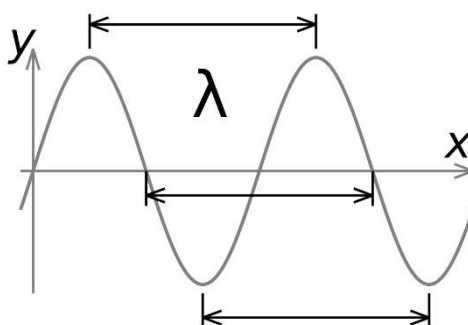


Figure 2.12 An illustration of a sine wave's plot with three pairs of related locations where the wavelength (λ) may be measured [100].

Infrared rays effective in material identification are in the range of 2.5 μm -25 μm , in

other words 400-4000 wave number. Each material has different absorption wavelengths of these infrared rays. The wave number of the material absorbing the rays sent from the Fourier transform infrared spectroscopy device is transferred to the computer connected to the device. From here, information about the recognition of the material is obtained from the data registered in the system.

2.3.6. Polarization

Polarization which is changing potential in electrode is a common technique to study electrochemical behavior of electrodes. Linear sweep voltammetry and cyclic voltammetry are type of polarization and used to reveal probable oxidation and reduction reactions of a process. Polarization methods were also used for studying biosensors, energy storage system. This technique is used in this work for corrosion properties of materials.

CHAPTER III

EXPERIMENTAL STUDIES

Fe-basis alloy was developed with the intention of being utilized as a corrosion-resistant coating for steel. Fe's sacrificial nature, low cost, and simplicity of application are factors in the use of Fe as a steel coating (hot-dipping or electroplating). An iron coating must, however, be sufficiently thick to withstand assault by a corrosive environment. It is necessary to create electrodeposited coatings that are thinner and have better corrosion resistance, ductility, and other qualities. Iron alloys have been developed by different growth conditions. Zn-Fe, Mn-Fe and Zn-Fe-Mn alloys were studied in this thesis. The use of a new metal is likely related to the alloys' ability to resist corrosion.

3.1. Materials

3.1.1. Growth of Metals/Alloys from Aqueous Solutions

Aqueous solution of zinc, iron and manganese salts were prepared from their salt form (Figure 3.1a). 0.2 M ZnSO_4 (Merck), 0.2 M FeSO_4 (Tekkim), 0.1 M MnCl_2 (Merck) were individually mixed with KH_2PO_4 and $\text{K}_4\text{P}_2\text{O}_7$ (Figure 3.1b). Pyrophosphate was added to the solutions to shift the growth potential [101]. 0.20 M of ZnSO_4 , FeSO_4 and MnCl_2 solutions were used to obtain Zn, Fe and Mn based electrodes. A constant potential of -2 V was applied for film growth. The alloys having two metals were obtained by mixing electrolyte solutions shown in Figure 3.1b. 0.20 M ZnSO_4 and 0.20 M FeSO_4 was mixed equally to use for Zn-Fe growth. ZnSO_4 and MnCl_2 were also mixed equally to have an electrolyte having 0.10 M ZnSO_4 and 0.10 M MnCl_2 , which was used to obtain Zn-Mn coating. Fe-Mn film was potentiostatically from the electrolyte having 0.10 M FeSO_4 and 0.10 M MnCl_2 . All electrolyte in this section had 0.10 M KH_2PO_4 and 0.50 M $\text{K}_4\text{P}_2\text{O}_7$ (Figure 3.1c). Ternary alloy of Zn-Fe-Mn was

obtained from an electrolyte which was the mixture of 0.20 M ZnSO_4 , 0.20 M FeSO_4 and 0.20 M MnCl_2 solutions. The photo of all growth solutions is given in Figure 3.1c.

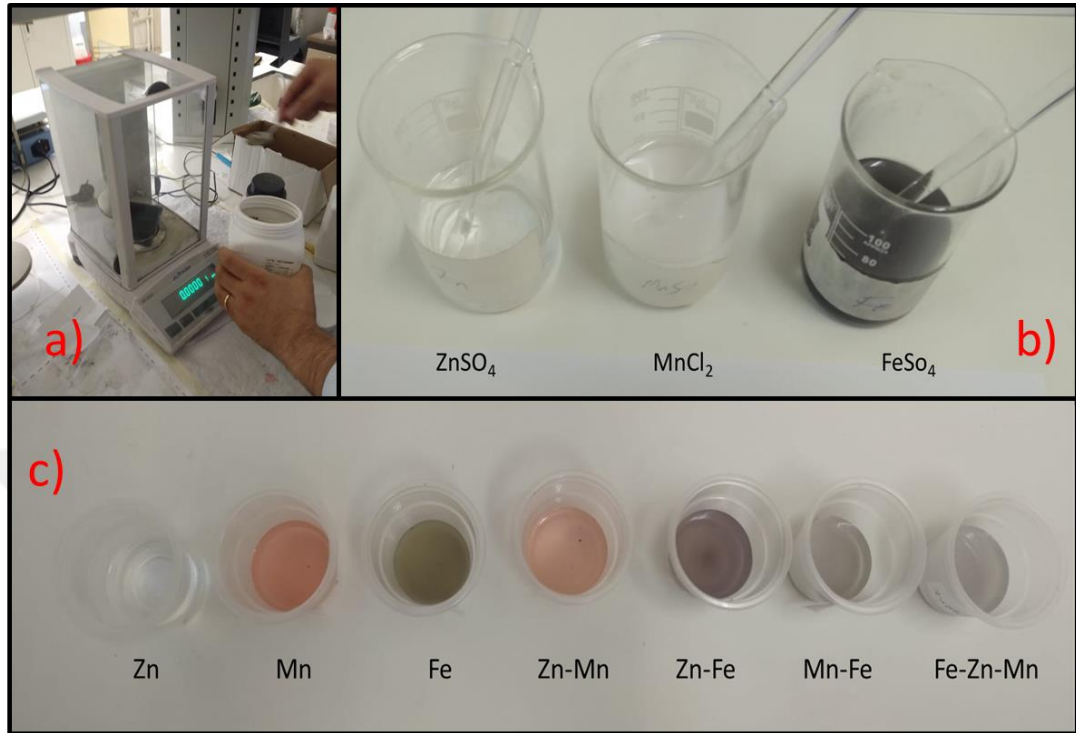


Figure 3.1 a) Weighting salts; b) electrolyte for metal growth and; c) all growth solutions. Metals/alloys written in panel c were fabricated from electrolytes.

It is known that steel could be corroded easily in chloride containing solution. If corrosion behavior of steel is analyzed after coating, the results could be dominated by steel itself. Therefore, a substrate which cannot be affected in NaCl solution is required. The substrate used in this work was graphite electrode because corrosion behavior of steel could be interfered with metals/alloys. Graphite electrodes were prepared on a tape. The tape was firstly attached to graphite surface (Figure 3.2a). The tape was taken off from the graphite surface and graphite particles were stay on tape (Figure 3.2b). As the tape having graphite become conductive, it could be used as substrate in electrodeposition process. The details of the substrate were explained in detail in the literature [102] 1cm^2 of graphite coated tape (Figure 3.2c) was immersed in growth potential explained in previous section.

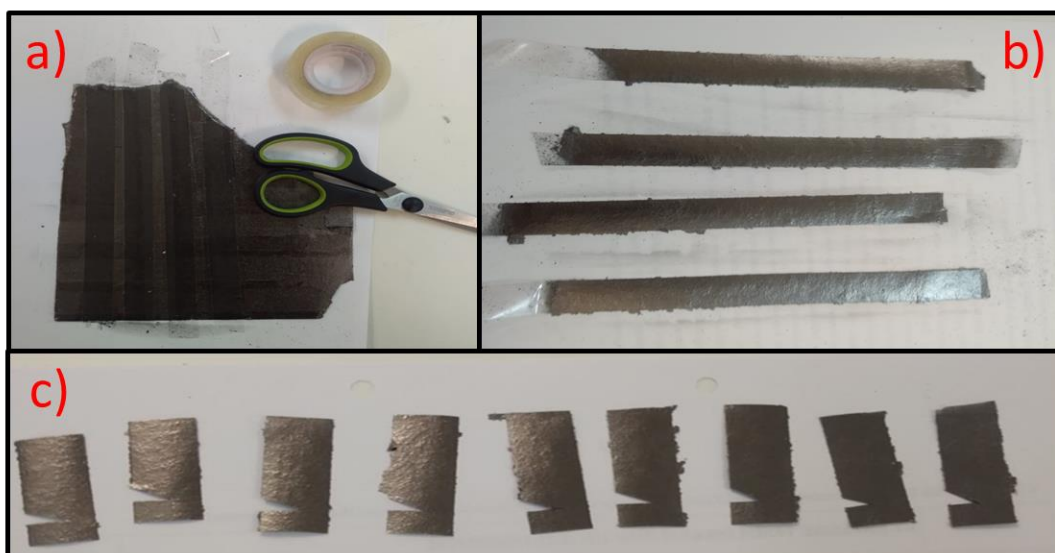


Figure 3.2 a) Graphite and tape to prepare graphite substrate. b) Graphite coated tape. c) Graphite (1 cm²) for immersing in growth electrolyte.

3.1.2. Growth of Metals/Alloys from Ionic Liquid

Without further purification, NaCl (Merck, 90%), FeSO₄·7H₂O (Merck, 99.5%), MnCl₂·4H₂O (Merck, 99%), ZnCl₂ (Merck, 98%), ethylene glycol (C₂H₆O₂, Merck, 99%) (EG) and choline chloride (HOC₂H₄N(CH₃)₃Cl, Merck, 98%) (ChCl) were utilized. Choline chloride and couple units' ethylene glycol (liquid) were combined to create ethaline ionic liquid, the molar ratio of ethylene glycol (liquid) to choline chloride was 1:2. Heating the mixture to 55 °C produced a homogenous liquid solution in about 30 minutes.

3.2. Procedure

3.2.1. Growth of Metals/Alloys from Aqueous Solution with Pyrophosphate Ligands

Bimetallic alloys and ternary alloy were obtained by applying constant potential of -2 V in pyrophosphate-based electrolyte. All films were fabricated at room conditions (around 1 atm and 25±2 °C). Computer-assisted Versa STAT device (Figure 3.3a) was used to perform Fe, Zn, Mn and alloys (Zn-Mn, Mn-Fe, Mn-Fe and Fe-Zn-Mn) electrodeposition. Experiment set up for metal/alloy coatings was based on three-

electrode electrodeposition system. Working, reference and counted electrodes are presented in Figure 3.3b. A constant potential (potentiostatic experiment set up (Figure 3.3c)) was applied to obtain metals/alloys on graphite (Figure 3.3d).

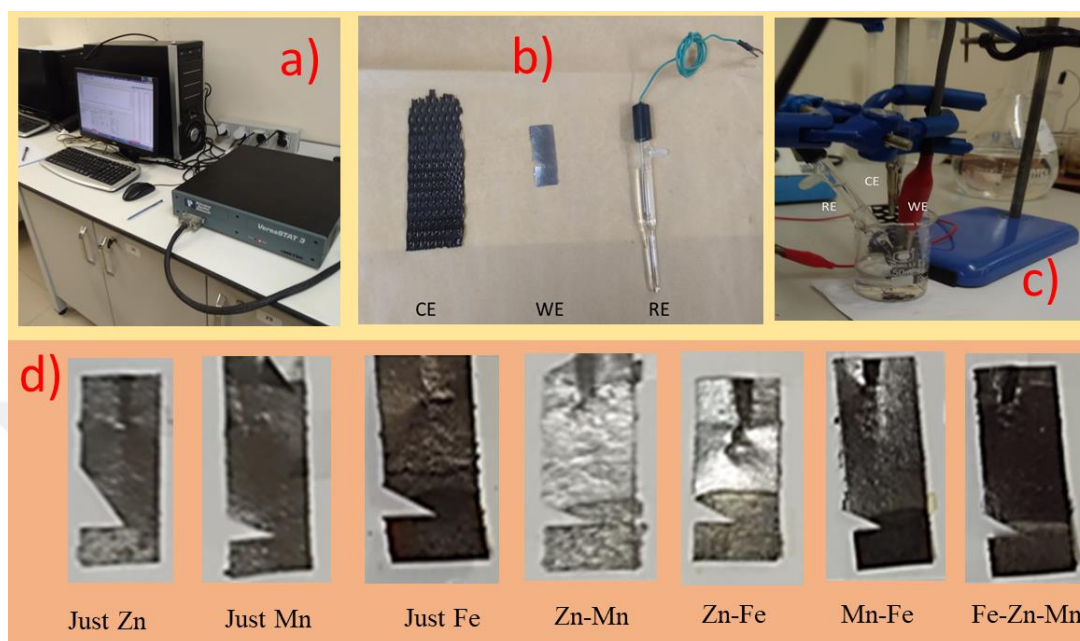


Figure 3.3 a) Experimental setup (potentiostat). b) Photo of the electrodes used in this research. WE, CE and RE refer to counter electrode, working electrode and reference electrode. c) Photo of three-cell electrodeposition system. d) Photo of the modified electrodes after electrodeposition process explained in the main text.

3.2.2. Growth of Coating on AISI 4140 Substrate with Different Ligands

All of the films were produced on an AISI 4140 stainless steel working electrode with a standard composition of %0.360 C, % 0.8 Mn, %0.005 Si, around 1%Cr, %0.30 Ni, less than 1 % Mo, % 0.075 V, % 0.070 S, nearly 0.15 % Cu and %0.034 P with an effective surface area [103]. A constant potential was applied in cathodic direction on a steel electrode with little current flow in an aqueous electrolyte having different ligands.

Before the deposition of steel layer some cleaning processes was applied as follow:

1. Steel plates were cut into discs with 2 mm thickness and 1.5 cm diameter in dimension.
2. Steel plates were mechanically polished with 300, 600, 1000 and 2000 mesh

sandpaper sequentially.

3. The polished surface of the steel plates was washed with distilled water.
4. Then, the steel plates were rinsed in the distilled water. In this way, its surface was freed from some kind of dirt and dusts.
5. Finally, the surface of the steel plates was dried with a dry paper.

At the end of all these processes, the steel substrate was ready for the application of electrodeposition.

3.2.2.1. Growth of Fe-Zn Alloy

$Zn_{1-x}Fe_x$ alloys [104] were deposited as of a chloride plating bath consisted of $ZnSO_4 \cdot 7H_2O$, $FeSO_4 \cdot 7H_2O$, $Na_2C_2O_4 \cdot 2H_2O$, H_3BO_3 . Contents of the solutions for preparing samples and their amounts are given in Table 3.1

Table 3.1 Contents of the liquids

Solution	Amounts (g/l)
$ZnSO_4 \cdot 7H_2O$	40
$FeSO_4 \cdot 7H_2O$	10,20,30,40,50
$Na_2C_2O_4 \cdot 2H_2O$	25
H_3BO_3	16

Hydrochloric acid is used to lower the pH of the bath to 4.7. The used electrolyte was made with double distilled water and p.a. chemicals (Merck). There were deposits made with a potential of -2 V. The experiment was conducted at 20 °C. Iron disks (AISI 4140) were the working electrodes (WE) utilized for electrodeposition. The data of prepared samples onto AISI 4140 code steel is given in Table 3.3.

Table 3.2 Sample used for the experiment and their data during the preparation of Fe-Zn samples.

No	Current (mA)	Potential (V)	CFe= FeSO ₄ *7H ₂ O (g/l)	Thickness d(μm)	pH	Temperature (°C)
FeZn-1	32	-2	10	2	4.7	20
FeZn-2	33	-2	20	2	4.7	20
FeZn-3	30	-2	30	2	4.7	20
FeZn-4	30	-2	40	2	4.7	20
FeZn-5	30	-2	50	2	4.7	20

3.2.2.2. Growth of Fe-Mn Alloy

Fe-Mn alloys were deposited from a plating bath that was acidic and included FeSO₄, MnSO₄H₂O, (NH₄)₂SO₄ whose amounts are given in the Table 3.3. Hydrochloric acid is used to bring the bath's pH level to 3,2. The used electrolyte was made with double distilled water and p.a. chemicals (Merck). Deposition was carried out at a current 30mA per area with cm² experimental temperature was taken 20 °C. The working electrodes (WE) used for electro deposition were iron (AISI 4140) disks. Area and thickness of thin film are 0.2 cm² and 3.4 μm respectively.

Table 3.3 Sample used for the experiment and their data during the preparation of Fe-Mn samples.

No	FeSO ₄ (g/L)	MnSO ₄ H ₂ O = 33.8g/l (NH ₄) ₂ SO ₄ = 200g/l pH = 3.2 Room Temperature Area = 1 cm ² J = 30mA/cm ² d = 3.4 μm
FeMn-1	2	
FeMn-2	2.72	
FeMn-3	5.44	
FeMn-4	13.6	
FeMn-5	27.2	

Contents of the solutions for preparing samples and amounts were given in Table 3.4.

Table 3.4. Insides of the solutions for Fe-Mn alloys.

Solutions	Amounts (g/l)
FeSO ₄	(2), (2.72), (5.44), (13.6), (27.2)
MnSO ₄ H ₂ O	33.8
(NH ₄) ₂ SO ₄	200

3.2.2.3. Growth of Fe-Zn-Mn Alloy

The data of prepared samples onto AISI 4140 code steel is given in Table 3.5.

Table 3.5 Sample used for the experiment and their data during the preparation of Fe-Zn-Mn samples.

Sample	Current (mA)	Potential (V)	CZn= ZnSO ₄ 7H ₂ O (g/L)	Thickness d(μm)	pH	T(°C)
FeZnMn-1	20	-1.7	10	2	3.2	20
FeZnMn-2	23	-1.7	20	2	3.2	20
FeZnMn-3	21	-1.7	30	2	3.2	20
FeZnMn-4	22	-1.7	40	2	3.2	20

Zn-Fe-Mn alloys were deposited from a chloride plating bath consisted of ZnSO₄7H₂O, FeSO₄, MnSO₄H₂O, (NH₄)₂ SO₄ whose amount were given in Table 3. 6. With the help of hydrochloric acid, the bath's pH level is brought down to 3.2. The used electrolyte was made with double distilled water and p.a. chemicals (Merck). Deposits were made with the potential of -1.7 V. Experimental temperature was taken 20.°C Iron disks (AISI 4140) were the working electrodes (WE) utilized for electrodeposition.

Table 3. 6 Contents of the solutions for the Fe-Zn-Mn alloys.

Solution	Amounts (g/L)
ZnSO ₄ 7H ₂ O	10,20,30,40
FeSO ₄	40
MnSO ₄ H ₂ O	62.5
(NH ₄) ₂ SO ₄	200

Potentiostat/galvanostat could be used for electrochemical applications including battery, corrosion, electrolysis, and electroplating that call for a sizable current and high compliance voltage. Galvanostat/ Potentiostat, Model 1100 Series (CHI) was used in the electrodeposition and corrosion studies presented in this thesis. The range of the equipment is 2 A and the potential range of it between -10 and 10 V [105]. The potential window was selected depending on the electrodes.

3.2.3. Preparation of Coating Electrodes for the Electrodeposition of Steel in Ionic Liquid

To make a deposition electrolyte, Ethaline ionic liquids containing individually FeSO_4 - ZnCl_2 , FeSO_4 - MnCl_2 , and a mixture of FeSO_4 , ZnCl_2 , and MnCl_2 were utilized. After being ground with sandpapers (200, 800, 1500 mesh), the steel substrate was washed with deionized water and dried. Steel substrates were immersed in an Ethaline solution including FeSO_4 and ZnCl_2 for Fe- Zn coating, FeSO_4 and MnCl_2 for Fe-Mn coating, and FeSO_4 , ZnCl_2 , and MnCl_2 for Fe-Zn-Mn coating. Electrodeposition was carried out by using -1.6 V for 300 seconds at a temperature of 55 °C. Each coating was developed on the steel surface independently in this manner. A platinum RE (reference electrode) and a titanium CE (counter electrode) were utilized when the WE (working electrode) was ground steel. Due to the absence of water in ionic liquid, an Ag-AgCl RE containing aqueous solution was not used during the electrodeposition of the films.

3.3. Characterization of the Electrodes

3.3.1. Metals/Alloys from Aqueous Solution with Pyrophosphate Ligands

Modified electrodes having mono metal (Zn, Fe and Mn), bimetallic alloy (Zn-Fe, Zn-Mn and Fe-Mn) and ternary alloy (Zn-Fe-Mn) were washed by deionized water after electrodeposition process explained above. The electrodes were transferred to 3.5wt.% NaCl solutions for corrosion test. The working and counter electrodes were metal/alloy coated graphite and Ir-Ru coated Ti mesh, respectively. The reference electrode in corrosion test was Ag-AgCl based electrode. The polarization was started at a potential which was 0.4 V less than open circuit potential. It means the starting point of

corrosion test was 0.4 V less than open circuit potential. The corrosion test was continued until +0.60 V vs Ag-AgCl RE (reference electrode). Two cycles were applied to all resulting electrodes to compare their passivation behavior. In this study CHI 1100 and Amatek Potentiostat devices have been used during experiment to get polarization curves.

3.3.2. Characterization of the Electrodes for The Electrodeposition of Steel in Ionic Liquid

The chemical structures of uncoated steel were determined using FT-IR (Perkin Elmer, Connecticut, USA), and the results were compared to the chemical structures of Zn-Fe, Fe-Mn, and Fe-Zn-Mn coated steel substrates. SEM morphological investigations of bare steel, Zn-Fe, Fe- Mn, and Zn-Fe-Mn alloy thin films on steel were performed (ZEISS Gemini FEGSEM 300, Germany). The phase of the fabricated thin films was determined using XRD. The electrodes in this work were electrochemically characterized using a potentiostat equipped with a three-electrode setup. The VersaSTAT3 (Oak Ridge, USA) potentiostat consisted of a reference, a working, and a counter electrode. In this study, coated steels were subjected to potentiodynamic polarization with 3.5 weight % NaCl to understand the corrosion process of the electrodes produced. In aqueous solution, an Ag-AgCl reference electrode was employed to maintain a consistent potential throughout the experiment. Steel (coated or uncoated) working and platinum coated titanium counter electrodes were utilized. The rationale for not using the Ag-AgCl (3 M KCl) RE (reference electrode) in the ionic solution is because the water in the Ag-AgCl RE (reference electrode) can combine with the ionic solution, altering the measurement potential. When the electrodes were cycled in aqueous NaCl solution, Ag/AgCl (with saturated KCl solution) was used as a reference electrode.

CHAPTER IV

RESULTS AND DISCUSSION

4.1. Electrodepositions of Fe and Fe Alloys (Fe-Zn, Fe-Mn and Fe-Zn-Mn) from Aqueous Electrolyte with Pyrophosphate Ligand

Metals and alloys were electrodeposited by applying constant potential as explained in Experimental section. Firstly, only metals (Zn, Fe and Mn) were grown on the substrate by applying -2 V for 300 seconds. Their chronoamperometric responses of only metals are shown in Figure 4.1a. The current of the elements during electrodeposition is different probably because of their thickness or hydrogen evolution reaction. Bimetallic alloys (Zn-Fe, Zn-Mn and Fe-Mn) and ternary alloy (Zn-Fe-Mn) were also obtained in the same conditions to compare metals and alloys corrosion behavior. Current responses of alloys during electrodeposition is presented in Figure 4.1b. Fluctuation of current occurs also during electrocoating of alloys. This fluctuation could be caused by different growth/nucleation reaction and different amount of hydrogen evolution reaction. As growth/nucleation process of the metals/alloys is out of the context of this thesis, we focused on corrosion responses of resulting electrodes.

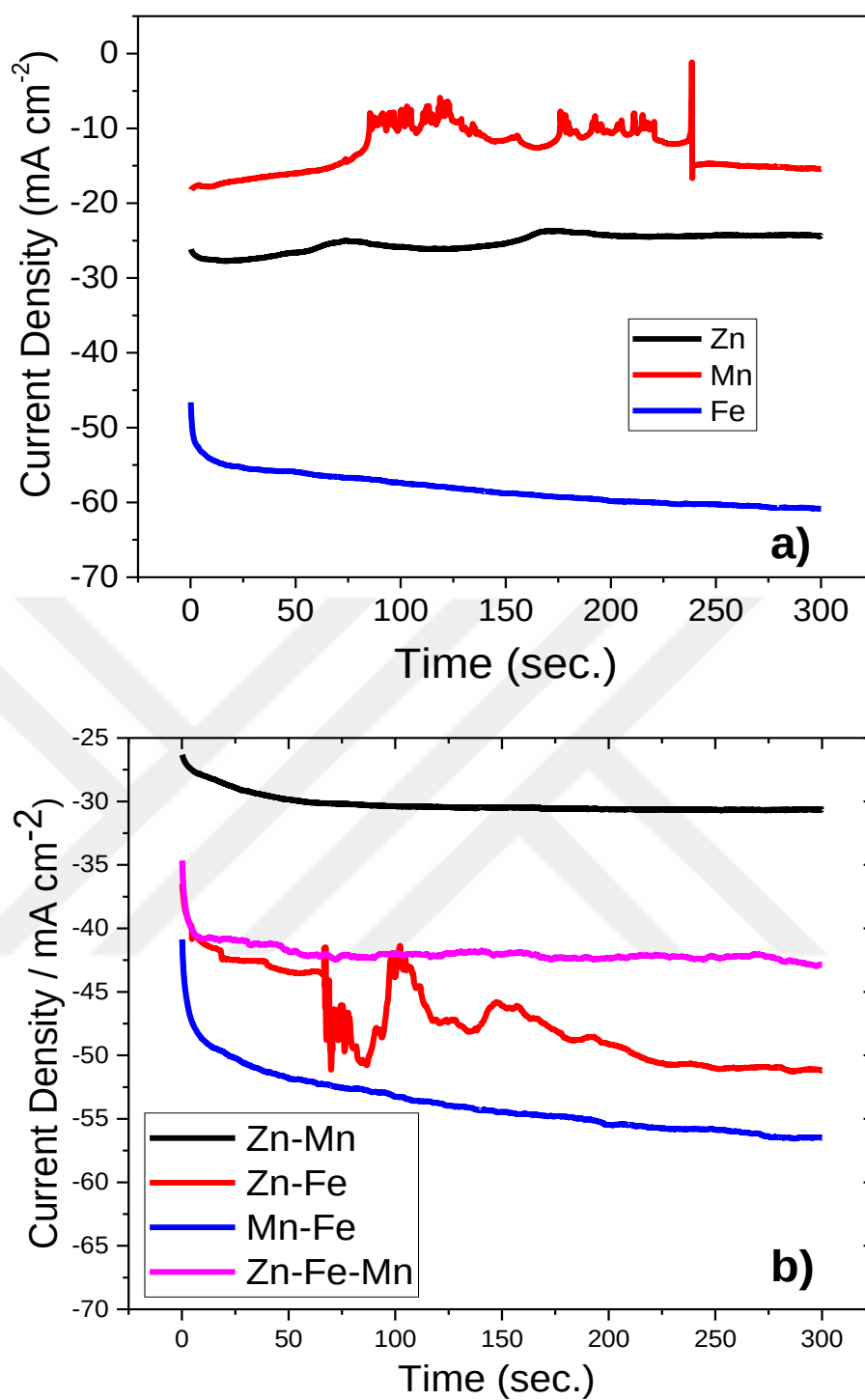


Figure 4.1 Chronoamperometric responses of potentiostatic growth of the films. Electrodeposited metals and alloys are indicated in the graphs.

After metals were electrodeposited potentiostatically by applying -2 V for 300 seconds, they were transferred to NaCl solution and their polarization is shown in Figure 4.2. It is known that iron could not have passive behavior and it can easily

corrode which is called pitting corrosion in NaCl media [106] Current responses of iron coating from aqueous solution increased significantly around 0 V indicating that iron could have pitting corrosion in NaCl solution (blue line of Figure 4.2a. Linear sweep voltammetry of Mn coated substrate is presented in Figure 4.2b to observe corrosion behavior clearly. All linear sweep voltammetry experiments were started at a negative potential which was 0.4 V less than open circuit potential. They were continued to 0.6 V to compare their corrosion behavior in the same conditions. The corrosion behavior of Mn in NaCl bath is similar to that of Fe. However, the current response of Mn (around 0.2 mA) is much lower than that of Fe (around 40 mA) at 0.6 V. It means that manganese could have higher corrosion resistivity than iron in these conditions.

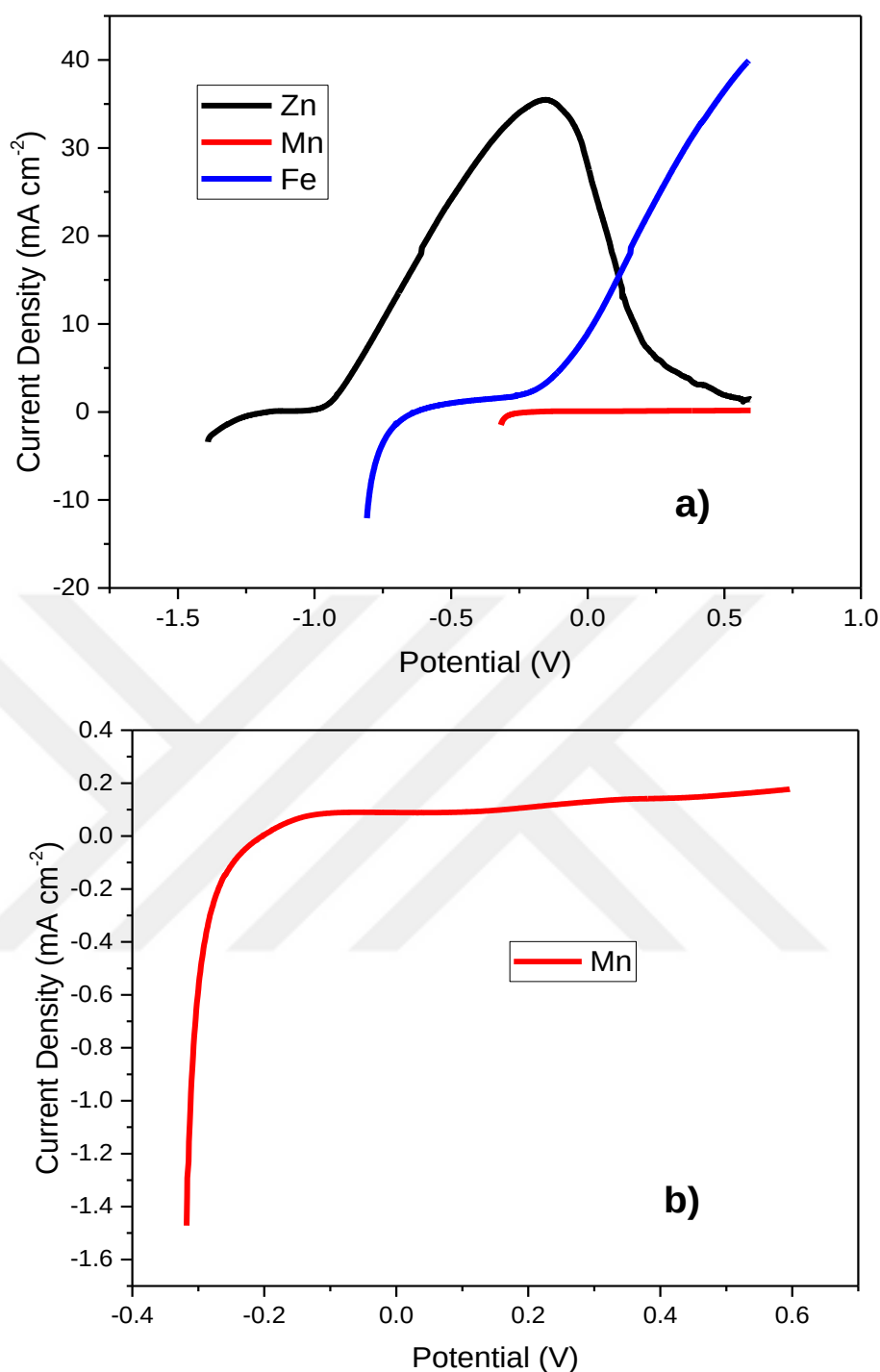


Figure 4.2 a) Linear sweep polarization of metals (obtained in aqueous solutions) in NaCl. b) linear sweep voltammetry responses of Mn.

Tafel plot of Figure 4.2 is drawn to compare corrosion properties of the films. The starting potential of cycles were at a potential less than open circuit potential and continued to positive direction (up to 0.6 V). Figure 4.2 illustrates corrosion behavior of mono metal (Zn, Fe and Mn film) in NaCl electrolyte. Passivation of Zn can be

proved by this experiment as current decreases after around 0 V. However, passivation of Mn or Fe was not observed. The pitting corrosion of iron could be deduced from this result because current significantly increased after around -0.2 V (blue line of Figure 4.3). Corrosion current of Mn (red line of Figure 4.3) is around ten times less than that of Fe (blue line of Figure 4.3). Pitting corrosion is not clear in Mn polarization as anodic polarization of Mn is almost constant.

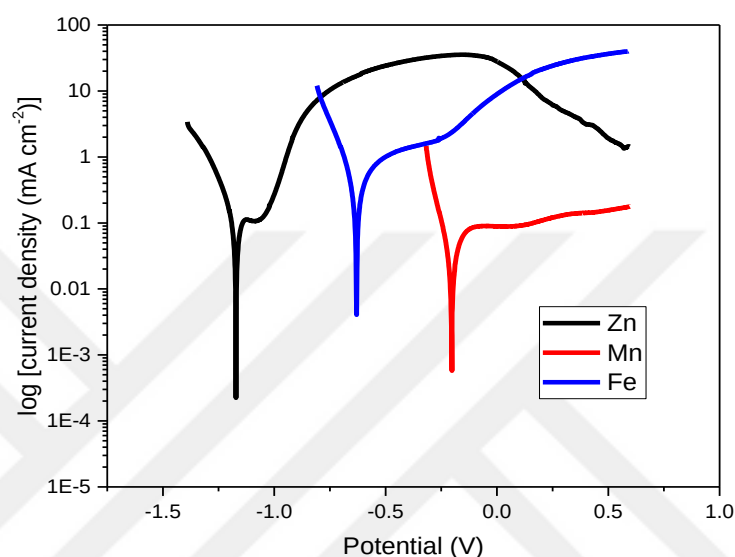


Figure 4.3 Tafel plot of Zn, Mn and Fe coating in NaCl. The data was retrieved from Figure 4.2.

Passivation of metals can prevent materials from corrosion. Therefore, it is usually a required properties for metals and alloys. Metals/alloys which could be passivated can be used for longer time. Linear sweep voltammetry and Tafel plot of metals showed that Zn can be passive in NaCl environment in Figure 4.2 and Figure 4.3, respectively. Second cycles of metals were compared in Figure 4.3. Zinc was cycled in NaCl and its polarization is given in Figure 4.4a. Corrosion current of zinc in second cycle (red line of Figure 4.4a) is more than ten times lower than that in first cycle (black line of Figure 4.4a) because it had a passive layer which could stop further corrosion. The first cycle was forward cycle and the second cycle was backward cycle. The first and second Tafel plot of Mn had similar corrosion current (Figure 4.4b). Corrosion behavior of Fe for cycles one and two are similar and they have similar current value due to pitting corrosion of iron (Figure 4.4c). After analyzing corrosion behavior of mono metal coatings, corrosion properties of alloys were examined.

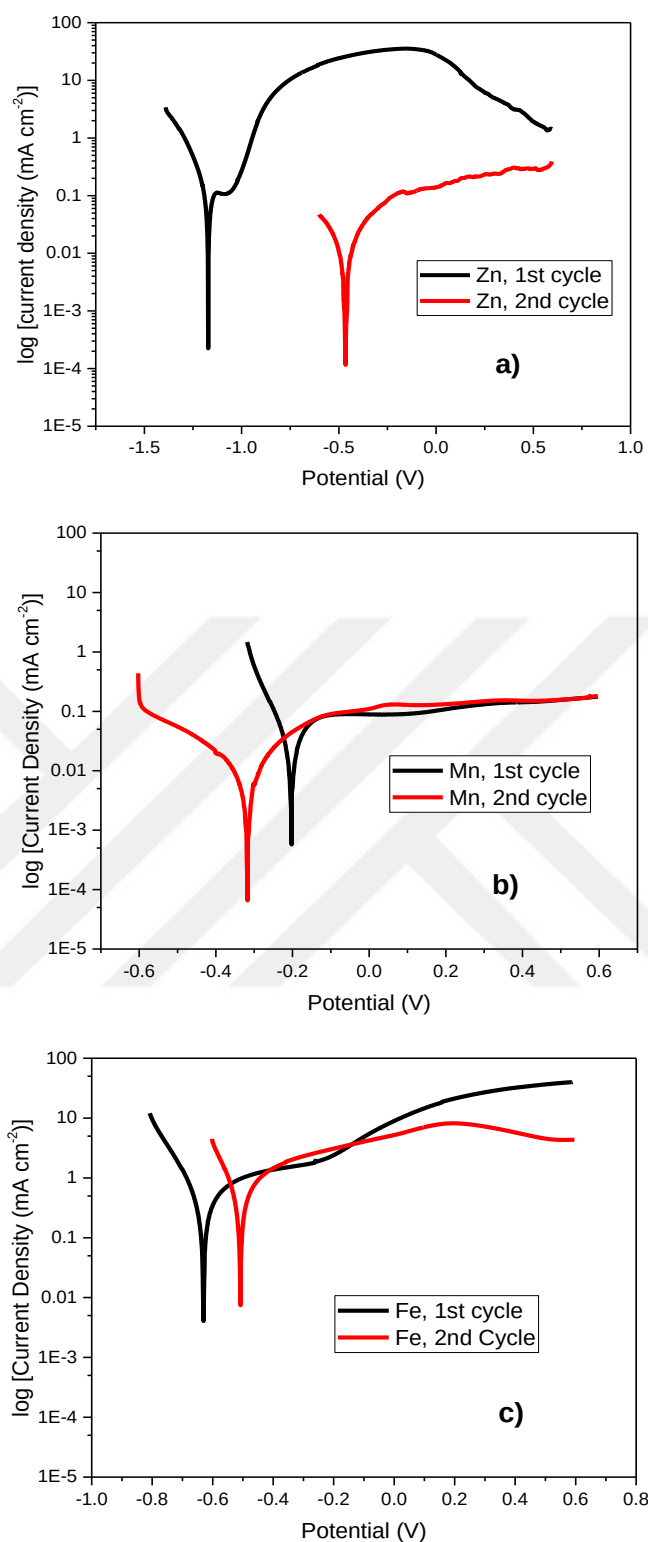


Figure 4.4 Tafel plot responses of a) Zn; b) Mn and; c) Fe coating in NaCl.

Alloys having two and three metals were obtained potentiostatically in aqueous solution. They were cleaned by deionized water and immersed in NaCl solution. Tafel plot of bimetallic alloys (Zn-Mn, Zn-Fe and Mn-Fe) were obtained in artificial

seawater (NaCl solution). Figure 4.5 illustrates polarization responses of bimetallic alloys. Oxidation peaks belonging to zinc-based alloys (Zn-Fe and Zn-Mn) were observed. These peaks could indicate passivation of Zn based alloys. Passivation of Zn-Mn (black line of Figure 4.5) and Zn-Fe (red line of Figure 4.5) occurred thanks to zinc addition because both of these alloys contained Zn metal. However, Mn-Fe film did show no passivation (blue line of Figure 4.5). Therefore, zinc could be used as alloying material to have higher corrosion resistivity.

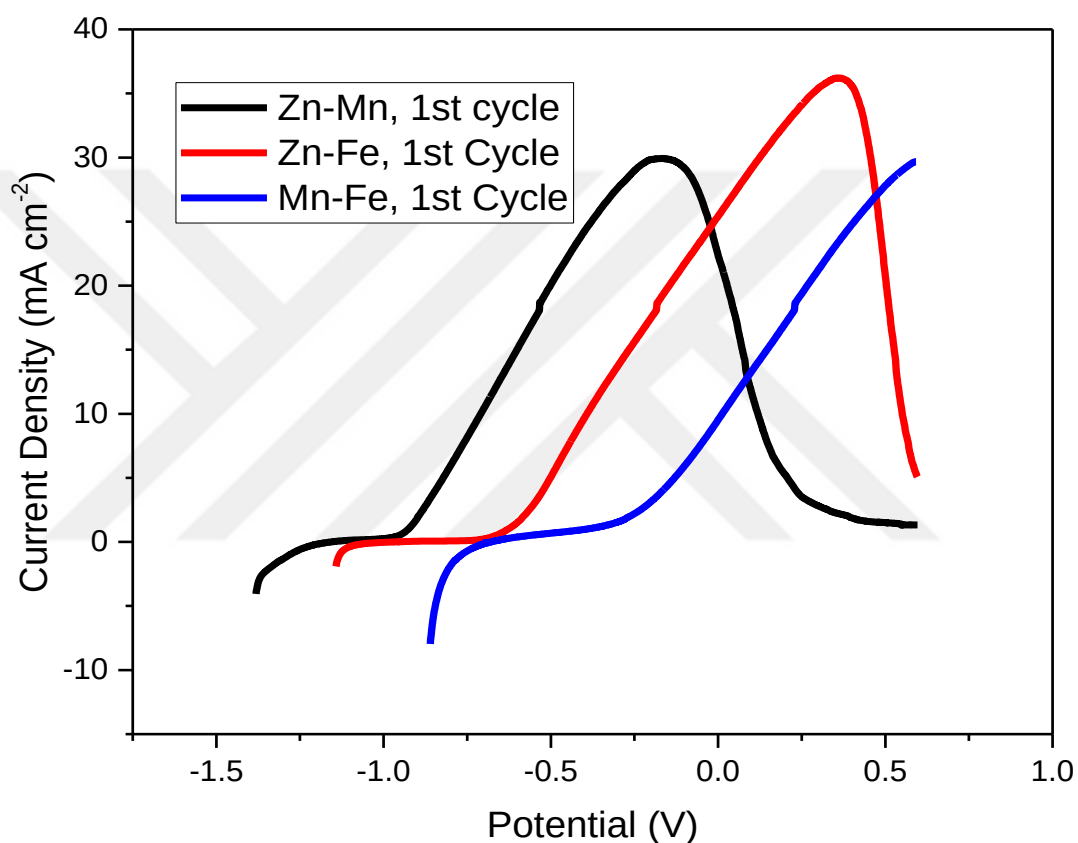


Figure 4.5 Linear sweep polarization of alloys (Zn-Mn, Zn-Fe and Mn-Fe obtained in aqueous solutions) in NaCl.

Logarithmic form of current in Figure 4.5 could be used to obtain Tafel plot of the films. Figure 4.6 demonstrates corrosion current and potential of bimetallic alloys in NaCl bath. Passivation of Zn-Fe and Zn-Mn are obvious as their current responses decreased around 0.5 V and .0.1 V, respectively. It could be deduced from Figure 4.6 that corrosion resistance of Zn-Fe film (red line in Figure 4.6) is higher than the others (either Mn-Fe or Zn-Mn) as Zn-Fe has lower corrosion current. Figure 4.6 also indicates

that a pitting corrosion could occur in Mn-Fe alloy. Addition of Zn could seize further corrosion as it causes passivation of the films. Therefore, it could be suggested that Zn could be added to alloys for higher corrosion resistivity of alloys. Electrodeposition is a suitable technique to form zinc-based alloys.

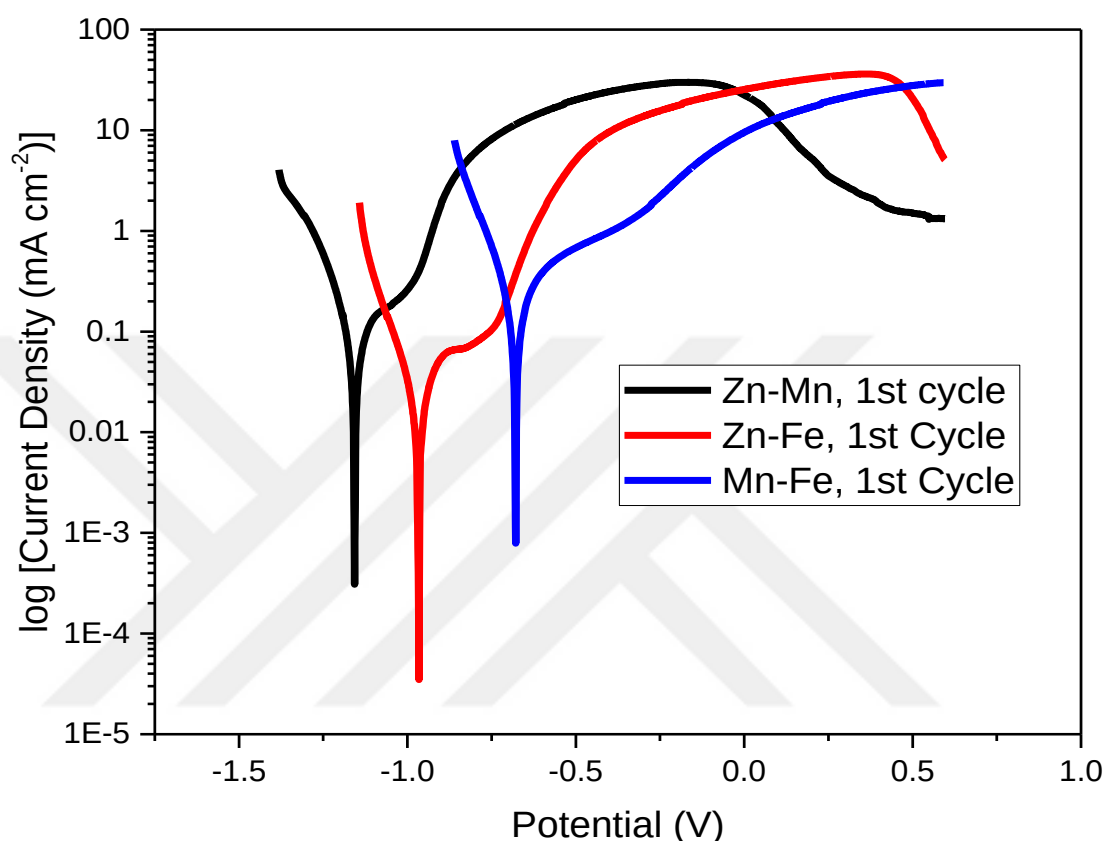


Figure 4.6 Tafel plot responses of Zn-Mn, Zn-Fe and Mn-Fe coating in NaCl.

First and second cycles of bimetallic alloys were compared to check their passivation/pitting corrosion behavior. Figure 4.7 is linear sweep voltametric responses of the alloys having two metals. Scanning of polarization potential was from negative side to positive side. As the corrosion current of the second cycle belonging to Zn-Mn is lower than that of the first cycle belonging to the same film, a passivation of Zn-Mn can be mentioned clearly.

The passivation of Zn-Mn was expected since it contains Zn. However, Figure 4.7 b did not display a significant passivation. Passivation was not expected for the film containing only Mn-Fe alloy. The corrosion current of Mn-Fe for the second cycle is

higher than that for the first cycle. It was concluded that addition of Zn could cause passivation and generally higher corrosion current. Therefore, Zn was also added to Mn-Fe to observe its corrosion properties.

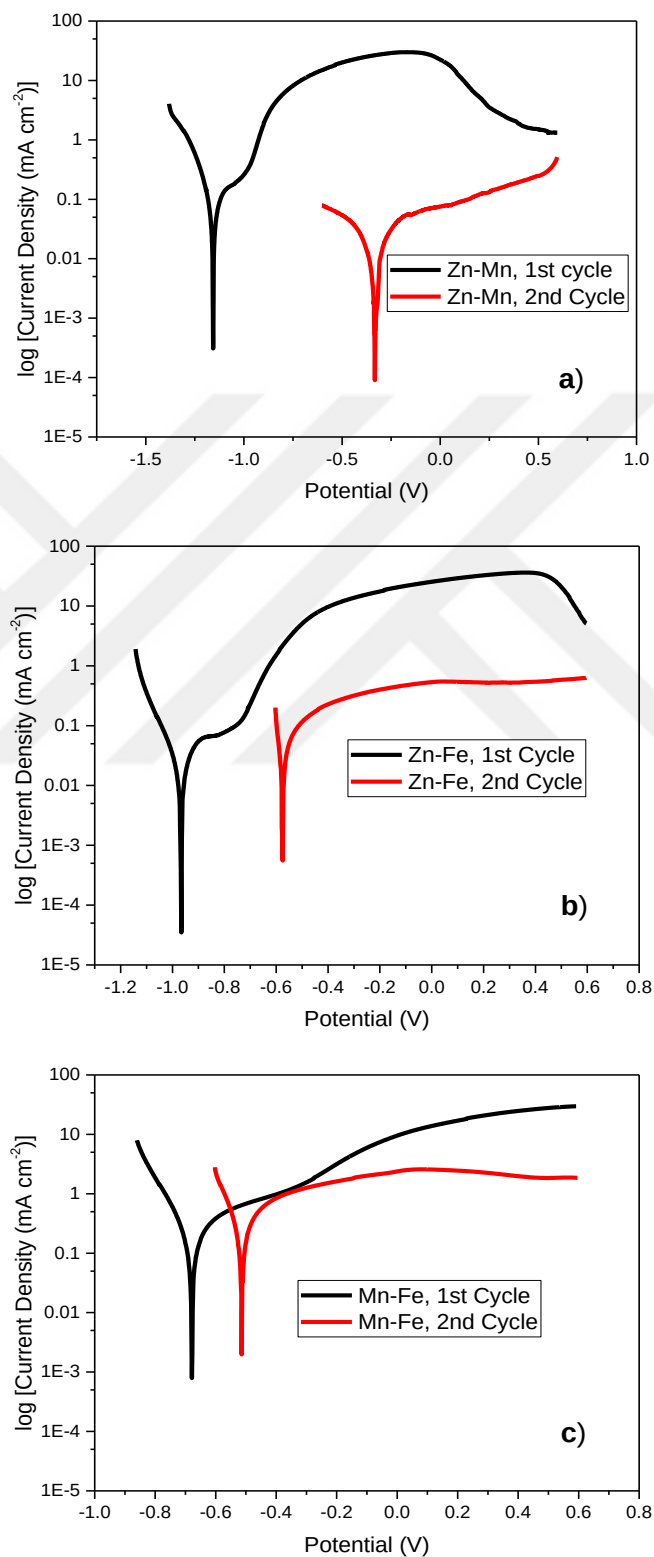


Figure 4.7. Tafel plot responses of a) Zn-Mn, b) Zn-Fe and c) Mn-Fe coating in NaCl.

When corrosion behavior of monometallic coating was analyzed, it was noticed that only Zn could have passivation behavior. Only Fe coating had pitting-like corrosion and its corrosion was higher than only Mn coating. Bimetallic alloys (Zn-Mn, Fe-Zn and Fe-Mn) were examined by means of linear sweep voltammetry and the alloys having Zn (Zn-Mn and Zn-Fe) illustrated passivation behavior. Ternary alloy having the three metals (Fe-Zn-Mn) studied in this work was obtained potentiostatically by applying constant potential for the same timescale (300 seconds). The ternary alloy was transferred to NaCl electrolyte for analyzing its corrosion behavior. Linear sweep voltammetry (cyclic polarization) responses of the ternary alloys is presented in Figure 4.8. The scanning was started from negative direction to 0.6 V shown in black line of Figure 4.8a. A clear oxidation peak for the first cycle of the ternary alloy was observed. However, current responses of this film for the second cycle are much lower than that for the first cycle which is due to passivation behavior of the alloy. The presence of Zn in its content (in Zn-Fe-Mn alloys) could cause this behavior. Figure 4.8b is Tafel Plot of the modified electrode given in Figure 10a. Current response of the film decreased significantly around 0.3 V shown in black line of Figure 4.8b due to passivation mentioned in Figure 4.8a. Second cycle of ternary alloy in NaCl bath is less than the first cycle of it after -0.4 V till 0.6 V. Corrosion current of the ternary alloy film did not increase in the second cycle because of the creation of a stable surface. Corrosion behavior of the metals (Zn, Fe and Mn) and alloys (Zn-Mn, Zn-Fe, Fe-Mn and Zn-Fe-Mn) indicated that addition of Zn could change electrochemical responses of the film. Zn metal and Zn based alloys could generally have higher corrosion resistivity and cause passivation of the surface.

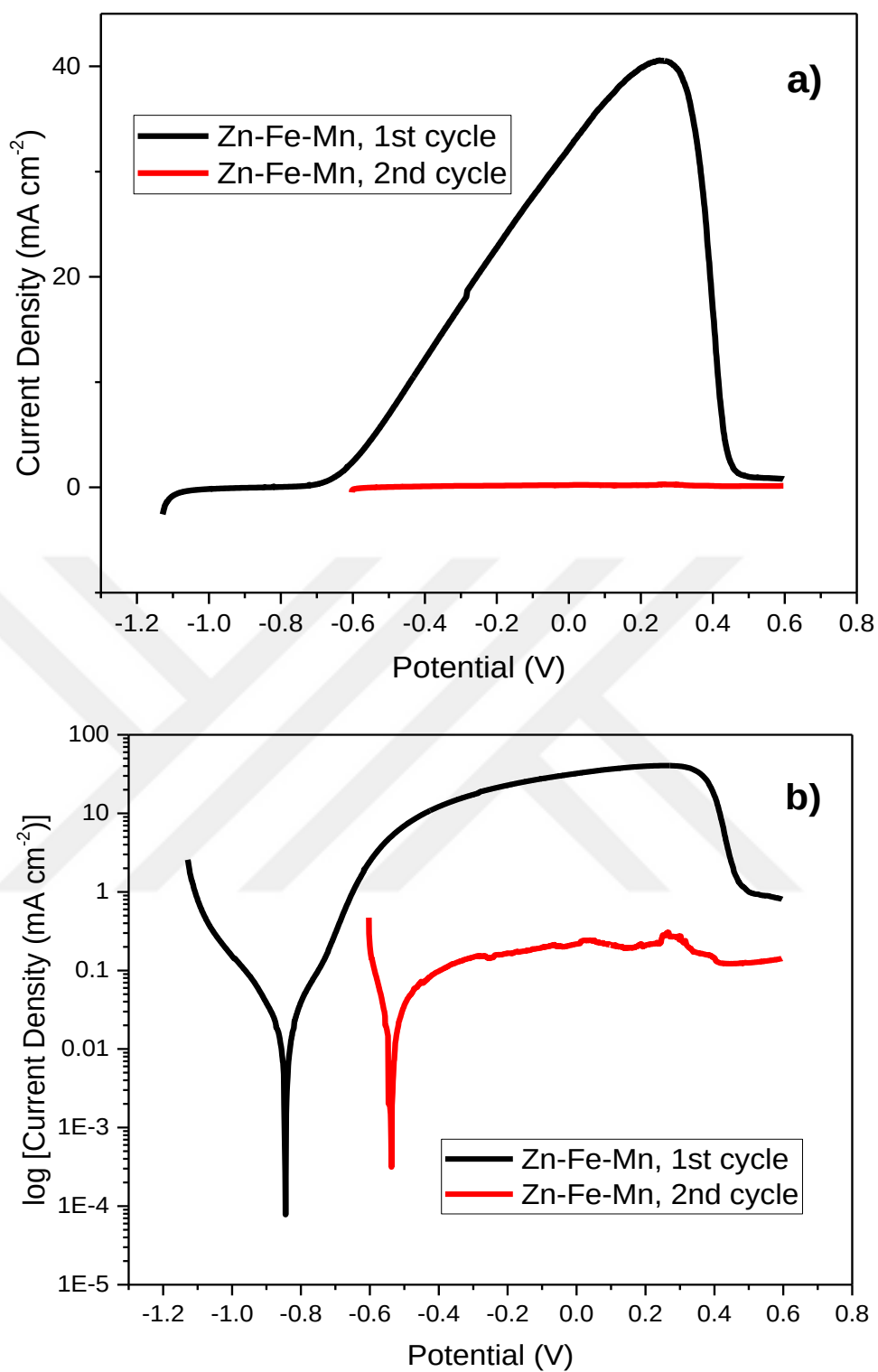


Figure 4.8 a) Linear sweep polarization and b) Tafel plot responses of metal alloys (Zn-Fe-Mn obtained in aqueous solutions) cycling in NaCl electrolyte.

4.2. Electrodepositions of Fe and Fe Alloys (Fe-Zn, Mn-Fe and Zn-Fe-Mn) from Aqueous Electrolyte with Different Ligands

4.2.1. Analysis of Fe-Zn alloy

4.2.1.1. Cyclic Voltammetry of Fe-Zn Alloy

The surface area of the steel substrate was 3.14 cm^2 and this substrate was used for Fe-Zn coating. The deposition potential of -2 V was applied for 5 minutes for each sample. This potential was found by cyclic voltammogram of steel in the electrolyte. The electrolyte consisted of 10, 20, 30, 40, 50 g/L Fe^{2+} concentrations.

shows the cyclic voltammograms of steel in the electrolyte having Fe^{2+} and Zn^{2+} . The electrolyte consisted of 10 g/L Fe^{2+} concentrations.

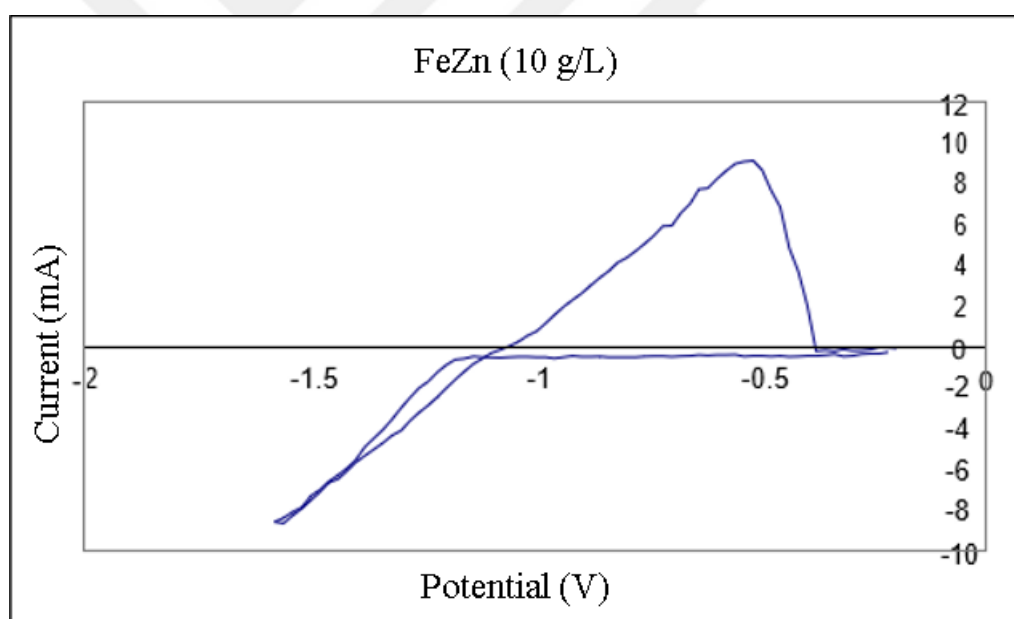


Figure 4.9 The cyclic voltammogram of Fe-Zn sample in solution containing (10g/L) of Fe concentration.

The pH value was adjusted to 4.7 and the potential was scanned the value between -0.22 V and -1.58 V for this sample. According to the results obtained from the data, it is seen in Figure 4.9 that the working electrode is not active between the potentials -0.22 V and -1.14 V. After the value of -1.14 V, the deposition of the Fe-Zn onto the iron substrate started and the cathodic current decreases until it arrives at the value of -1.58

V and sharp peak is observed at -8.41 mA. After the value of -1.58 V, the anodic current starts to rise. In the graph, it is observed the sharp peak around 9.28 mA and is seen the oxidation at -0.52 V. This oxidation means that the alloy electrodeposited at negative potential started to dissolve.

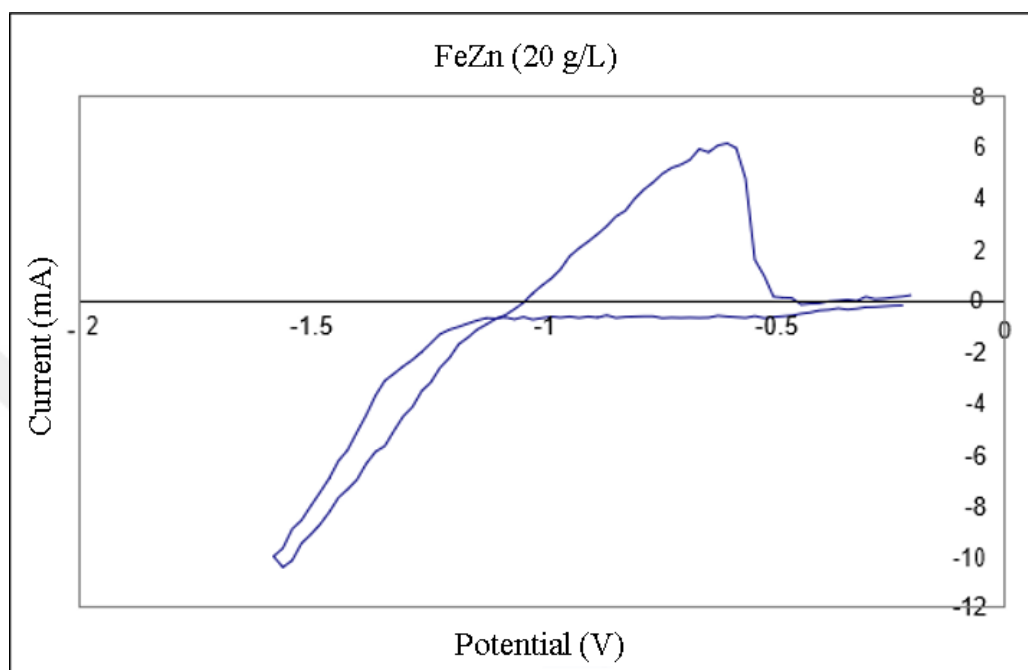


Figure 4.10 The cyclic voltammogram of Fe-Zn sample in solution containing (20g/L) of Fe concentration.

The pH value is 4,7, applied current 33 mA and the cathodic potential is scanned the value between -0.2 V and - 1.58 V for this sample. As seen in Figure 4.10 the working electrode is passive between the potentials -0.2 V and -1.14 V. The deposition of the Fe- Zn onto the iron substrate starts from the beginning of the value of -1.14 V and the cathodic current decreases until it arrives at the rate of -1.58 V and sharp peak is observed at -9.98 mA. The anodic current starts to increase after the value of -1.58 V. In the graph, the sharp peak around 6.19 mA and the oxidation at -0.6 V are observed.

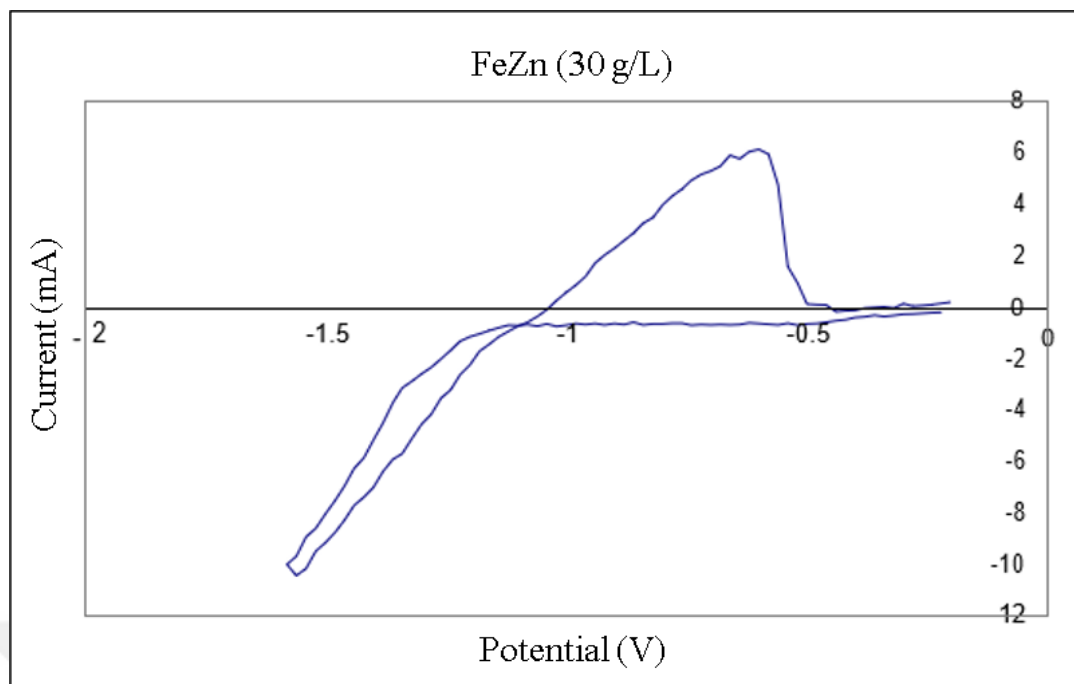


Figure 4.11 The cyclic voltammogram of Fe-Zn sample in solution containing (30g/L) of Fe concentration.

The pH value is 4.7, applied current 30 mA and according to the Figure 4.11 the scanning range of the cathodic potential value is between -0.24 V and 1.58 V for this sample. It is seen that the working electrode is passive between the potentials -0.24 V and -1.12 V. From the value of -1.12 V, the deposition of the Fe-Zn starts onto the iron substrate. The cathodic current decreases the sharp peak is at - 9.98 mA until the potential reaches -1.58 V. Then the anodic current starts to increase after the value of -1.58 V. In this status the sharp peak around 6.19 mA and is seen the oxidation at -0.6 V according to the graph.

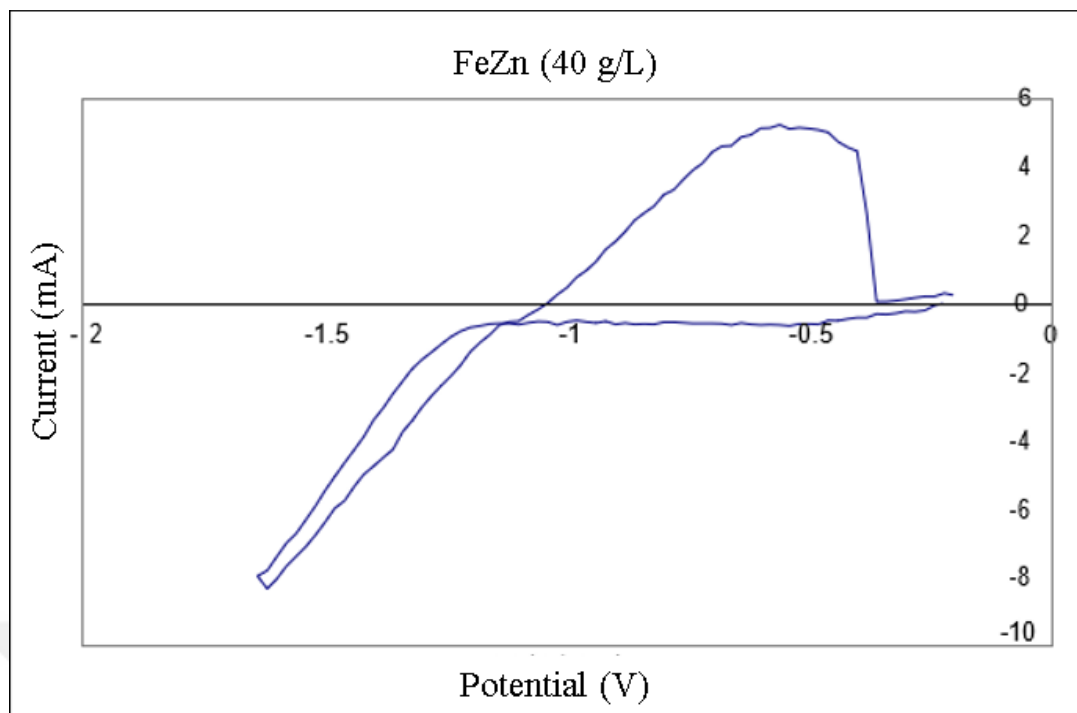


Figure 4.12 The cyclic voltammogram of Fe-Zn sample in solution containing (40g/L) of Fe concentration.

The pH value is 4.7, applied current 30 mA and as seen in Figure 4.12 the cathodic potential is scanned the value between -0.22 V and -1.64 V for this sample. Passivation potential value of the working electrode is between -0.22 V and -1.18 V. The deposition of the Fe-Zn onto the iron substrate starts from the beginning of the value of -1.18 V and the cathodic current decreases till it reaches the value of -1.64 V and -7.94 mA current value is observed. Increasing of the anodic current is seen after the value of -1.64 V. The sharp peak around 5.26 mA and the oxidation at -0.56 V are seen in the graph.

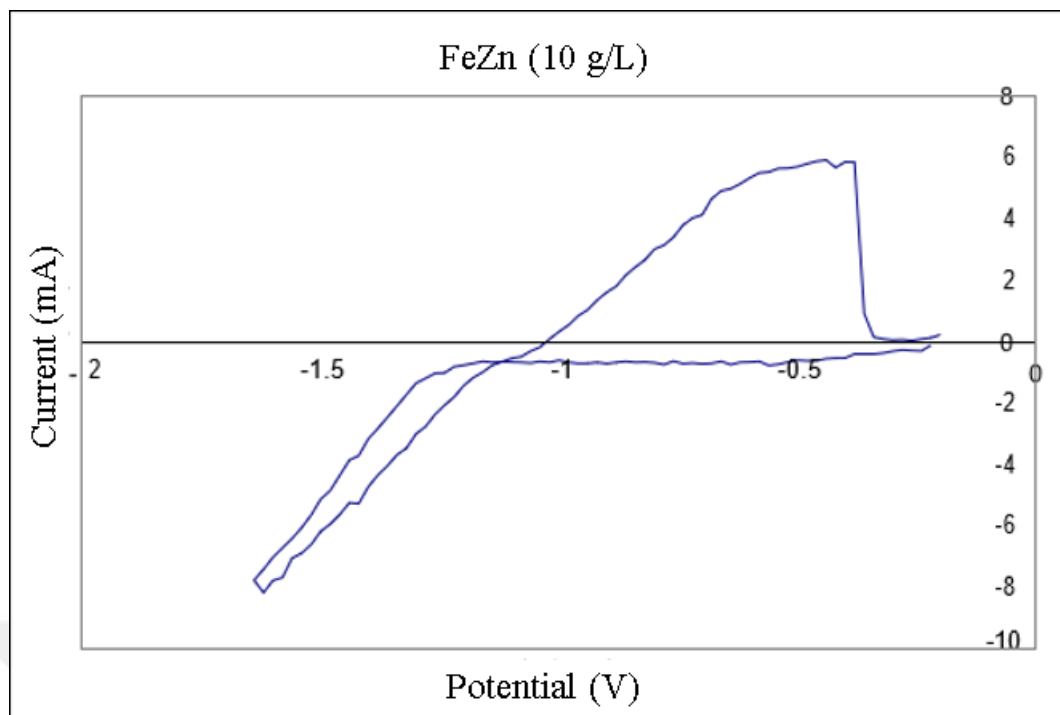


Figure 4.13 The cyclic voltammogram of Fe-Zn sample in solution containing (50g/L) of Fe concentration.

The pH value is 4.7, applied current 30 mA and as seen in Figure 4.13 the cathodic potential is observed between -0.24 V and -1.64 V scanning ranges for this sample. The working electrode is passive between the potentials -0.24 V and -1.16 V values. From the beginning of the value of -1.16 V, the deposition of the Fe-Zn onto the iron substrate starts and the cathodic current decreases up to it reaches the value of -1.64 V and sharp peak is observed at -7.7 mA. After the value of -1.64 V, the anodic current starts to increase. In this graph, it is observed that the sharp peak around 5.95 mA and the oxidation at -0.44 V are seen.

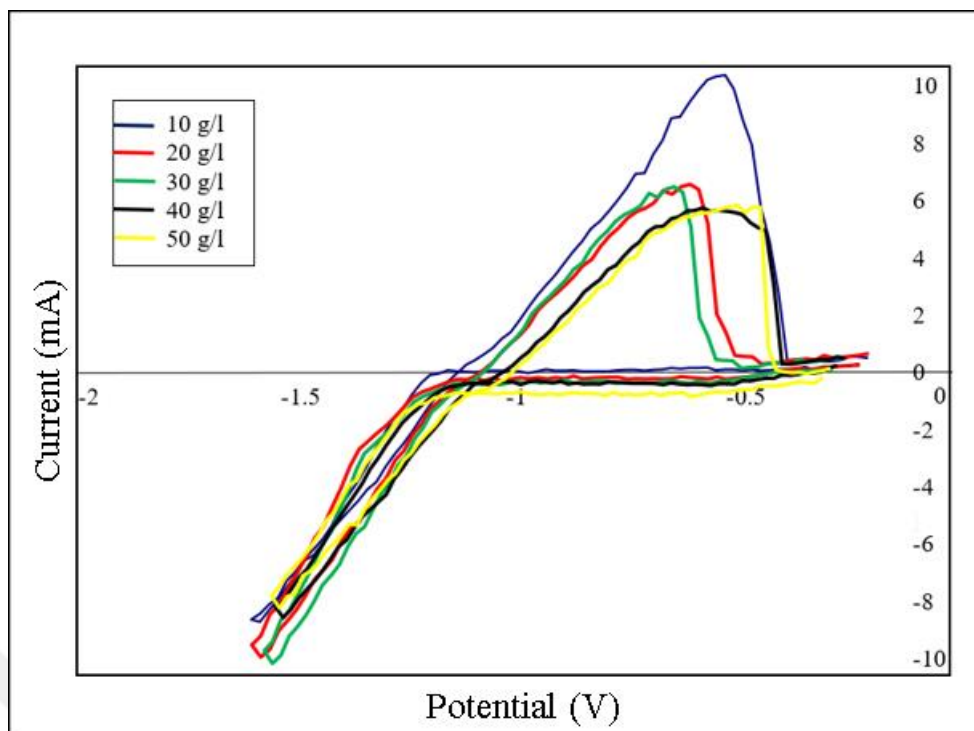


Figure 4.14 The overlapped cyclic voltammogram of Fe-Zn sample containing (10-50 g/L) of Fe concentration.

4.2.1.2. Scanning Electron Microscope (SEM) Pictures of Fe-Zn Alloy

Cyclic voltammograms in Section 4.2.1.1 showed that the application of a potential lower than -1.5 V could lead to electrodeposition of alloys. Therefore, a cathodic potential was applied to obtain alloys. After electrocoating of steel by various alloys, they were characterized by SEM, XRD, EDX and linear sweep voltammetry. SEM images of the Fe-Zn alloys electrodeposited onto the iron substrate show the crystal structure of the films by choosing an area with a 5000X magnification.

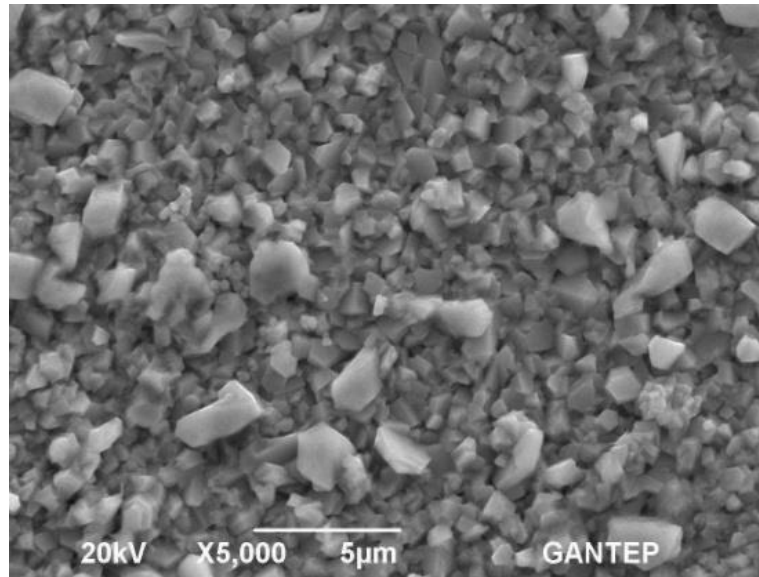


Figure 4.15 The SEM images of Fe-Zn containing 10g/L of Fe concentration.

The SEM picture of a Fe-Zn alloy made from an electrolyte with a 10 g/L Fe content and a pH of 4.7 is shown in Figure 4.15. The size of the granules is variable. Polygonal shapes are assembled to form the deposit.

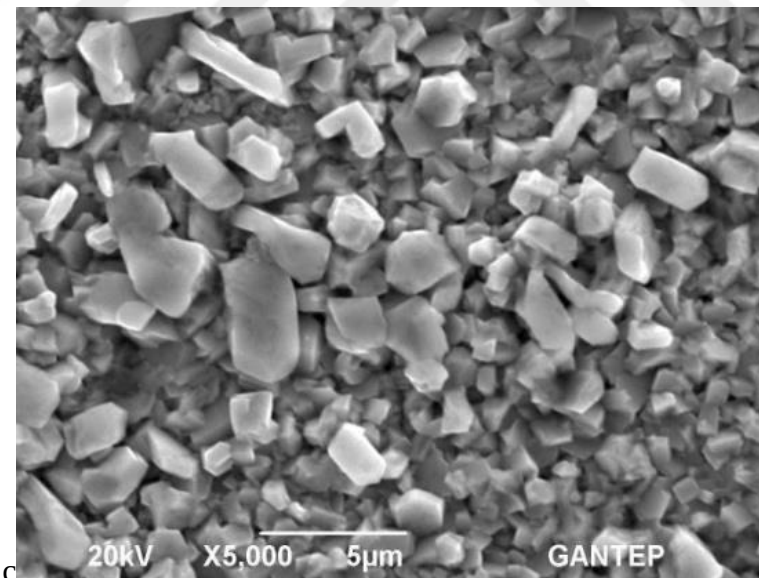


Figure 4.16 The SEM image of Fe-Zn containing 20g/L of Fe concentration.

Figure 4.16 gives the SEM image about the sample Fe-Zn alloy contains 20 g/L Fe composition with pH value of 4.7. There are bigger granules than the granules of SEM image in Figure 4.15.

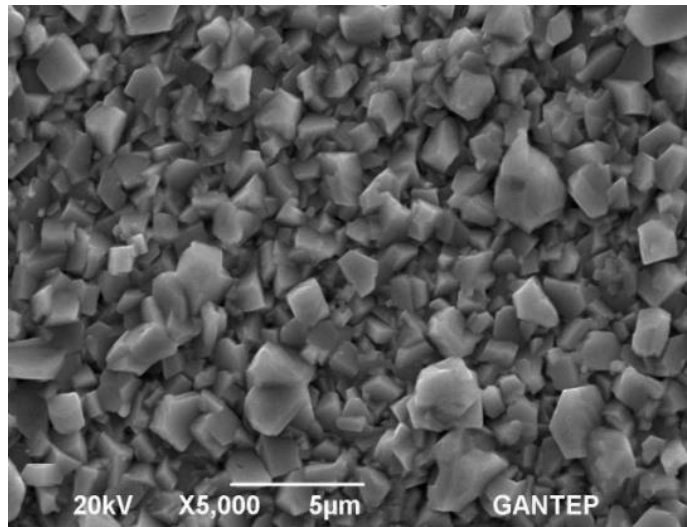


Figure 4.17 The SEM image of Fe-Zn containing 30g/L of Fe concentration.

Figure 4.17 shows a SEM image of a sample Fe-Zn alloy with a pH value of 4.7 and a Fe content of 30 g/L. The graphic shows that the average granular size, which is the largest among the other samples, is nearly equivalent to the average granular size of the Fe-Zn alloy electrodeposited onto the iron substrate. It proves the film has better crystalline, according to this.

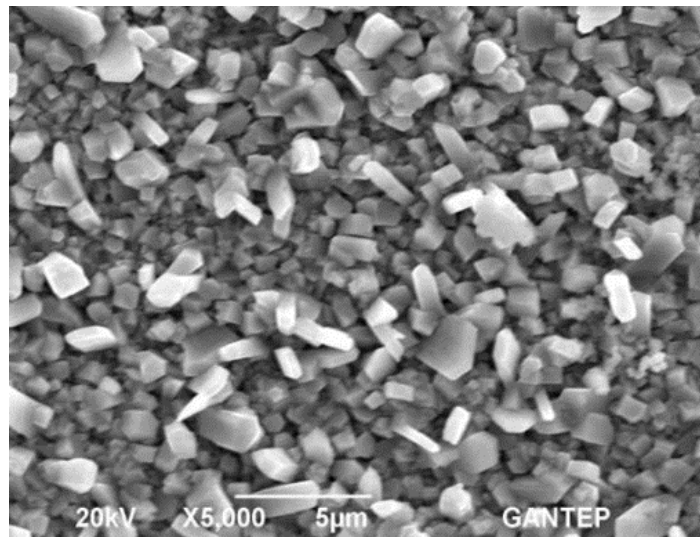


Figure 4.18 The SEM image of Fe-Zn containing 40g/L of Fe concentration.

Figure 4.18 screens SEM image about the sample Fe-Zn alloy contains 40 g/L Fe composition with pH value of 4.7. The image indicates that Fe- Zn alloy which is

electrodeposited onto the iron substrate homogeneously and almost equally to the average granular sizes which are smaller than the other samples have.

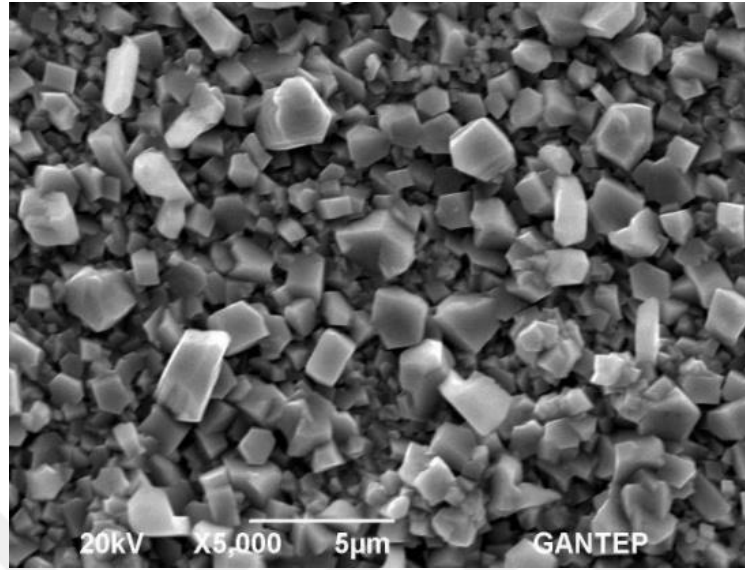


Figure 4.19 The SEM image of Fe-Zn containing 50g/L of Fe concentration.

Figure 4.19 gives the SEM images about the sample Fe-Zn alloy contains 50 g/L Fe composition with pH value of 4.7. In this image, the grains have more 3-D shapes and hexagonal shapes which are more marked. But gaps between granules are bigger and deeper than the other samples. This can create risks to protect substrate from the corrosion. Big gaps can allow getting foreign substances like water, dust etc. which cause corrosion to the surface of the sample.

4.2.1.3. Energy Dispersive X-Ray (EDX) Analysis of Fe-Zn Alloy

Following SEM investigation, EDX data of a Fe-Zn alloy electrodeposited from an electrolyte containing 10 g/L Fe^{2+} ions were obtained. Figure 4.20 and Table 3.7 illustrate EDX result of Fe-Zn alloy. Iron and zinc ratio in this alloy is 10.9% and 89.1%, respectively.

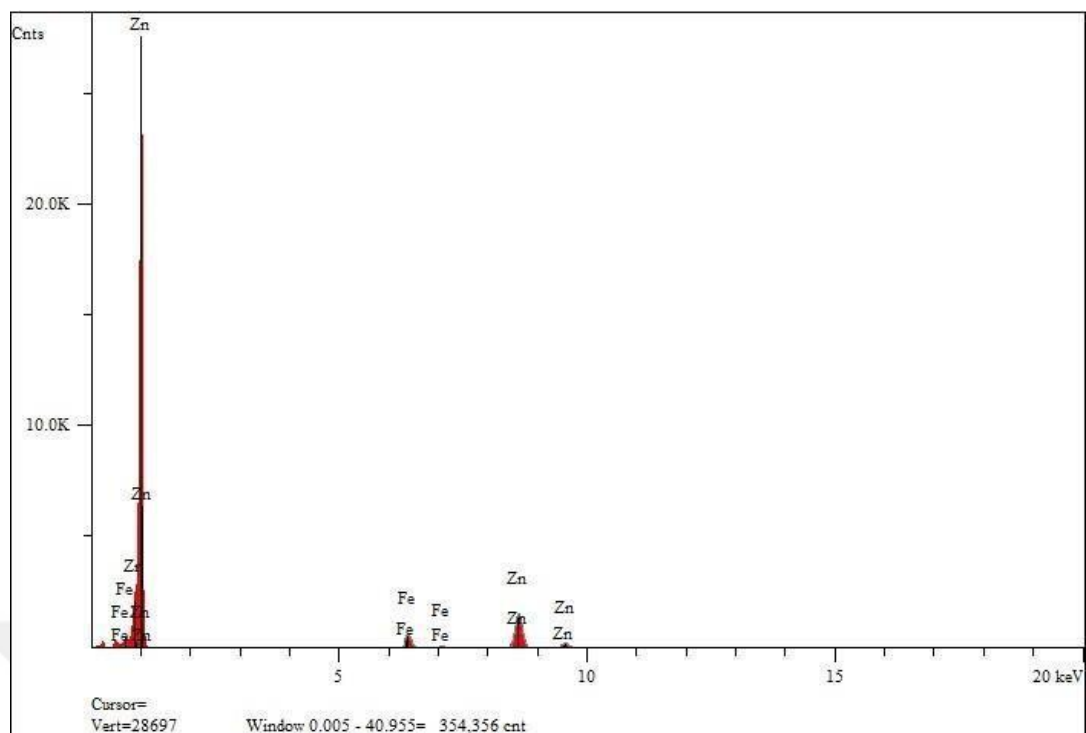


Figure 4.20 EDX image of Fe-Zn with 10 g/L Fe concentration.

Table 3.7 EDX Results Fe-Zn with 10 g/L Fe concentration.

Element	Line	Intensity (c/s)	Concentration	Units
Fe	Ka	98.65	10.889	wt. %
Zn	Ka	269.65	89.111	wt. %
			100.000	wt. %

EDX data of a Fe-Zn alloy electrodeposited from an electrolyte containing 20 g/L Fe^{2+} ions were obtained following SEM analysis. Fe-Zn alloy EDX results are illustrated in Figure 4.21 and Table 3.8 This alloy's iron and zinc content are 6.8% and 93.2%, respectively.

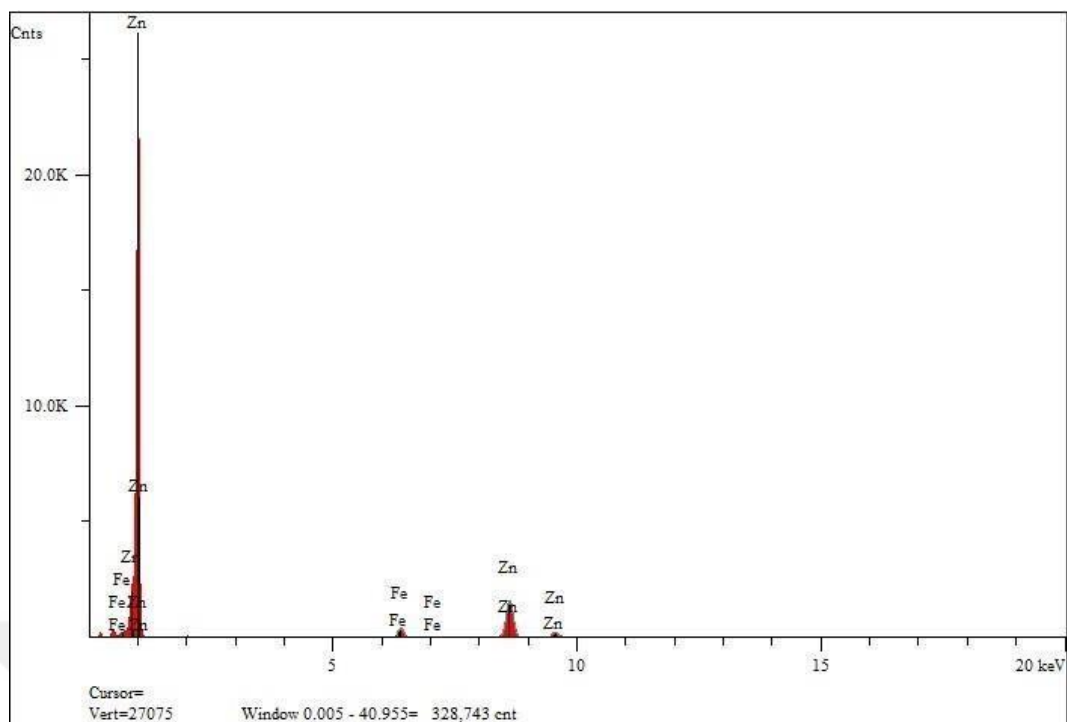


Figure 4.21 EDX image of Fe-Zn with 20 g/L Fe concentration.

Table 3.8 EDX Results Fe-Zn with 20 g/L Fe concentration.

Element	Line	Intensity (c/s)	Concentration	Units
Fe	Ka	60.02	6.765	wt.%
Zn	Ka	274.15	93.235	wt.%
			100.000	wt.%

EDX information of a Fe-Zn alloy electrodeposited from an electrolyte containing 30 g/L Fe^{2+} ions were acquired after SEM analysis. Figure 4.22 and Table 3.9 show the results of the EDX analysis on the Fe-Zn alloy. Fe-Zn with a 30 g/L Fe content was found using EDX. Iron and zinc make up 6.3% and 93.7%, respectively, of this alloy.

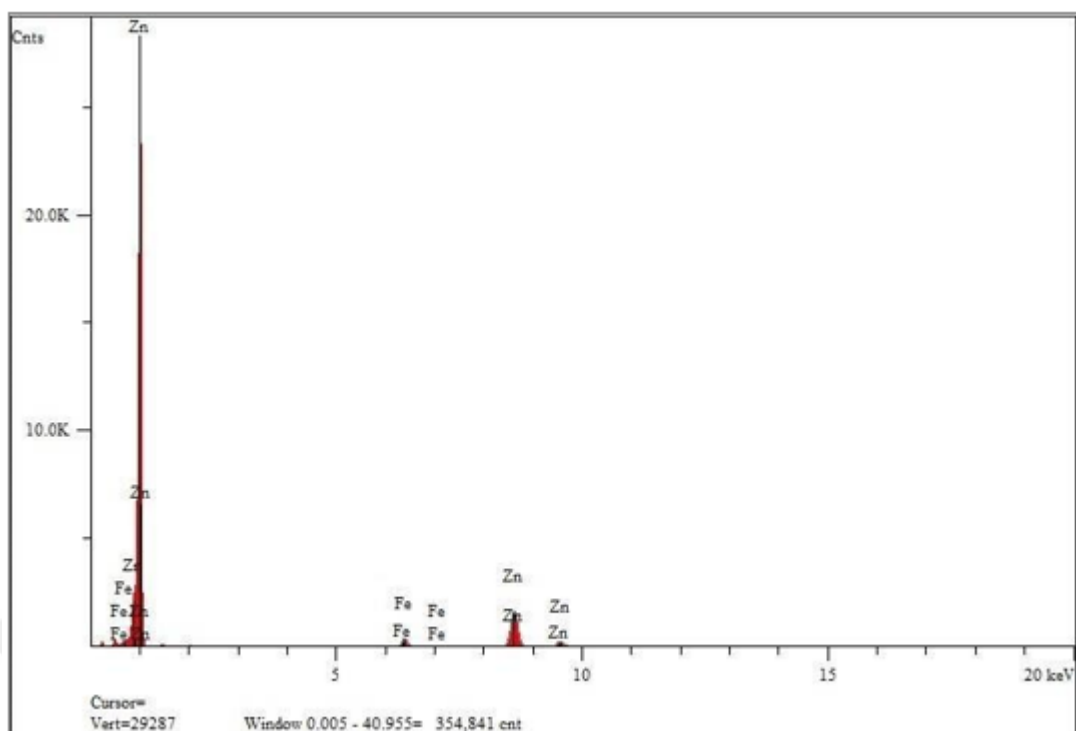


Figure 4.22 EDX image of Fe-Zn with 30 g/L Fe concentration.

Table 3.9 EDX Results Fe-Zn with 30 g/L Fe concentration.

Element	Line	Intensity (c/s)	Concentration	Units
Fe	Ka	58.84	6.255	wt.%
Zn	Ka	291.94	93.745	wt.%
			100.000	wt.%

EDX data of a Fe-Zn alloy electrodeposited from an electrolyte containing 40 g/L Fe^{2+} ions were obtained after SEM investigation. The outcomes of the EDX investigation on the Fe-Zn alloy are displayed in Figure 4.23 and Table 3.10. Using Fe-Zn with a concentration of 40 g/L was found using EDX. 6.3% iron and 93.7% zinc, respectively, make up this alloy.

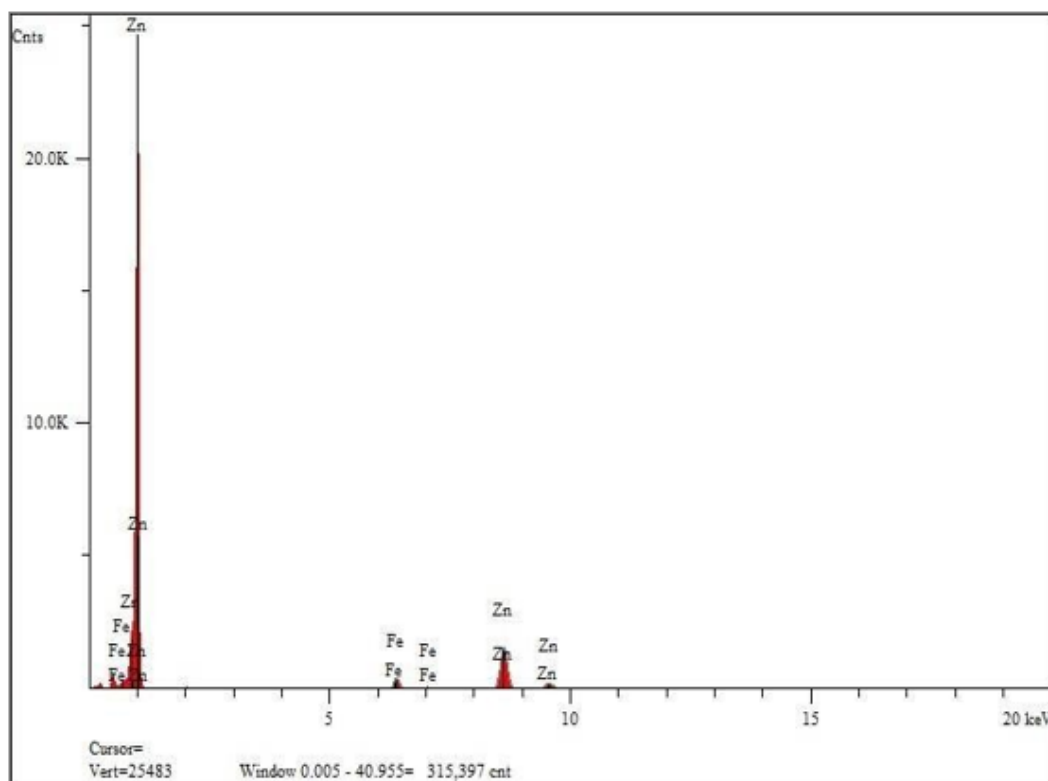


Figure 4.23 EDX image of Fe-Zn with 40 g/L Fe concentration.

Table 3.10 EDX Results Fe-Zn with 40 g/L Fe concentration.

Element	Line	Intensity (c/s)	Concentration	Units
Fe	Ka	64.09	7.194	wt. %
Zn	Ka	274.22	92.806	wt. %
			100.000	wt. %

A Fe-Zn alloy that was electrodeposited from an electrolyte containing 50 g/L Fe^{2+} ions was discovered using EDX data after SEM analysis. Figure 4.24 and Table 3.11 show the determinations of the EDX experiment on the Fe-Zn alloy. Fe-Zn with a 50 g/L Fe content was found using EDX. 7.7% iron and 92.3% zinc, respectively, make up this alloy.

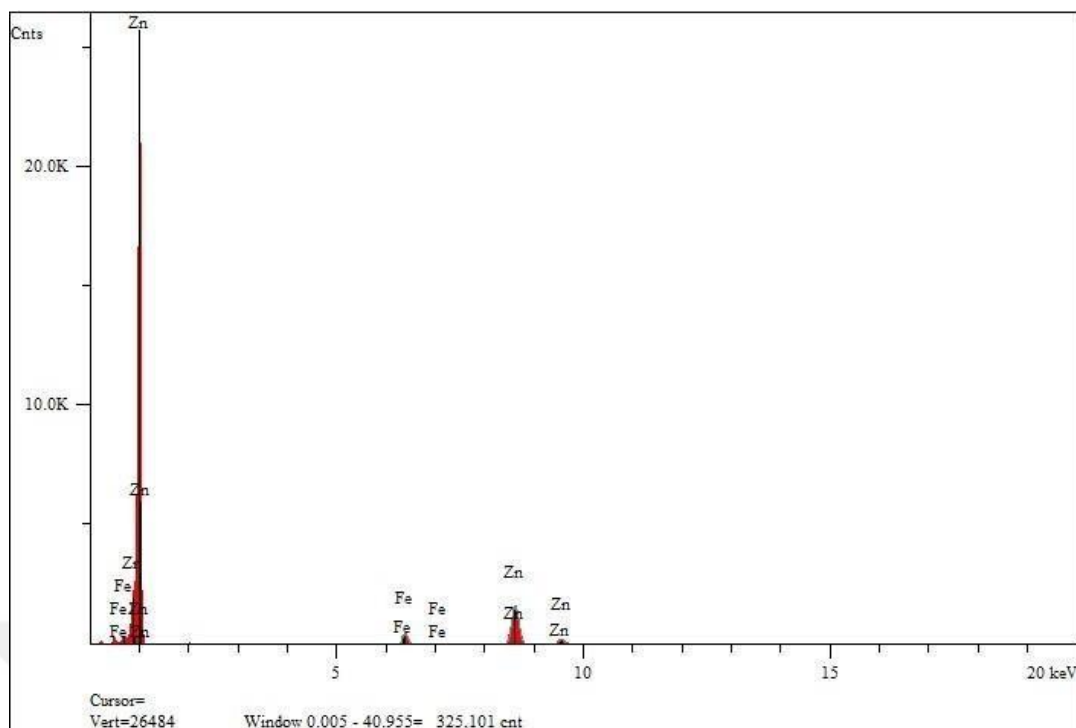


Figure 4.24 EDX image of Fe-Zn with 50 g/L Fe concentration.

Table 3.11 EDX Results Fe-Zn with 50 g/L Fe concentration.

Element	Line	Intensity (c/s)	Concentration	Units
Fe	Ka	69.49	7.656	wt.%
Zn	Ka	278.30	92.344	wt.%
			100.000	wt.%

The EDX results of alloys are listed in the tables. It shows the concentrations of the Zn and Fe. The peak related to zinc is dominant in the figures. According to the results, Zn concentration of the sample electroplated from an electrolyte containing 30 g/L Fe has a higher ratio than the other concentrations. The decrease rate of this metal tends to be higher than that of Zn once Fe electrodeposition is practical. The peak intensity of Zn gives information about Fe-Zn film condition. If Zn peak is higher, Fe-Zn film could have passivation behavior. The SEM images demonstrate the better crystallinity at the 30 g/L Fe composition.

4.2.1.4. X- Ray Diffraction (XRD) of Fe-Zn Alloy

Steel (AISI 4140) was used as a substrate and coated by metals and alloys. Before analyzing XRD of the modified electrodes, XRD pattern of non-coated steel was obtained. Figure 4.25 illustrates XRD results of bare steel used in this work.

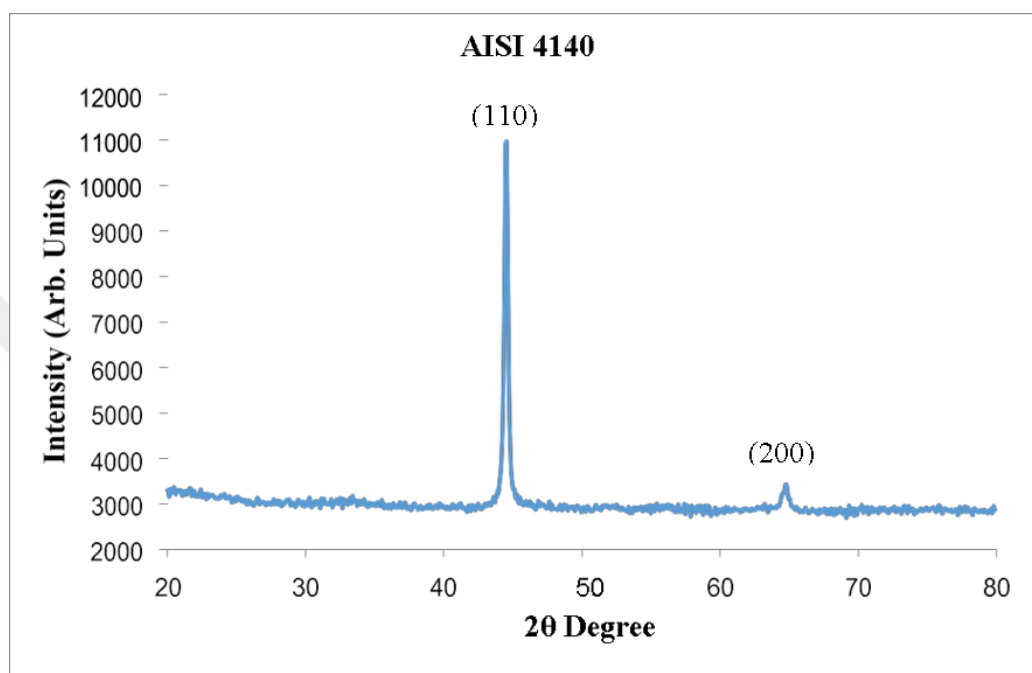


Figure 4.25 XRD patterns of AISI 4140 iron substrate

Table 3. 12 Diffraction indices of the peaks of AISI 4140 iron substrate with respect to Miller indices

Number	h	k	l	2 Theta [degree]
1	1	1	0	44.58
2	2	0	0	64.84

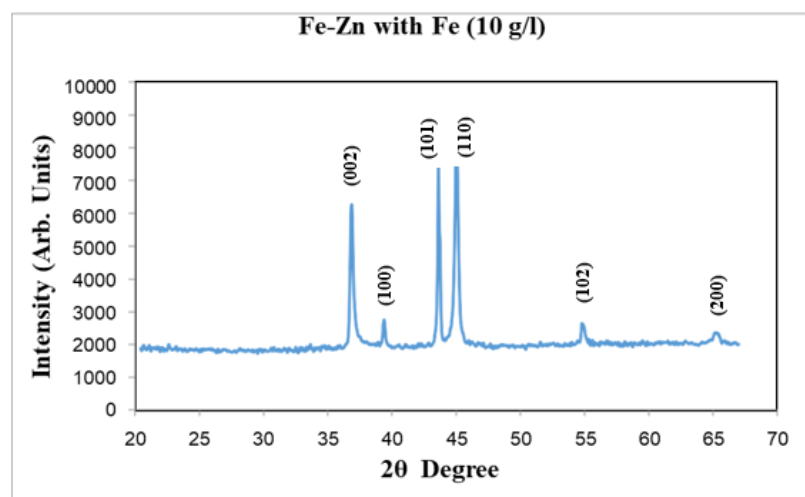


Figure 4.26 XRD patterns of Fe-Zn alloy containing (10g/L) of Fe concentration.

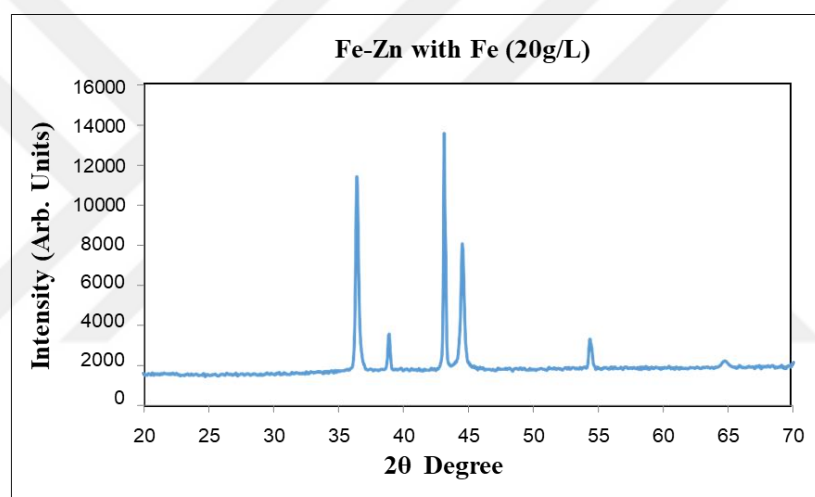


Figure 4.27 XRD patterns of Fe-Zn alloy containing (20g/L) of Fe concentration.

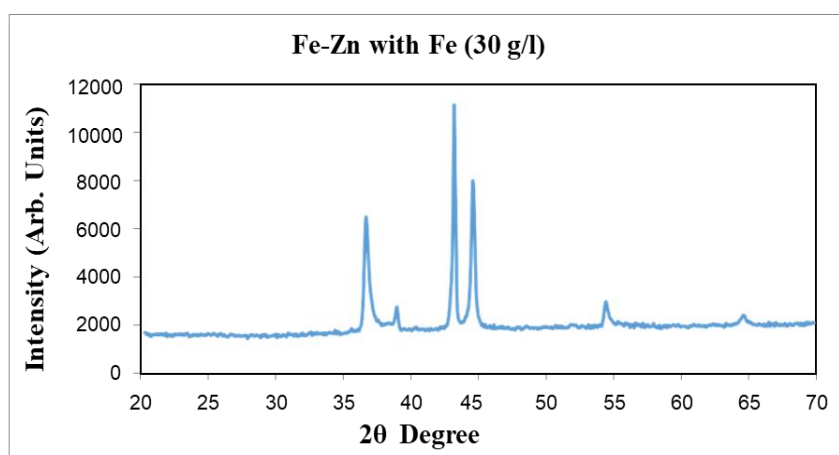


Figure 4.28 XRD patterns of Fe-Zn alloy containing (30g/L) of Fe concentration.

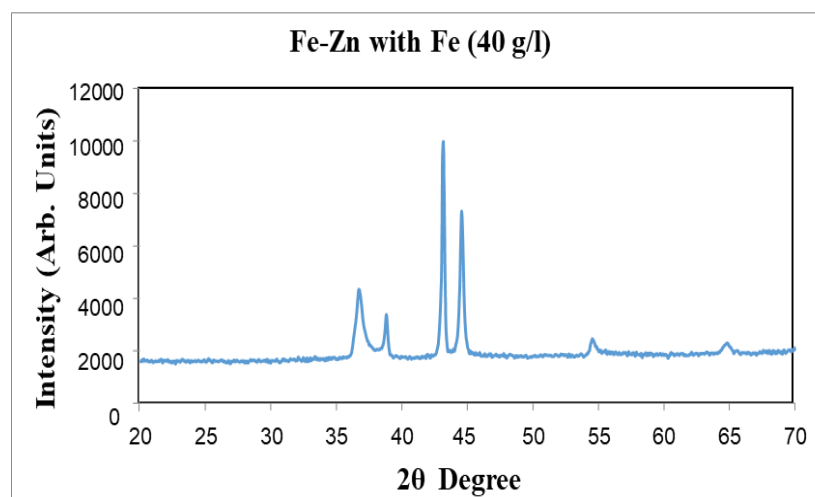


Figure 4.29 XRD patterns of Fe-Zn alloy containing (40g/L) of Fe concentration.

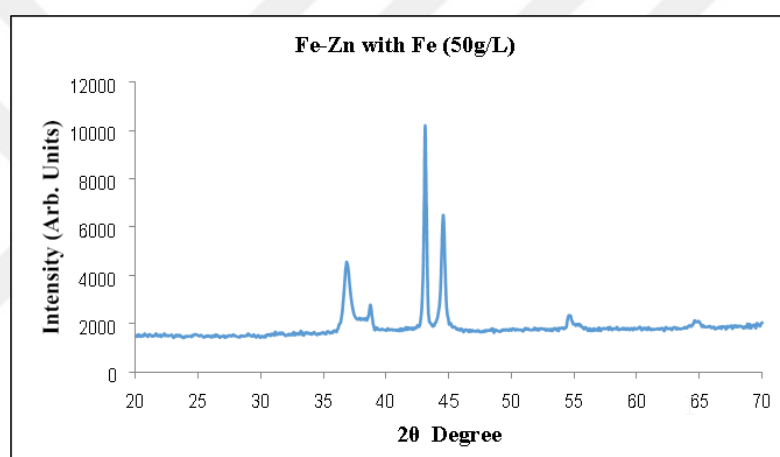


Figure 4.30 XRD patterns of Fe-Zn alloy containing (50g/L) of Fe concentration.

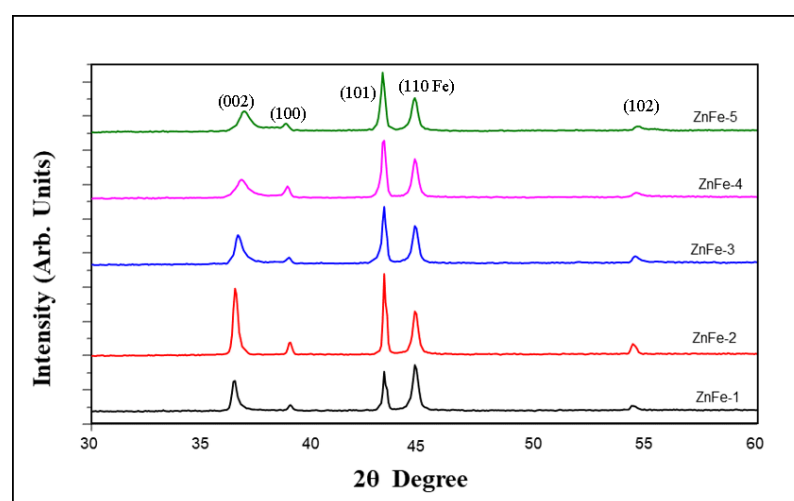


Figure 4.31 Overlap XRD patterns of Fe-Zn alloy containing (from 10 to 50 g/L) of Fe concentration.

The XRD results of films in different Fe values seen in Figure 4.26 Figure 4.30), are shown below. The peaks represent the crystallinity of the films and the changing Fe concentration value of Fe-Zn alloys effects the results. The structure of the Fe-Zn alloy coatings is the same as zinc [107] but different crystallographic orientation, which is the consequence of minimal quantity of iron [108]. As a result of research of articles related with Fe-Zn alloys, it was reached given results.

Table 3.13 Peak numbers, planes (hkl), diffraction angles and diffracted elements for the measured XRD of five samples in different Fe concentration of Fe-Zn alloys.

No	Plane (hkl)	2 Theta (Degree)	Element diffracts
1	0 0 2	36.32	Zn
2	1 0 0	38.97	Zn
3	1 0 1	43.19	Zn
4	1 1 0	44.58	Fe
5	1 0 2	54.28	Zn
6	2 0 0	63.84	Fe

These results seen in Table 3.13 show which element in which 2 theta angle and planes, give peak on the XRD pattern Fe-Zn Alloy films deposited on to iron substrate. For the plane (hkl = 100) rate of Zn 5.71 %, Fe-Zn is 0,02 % and for 101 plane Zn 0.99 %, Fe-Zn is 0.51 % for electrodeposit system [109]. Among the XRD patterns of Fe-Zn alloy containing from 10 g/L to 50 g/L of Fe concentration, the sharpest Zn peak at 101 plane (at the same time represent the peak of Fe-Zn alloy) is seen for the second sample prepared with Fe-Zn alloy containing 20 g/L of Fe concentration. The others have about same peaks. At 2 theta= 44.58 and (100) plane and 2 theta= 63.84 and (200) Fe diffraction peaks caused by iron substrate because as it seen the XRD patterns these peaks are the same.

4.2.1.5. Polarization Curve Analysis of Fe-Zn

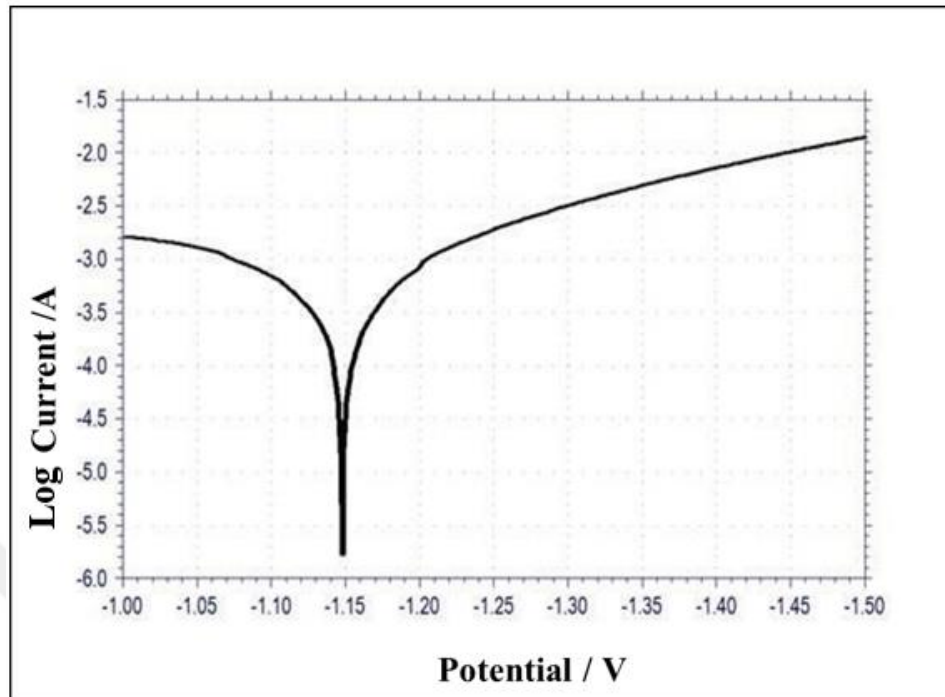


Figure 4.32 Polarization curve of the AISI 4140 corrosion potential and corrosion current of the substrate have been obtained -1.148 V, and $10^{-3.2}$ A respectively.

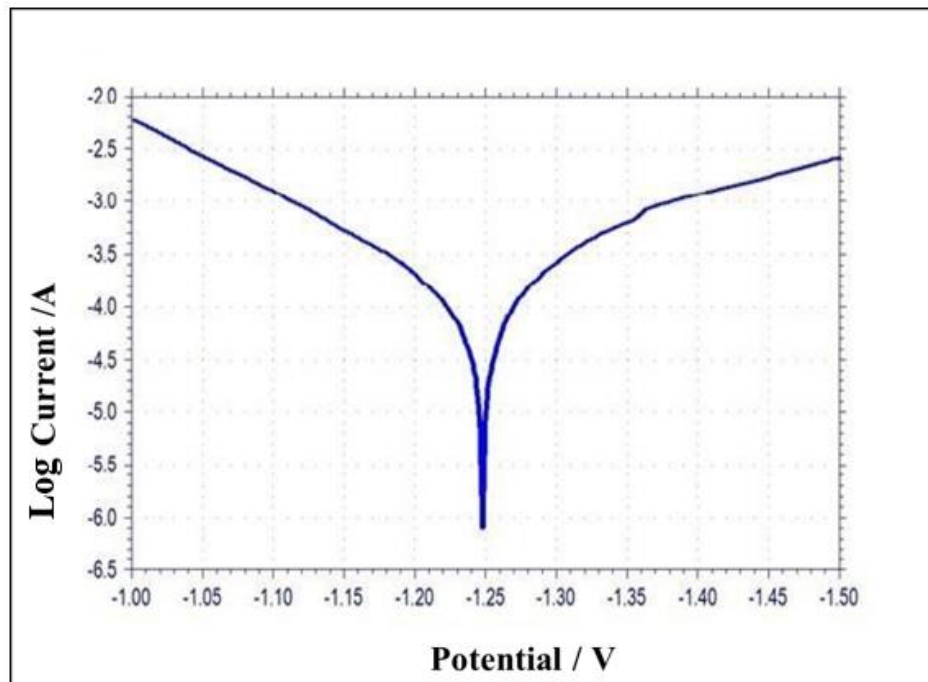


Figure 4.33 Polarization curve of the Fe-Zn including 10.889 wt. % of Fe.

Fe-Zn alloy was electrodeposited on steel substrate and immersed in NaCl solution for polarization. Tafel Plot belonging to Fe-Zn alloy was obtained by taking logarithm of current. Figure 4.33 illustrates Tafel Plot of Fe-Zn alloy having 10.9% Fe electrodeposited from an electrolyte having 10 g/L Fe^{2+} concentration. Corrosion current and potential of Fe-Zn alloy with 10.9% Fe is $10^{-3.81}$ A and -1.25 V, respectively. Corrosion current of this alloy is more than six times lower than that of bare steel.

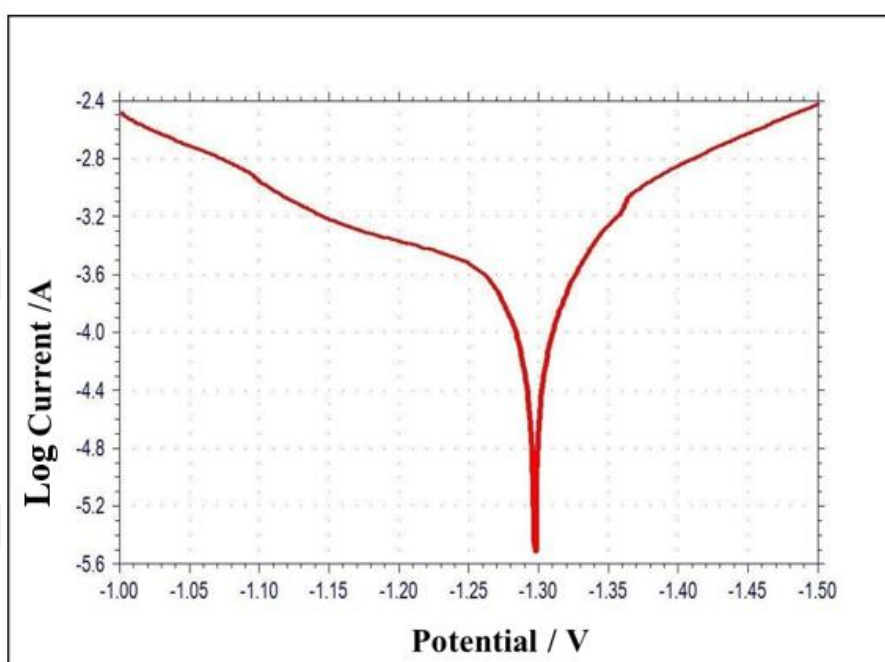


Figure 4.34 Polarization curve of the Fe-Zn for 6.765 wt. % concentration of Fe

Fe-Zn alloy was electrodeposited on steel substrate and immersed in NaCl solution for polarization. Tafel Plot belonging to Fe-Zn alloy was obtained by taking logarithm of current. Figure 4.34 illustrates Tafel Plot of Fe-Zn alloy having 6.77% Fe electrodeposited from an electrolyte having 20 g/L Fe^{2+} concentration. Corrosion current and potential of Fe-Zn alloy with 6.77% Fe is $10^{-3.62}$ A and -1.30 V, respectively. Corrosion current of this alloy is less than that of bare steel and corrosion resistivity of alloy is greater than bare steel.

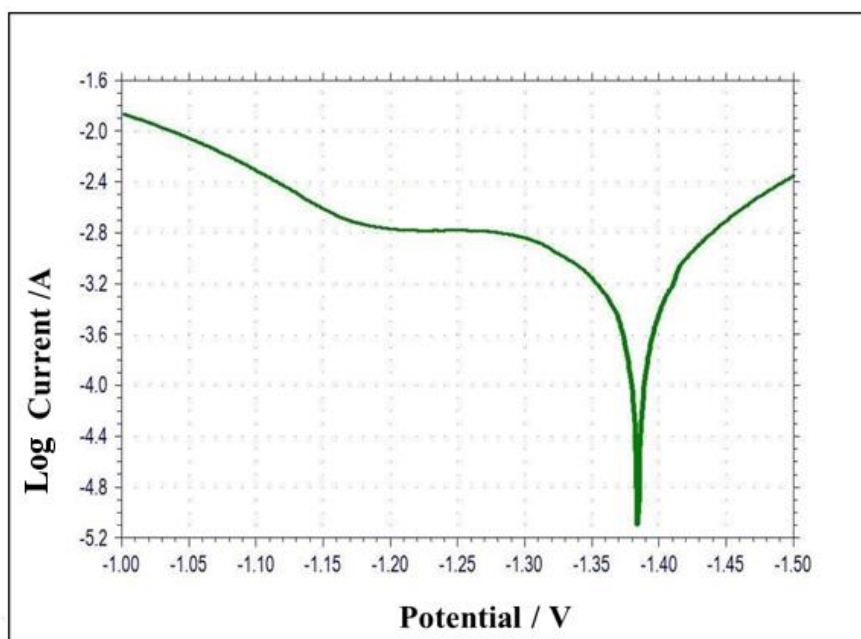


Figure 4.35 Polarization curve of the Fe-Zn for 6.255 wt. % concentration of Fe

Fe-Zn alloy electrodeposited on steel substrate was immersed in 3.5% NaCl electrolyte for linear sweep voltammetry experiment. Tafel Plot of this Fe-Zn alloy is presented in Figure 4.35. This graph is Tafel Plot of Fe-Zn alloy having 6.26% Fe electrodeposited from an electrolyte having 30 g/L Fe^{2+} concentration. Corrosion current and potential of Fe-Zn alloy with 6.26% Fe is $10^{-2.92}$ A and -1.38 V, respectively. Corrosion current of this alloy is different (higher) than that of previous coated steel. This could occur due to structural differences of modified electrode because the ratio of iron in this alloy was not significantly different than other films.

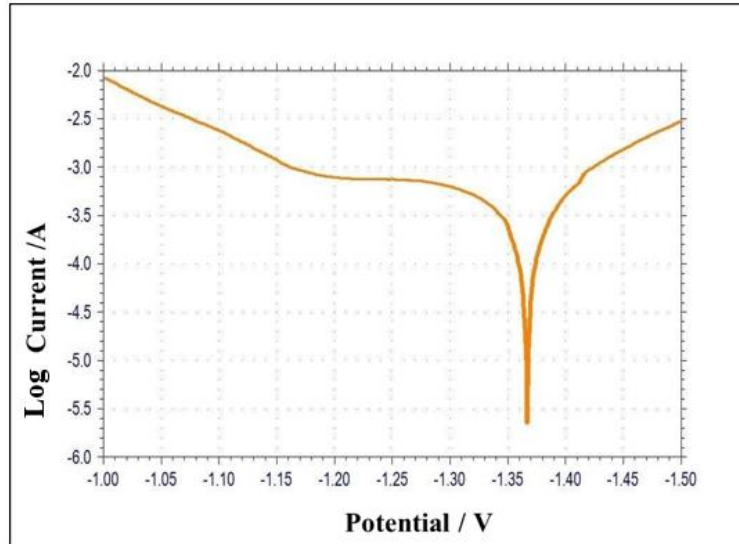


Figure 4.36 Polarization curve of the Fe-Zn for 7.194 wt. % concentration of Fe

Fe-Zn alloy was electrodeposited on steel substrate and immersed in NaCl solution for polarization. Tafel Plot belonging to Fe-Zn alloy was obtained by taking logarithm of current. Figure 4.36 illustrates Tafel Plot of Fe-Zn alloy having 7.2% Fe electrodeposited from an electrolyte having 40 g/L Fe^{2+} concentration. Corrosion current and potential of Fe-Zn alloy with 7.2% Fe is $10^{-3.41}$ A and -1.37 V, respectively. Corrosion current of this alloy is less than that of bare steel and corrosion resistivity of alloy is greater than bare steel.

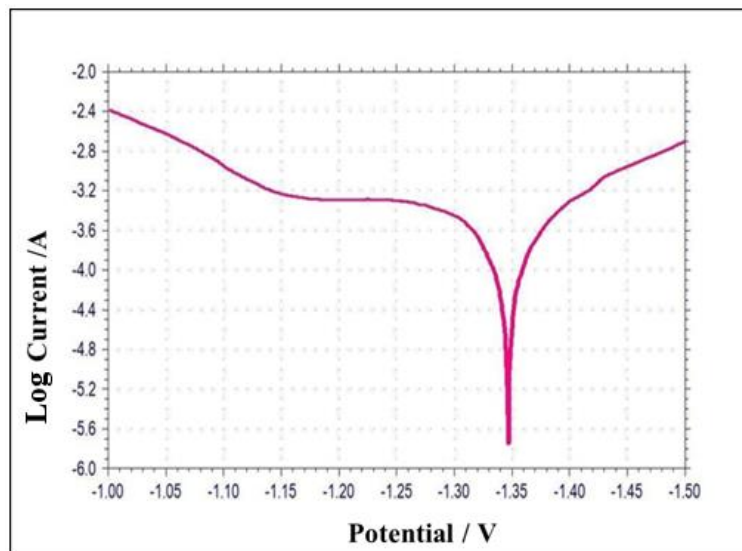


Figure 4.37 Polarization curve of the Fe-Zn for 7.656 wt. % concentration of Fe.

Fe-Zn alloy electrodeposited on steel substrate was immersed in 3.5% NaCl electrolyte for linear sweep voltammetry experiment. Tafel Plot of this Fe-Zn alloy is presented in Figure 4.37. This graph is Tafel Plot of Fe-Zn alloy having 7.66% Fe electrodeposited from an electrolyte having 50 g/L Fe^{2+} concentration. Corrosion current and potential of Fe-Zn alloy with 7.66% Fe is $10^{-3.62}$ A and -1.34 V, respectively. Corrosion current of this alloy is less than that of previous coated steel and thus corrosion resistivity of alloy is greater than bare steel.

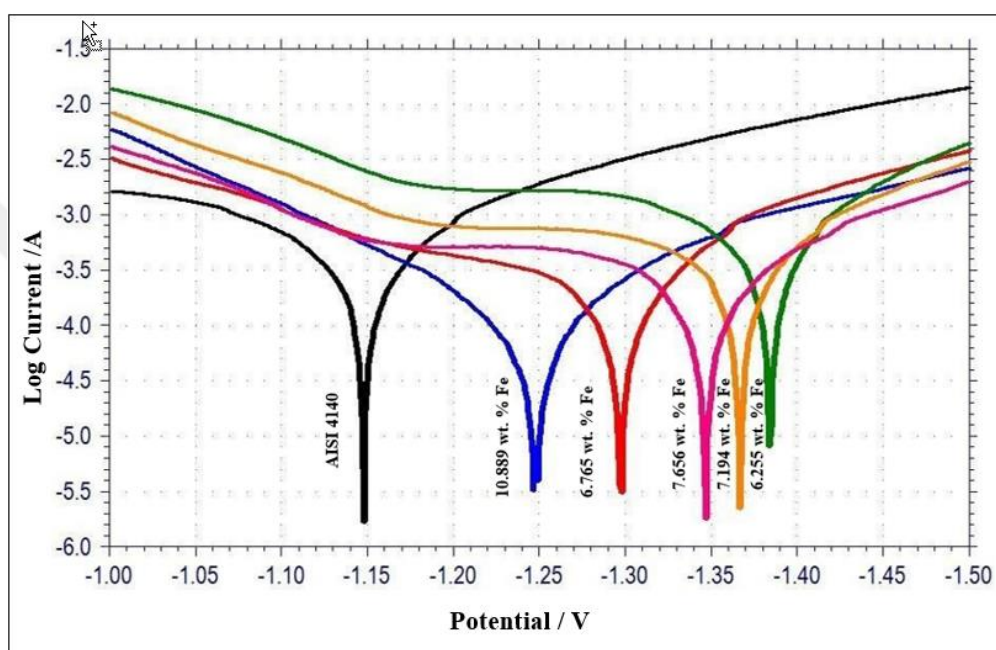


Figure 4.38 Potentiodynamic polarization curve of electrodeposited Fe-Zn alloys for all concentrations of Fe on AISI 4140 substrate [57].

Table 3.14 The definition of samples in Figure 4.38.

Black Line	AISI 4140 (Reference)
Blue Line	10.889wt. % Fe (Fe content in Fe-Zn sample)
Red Line	6.765wt. % Fe
Green Line	6.255wt. % Fe
Orange Line	7.194wt. % Fe
Pink Line	7.656wt. % Fe

In Figure 4.38 all sweep voltametric curves belonging to Fe-Zn alloys electrodeposited in

an electrolyte having different iron ion concentration are presented. They have the meaning as follows: According to the Figure 4.38 the sample (in blue line of Figure 4.38) with 10.889 wt.% of Fe which has more positive corrosion potential than the other samples. The sample (the curve shown in green line of Figure 4.38) with concentration of 6.255 wt.% of Fe has more negative corrosion potential. Potentials for corrosion of these samples are between -1.248 V and -1.384 V [110]. The obtained values (corrosion potential E_p and corrosion current I_p for the AISI 4140 steel substrate and the sample Fe-Zn for the different concentration of Fe determined by EDX after electroplating) are shown in Table 3.15.

The corrosion rate of the samples was calculated by the equation given below:

$$CR = \frac{i_{corr} \cdot M_m \cdot K}{n \cdot \rho \cdot A}$$

In which CR is corrosion rate in $\mu\text{m year}^{-1}$. i_{corr} and M_m represent corrosion current in ampere and molar mass of the material in g mol^{-1} , respectively. n is mol number of electrons causing oxidation. ρ is the symbol of density in g cm^{-3} . A is the area of the working electrode immersed in corrosion electrolyte used in corrosion study. K is a constant value (3,268,487) to calculate corrosion rate in $\mu\text{m year}^{-1}$.

Table 3.15 The corrosion potential E_{corr} and corrosion current I_{corr} of AISI 4140 steel substrate and Fe-Zn obtained in different concentrations of Fe^{2+} .

		pH	$E_{corr}(\text{V})$	$I_{corr}(\text{A})$	CR (mm/year)
AISI 4140		4.7	-1.148	-3.2	7.33
Fe-Zn sample for					
10.889 wt. % Fe	Sample CA-1	4.7	-1.24	-3.81	2.26
6.765 wt. % Fe	Sample CA-2	4.7	-1.30	-3.62	3.54
6.255 wt. % Fe	Sample CA-3	4.7	-1.38	-3.32	7.40
7.194 wt. % Fe	Sample CA-4	4.7	-1.37	-3.41	5.73
7.656 wt. % Fe	Sample CA-5	4.7	-1.35	-3.73	2.93

The Fe concentration plays crucial role in corrosion resistivity that has already obtained and revealed in Figure 4.33 means that the obtained corrosion potential value is -1.248 V for Fe-Zn sample with the 10.889 wt.% of Fe concentration in substrate group. On the other side the corrosion potential of Fe-Zn alloys with concentration of 47.856 wt. % Fe is -1.384 V that has the meaning of the least corrosion resistive among the other Fe- Zn coatings.

The values from the Table 3.15 shows that sample contains 10.889 wt. % Fe concentration after electrodeposition has higher corrosion resistance. Because its CR rate is the lowest one as 2.26 mm/year among the other samples which are electrodeposited with Fe-Zn alloy. The sample with concentration of 6.255 wt.% of Fe has CR as 7.40 mm/year. This show that the sample has lower corrosion resistant than the others.

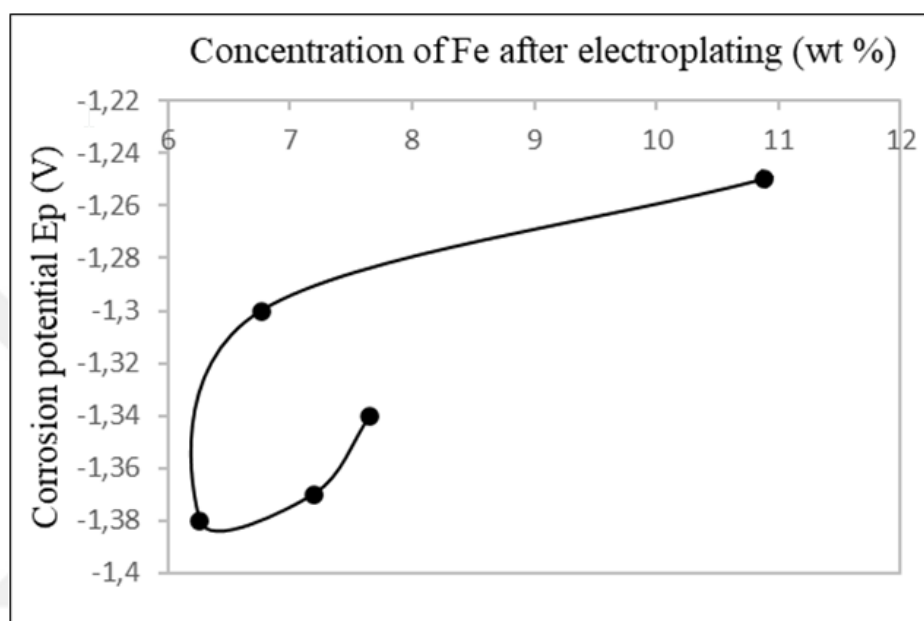


Figure 4.39 Corrosion potential of the Fe-Zn alloy coatings.

Figure 4.39 implies that Fe-Zn sample with concentration of 10.889 wt. % Fe has higher corrosion potential than other Fe-Zn samples.

4.2.2. Analysis of Fe-Mn Alloys

4.2.2.1. Scanning Electron Microscope (SEM) Pictures of Fe-Mn Alloy

SEM micrograph (top view) of Fe-Mn alloy deposits [111] onto AISI 4140 code steel substrate with different amounts of % Fe and Mn weight concentrations. The images of Fe-Mn alloy show the crystal structure of the film by choosing an area with a 5000x magnification apart from the image shown in Figure 4.43. For this image 4300 X magnification was used to get better view.

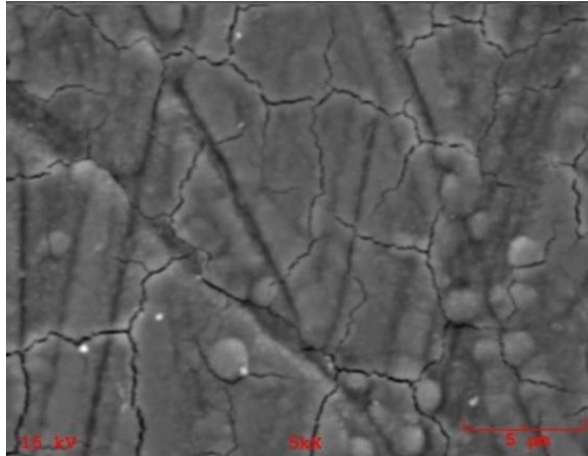


Figure 4.40 The SEM image of Fe-Mn containing 83.692 % of Fe and 16.308 wt. % of Mn weight concentration with pH=3.2.

In Figure 4.40 SEM image shows the surface morphologies of optimized [112] Fe-Mn coating contains 83.692 of Fe and 16.308 of Mn weight % concentration with pH=3.2. The sample resembles the structure it had after the river bed was drained. The lines seen with gray bubbles are traces left by sanding the steel substrate.

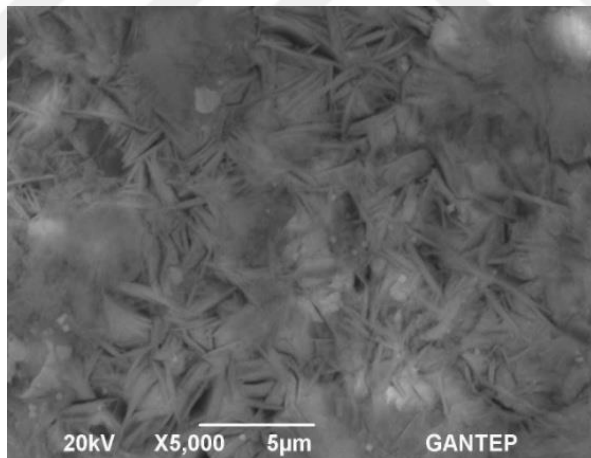


Figure 4.41 The SEM image of Fe-Mn containing 21.971% of Fe and 78.029 wt. % of Mn weight concentration.

SEM image seen in Figure 4.41 demonstrates the typical surface configuration of Fe-Mn coating contains 21.971% of Fe and 78.029% of Mn weight concentration with pH=3.2. In this image, the film of Fe-Mn, contains 21.971 % of Fe and 78.029% of Mn weight concentration has severe fibrous structure.

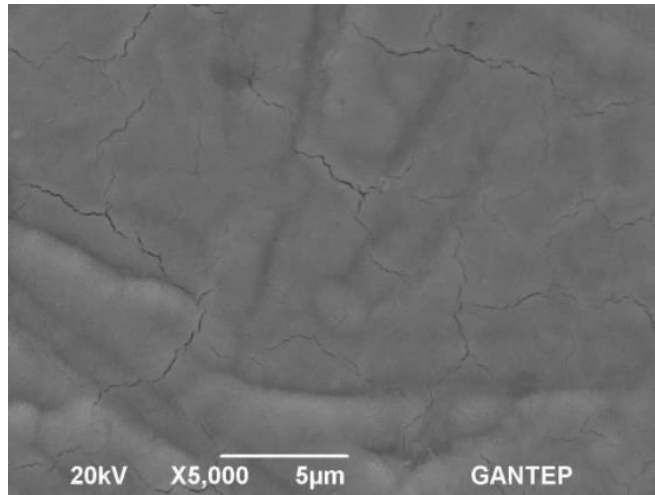


Figure 4.42 The SEM image of Fe-Mn containing 86.231% of Fe and 13.769 wt. % of Mn weight concentration.

SEM image in Figure 4.42 can be seen the typical surface structure of optimized Fe-Mn coating contains 86.231% of Fe and 13.769% of Mn weight concentration with pH=3.2.

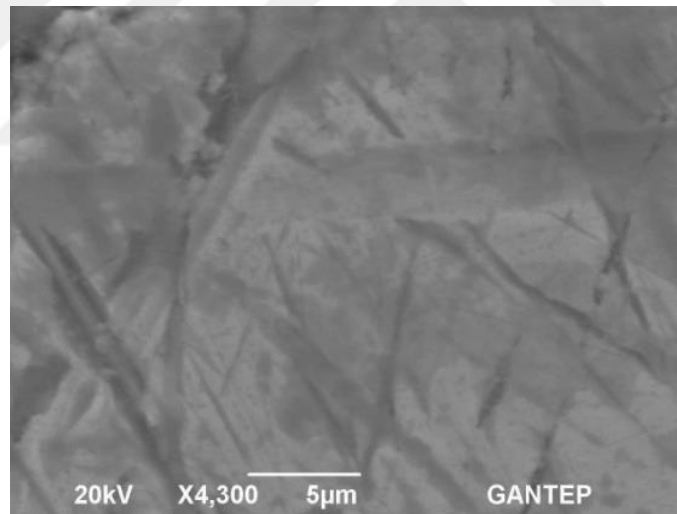


Figure 4.43 The SEM image of Fe-Mn containing 89.360 of Fe and 10.640 of Mn weight % concentration.

SEM image in Figure 4.43 shows the surface morphologies of Fe-Mn coating contains 89.360 %of Fe and 10.640 % of Mn weight concentration with pH=3.2. After forming electrodeposition of Fe-Mn on the substrate; we ground the film with sand paper.

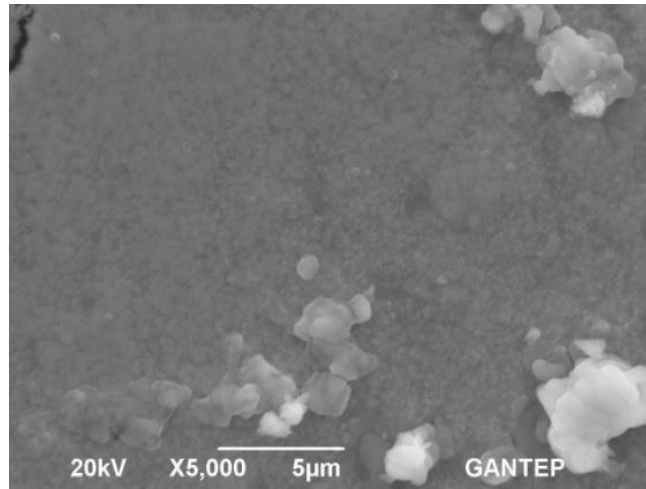


Figure 4.44 The SEM image of Fe-Mn containing 94.386 of Fe and 5.614 of Mn weight % concentration.

SEM image in Figure 4.44 reveals the typical surface morphologies of optimized Fe-Mn coating contains 94.386 % of Fe and 5.614 % of Mn weight concentration with pH=3.2. The image of Fe-Mn alloy shows the film's crystal structure by choosing an area with a 5000x magnification. White particles are dust remained environment.

4.2.2.2. Energy Dispersive X-Ray (EDX) Analysis of Fe-Mn Alloy

Afterwards SEM inspection, EDX data was used to identify a Fe-Mn alloy that was electrodeposited from an electrolyte containing 2g/L Fe^{2+} ions. The results of the EDX experiment on the Fe-Mn alloy are presented in Figure 4.45 and Table 3.16. Using EDX, Fe-Mn with a 2 g/L Fe concentration was discovered. This alloy is composed of 16.3% manganese and 83.7% iron respectively.

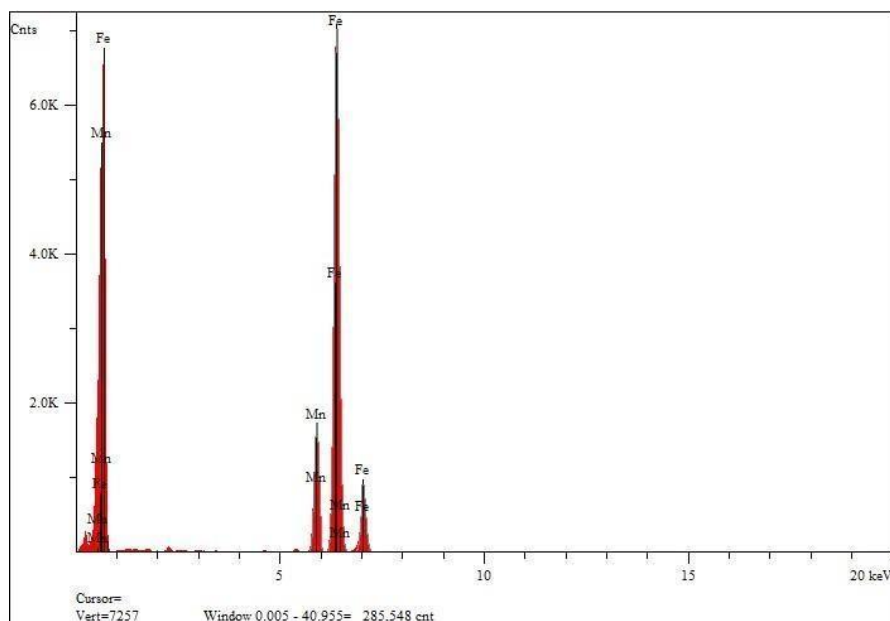


Figure 4.45 EDS spectra [113] of Fe-Mn alloy contains 16.308 Mn at % weight

Figure 4.45 shows the peaks of Fe and Mn. Distinct peaks are observed by applying various potential approximately 0.5, 5.8, 6.5 and 7 keV. The manganese contents in the coatings measured via EDS analyses are listed [114] in Table 3.16-Table 3.20.

Table 3.16 The manganese content as 16.308 at % weight in the coatings measured via EDS analyses.

Element	Line	Intensity (c/s)	Concentration	Units
Mn	Ka	252.76	16.308	wt. %
Fe	Ka	1,077.33	83.692	wt. %
			100.000	wt. %

Subsequently SEM analysis, EDX data was used to pinpoint an electrodeposited Fe-Mn alloy from an electrolyte containing 2.72 g/L Fe^{2+} ions. Figure 4.46 and Table 3.17 show the outcomes of the EDX experiment on the Fe-Mn alloy. Fe-Mn with a Fe content of 2.72 g/L was found using EDX. This alloy consists of 78 % manganese and 22 % iron, respectively.

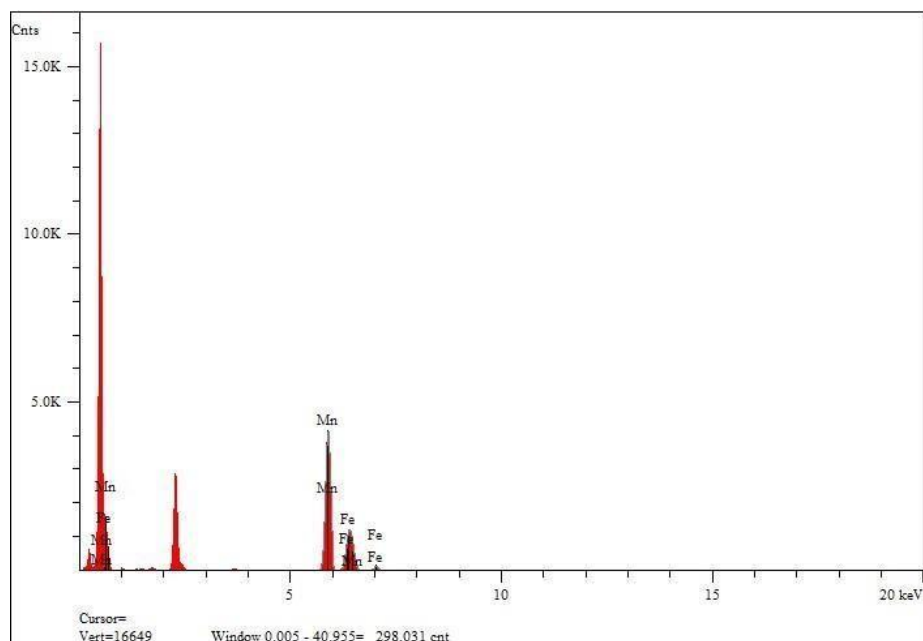


Figure 4.46 EDS spectra of Fe-Mn alloy contains 78.029 Mn at % weight

Figure 4.46 shows the peaks of Fe and Mn. Distinct peaks are observed by applying various potential approximately 0.5, 2.3, 5.9, 6.5 and 7keV.

Table 3.17 The manganese content as 78.029 at % weight in the coatings measured via EDS analyses.

Element	Line	Intensity (c/s)	Concentration	Units
Mn	Ka	620.94	78.029	wt. %
Fe	Ka	148.67	21.971	wt. %
			100.000	wt. %

Afterwards SEM inspection, an electrolyte containing 5.44 g/L Fe^{2+} ions was used to identify an electrodeposited Fe-Mn alloy using EDX data. The results of the EDX experiment on the Fe-Mn alloy are displayed in Figure 4.47 and Table 3.18. Using EDX, Fe-Mn with a Fe concentration of 5.44 g/L was discovered. This alloy is composed of 13.8 % manganese and 86.2 % iron correspondingly.

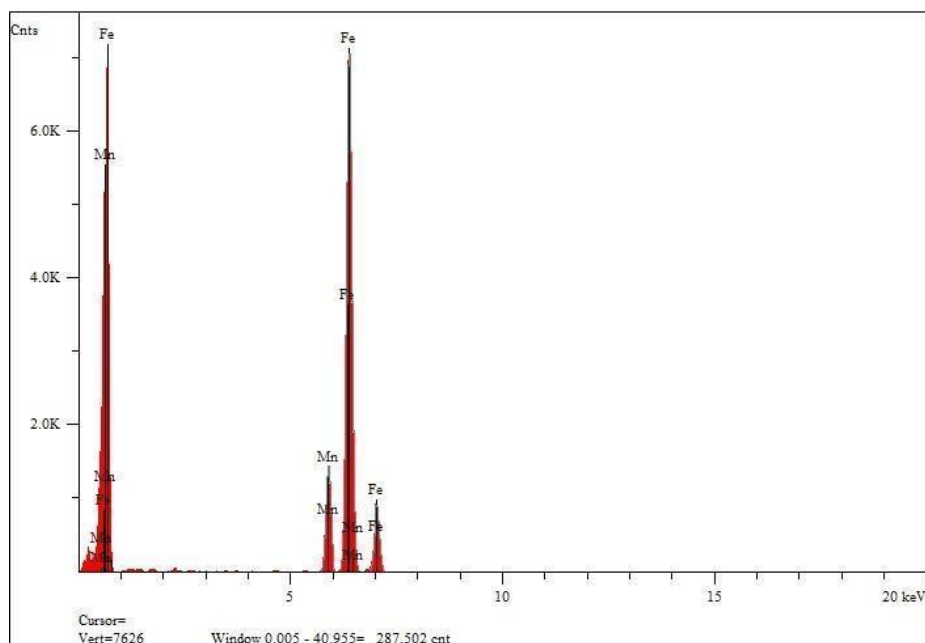


Figure 4.47 EDS spectra of Fe-Mn alloy contains 13.769 Mn at % weight

Fe and Mn peak are shown in Figure 4.47. Applying potentials between 0.5, 5.9, 6.5, and 7 keV allows for the observation of distinct peaks.

Table 3.18 The manganese contents as 13.769 at % weight in the coatings measured via EDS analyses.

Element	Line	Intensity (c/s)	Concentration	Units
Mn	Ka	210.97	13.769	wt.%
Fe	Ka	1,094.93	86.231	wt.%
			100.000	wt.%

Afterwards SEM inspection, an electrodeposited Fe-Mn alloy from an electrolyte containing 13.6 g/L Fe^{2+} ions were identified using EDX data. Figure 4.48 and Table 3.19 show the outcomes of the EDX experiment on the Fe-Mn alloy. Fe-Mn was found to have a Fe content of 13.6 g/L using EDX. 10.6 % manganese and 89.4 % iron respectively, make up this alloy.

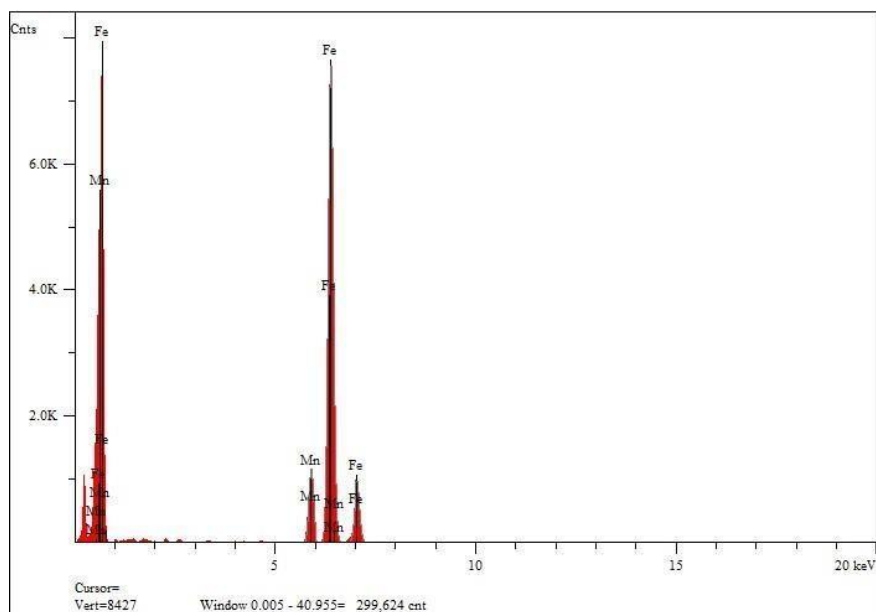


Figure 4.48 EDS spectra of Fe-Mn alloy contains 10.640 Mn at % weight

Figure 4.48 shows the peaks of Fe and Mn. Distinct peaks are observed by applying various potential approximately 0.2, 0.5, 5.9, 6.5 and 7 keV.

Table 3.19 The manganese content as 10.640 at % weight in the coatings measured via EDS analyses.

Element	Line	Intensity (c/s)	Concentration	Units
Mn	Ka	168.62	10.640	wt. %
Fe	Ka	1,169.90	89.360	wt. %
			100.000	wt. %

Following SEM inspection, EDX data was used to pinpoint an electrodeposited Fe-Mn alloy from an electrolyte containing 13.6 g/L Fe^{2+} ions. The results of the EDX experiment on the Fe-Mn alloy are displayed in Figure 4.49 and Table 3.20. Using EDX, it was discovered that Fe-Mn had a Fe concentration of 13.6 g/L. This alloy is composed of 5.6 % manganese and 94.4% iron, respectively.

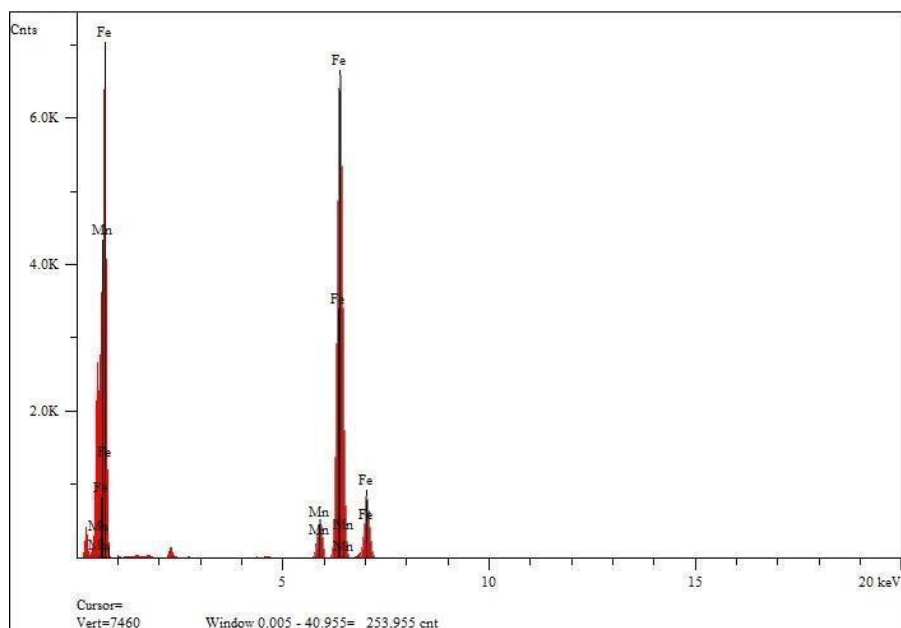


Figure 4.49 EDS spectra of Fe-Mn alloy contains 5.614 Mn at % weight

Fe and Mn's peaks are depicted in Figure 4.49. Different potentials used resulted in distinct peaks that were around 0.2, 0.5, 5.9, 6.5, and 7 keV.

Table 3.20 The manganese content as 5.614 at % weight in the coatings measured via EDS analyses.

Element	Line	Intensity (c/s)	Concentration	Units
Mn	Ka	74.13	5.614	wt. %
Fe	Ka	1,023.43	94.386	wt. %
			100.000	wt. %

4.2.2.3.X-Ray Diffraction (XRD) of Fe-Mn Alloy

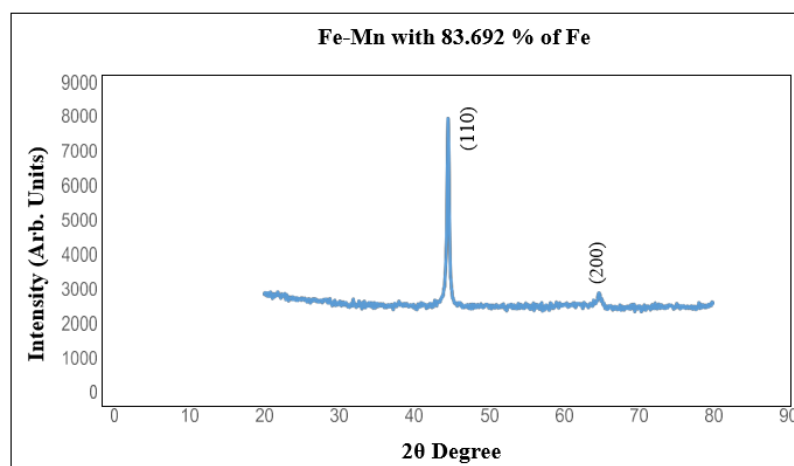


Figure 4.50 XRD images of a Fe-Mn alloy with a content of 83.692% Fe.

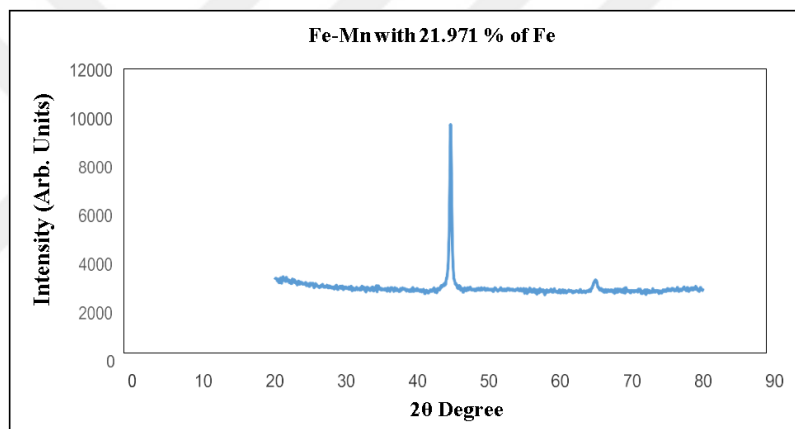


Figure 4.51 XRD images of a Fe-Mn alloy with a content of 21.971% Fe.

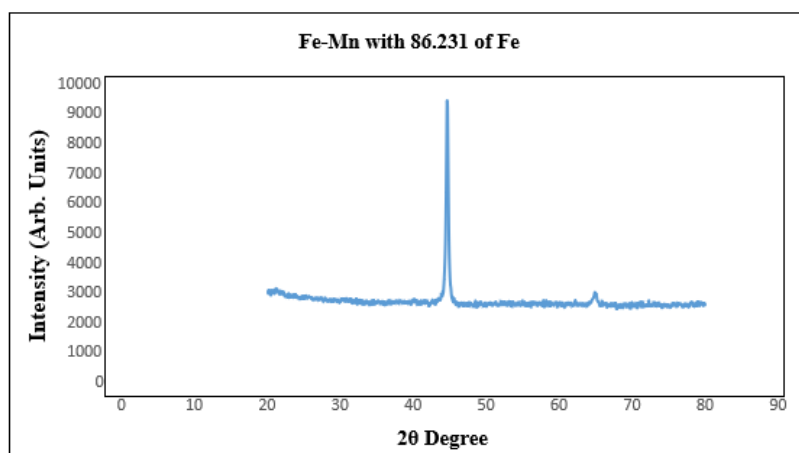


Figure 4.52 XRD images of a Fe-Mn alloy with a content of 86.231 Fe.

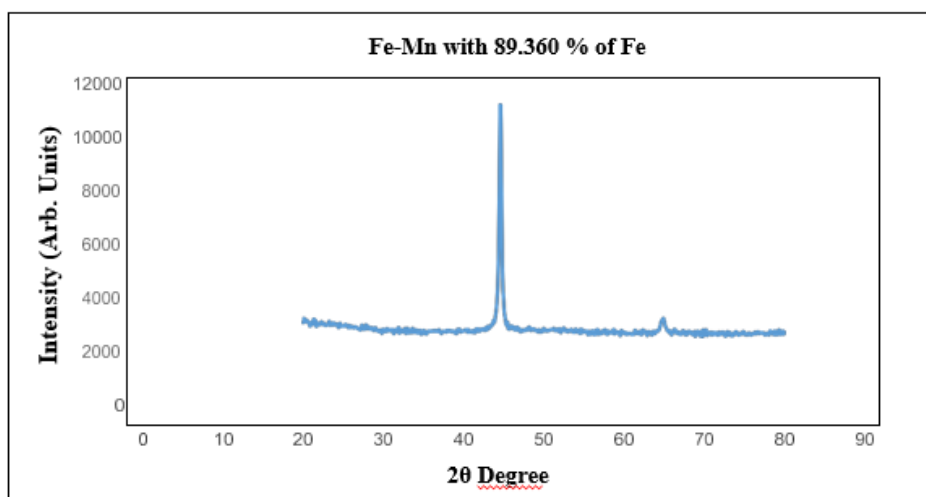


Figure 4.53 XRD images of a Fe-Mn alloy with a content of 89.360 % Fe.

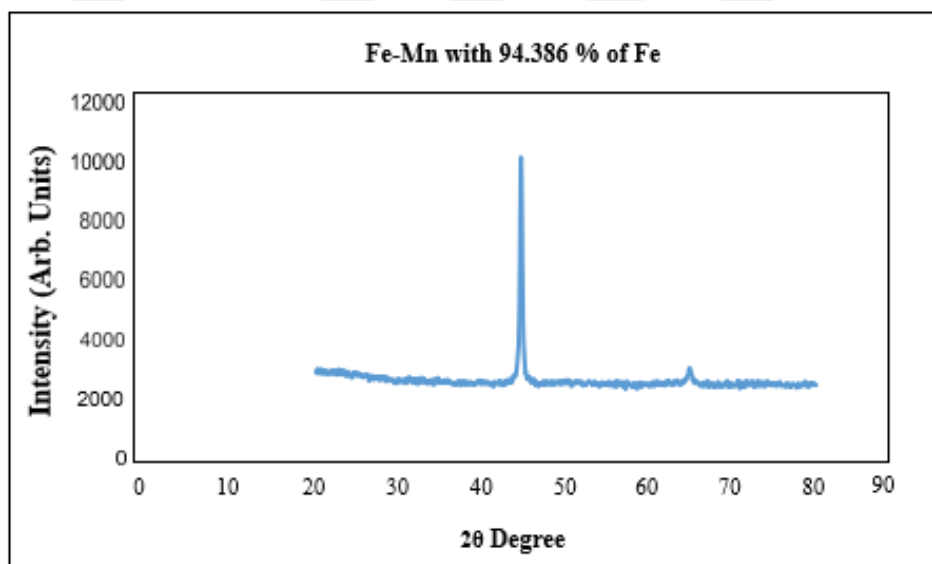


Figure 4.54 XRD images of a Fe-Mn alloy with a content of 94.386 Fe.

When the XRD graphs of the samples produced from the aqueous solutions of FeMn alloys are examined. It is understood that the two dominant peaks (shown in Figure 4.50 -Figure 4.54) belong to the iron element. This may be due to the fact that the signals from the steel substrate of the sample were read. The intensity differences are due to the Mn element in the sample. In other words, the observation of different intensity indicates the presence of Mn element in the sample.

4.2.2.4. Polarization Curve Analysis of Fe-Mn

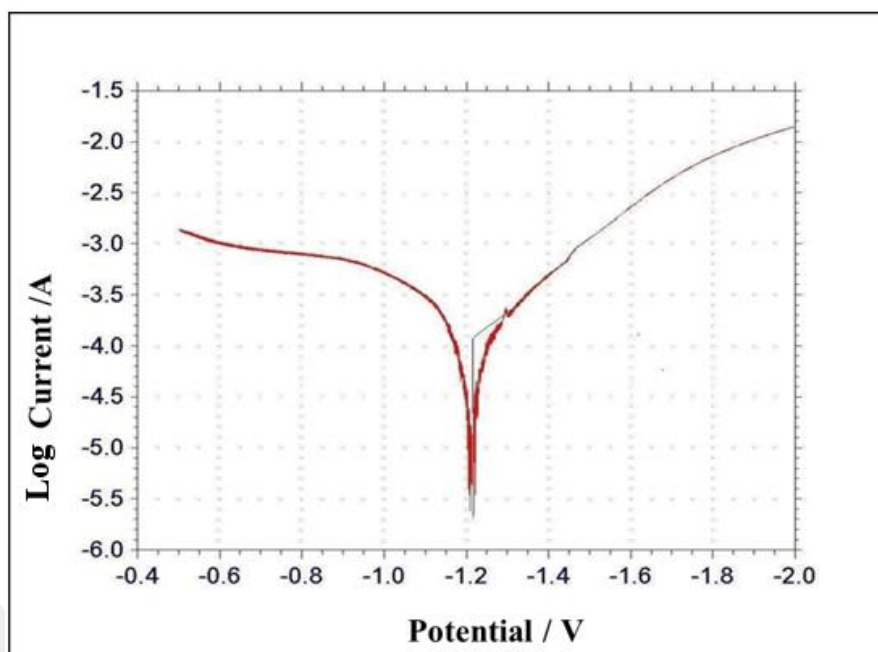


Figure 4.55 Polarization curve of the Fe-Mn sample for 16.308 wt.% concentration of Mn.

Fe-Mn alloy electrodeposited on steel substrate was immersed in 3.5% NaCl electrolyte for linear sweep voltammetry experiment. Tafel Plot of this Fe-Zn alloy is presented in Figure 4.55 This graph is Tafel Plot of Fe-Mn alloy having 16.308 wt.% Mn electrodeposited from an electrolyte having 2 g/L FeSO_4 (which is the variant in solution) concentration. Corrosion current and potential of Fe-Mn alloy 16.308 wt.% concentration of Mn. is $10^{-3.8}$ A and -1.22 V, respectively. This alloy has a lower corrosion current than previously coated steel, making it more corrosion resistant than naked AISI 4140 steel substrate have been obtained -1.148 V of E_{corr} , and $10^{-3.2}$ A I_{corr} respectively.

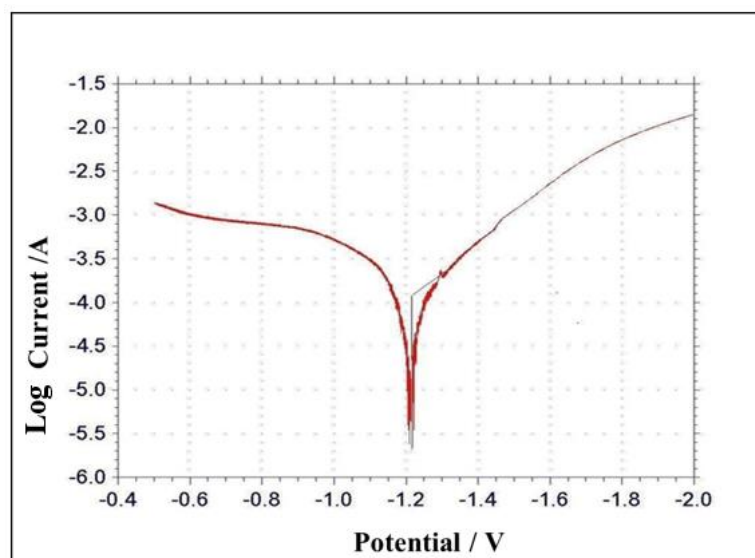


Figure 4.56 Polarization curve of the Fe-Mn sample for 13,769 wt. % concentration of Mn.

For a linear sweep voltammetry experiment, Fe-Mn alloy electrodeposited on steel substrate was submerged in 3.5% NaCl electrolyte. A Tafel Plot of this Fe-Zn alloy is shown in Figure 4.56. This graph is a Tafel Plot of a Fe-Mn alloy with 13,769 weight percent Mn electrodeposited from an electrolyte with a concentration of 2.72 g/L FeSO₄. The corrosion current and potential of an alloy of Fe and Mn with a Mn content of 13,769 weight percent are respectively $10^{-3.9}$ A and -1.23 V.

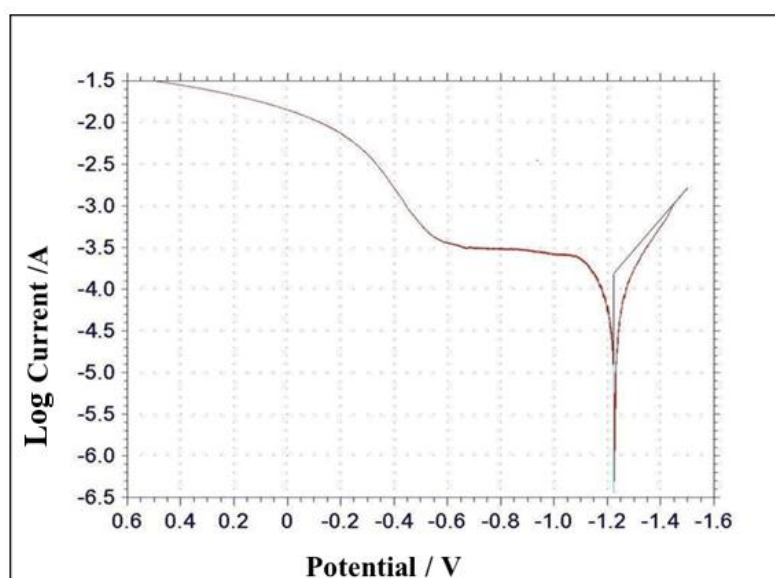


Figure 4.57 Polarization curve of the Fe-Mn sample for 10,640 % concentration of Mn.

Fe-Mn alloy electrodeposited on steel substrate was immersed in 3.5% NaCl solution for a linear sweep voltammetry experiment. A Tafel Plot of this Fe-Zn alloy is displayed in Figure 4.57. Using an electrolyte with a FeSO₄ concentration of 5.44 g/L, this graph shows the Tafel plot of an electrodeposited Fe-Mn alloy with 10,640 weight percent Mn. An alloy of Fe and Mn with a 10.640 weight percent Mn content has corrosion current and potential of, respectively, $10^{-3.8}$ A and -1.24V.

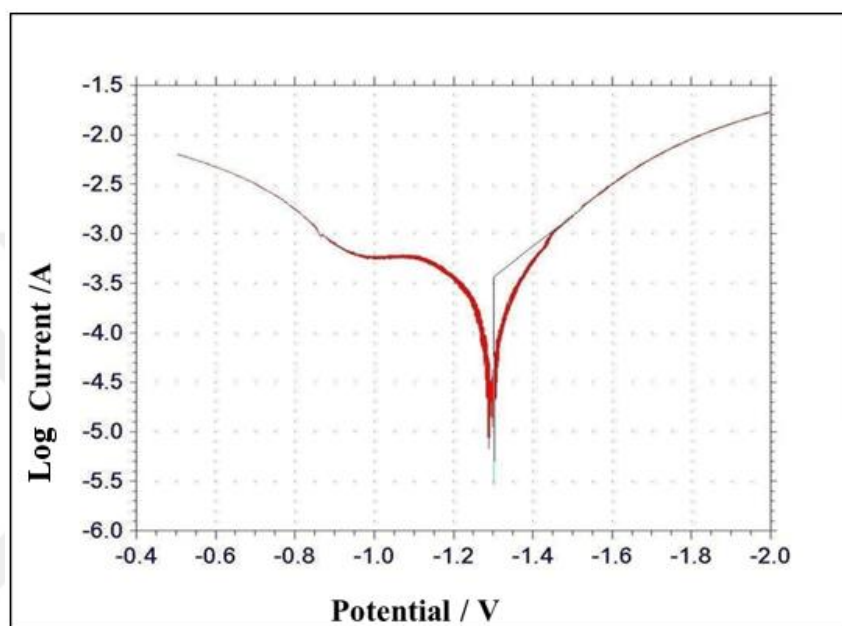


Figure 4.58 Polarization curve of the Fe-Mn sample for 5,614 % concentration of Mn.

For a linear sweep voltammetry experiment, Fe-Mn alloy electrodeposited on steel substrate was submerged in 3.5% NaCl solution. Figure 4.58 shows a Tafel Plot of this Fe-Zn alloy. This graph displays the Tafel plot of an electrodeposited Fe-Mn alloy with 5,614 weight percent Mn using an electrolyte with a FeSO₄ concentration of 13.6 g/L. Corrosion current and potential for an alloy of Fe and Mn with 5,614 weight percent Mn are, respectively, $10^{-3.3}$ A and -1.3V. It is known that addition of manganese to iron could increase ductility of Fe-Mn alloy [115]. Mechanical behavior of iron-based alloys could be changed by alloying them with manganese. This study shows that electrochemical (corrosion) behavior of these alloys could be controlled by changing the ratio of manganese in iron.

Table 3.21 The corrosion potential E_{corr} , corrosion current I_{corr} and carried charge Ah of AISI 4140 steel substrate and Fe-Mn samples for different concentrations of Mn.

		pH	E_{corr} (V)	I_{corr} (A)	CR (mm/year)
AISI 4140		3.2	-1.148	-3.2	7.33
Fe-Mn sample for concentration of					
16,308 %Mn	Sample CA-6	3.2	-1.22	-3.8	1.95
13,769 %Mn	Sample CA-7	3.2	-1.23	-3.9	1.55
10,640 %Mn	Sample CA-8	3.2	-1.22	-3.8	1.96
5,614 %Mn	Sample CA-9	3.2	-1.30	-3.3	6.22

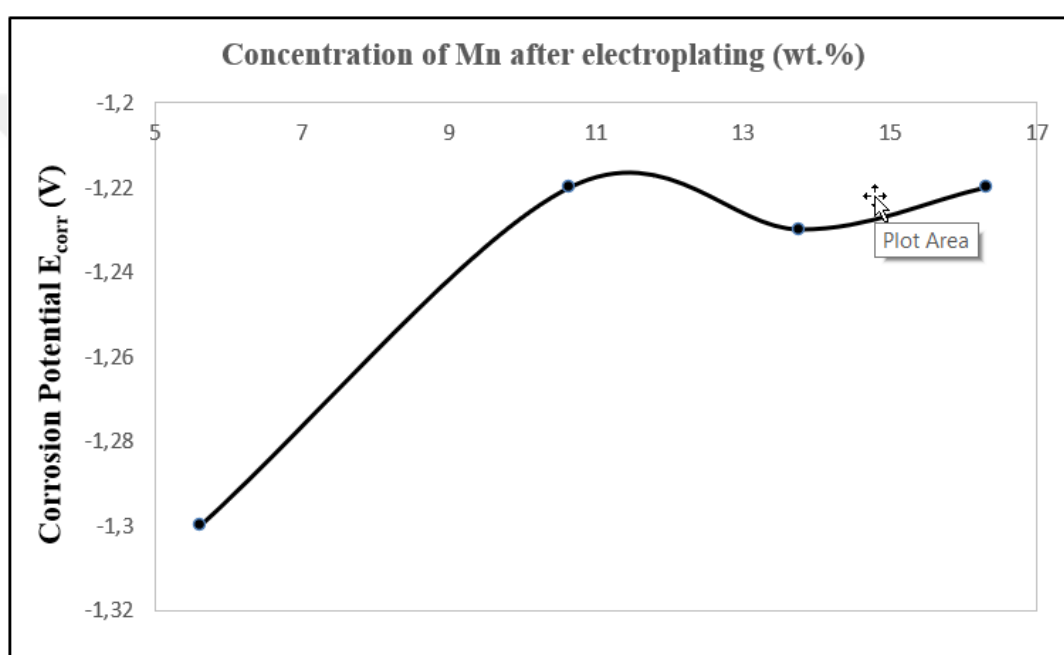


Figure 4.59 Corrosion potential of the Fe-Mn alloy coatings.

Figure 4.59 shows corrosion potential (E_{corr}) versus Concentration of Mn (wt%) after electroplating of FeMn alloys. From the Table 3.21, Fe-Mn electroplated sample for the concentration of 13.769 wt. % Mn, has lower corrosion rate (CR) than the other Fe-Mn electroplated samples examined experimentally in this study. On the other hand, Fe-Mn electroplated sample for the concentration of 5.614 wt. % Mn has higher CR than the other Fe-Mn sample fabricated in this study. If a sample has a low corrosion rate, it can be said to be more resistant to corrosion.

4.2.3. Studies on Fe-Zn-Mn Alloy

4.2.3.1. Cyclic Voltammetry of Fe-Zn-Mn Alloy

In this study, the surface area, the applied voltage and time are 1 cm², 1,7 V and 5 minutes respectively for each sample. Figure 4.60 - Figure 4.64 shows the cyclic voltammograms of Fe- Zn-Mn samples consists of 10, 20, 30, 40 g/L Zn concentrations in the solutions respectively in the solutions by using electrodeposition technique.

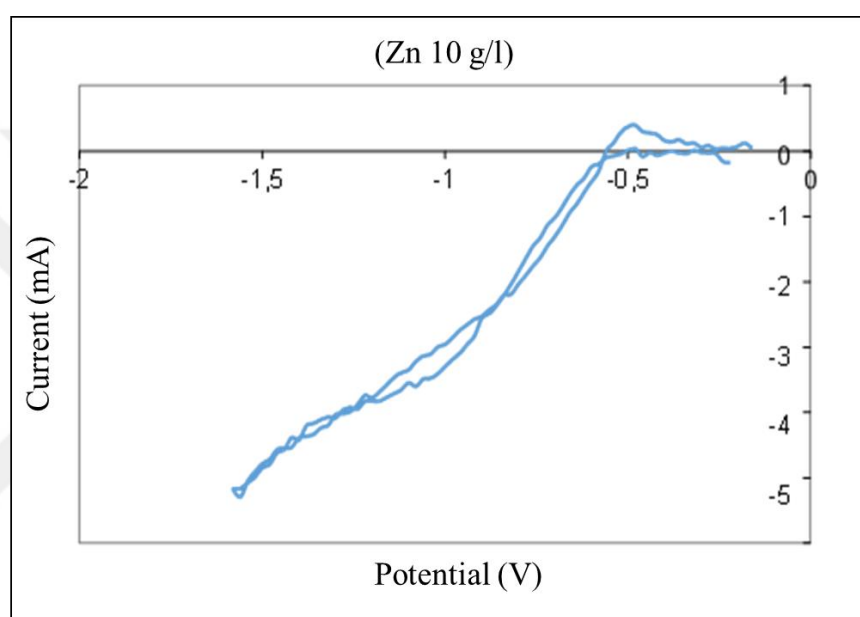


Figure 4.60 The cyclic voltammogram of Fe-Zn-Mn sample containing (10g/L) of Zn concentration.

In this experiment, the pH value is 3,2 applied current 20 mA and considering Figure 4.60 the cathodic potential is scanned between -0.2 V and -1.56 V values. According to the results obtained from the data, it is seen that the working electrode is passive between the potentials -0.2 V and -0.54 V. The deposition of the Fe-Zn-Mn onto the iron substrate starts from the beginning of -0.54 V value, and the cathodic current decreases until potential reaches the value of -1.56 V and sharp peak is observed at -5.29 mA. After the returning point at negative potential side [at potential value of -1.56 V], the anodic current starts to increase clearly. From this graph one can see that the sharp peak is around 0.39 mA and also the oxidation is around at -0.48 V.

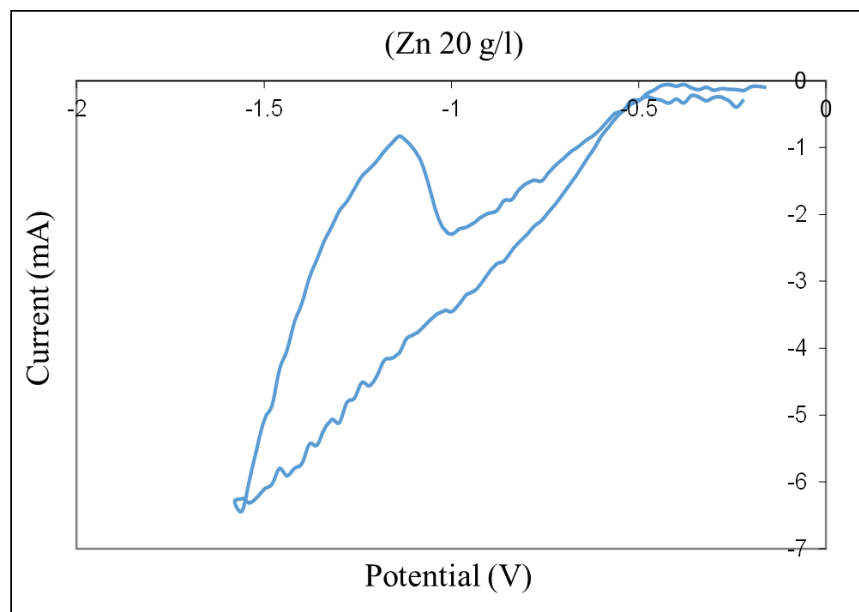


Figure 4.61 The cyclic voltammogram of Fe-Zn-Mn sample containing (20g/L) of Zn concentration.

The pH value is 3.2 and applied current is 23 mA in this experiment. The cathodic potential is scanned between -0.22 V and -1.58 V values as seen in Figure 4.61. According to the results from the data, it is seen that the working electrode is passive between the potentials - 0.22 V and -0.49V. From the start up -0.49 V value, the deposition of the Fe- Zn-Mn onto the iron substrate starts and the cathodic current decreases until potential figures out at the value of -1.58 V and sharp peak is observed at -6.28 mA. After the returning point at potential value of -1.58 V, the anodic current starts to increase. From this graph it seen that the sharp peak is around 0.049 mA and the oxidation is also around at -0.38 V.

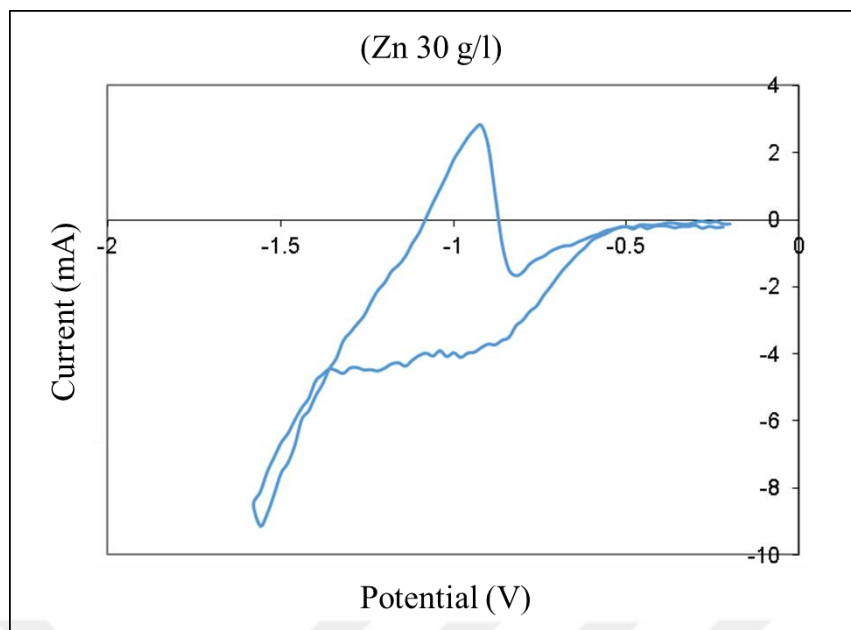


Figure 4.62 The cyclic voltammogram of Fe-Zn-Mn sample containing (30g/L) of Zn concentration.

In this study, the pH value is 3.2 applied current 21 mA. Scanning range of the cathodic potential is between -0.22 V and -1.58V values. The results obtained from the Figure 4.62 that the working electrode is passive between the potentials -0.22 V and -0.44 V. The deposition of the Fe-Zn-Mn onto the iron substrate starts from the beginning of -0.44 V value, and the cathodic current decreases until it gets at the value of -1.58 V and sharp peak is observed at -8.51 mA. After the returning point at the value of -1.58 V, the anodic current starts to increase pointedly. From this graph one can see that the sharp peak is around 2.81 mA and also the oxidation is around at -0.92 V.

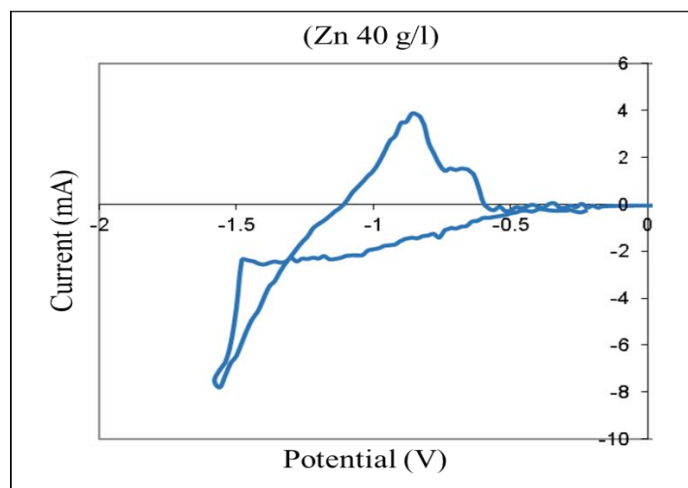


Figure 4.63 The cyclic voltammogram of Fe-Zn-Mn sample containing (40g/L) of Zn concentration.

For this sample the pH value 3.2 applied current 22 mA are performed. The cathodic potential is scanned between 0.02 V and -1.58V values. As for that the results come by the data, it is seen that the working electrode passivation potential is between -0.2 V and -0.46 V. From the beginning of -0.46 V value, the deposition of the Fe-Zn- Mn onto the iron substrate starts and the cathodic current increases until it progresses to the value of -1.58 V and sharp peak is observed at -7.49 mA. The returning point as a potential in which the anodic current starts to increase is -1.58 V. As seen in Figure 4.63 that the sharp peak is around 3.88 mA and the oxidation is around at -0.86 V.

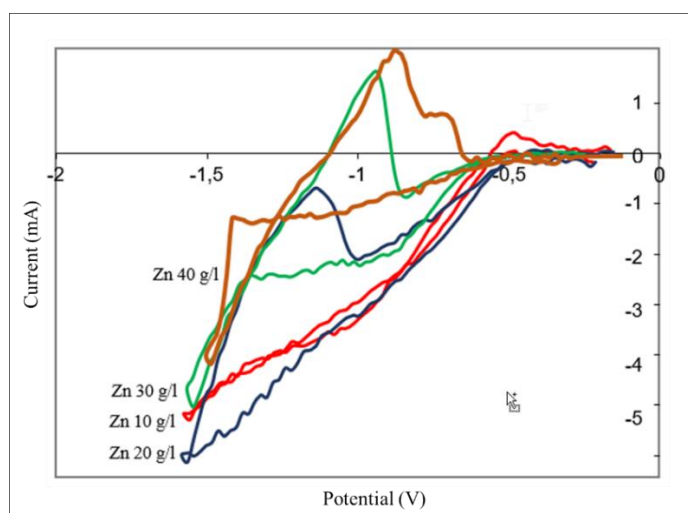


Figure 4.64 The overlapped cyclic voltammogram of Fe-Zn-Mn sample containing (10,20,30, and 40g/L) of Zn concentration.

4.2.3.2. Scanning Electron Microscope (SEM) Pictures of Fe-Zn-Mn Alloy

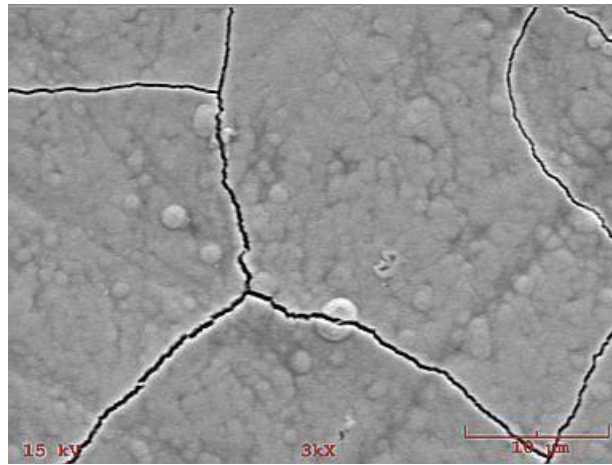


Figure 4.65 The SEM picture of Fe-Zn-Mn containing (10g/L) of Zn concentration

Figure 4.65 shows the SEM image of the sample fabricated from aqueous solution of FeZnMn alloy surface of the sample has papilla and cracks. These cracks are unwanted for a sample. This will reduce the resistance of the sample against corrosion due to the possibility of dust and water accumulating in these cracks.

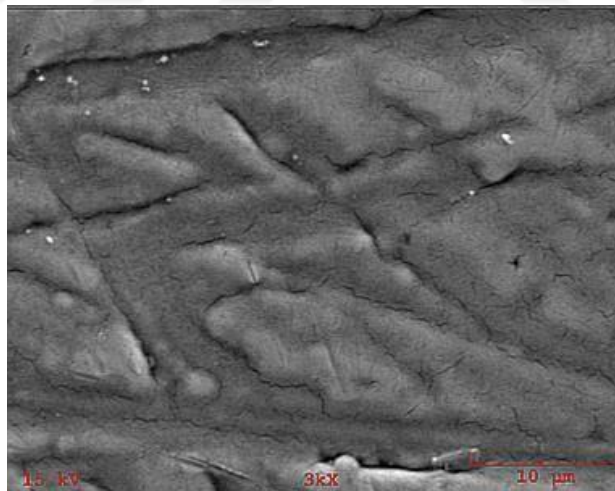


Figure 4.66 The SEM picture of Fe-Zn-Mn containing (20g/L) of Zn concentration.

It can be mentioned that there are irregular bulges formed on the surface of the sample seen in Figure 4.66 and that there are small cracks in the lower parts of them. on the surface, it can be seen with the scratch left from the sanding process while preparing the steel substrate for the experiment.

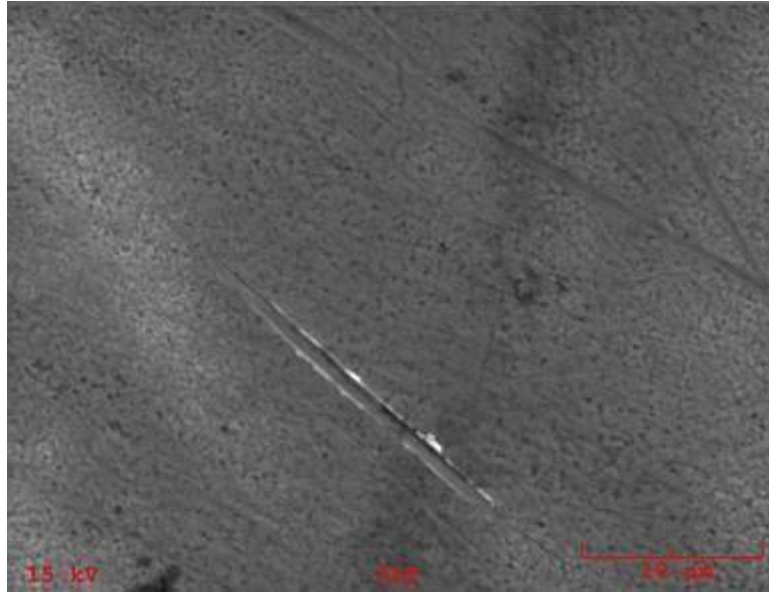


Figure 4.67 The SEM picture of Fe-Zn-Mn containing (30g/L) of Zn concentration

The sample seen in Figure 4.67 surface resembles large porous pebbles near the sea.

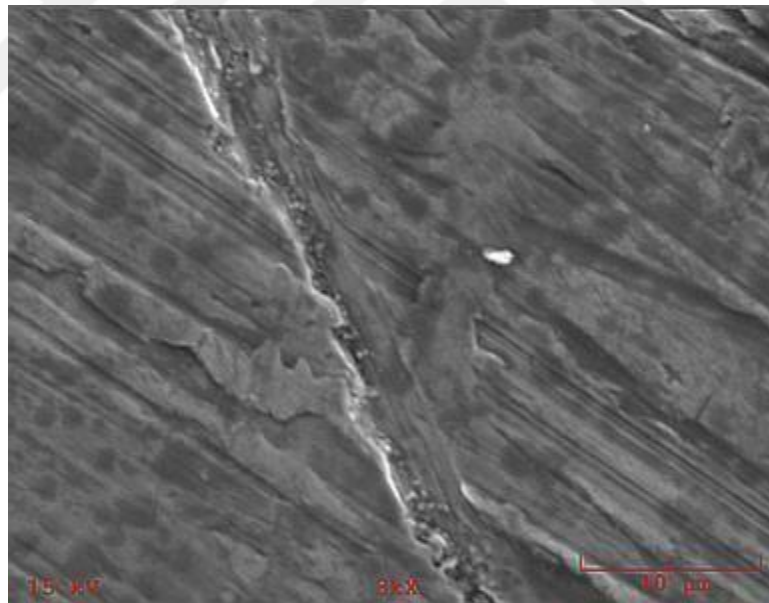


Figure 4.68 The SEM picture of Fe-Zn-Mn containing (40g/L) of Zn concentration

It can be said that there are irregular accumulations and parallel lines for the image in Figure 4.68. In addition, the thick line passing through the middle of the parallel lines at an angle of about 60 degrees in the middle of the picture resembles a broken fault line in a field.

4.2.3.3. Energy Dispersive X-Ray (EDX) Analysis of Fe-Zn-Mn Alloy

After SEM examination, an electrodeposited Fe-Mn alloy from an electrolyte containing 10 g/L Zn^{+2} ions were identified using EDX data. Figure 4.69 and Table 3.22 show the outcomes of the EDX experiment on the Fe-Zn-Mn alloy. Fe-Zn-Mn with a Zn content of 10 g/L was found using EDX. This alloy consists of 2.3 % manganese, 67 % iron and 30.7 % Zn.

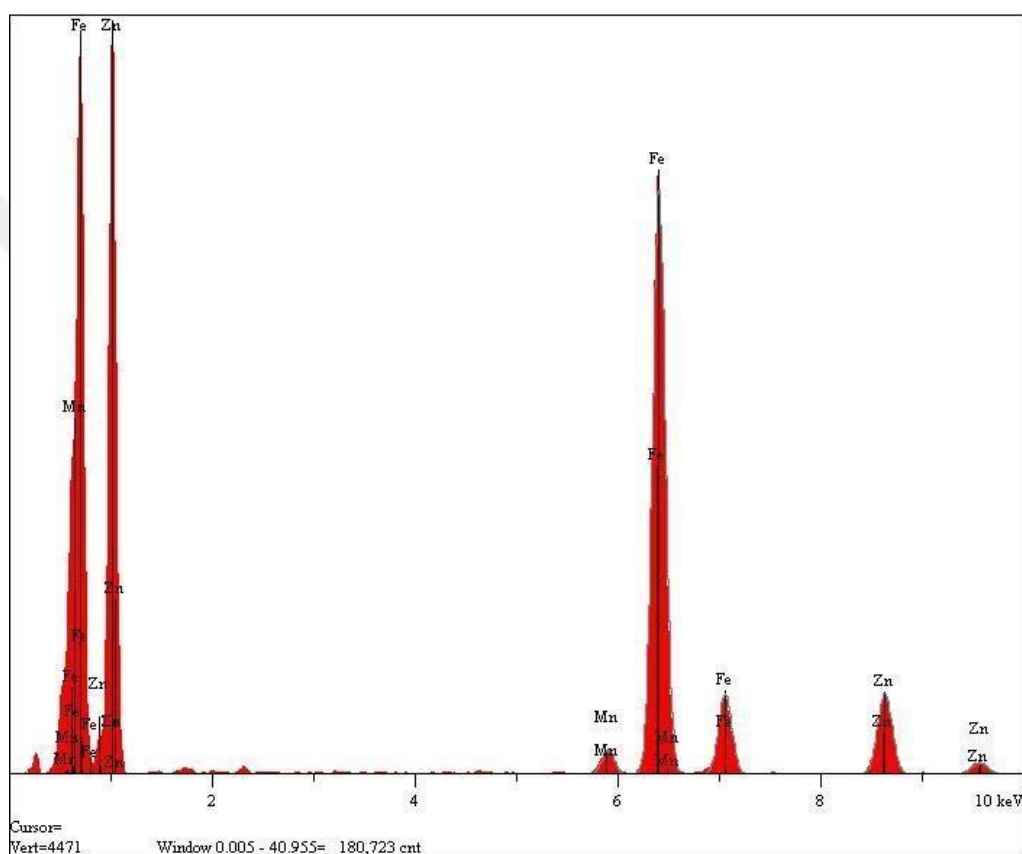


Figure 4.69 EDX image of Fe-Zn-Mn with 10 g/L Zn concentration.

Table 3.22 Mn with 10 g/L Zn concentration.

Element	Line	Intensity (c/s)	Concentration	Units
Mn	Ka	21.90	2.297	wt. %
Fe	Ka	535.18	66.918	wt. %
Zn	Ka	85.81	30.785	wt. %
			100.000	wt. %

After SEM analysis, EDX data was used to pinpoint an electrodeposited Fe-Mn alloy from an electrolyte containing 20 g/L Zn^{+2} ions. The results of the EDX experiment on the Fe-Zn-Mn alloy are presented in Figure 4.70 and Table 3.23. Using EDX, Fe-Zn-Mn with a Zn concentration of 20 g/L was discovered. 0.2 % manganese, 17.6 % iron, and 82.2 % zinc make up this alloy.

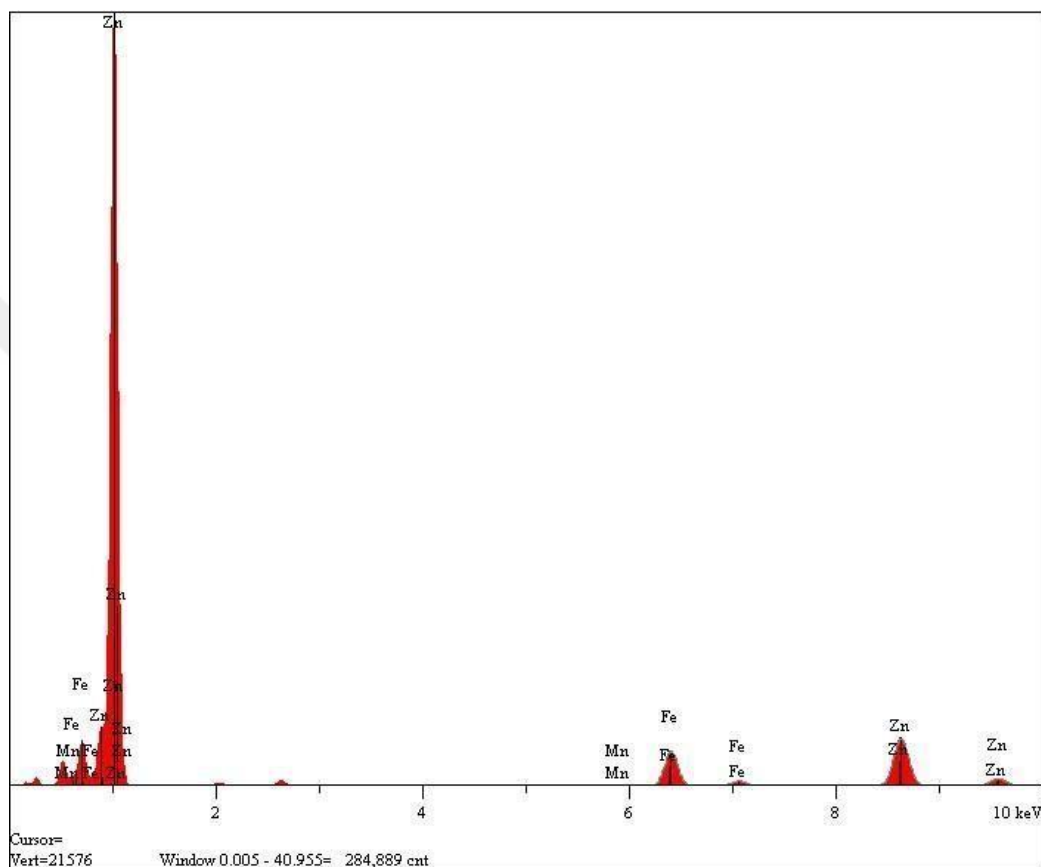


Figure 4.70 EDX image of Fe-Zn-Mn with 20 g/L Zn concentration.

Table 3.23 Mn with 20 g/L Zn concentration.

Element	Line	Intensity (c/s)	Concentration	Units
Mn	Ka	1.53	0.160	wt.%
Fe	Ka	148.40	17.628	wt.%
Zn	Ka	233.60	82.212	wt.%
			100.000	wt.%

An electrodeposited Fe-Mn alloy from an electrolyte containing 30 g/L Zn^{+2} ions was located using EDX data after SEM investigation. Figure 4.71 and Table 3.24 exhibit

the findings of the EDX experiment performed on the Fe-Zn-Mn alloy. Fe-Zn-Mn with a 30 g/L Zn content was found using EDX. This alloy has 80.1% zinc, 19.5% iron, and 0.4 % manganese.

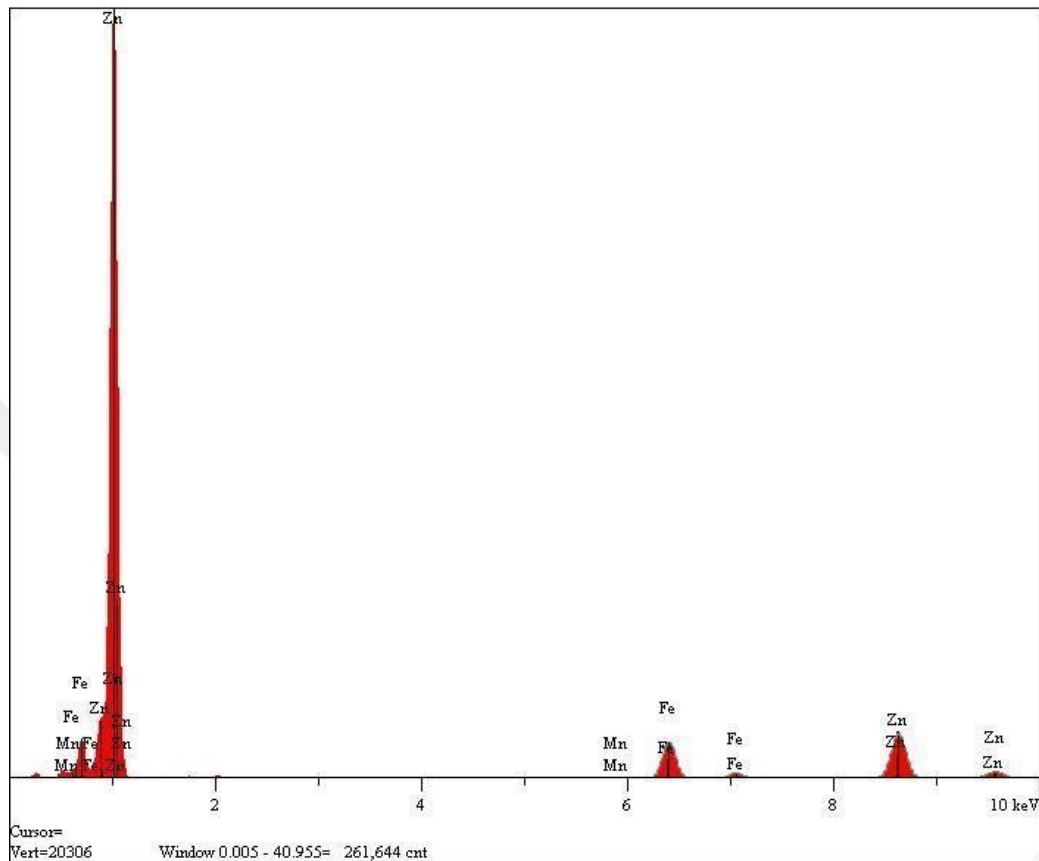


Figure 4.71 EDX image of Fe-Zn-Mn with 30 g/L Zn concentration.

Table 3.24 Mn with 30 g/L Zn concentration.

Element	Line	Intensity (c/s)	Concentration	Units
Mn	Ka	3.22	0.370	wt.%
Fe	Ka	148.76	19.514	wt.%
Zn	Ka	206.70	80.116	wt.%
			100.000	wt.%

After a SEM investigation, an electrodeposited Fe-Mn alloy from an electrolyte containing 40 g/L Zn²⁺ ions were discovered using EDX data. The results of the EDX experiment conducted on the Fe-Zn-Mn alloy are shown in Figure 4.72 and Table 3.25. Using EDX, Fe-Zn-Mn with a Zn concentration of 40 g/L was discovered. This alloy has 0.6 % manganese, 51.5 % iron, and 47.9 % zinc.

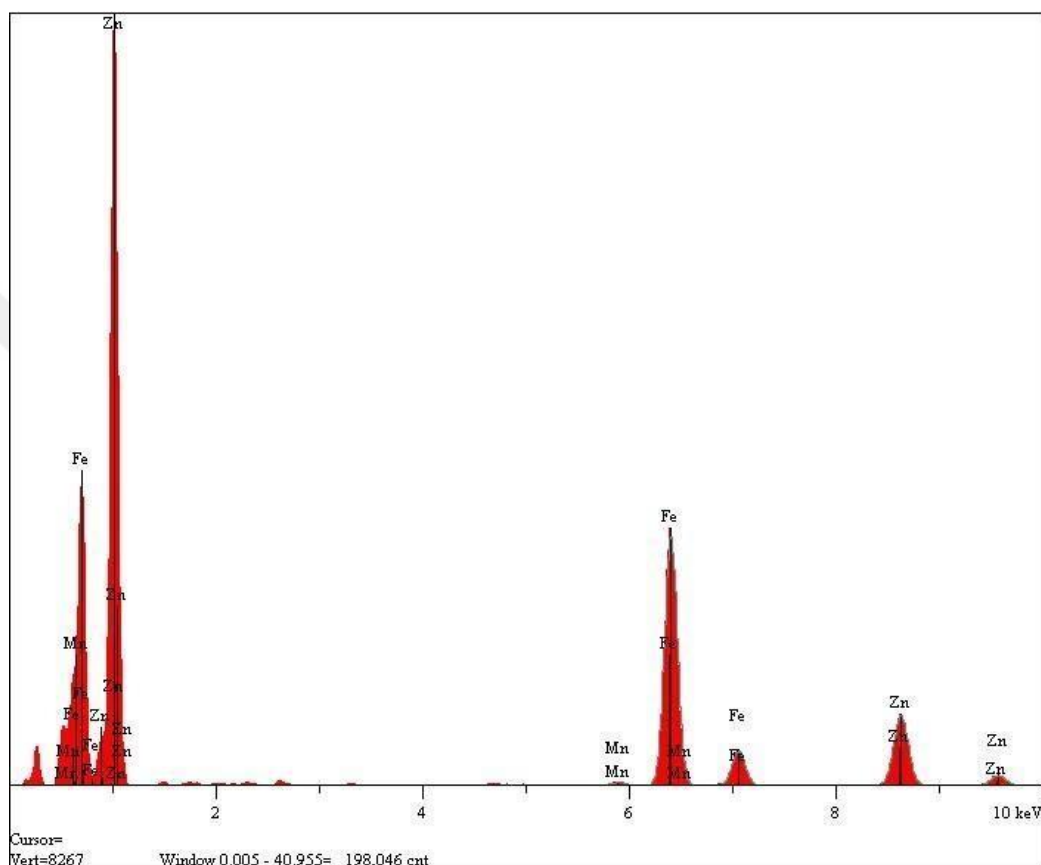


Figure 4.72 EDX image of Fe-Zn-Mn with 40 g/L Zn concentration.

Table 3.25 Mn with 40 g/L Zn concentration.

Element	Line	Intensity (c/s)	Concentration	Units
Mn	Ka	5.64	0.602	wt.%
Fe	Ka	410.62	51.542	wt.%
Zn	Ka	132.18	47.856	wt.%
			100.000	wt.%

Table 3.26 Amounts of Zn, Fe, Mn before and after the electrodeposition.

Number of the Samples	Before Electrodeposition (g/l)			After Electrodeposition (%)		
	ZnSO ₄ ·7H ₂ O	FeSO ₄	MnSO ₄ ·H ₂ O	Zn	Fe	Mn
FeZnMn-1	10	40	62.5	30.785	66.918	2.297
FeZnMn-2	20	40	62.5	82.212	17.628	0.160
FeZnMn-3	30	40	62.5	80.116	19.514	0.370
FeZnMn-4	40	40	62.5	47.856	51.542	0.602

Table 3.26 shows amounts Zn, Fe, Mn elements in the solution before electrodeposition and deposited these three elements on the AISI 4140 code steel substrate after electrodeposition. According to the EDX results of electrodeposited Fe-Zn-Mn alloys and concentrations of Fe, Zn and Mn (shown in Table 3.26) after electroplating there are high Zn concentrations values. Zn figures in passivation which is effects corrosion resistivity. Samples containing 20% and 30% zinc concentration in the solution before electrodeposition show more passivation after electrodeposition due to the high zinc content. which means that these samples are better than the other two.

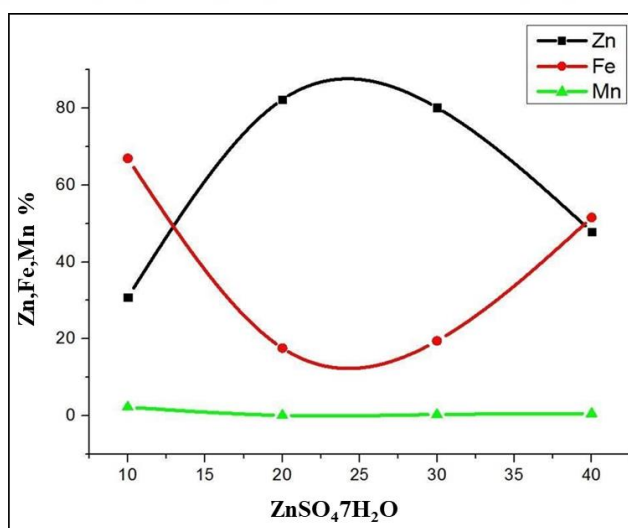


Figure 4.73 Zn amounts before electrodeposition versus Zn, Fe and Mn concentrations after electrodeposition.

Figure 4.73 illustrates wt.% concentrations of iron, zinc and magnesium formed by electrodeposition in the solution containing Zn at different concentrations prepared before electrodeposition.

4.2.3.4. X-Ray Diffraction (XRD) of Fe-Zn-Mn Alloy

In this part it had to be shown the assessment the value of XRD measurements. However, the obtained Fe-Zn-Mn thin film was not effective because measured signal of this film and the signal coming from substrate were fitting into another.

4.2.3.5. Polarization curve analysis of Fe-Zn-Mn

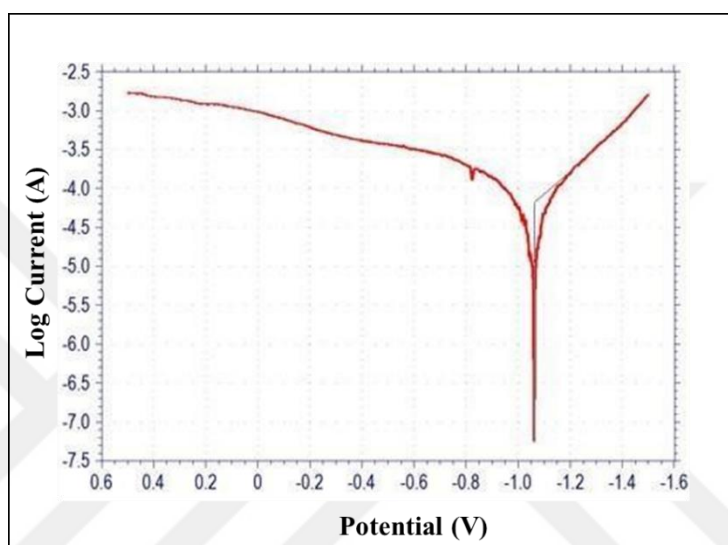


Figure 4.74 Polarization curve of the Fe-Zn-Mn for 30.785 % concentration of Zn.

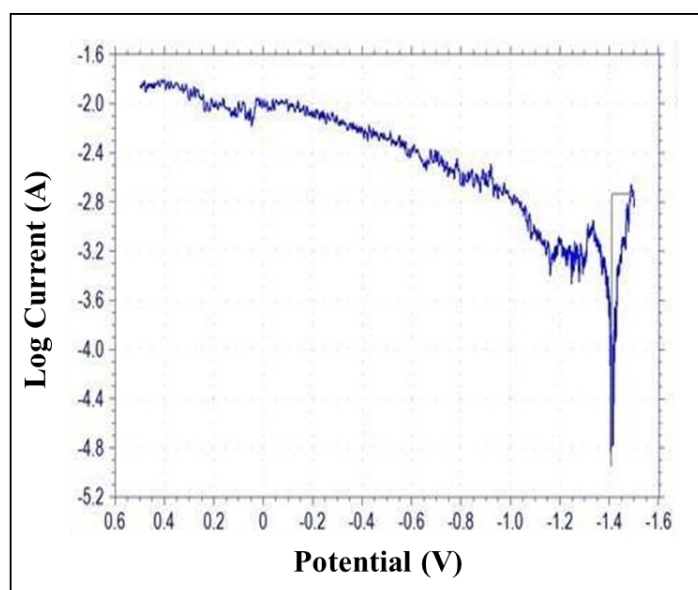


Figure 4.75 Polarization curve of the Fe-Zn-Mn for 82.212 % concentration of Zn.

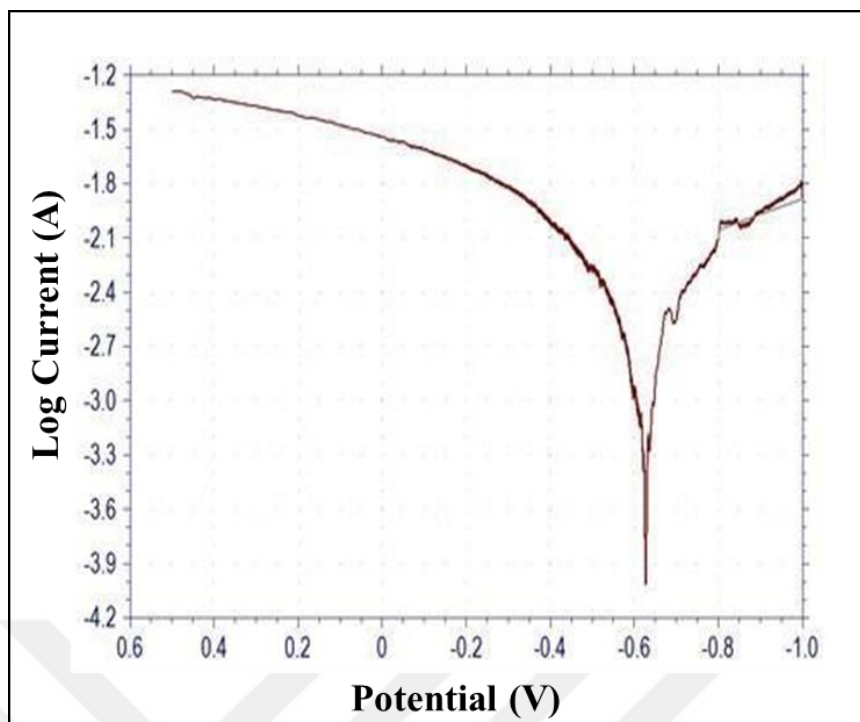


Figure 4.76 Polarization curve of the Fe-Zn-Mn for 80.116 % concentration of Zn.

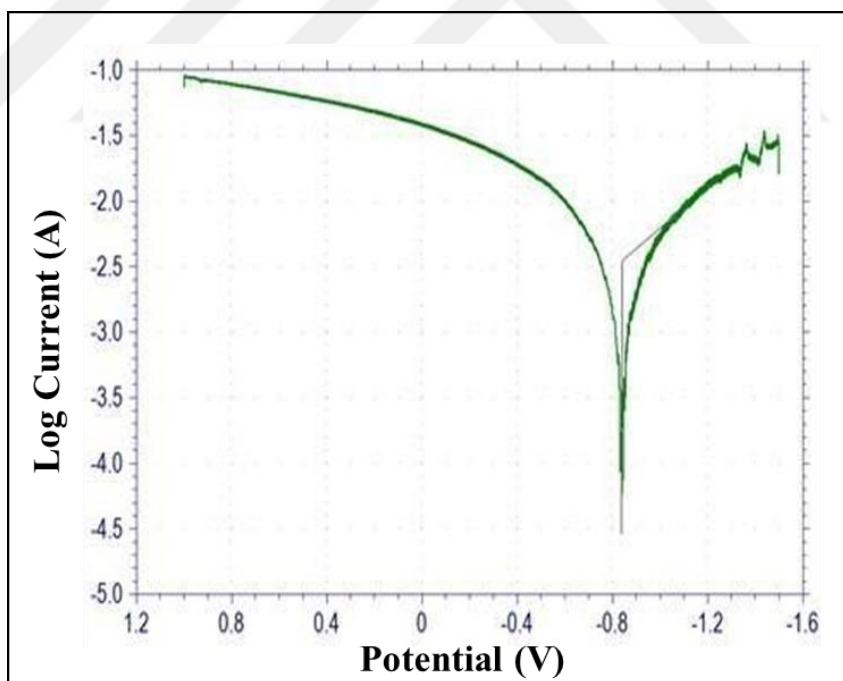


Figure 4.77 Polarization curve of the Fe-Zn-Mn for 47.856 % concentration of Zn.

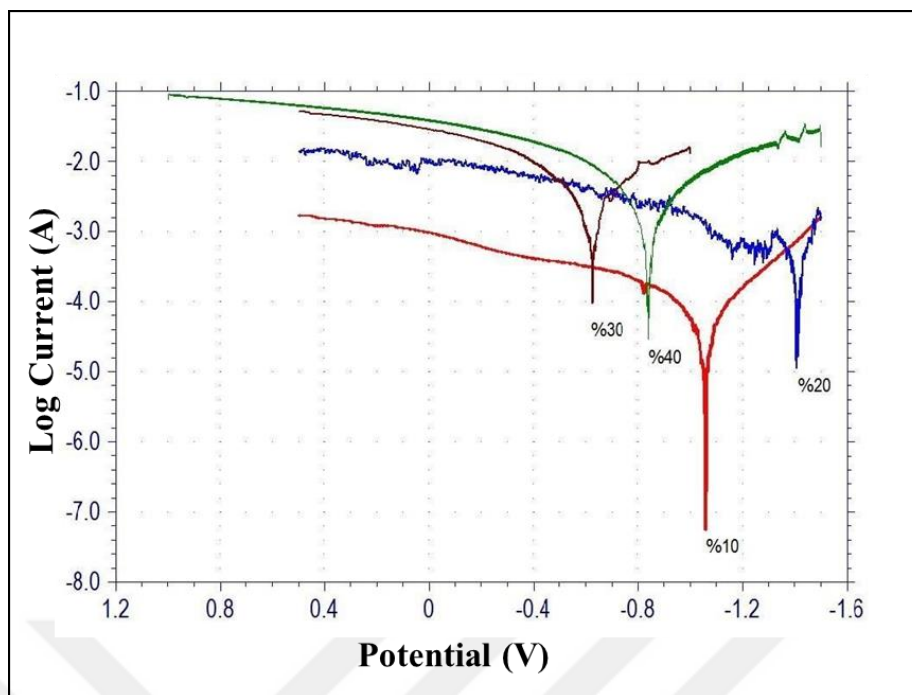


Figure 4.78 Linear sweep voltammogram [116] of electrodeposited of electro - deposited Fe-Zn- Mn alloys for all concentrations of Zn on AISI 4140 substrate.

I_{corr} and E_{corr} values determined from Figure 4.74- Figure 4.77 are shown in Table 3.27 and corrosion rates of the samples electrodeposited FeZnMn alloys, are calculated and added.

Table 3.27 The corrosion potential E_{corr} and corrosion current I_{corr} AISI 4140 steel substrate and Fe-Zn-Mn for different concentrations of Zn.

		pH	$E_{corr}(V)$	$I_{corr} (A)$	CR (mm/year)
AISI 4140		3.2	-1.148	-3.2	7.33
Fe-Zn-Mn sample for					
30.785 wt.% Zn	Sample 1	3.2	-1.061	-4.210	0.51
82.212 wt.% Zn	Sample 2	3.2	-1.409	-2.820	3.38
80.116 wt.% Zn	Sample 3	3.2	-0.640	-2.636	5.77
47.856 wt.% Zn	Sample 4	3.2	-0.830	-2.530	18.72

In this part corrosion behaviors of Fe-Zn and Fe-Mn Fe-Zn-Mn alloys electrodeposited on the iron (AISI 4140) substrate from an acidic chloride bath by using three-electrode system have been studied.

It can be concluded that the obtained values (corrosion potential E_{corr} and corrosion current I_{corr} for the AISI 4140 steel substrate and the sample Fe-Zn-Mn for the different concentration of Zn determined by EDX after electroplating) are in Table 3.27.

According to these data our searched corrosion potential varies between -1.409 and 0.830 Volt for different amount of Zn values. As seen from these results, obtained after coating, corrosion potential E_{corr} s are not showing the steady manner. This case is also related to other data of our experiments like corrosion current I_{corr} . All parameters as mentioned are obtained under pH = 3.2.

When the corrosion rates of the samples which are fabricated from aqueous solutions of FeZnMn alloys are analyzed, the sample which contains 30.785 wt% Zn after electroplating, has lower CR as 0.51 mm/year than the other samples. This shows the sample has high corrosion resistance than the others. On the other hand, the sample which contains 47.856 wt% Zn after electroplating and has 18.72 mm/year CR is the poorer sample than the others for the corrosion prevention. For Fe-Zn-Mn Alloys. From the CV figures of Fe-Zn-Mn alloys the sharpest peak is around 2.81 mA and also the oxidation is around at -0.92 V for the 10 g/L of Zn in the liquid. The weakest peak is around 0.39 mA and also the oxidation is around at -0.48 V. According to the SEM images in this experiment the best Fe-Zn-Mn alloy film electrodeposited on the substrate surface is for the 30 g/L of Zn and the poorest film is for 10 g/L of Zn concentration.

Upon the graphs of EDX analyses of Fe-Zn-Mn, the peaks of Zn for 20 g/L and 30g/L have almost the same concentration values as 82.212 % and 80, 116 % respectively. On the other hand, the concentrations of Fe are as 17.628 % and 19.514 % and that of Mn are as 0.370 % and 0.602 % respectively. From electrodeposition and Zn concentrations after electrodeposition change inversely proportional for the electrodeposited films consisting 10, 20, 30 g/L of Zn amounts in solution before the electrodeposition. The concentration values have near to each other for 40 g/L of Zn, Fe and Zn %. At the same time for Mn % concentrations, the values are very close to each other and very lower than Fe and Zn % concentrations. Here we can claim that if the amount of % Zn lies in higher levels and that of % Mn in lower levels the formation of the film on substrate is obtained smooth and orderly.

4.3. Electrodepositions of Fe and Fe Alloys (Fe-Zn, Fe-Mn and Fe-Zn-Mn) from Ionic Liquid Electrolyte

4.3.1. Growth of Fe-Zn, Fe-Mn and Fe-Zn-Mn Alloy Films in Ionic Liquid

Using a cyclic voltammogram, the steel working electrode was immersed in Ethaline ionic liquid to investigate the growth conditions of Fe-Zn, Fe-Mn, and Fe-Zn-Mn on steel. The cyclic voltammogram curves of a bare steel electrode in pure Ethaline solution (red line of Figure 4.79 a) and in Ethaline solution containing both Fe^{2+} and Zn^{2+} salts (black line of Figure 4.79 b) and Fe^{2+} and Mn^{2+} salts are shown (red line of Figure 4.79 b). All electrolytes' cyclic voltammograms were started at 0 V and scanned to -1.7 V, and then scanned back to 0.5 V at the same scan rate. When a bare steel electrode was immersed in Ethaline ionic liquid at 0 V, it oxidized because the ionic liquid can directly oxidize the steel. The direction of scanning was from 0 V to the negative side. Steel oxidation was halted at around -0.5 V. Between -0.5 V and around -1.3 V, no redox reaction occurred since the current through steel was around 0 A (red line in Figure 4.79 a) , indicating that there were no ions that could be reduced in Ethaline at this potential range. Normally, Ethaline did not contain any metal salt at the start (before polarization). As the steel working electrode did not oxidize again when the cycle potential was increased from -1.7 V to roughly -0.4 V, current was around 0 V and no reduction or oxidation occurred. As no oxidation peak was recorded following the reduction at roughly -1.7 V, it may be concluded that the reduction happened as a result of hydrogen evolution. At nearly -0.45 V, steel was oxidized (Figure 4.79 a-red line).

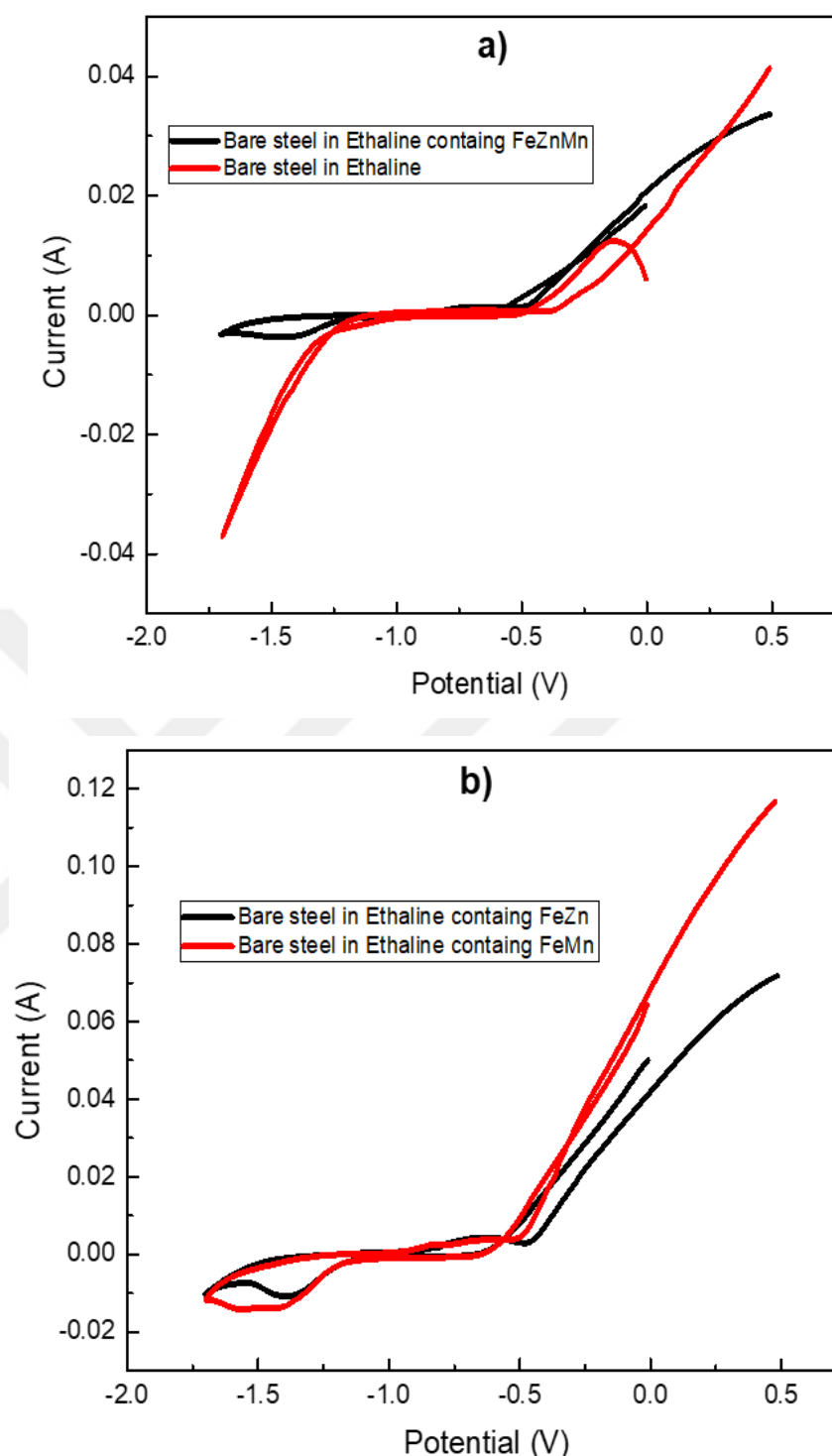


Figure 4.79 (a) Cyclic voltammogram curve of bare steel working electrode in pure Ethaline solution (black line) and in Ethaline liquid comprising Fe^{2+} , Zn^{2+} and Mn^{2+} ions (red line); (b) Cyclic voltammogram curve of bare steel working electrode in Ethaline liquid comprising Fe^{2+} and Zn^{2+} (black line) and Fe^{2+} and Mn^{2+} (red line). $\nu = 20 \text{ mV s}^{-1}$.

When bare steel was submerged in Ethaline containing Fe and Mn salts (red line in Figure 4.79b), the steel electrode reduced at potentials ranging from 0 to -0.5 V. This is due to the reduction of the steel electrode observed when bare steel was cycled in pure Ethaline. There was no appreciable current between -0.5 V and roughly -1.2 V, indicating that there was no reduction or oxidation of the steel in Ethaline containing Fe and Mn salts. Then, a slight reduction peak occurred between -1.2 V and roughly -1.4 V, and there is no current changing between -1.4 V and -1.6 V. This cathodic current (reduction) happened as a result of Mn^{2+} and/or Fe^{2+} ion reduction. Between -1.4 V to approximately -0.8 V, current was near zero, with no evidence of reduction or oxidation. At around -0.7 V, a tiny oxidation peak was noticed, which could be due to film dissolution. Finally, an oxidation was noticed between -0.5 V and 0.5 V. This peak cannot provide information on film dissolution since steel can oxidize in this range of potentials.

When bare steel is examined in Ethaline containing both Fe^{2+} and Zn^{2+} based salts (black line in Figure 4.79b), an oxidation in bare steel is found between 0 and -0.5 V. The cyclic voltammogram pattern for steel in Ethaline containing iron and zinc salt (black line in Figure 4.79b) is similar to the pattern for steel in Ethaline containing Fe^{2+} and Mn^{2+} salt (red line of Figure 4.79b). As a result, both electrolytes undergo identical reduction and oxidation. When bare steel was immersed in Ethaline containing Fe^{2+} , Zn^{2+} , and Mn^{2+} salts (black line in Figure 4.79a), the current of steel electrode decreased between 0 and approximately -0.5 V. Due to the fact that the ampere is zero when scanning between -0.5 V and approximately -1.25 V, there was no reduction or oxidation of the salt or steel electrode at these voltages. Between -1.25 and -1.7 V, a decrease in voltage was noticed, which could be due to the deposition of the alloy-based coating. Thus, by applying -1.6 V, these films (Fe-Zn, Fe-Mn, and Fe-Zn-Mn) may be formed.

4.3.2. Characterization of the Electrodes

Fe-Zn, Fe-Mn, and Fe-Zn-Mn films were electrodeposited on steel surfaces using Ethaline containing their salts. Before disclosing their corrosion behavior, these electrodes were characterized. EDAX and SEM analyses were used to establish the coatings' elemental and morphological compositions [117]. SEM pictures of Fe-Zn,

Fe-Mn, and Fe-Zn-Mn alloys coated steel electrodeposited from an ionic liquid media are shown in Figure 4.80. Picture of steel inset in Figure 4.80a reveals scratches on the steel surface caused by the grinding operation. Clustered nanoparticles were found in Figure 4.80b's SEM image of a Fe-Zn coating on steel. The SEM picture of Fe-Mn in Figure 4.80c resembles a cloudy sky. On the other hand, as shown in Figure 4.80d, the SEM image of Fe-Zn-Mn electrodeposited on steel looks like an uneven heterogeneous sheet.

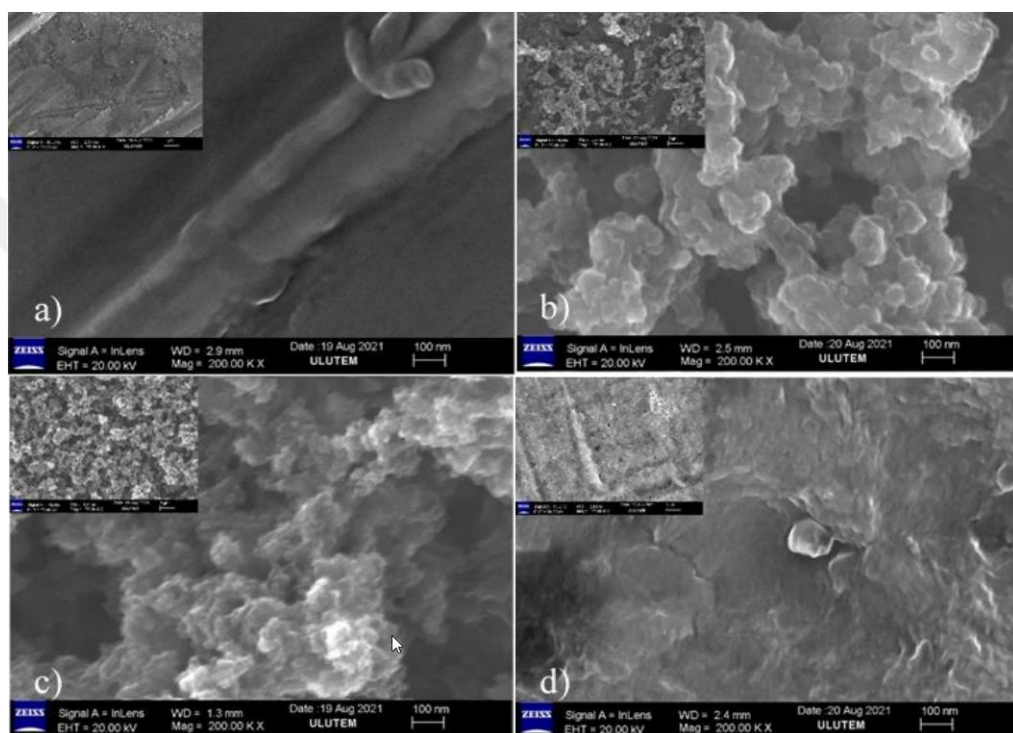


Figure 4.80 SEM pictures of a) bare steel, b) electrodeposited Fe-Zn based alloy on steel; c) electrodeposited Fe-Mn based alloy on steel and; d) electrodeposited Fe-Zn-Mn basis alloy on steel. The films were fabricated potentiostatically from Ethaline ionic solution.

Before presenting the XRD, FTIR, and corrosion data for the coating, the EDAX analysis of uncoated and alloy coated electrodes are presented in Table 3.28. On steel, Fe-Zn and Fe-Mn coatings contain 3.5 % Zn and 3.5 % Mn, respectively. Both of them have an Fe content of 96.5 %, as steel is mostly composed of iron. Due to the thinness of the coatings, EDX was able to detect significantly the underlying iron. The elemental composition of the Fe-Zn-Mn alloy indicates that it contains 1.7 % Mn and 0.5 % Zn.

Table 3.28 Elemental ratio in Fe-Zn, Fe-Mn and Fe-Zn-Mn alloys electrodeposited on steel.

Alloys →	Fe-Zn	Fe-Mn	Fe-Zn-Mn
Element ↓	Wt%	Wt%	Wt%
Mn	0	3.5	1.7
Fe	96.5	96.5	97.8
Zn	3.5	0	0.5

XRD is a technique for determining the crystal structure of a material using the scattered X-rays in various directions [118]. XRD was employed to analyze the crystal composition of electrochemically deposited coatings on steel. Figure 4.81 shows the XRD patterns of the bare steel electrode with Fe-Zn, Fe-Mn, and Fe-Zn-Mn alloy samples put on it. Because the films are thin and the XRD results are dominated by the steel substrate, the XRD peaks of Fe-Zn, Fe-Mn, and Fe-Zn-Mn alloys coated steel were like to those of basis steel electrode (Figure 4.81). The peaks of the supplied electrodes correspond to the steel orientations (110), (200), and (211) [119].

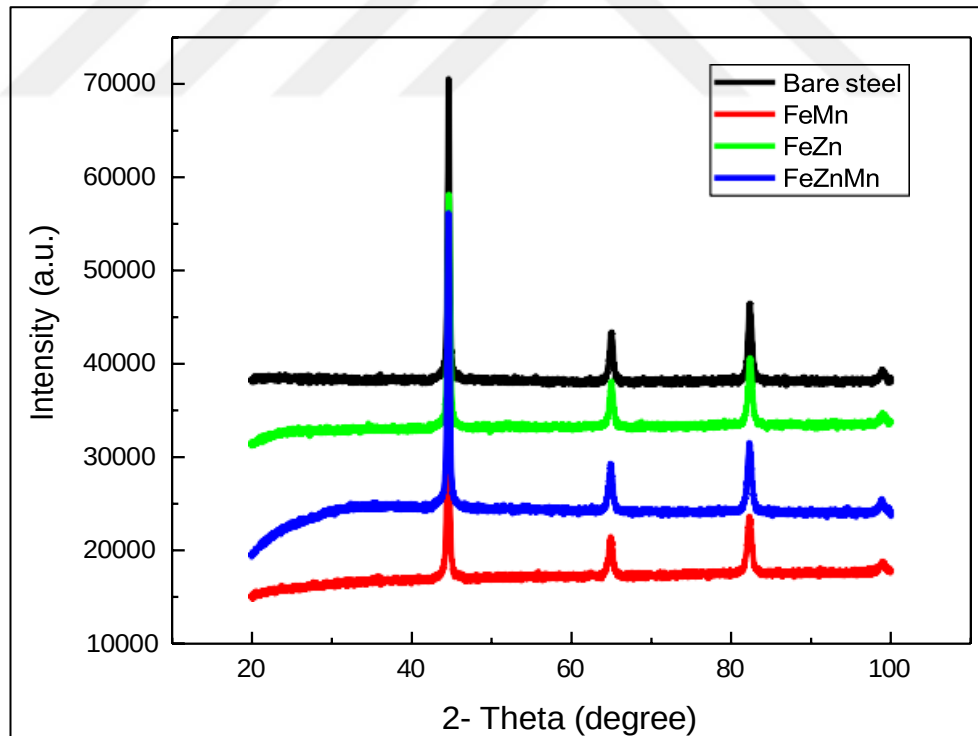


Figure 4.81 The patterns of X-ray diffraction (XRD) of a) bare steel; b) Fe-Mn; c) Fe-Zn and; d) Fe-Zn-Mn coated steel.

FTIR is a technique for obtaining the infrared absorption and emission spectra of a substance [120]. Figure 4.82 shows the vibration spectra of modified and untreated steel electrodes. Figure 4.82 illustrates the FTIR spectrum of uncoated steel. In the spectra of bare steel, there is only one peak about 410 cm^{-1} (black line of Figure 4.82). The FTIR spectrum of the Fe-Mn alloy electrochemically coated onto the steel is shown in Figure 4.82 (red line). The Fe-Mn alloy's FTIR spectra (Figure 4.82) showed peaks at $451, 700, 1111, 1586,$ and 3255 cm^{-1} . Figure 4.82 depicts the FTIR spectrum of the Fe-Zn alloy. When the Fe-Zn alloy's FTIR spectrum is investigated, it is discovered to have peaks around $450, 500, 700, 1080$ and 1580 cm^{-1} (green line, Figure 4.82). These peaks indicate that the electrochemically formed alloy coatings may be in the form of their oxide or hydroxide in nature. Figure 4.82 depicts the FTIR spectrum of the Fe-Zn-Mn ternary alloy. Its peaks are located at around $665, 1634, 1653,$ and $1700, 2313,$ and 3407 cm^{-1} (blue line, Figure 4.82).

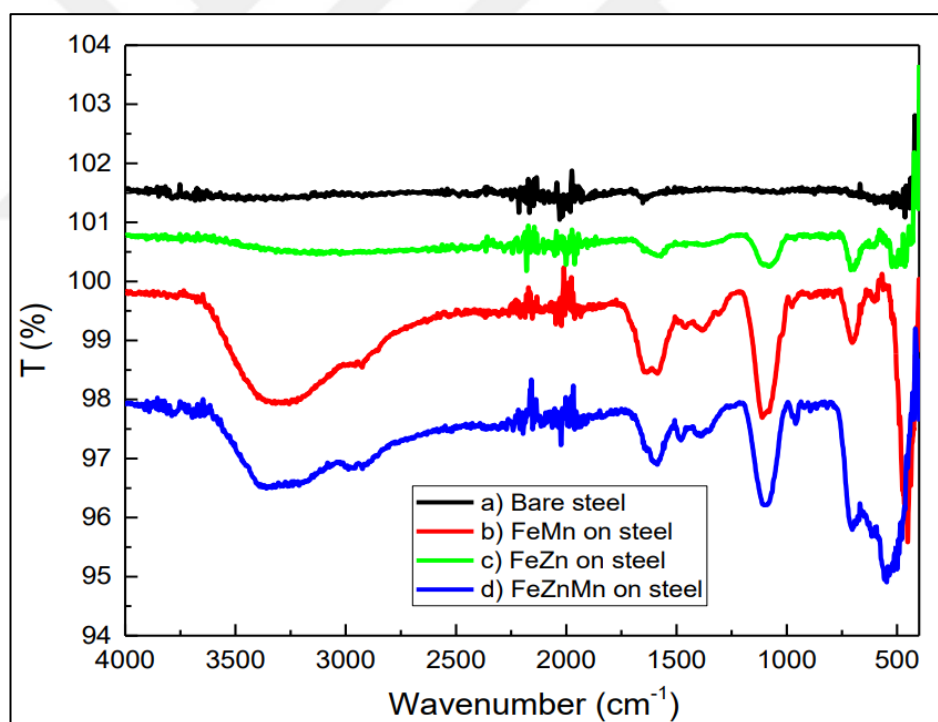


Figure 4.82 FTIR spectra of a) bare steel electrode (black line); b) Fe-Mn (red line); c) Fe-Zn (green line); and d) Fe-Zn-Mn (blue line) alloy deposited on steel electrode.

4.3.3. Corrosion Study of the Electrodes

E_{corr} and I_{corr} values can be computed from the Tafel values by intersecting the oxidation and reduction lines of the corrosion potential and corrosion current density on the Tafel plot. Tafel plots were obtained by immersing Fe-Zn, Fe-Mn, and Fe-Zn-Mn alloys coated on steel and platinum Figure 4.83a substrates in an aqueous 3.5 wt.% NaCl solution. To examine the corrosion behavior of Fe-Zn, Fe-Mn, and Fe-Zn-Mn coated steel and platinum electrodes generated electrochemically, they were compared with the corrosion behavior of uncoated steel and platinum electrodes. The Tafel plot of Fe-Zn, Fe-Mn, and Fe-Zn-Mn alloys coated on steel is shown in Figure 4.83a. Prior to coating a steel from this ionic liquid electrolyte, any aqueous residues in the ionic liquid were eliminated by heating to around 60 °C. Additionally, the reference, counter, and working electrodes were dried with hot air to remove any remaining moisture on their surfaces. Corrosion current and potential values of modified electrodes in 3.5 wt.% NaCl media can be estimated using the logarithm of current in linear sweep voltammeter responses. Figure 4.83b shows Tafel plots of the bare platinum electrode and electrochemically deposited Fe-Zn, Fe-Mn, and Fe-Zn-Mn alloys on the platinum substrate in a 3.5 percent NaCl solution (25 °C).

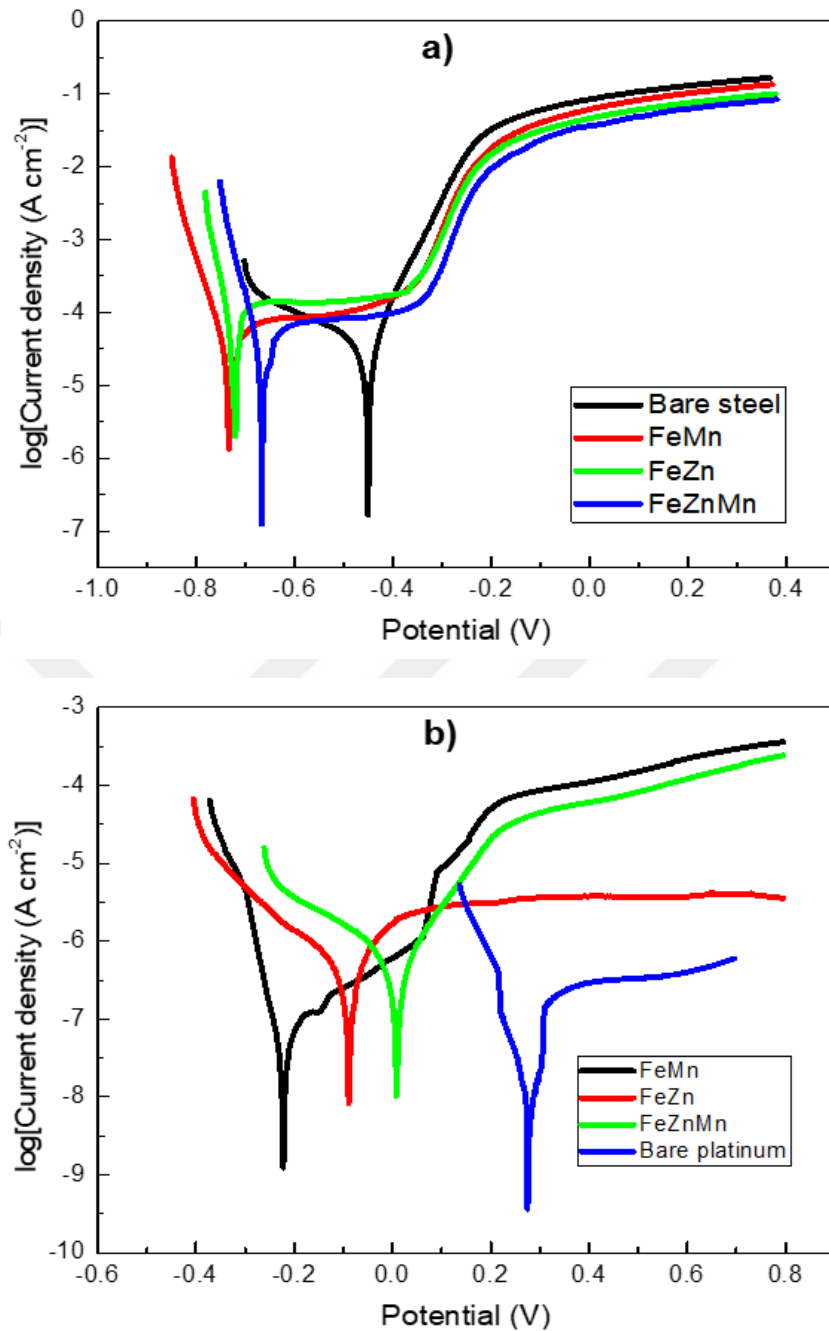


Figure 4.83 a) Potentiodynamic polarization responses of bare steel (black line) electrode, iron manganese alloy (red line), iron zinc alloy (green line), and iron, zinc and manganese alloy (blue line) electrodes coated on steel substrate electrochemically in 3.5% NaCl solution at 25 °C. b) Potentiodynamic polarization responses behavior of bare platinum (blue line) electrode, iron manganese alloy (black line), iron zinc alloy (red line), and iron, zinc and manganese alloy (green line) alloy electrodes electrochemically coated on platinum substrate in 3.5% NaCl solution at 25 °C.

I_{corr} is a critical metric for determining the kinetics of corrosion reactions. The lower the I_{corr} value, the slower the corrosion rate and the greater the material's corrosion resistance [121]. Table 3.29 summarizes the corrosion current and potential of the electrodes utilized in this study. When I_{corr} values of electroplated samples are examined, it is discovered that the corrosion rate of bare steel did not rise after it was coated with alloys, owing to the fact that the corrosion responses obtained using linear sweep voltammetry were dominated by the steel substrate. As a result, the alloys were electrodeposited on the Pt surface to demonstrate the coating effect. All alloy coatings had a lower corrosion current (less than 1 A cm^{-2}) than steel (63 A cm^{-2}). Fe-Zn, Fe-Mn, and Fe-Zn-Mn alloys coated on steel can be used to protect steel against corrosion. Due to the more positive potential of ZnFeMn alloy, it can be the highest corrosion protection materials compared to other alloys.

Table 3.29 Electrochemical parameters of Fe-Zn, Fe-Mn, and Fe-Zn-Mn alloys synthesized electrochemically on steel and platinum electrode and shifted into 3.5% NaCl solution. The data given in Figure 4.83a were used for I_{corr} and E_{corr} of the electrodes.

Electrode	I_{corr} (μA)	E_{corr} (V)	CR (mm/year)
Bare steel	63	-0.487	0.755
Fe-Zn on steel	56	-0.722	0.657
Fe-Mn on steel	104	-0.786	1.210
Fe-Zn-Mn on steel	75	-0.665	0.873
Fe-Zn on platinum	0.62	-0.081	0.0073
Fe-Mn on platinum	0.11	-0.224	0.0013
Fe-Zn-Mn on platinum	0.76	+0.023	8.853

Ag-AgCl was used as the reference electrode in this study with non-aqueous ionic solution. According to corrosion rates from Tafel curves and the data in Table 3.29, it is seen that the FeZn alloy film on the steel is a better sample with a corrosion rate of 0.657 mm/year. In electroplating on platinum, it can be said that the FeMn sample with a corrosion rate of 0.0013 mm/year is better than the others. On the other hand, samples in addition, considering the corrosion rates, it is seen that the corrosion resistance of samples FeZn, FeMn and FeZnMn alloys electroplated on platinum have better

corrosion resistant. The reason for this is that the platinum used as a substrate has less effect on electroplating than the steel substrate.



CHAPTER V

CONCLUSION

Metals and alloys were electrodeposited by applying constant potential in aqueous and ionic liquid environments. Firstly, only metals (Zn, Fe and Mn) were grown on the substrate by applying -2 V for 300 seconds in aqueous solutions having pyrophosphate ligands. The current of the elements during electrodeposition had different thickness or hydrogen evolution reaction. Bimetallic alloys (Zn-Fe, Zn-Mn and Fe-Mn) and ternary alloy (Zn-Fe-Mn) were also obtained in the same conditions to compare metals and alloys corrosion behavior. Fluctuation of current occurs also during electrocoating of alloys. This fluctuation could be caused by different growth/nucleation reaction and different amount of hydrogen evolution reaction.

After metals were electrodeposited potentiostatically by applying -2 V for 300 seconds in aqueous solutions with pyrophosphate ligands, they were transferred to NaCl solution. It is known that iron could not have passive behavior and it can easily corrode which is called pitting corrosion in NaCl media. Current responses of iron coating from aqueous solution increased significantly around 0 V indicating that iron could have pitting corrosion in NaCl solution. All linear sweep voltammetry experiments were started at a negative potential which was 0.4 V less than open circuit potential. They were continued to 0.6 V to compare their corrosion behavior in the same conditions. The corrosion behavior of Mn in NaCl bath is similar to that of Fe. However, the current response of Mn (around 0.2 mA) is much lower than that of Fe (around 40 mA) at 0.6 V. Manganese could have higher corrosion resistivity than iron in these conditions.

The starting potential of cycles were at a potential less than open circuit potential and continued to positive direction (up to 0.6 V). Passivation of Zn can be proved by this experiment as current decreases after around 0 V. However, passivation of Mn or Fe

was not observed. The pitting corrosion of iron could be deduced from this result because current significantly increased after around -0.2 V. Corrosion current of Mn is around ten times less than that of Fe. Pitting corrosion is not clear in Mn polarization as anodic polarization of Mn is almost constant.

Passivation of metals can prevent materials from corrosion. Therefore, it is usually a required properties for metals and alloys. Metals/alloys which could be passivated can be used for longer time. Corrosion behavior of Fe for the first and second cycles are similar and they have similar current value due to pitting corrosion of iron. After analyzing corrosion behavior of mono metal coatings, corrosion properties of alloys were examined.

Alloys having two and three metals were obtained potentiostatically in aqueous solution with pyrophosphate media. They were cleaned by deionized water and immersed in NaCl solution. Tafel plot of bimetallic alloys (Zn-Mn, Zn-Fe and Mn-Fe) were obtained in artificial seawater (NaCl solution). Oxidation peaks belonging to zinc-based alloys (Zn-Fe and Zn-Mn) were observed. These peaks could indicate passivation of Zn based alloys. Passivation of Zn-Mn and Zn-Fe occurred thanks to zinc addition because both of these alloys contained Zn metal. However, Mn-Fe film did show no passivation. Therefore, zinc could be used as alloying material to have higher corrosion resistivity.

Passivation of Zn-Fe and Zn-Mn are obvious as their current responses decreased around 0.5 V and 0.1 V, respectively. Corrosion resistance of Zn-Fe film is higher than the others (either Mn-Fe or Zn-Mn) as Zn-Fe has lower corrosion current. Addition of Mn or Zn can decrease corrosion rate of uncoated steel. The lifetime of steel could be increased by this method. A pitting corrosion could occur in Mn-Fe alloy. Addition of Zn could seize further corrosion as it causes passivation of the films. Therefore, it could be suggested that Zn could be added to alloys for higher corrosion resistivity of alloys. Electrodeposition is a suitable technique to form zinc-based alloys.

First and second cycles of bimetallic alloys were compared to check their passivation/pitting corrosion behavior. Scanning of polarization potential was from

negative side to positive side. As the corrosion current of the second cycle belonging to Zn-Mn is lower than that of the first cycle belonging to the same film, a passivation of Zn-Mn can be mentioned clearly. The passivation of Zn-Mn was expected since it contains Zn. Passivation was not expected for the film containing only Mn-Fe alloy. The corrosion current of Mn-Fe for the second cycle is higher than that for the first cycle. It was concluded that addition of Zn could cause passivation and generally higher corrosion current. Therefore, Zn was also added to Mn-Fe to observe its corrosion properties.

When corrosion behavior of monometallic coating was analyzed, it was noticed that only Zn could have passivation behavior. Only Fe coating had pitting-like corrosion and its corrosion was higher than only Mn coating. Bimetallic alloys (Zn-Mn, Zn-Fe and Fe-Mn) were examined by means of linear sweep voltammetry and the alloys having Zn (Zn-Mn and Zn-Fe) illustrated passivation behavior. Ternary alloy having the three metals (Zn-Fe-Mn) studied in this work was obtained potentiostatically by applying constant potential for the same timescale (300 seconds). The ternary alloy was transferred to NaCl electrolyte for analyzing its corrosion behavior. The scanning was started from negative direction to 0.6 V. A clear oxidation peak for the first cycle of the ternary alloy was observed. However, current responses of this film for the second cycle are much lower than that for the first cycle which is due to passivation behavior of the alloy.

The presence of Zn in its content (in Zn-Fe-Mn alloys) could cause this behavior. Current response of the film decreased significantly around 0.3 V. Second cycle of ternary alloy in NaCl bath is less than the first cycle of it after -0.4 V till 0.6 V. Corrosion current of the ternary alloy film did not increase in the second cycle because of the creation of a stable surface. Corrosion behavior of the metals (Zn, Fe and Mn) and alloys (Zn-Mn, Zn-Fe, Fe-Mn and Zn-Fe-Mn) indicated that addition of Zn could change electrochemical responses of the film. Zn metal and Zn based alloys could generally have higher corrosion resistivity and cause passivation of the surface.

The steel substrate was used for Fe-Zn coating in an electrolyte having different ligands. The deposition potential of -2 V was applied for 5 minutes for each sample. This potential was found by cyclic voltammogram of steel in the electrolyte. The pH

value was adjusted to 4.7 and the potential was scanned the value between -0.22 V and - 1.58 V for this sample. The working electrode is not active between the potentials - 0.22 V and -1.14 V. After the value of -1.14 V, the deposition of the Fe-Zn onto the iron substrate started and the cathodic current decreases until it reaches the value of -1.58 V and sharp peak is observed at -8.41 mA. After the value of -1.58 V, the anodic current starts to increase. In the graph, it is observed the sharp peak around 9.28 mA and is seen the oxidation at -0.52 V. This oxidation means that the alloy electrodeposited at negative potential started to dissolve.

The pH value is 4.7, applied current 33 mA and the cathodic potential is scanned the value between -0.2 V and - 1.58 V for this sample. The working electrode is passive between the potentials -0.2 V and -1.14 V. The deposition of the Fe- Zn onto the iron substrate starts from the beginning of the value of -1.14 V and the cathodic current decreases until it reaches the value of -1.58 V and sharp peak is observed at -9.98 mA. The anodic current starts to increase after the value of -1.58 V. In the graph, the sharp peak around 6.19 mA and the oxidation at -0.6 V are observed.

Cyclic voltammograms showed that the application of a potential less than -1.5 V could cause electrodeposition of alloys. Therefore, a cathodic potential was applied to obtain alloys. After electrocoating of steel by various alloys, they were characterized by SEM, XRD, EDAX and linear sweep voltammetry. SEM images of the Fe-Zn alloys electrodeposited onto the iron substrate show the crystal structure of the films by choosing an area with a 5000X magnification.

The SEM picture of a Fe-Zn alloy was obtained from an electrolyte with different concentration (10 to 50 g/L Fe^{2+} content). The size of the granules of Fe-Zn electrodeposited from 10 g/L Fe^{2+} content is variable. Polygonal shapes are assembled to form the deposit. SEM image about the sample Fe-Zn alloy contains 20 g/L Fe composition with pH value of 4.7 showed bigger granules than the granules electrodeposited from 10 g/L Fe^{2+} content. SEM image of a sample Fe-Zn alloy with a pH value of 4.7 and a Fe content of 30 g/L had the average granular size, which is the largest among the other samples, is nearly equivalent to the average granular size of the Fe-Zn alloy electrodeposited onto the iron substrate. It proves the film has better crystalline structure. SEM image of Fe-Zn alloy contained 40 g/L Fe composition and

electrodeposited onto the iron had homogeneously and almost equal average granular sizes which are smaller than the other samples have. SEM images of the sample Fe-Zn alloy formed from 50 g/L Fe composition with pH value of 4.5 had the grains with more 3-D shapes and hexagonal shapes. However, gaps between granules are bigger and deeper than the other samples. This can create risks to protect substrate from the corrosion. Big gaps can allow getting foreign substances like water, dust etc. which cause corrosion to the surface of the sample.

EDX results of Fe-Zn alloy electrodeposited from an electrolyte having different concentration of Fe^{2+} (10 g/L Fe^{2+} to 50 g/L Fe^{2+}) ions were obtained after SEM analysis. Iron and zinc ratio in the alloy fabricated in 10 g/L Fe^{2+} is 10.9% and 89.1%, respectively. EDX data of a Fe-Zn alloy electrodeposited from an electrolyte containing 20 g/L Fe^{2+} ions illustrated that iron and zinc content are 6.8% and 93.2%, respectively. EDX information of a Fe-Zn alloy electrodeposited from an electrolyte containing 30 g/L Fe^{2+} ions were acquired after SEM analysis. Fe-Zn with a 30 g/L Fe content was found using EDX. Iron and zinc make up 6.3% and 93.7%, respectively, of this alloy. EDX data of a Fe-Zn alloy electrodeposited from an electrolyte containing 40 g/L Fe^{2+} ions showed that this alloy is made up of 6.3% iron and 93.7% zinc, respectively.

A Fe-Zn alloy that was electrodeposited from an electrolyte containing 50 g/L Fe^{2+} ions had 7.7% iron and 92.3% zinc, respectively. The EDX results of alloys proved that zinc is dominant in the alloys. According to the results, Zn concentration of the sample electroplated from an electrolyte containing 30 g/L Fe has a higher ratio than the other concentrations. When Fe electrodeposition becomes feasible, the reduction rate of this metal tends to be enhanced in comparison with that of Zn. The Zn ratio in the alloy gives information about Fe-Zn film condition. If Zn peak is higher, Fe-Zn film could have passivation behavior. Steel (AISI 4140) was used as a substrate and coated by metals and alloys. Before analyzing XRD of the modified electrodes, XRD pattern of non-coated steel was obtained. The peaks represent the crystallinity of the films and the changing Fe concentration value of Fe-Zn alloys effects the results. The Fe-Zn alloy coatings have the same structure as zinc but different crystallographic orientation, which is the consequence of the small iron amount. As a result of research

of articles related with Fe-Zn alloys, it was reached given results.

Among the XRD patterns of Fe-Zn alloy containing from 10 g/L to 50 g/L of Fe concentration, the sharpest Zn peak at 101 planes (at the same time represent the peak of Fe-Zn alloy) is seen for the second sample prepared with Fe-Zn alloy containing 20 g/L of Fe concentration. The others have about same peaks. At $2\theta = 44.58$ and (100) plane and $2\theta = 63.84$ and (200) Fe diffraction peaks caused by iron substrate because as it seen the XRD patterns these peaks are the same.

Bare and alloy coated AISI 4140 steel substrate was immersed in aqueous 3% NaCl solution for 40 minutes. Corrosion potential and corrosion current of bare substrate have been obtained -1.148 V, and $10^{-3.2}$ A respectively. The corrosion current of the modified electrode was generally decreased after coating. This shows that corrosion resistivity of the coating was higher than bare steel. This method (electrodeposition of alloy) could be used to prevent metals from corrosion.

SEM micrograph (top view) of Fe-Mn alloy deposits onto AISI 4140 code steel substrate with different amounts of % Fe and Mn weight concentrations. SEM image showed the surface morphologies of optimized Fe-Mn coating contains 83.692 of Fe and 16.308 of Mn weight % concentration with pH=3.2. SEM image of the alloy with 21.971% of Fe and 78.029% of Mn weight had severe fibrous structure. SEM image of the sample with 86.231% of Fe and 13.769% of Mn in Fe-Mn alloy had crack-like structure. The top of Fe-Mn coating contained 89.360 % of Fe and 10.640 % of Mn had crack-free surface.

After SEM inspection, EDX data was used to identify a Fe-Mn alloy that was electrodeposited from an electrolyte containing 2 g/L Fe^{2+} ions. Using EDX, Fe-Mn with a 2 g/L Fe concentration was discovered. This alloy is composed of 16.3% manganese and 83.7% iron respectively.

After SEM examination, an electrodeposited Fe-Mn alloy from an electrolyte containing 2.72 g/L Fe^{2+} ions were identified using EDX data. Fe-Mn consists of 78 % manganese and 22 % iron, respectively. Fe-Mn alloy electrodeposited from an electrolyte containing 5.44 g/L Fe^{2+} ions composed of 13.8 % manganese and 86.2 %

iron. EDX experiment with the Fe-Mn alloy obtained from 13.6 g/L Fe^{2+} ions had 10.6 % manganese and 89.4 % iron respectively. Fe-Mn alloy electrodeposited from an electrolyte containing 13.6 g/L Fe^{2+} ions had 5.6 % manganese and 94.4% iron.

Using a cyclic voltammogram, the steel working electrode was immersed in Ethaline ionic liquid to investigate the growth conditions of Fe-Zn, Fe-Mn, and Fe-Zn-Mn on steel. The cyclic voltammogram curves of a bare steel electrode in pure Ethaline solution and in Ethaline solution containing Fe^{2+} , Zn^{2+} and Mn^{2+} salts. All electrolytes' cyclic voltammograms were started at 0 V and scanned to -1.7 V, and then scanned back to 0.5 V at the same scan rate. When a bare steel electrode was immersed in Ethaline ionic liquid at 0 V, it oxidized because the ionic liquid can directly oxidize the steel. The direction of scanning was from 0 V to the negative side. Steel oxidation was halted at around -0.5 V. Between -0.5 V and around -1.3 V, no redox reaction occurred since the current through steel was around 0 A, indicating that there were no ions that could be reduced in Ethaline at this potential range. Normally, Ethaline did not contain any metal salt at the start (before polarization). As the steel working electrode did not oxidize again when the cycle potential was increased from -1.7 V to roughly -0.4 V, current was around 0 V and no reduction or oxidation occurred. As no oxidation peak was recorded following the reduction at roughly -1.7 V, it may be concluded that the reduction happened as a result of hydrogen evolution. At approximately -0.45 V, steel was oxidized.

When bare steel was immersed in Ethaline containing Fe and Mn salts, the steel electrode reduced at potentials ranging from 0 to -0.5 V. This is due to the reduction of the steel electrode observed when bare steel was cycled in pure Ethaline. There was no appreciable current between -0.5 V and roughly -1.2 V, indicating that there was no reduction or oxidation of the steel in Ethaline containing Fe and Mn salts. Then, a slight reduction peak occurred between -1.2 V and roughly -1.4 V, and there is no current changing between -1.4 V and -1.6 V. This cathodic current (reduction) happened as a result of Mn^{2+} and/or Fe^{2+} ion reduction. Between -1.4 V to approximately -0.8 V, current was near zero, with no evidence of reduction or oxidation. At around -0.7 V, a tiny oxidation peak was noticed, which could be due to film dissolution. Finally, an oxidation was observed between -0.5 V and 0.5 V. This

peak cannot provide information on film dissolution since steel can oxidize in this range of potentials.

When bare steel is examined in Ethaline containing both Fe^{2+} and Zn^{2+} -based salts, an oxidation in bare steel is found between 0 and -0.5 V. The cyclic voltammogram pattern for steel in Ethaline containing iron and zinc salt is similar to the pattern for steel in Ethaline containing Fe^{2+} and Mn^{2+} . As a result, both electrolytes undergo identical reduction and oxidation. When bare steel was immersed in Ethaline containing Fe^{2+} , Zn^{2+} , and Mn^{2+} salts, the current of steel electrode decreased between 0 and approximately -0.5 V. Due to the fact that the ampere is zero when scanning between -0.5 V and approximately -1.25 V, there was no reduction or oxidation of the salt or steel electrode at these voltages. Between -1.25 and -1.7 V, a decrease in voltage was noticed, which could be due to the deposition of the alloy-based coating. Thus, by applying -1.6 V, these films (Fe-Zn, Fe-Mn, and Fe-Zn-Mn) may be formed.

Fe-Zn, Fe-Mn, and Fe-Zn-Mn films were electrodeposited on steel surfaces using Ethaline containing their salts. Before disclosing their corrosion behavior, these electrodes were characterized. EDAX and SEM analyses were used to establish the coatings' elemental and morphological compositions. SEM pictures of Fe-Zn, Fe-Mn, and Fe-Zn-Mn alloys coated steel electrodeposited from an ionic liquid media were obtained. Scratches on the steel surface caused by the grinding operation was observed. The SEM picture of Fe-Mn resembles a cloudy sky. On the other hand, the SEM picture of Fe-Zn-Mn electrodeposited on steel resembles an uneven heterogeneous sheet.

Before presenting the XRD, FTIR, and corrosion data for the coating, the EDAX analysis of uncoated and alloy coated electrodes are presented. On steel, Fe-Zn and Fe-Mn coatings contain 3.5 % Zn and 3.5 % Mn, respectively. Both of them have an Fe content of 96.5 %, as steel is mostly composed of iron. Due to the thinness of the coatings, EDAX was able to detect significantly the underlying iron. The elemental composition of the Fe-Zn-Mn alloy indicates that it contains 1.7 % Mn and 0.5 % Zn. XRD was used to analyze the crystal structure of electrochemically deposited coatings on steel. The XRD patterns of the bare steel electrode with Fe-Zn, Fe-Mn, and Fe-Zn-

Mn alloy samples put on it. Because the films are thin and the XRD results are dominated by the steel substrate, the XRD peaks of Fe-Zn, Fe-Mn, and Fe-Zn-Mn alloys coated steel were similar to those of bare steel electrode. The peaks of the supplied electrodes correspond to the steel orientations (110), (200), and (211).

FTIR illustrates the vibration spectra of modified and untreated steel electrodes. In the spectra of bare steel, there is only one peak about 410 cm^{-1} . The FTIR spectrum of the Fe-Mn alloy electrochemically coated onto the steel is presented. The Fe-Mn alloy's FTIR spectra showed peaks at 451, 700, 1111, 1586, and 3255 cm^{-1} . When the Fe-Zn alloy's FTIR spectrum is investigated, it is discovered to have peaks around 450, 500, 700, 1080 and 1580 cm^{-1} . These peaks indicate that the electrochemically formed alloy coatings may be in the form of their oxide or hydroxide in nature. FTIR spectrum of the Fe-Zn-Mn ternary alloy had some peaks located at around 665, 1634, 1653, and 1700, 2313, and 3407 cm^{-1} .

E_{corr} and I_{corr} values can be computed from the Tafel values by intersecting the oxidation and reduction lines of the corrosion current density and corrosion potential on the Tafel plot. Tafel plots were obtained by immersing Fe-Zn, Fe-Mn, and Fe-Zn-Mn alloys coated on steel and platinum substrates in an aqueous 3.5 wt.% NaCl solution. To examine the corrosion behavior of Fe-Zn, Fe-Mn, and Fe-Zn-Mn coated steel and platinum electrodes generated electrochemically, they were compared with the corrosion behavior of uncoated steel and platinum electrodes. The Tafel plot of Fe-Zn, Fe-Mn, and Fe-Zn-Mn alloys coated on steel is obtained.

Prior to coating a steel from this ionic liquid electrolyte, any aqueous residues in the ionic liquid were eliminated by heating to around $60\text{ }^{\circ}\text{C}$. Additionally, the reference, counter, and working electrodes were dried with hot air to remove any remaining moisture on their surfaces. Corrosion current and potential values of modified electrodes in 3.5 wt% NaCl media can be estimated using the logarithm of current in linear sweep voltammeter responses. Tafel plots of the bare platinum electrode and electrochemically deposited Fe-Zn, Fe-Mn, and Fe-Zn-Mn alloys on the platinum substrate in a 3.5 percent NaCl solution ($25\text{ }^{\circ}\text{C}$) are presented.

I_{corr} is a critical metric for determining the kinetics of corrosion reactions. The lower

the I_{corr} value, the slower the corrosion rate and the greater the material's corrosion resistance. The corrosion current and potential of the electrodes utilized in this study were summarized. When I_{corr} values of electroplated samples are examined, it is discovered that the corrosion rate of bare steel did not rise after it was coated with alloys, owing to the fact that the corrosion responses obtained using linear sweep voltammetry were dominated by the steel substrate. As a result, the alloys were electrodeposited on the Pt surface to demonstrate the coating effect. All alloy coatings had a lower corrosion current (less than 1 A cm^{-2}) than steel (63 A cm^{-2}). Fe-Zn, Fe-Mn, and Fe- Zn-Mn alloys coated on steel can be used to protect steel against corrosion.

When evaluated according to corrosion rates, the following can be said for the samples obtained from aqueous solutions of FeZn, FeMn and FeZnMn alloys.

According to the data in Table 3.15, the sample with 10.889 weight percent of Fe after electrodeposition had a higher corrosion resistance. Since among the samples that have an electrodeposited Fe-Zn alloy, its CR rate is the lowest at 2.26 mm/year. Fe concentration of 6.255 weight percent in the sample results in a CR of 7.40 mm/year. This demonstrates that the sample is less resistant to corrosion than the others.

According to Table 3.21, the corrosion rate (CR) of the Fe-Mn electroplated sample with 13.769 weight percent Mn is lower than that of the other Fe-Mn electroplated samples tested experimentally in this work. In contrast, the Fe-Mn electroplated sample with 5.614 weight percent Mn had a greater CR than the other Fe-Mn sample created for this investigation. A sample is said to be more corrosion-resistant if its corrosion rate is low.

When the corrosion rates of the samples made from aqueous FeZnMn alloy solutions were examined, it was found that the sample with 30.785 weight percent Zn after electroplating had a lower CR of 0.51 mm/year (seen in Table 3.27) than the other samples. This demonstrates the sample has stronger corrosion resistance than the others. On the other hand, the sample that has 18.72 mm/year CR and has a Zn content of 47.856 weight percent after electroplating is worse than the others for preventing corrosion.

For the samples obtained from anhydrous ethaline solutions of FeZn, FeMn and FeZnMn alloys, the following conclusions can be reached.

According to corrosion rates from Tafel curves and the data in Table 3.29, it is seen that the FeZn alloy film on the steel is a better sample with a corrosion rate of 0.657 mm/year. In electroplating on platinum, it can be said that the FeMn sample with a corrosion rate of 0.0013 mm/year is better than the others. On the other hand, samples in addition, considering the corrosion rates, it is seen that the corrosion resistance of samples FeZn, FeMn and FeZnMn alloys electroplated on platinum have better corrosion resistant. The reason for this is that the platinum used as a substrate has less effect on electroplating than the steel substrate.

REFERENCES

- [1] P. S. Wells, "Iron Age Temperate Europe: Some Current Research Issues," 1990.
- [2] A. M. Helmenstine, *Ph.D. Interesting and Useful Facts about Iron*.
- [3] A. Popoola, O. Olorunniwo, and O. Ige, "Corrosion Resistance Through the Application of Anti- Corrosion Coatings," in *Developments in Corrosion Protection*, InTech, 2014.
- [4] H. Tamura, "The role of rusts in corrosion and corrosion protection of iron and steel," *Corros Sci*, vol. 50, no. 7, pp. 1872–1883, 2008.
- [5] I. Odnevall Wallinder, X. Zhang, S. Goidanich, N. le Bozec, G. Herting, and C. Leygraf, "Corrosion and runoff rates of Cu and three Cu-alloys in marine environments with increasing chloride deposition rate," *Science of the Total Environment*, vol. 472, pp. 681–694, 2014.
- [6] T. Li, X. G. Li, C. F. Dong, and Y. F. Cheng, "Characterization of atmospheric corrosion of 2A12 aluminum alloy in tropical marine environment," *J Mater Eng Perform*, vol. 19, no. 4, pp. 591–598, 2010.
- [7] L. Cao, Y. Wan, Y. Li, and S. Yang, "Corrosion-resistant and friction-reducing performance of super-hydrophobic coating on hot-dip galvanised steel in a 3.5% NaCl solution," *Lubrication Science*, vol. 33, no. 6, pp. 325–334, 2021.
- [8] L. S. Selwyn, P. J. Sirois, and V. Argyropoulos, "The corrosion of excavated archaeological iron with details on weeping and akaganeite," *Studies in Conservation*, vol. 44, no. 4, pp. 217–232, 1999.
- [9] S. A. Bradford and J. E. Bringas, *Corrosion control*, vol. 115. Springer, 1993.
- [10] F. H. Haynie, "Environmental Factors Affecting the Corrosion of Galvanized Steel", 1987.
- [11] R. Suraj, "Hardfacing and its effect on wear and corrosion performance of various ferrous welded mild steels," *Mater Today Proc*, vol. 42, pp. 842–850, 2020.

- [12] “Chemical properties of iron - Health effects of iron - Environmental effects of iron”, [Online]. Available: <http://www.lenntech.com/periodic/elements/fe.htm>.
- [13] M. Izaki, “Electrodeposition of iron and iron alloys,” *Modern electroplating*, vol. 5, 2010.
- [14] S. Pandiyarajan, M. Ganesan, A. H. Liao, S. S. M. Manickaraj, S. T. Huang, and H. C. Chuang, “Ultrasonic-assisted supercritical-CO₂ electrodeposition of Zn-Co film for high-performance corrosion inhibition: A greener approach,” *Ultrason Sonochem*, vol. 72, no. December 2020, p. 105463, 2021.
- [15] H. Wang, J. Xu, X. Du, Z. Du, X. Cheng, and H. Wang, “A self-healing polyurethane-based composite coating with high strength and anti-corrosion properties for metal protection,” *Compos B Eng*, vol. 225, no. August, p. 109273, 2021.
- [16] S. Harsimran, K. Santosh, and K. Rakesh, “Overview of Corrosion and Its Control: a Critical Review,” *Proceedings on Engineering Sciences*, vol. 3, no. 1, pp. 13–24, 2021.
- [17] L. F. Mondolfo, “Aluminum–Magnesium, Aluminum–Manganese Alloys,” *Aluminum Alloys*, pp. 806–841, 1976.
- [18] H. P. Godard. P.M. Aziz, “Corrossion,” vol. 10, p. 269, 1954.
- [19] G. W. W. Hubner, “Studies on the Mechanism of the Pitting Corrosion of Aluminum,” *Current Corrosion Research in Scandinavia*, 1964.
- [20] A. P. Bond, G. F. Bolling, H. A. Domian, and H. Biloni, “Microsegregation and the Tendency for Pitting Corrosion in High-Purity Aluminum,” *J Electrochem Soc*, vol. 113, no. 8, p. 773, 1966.
- [21] G. I. K. Goto, Y. Shimizu, “No Title,” *Trans. Nat. Res. Inst. Metals (Japan)*, vol. 22, p. 86, 1980.
- [22] G. D. Wilcox and D. R. Gabe, “Electrodeposited zinc alloy coatings,” *Corros Sci*, vol. 35, no. 5–8, pp. 1251–1258, 1993.
- [23] Z. F. Lodhi, F. D. Tichelaar, C. Kwakernaak, J. M. C. Mol, H. Terryn, and J. H. W. de Wit, “A combined composition and morphology study of electrodeposited Zn-Co and Zn-Co-Fe alloy coatings,” *Surf Coat Technol*, vol. 202, no. 12, pp. 2755–2764, 2008.
- [24] J. H. W. de Wit. Z.F. Lodhi , J.M.C. Mol , A. Hovestad , L. ’t Hoen-Velterop , H. Terryn, “Corrosion resistance of Zn–Co–Fe alloy coatings on high strength

- steel,” *Surf Coat Technol*, vol. 203, pp. 1415–1422, 2009.
- [25] A. Chansena and S. Sutthiruangwong, “Corrosion behavior of electrodeposited Co-Fe alloys in aerated solutions,” *J Magn Magn Mater*, vol. 429, no. October 2016, pp. 251–256, 2017.
 - [26] A. C. H. Yathish Ullal, “Electrodeposition and electro-catalytic study of Nanocrystalline Ni-Fe Alloy,” *Int J Hydrogen Energy*, vol. 39, pp. 10485–10492, 2014.
 - [27] I. H. Karahan, “Electrodeposition and Properties of ZnFeNi Alloys,” *Chinese Journal of Physics*, vol. 46, p. 1, 2008.
 - [28] Z. N. Yang, Z. Zhang, and J. Q. Zhang, “Electrodeposition of decorative and protective Zn-Fe coating onto low-carbon steel substrate,” *Surf Coat Technol*, vol. 200, no. 16–17, pp. 4810–4815, 2006.
 - [29] M. M. Abou-Krishna, A. G. Alshammari, F. H. Assaf, and F. A. El-Sheref, “Electrochemical behavior of Zn–Co–Fe alloy electrodeposited from a sulfate bath on various substrate materials,” *Arabian Journal of Chemistry*, vol. 12, no. 8, pp. 3526–3533, 2019.
 - [30] J. Winiarski, A. Leśniewicz, P. Pohl, and B. Szczygieł, “The effect of pH of plating bath on electrodeposition and properties of protective ternary Zn–Fe–Mo alloy coatings,” *Surf Coat Technol*, vol. 299, pp. 81–89, 2016.
 - [31] J. Winiarski, W. Tylus, M. S. Krawczyk, and B. Szczygieł, “The influence of molybdenum on the electrodeposition and properties of ternary Zn-Fe-Mo alloy coatings,” *Electrochim Acta*, vol. 196, pp. 708–726, 2016.
 - [32] M. Kanagasabapathy and S. Jayakrishnan, “Textural and morphological studies on zinc-iron alloy electrodeposits,” *Journal of Chemical Sciences*, vol. 123, no. 3, pp. 357–364, 2011.
 - [33] A. P. Ordine, S. L. Díaz, I. C. P. Margarit, and O. R. Mattos, “Zn-Ni and Zn-Fe alloy deposits modified by P incorporation: Anticorrosion properties,” *Electrochim Acta*, vol. 49, no. 17–18, pp. 2815–2823, 2004.
 - [34] S. A. E.-N. M.M. Abou-Krishna , F.H. Assaf, “The influence of Fe^{2+} concentration and deposition time on the corrosion resistance of the electrodeposited zinc–nickel– iron alloys,” *Arabian Journal of Chemistry*, vol. 9, pp. 1349–1356, 2016.
 - [35] A. C. Hegde, K. Venkatakrishna, and N. Eliaz, “Electrodeposition of Zn-Ni,

- Zn-Fe and Zn-Ni-Fe alloys,” *Surf Coat Technol*, vol. 205, no. 7, pp. 2031–2041, 2010.
- [36] K. O. Nayana, T. v. Venkatesha, and K. G. Chandrappa, “Influence of additive on nanocrystalline, bright Zn-Fe alloy electrodeposition and its properties,” *Surf Coat Technol*, vol. 235, pp. 461–468, 2013.
- [37] S. Yogesha and A. Chitharanjan Hegde, “Optimization of deposition conditions for development of high corrosion resistant Zn-Fe multilayer coatings,” *J Mater Process Technol*, vol. 211, no. 8, pp. 1409–1415, 2011.
- [38] H. Adelkhani and M. R. Arshadi, “Properties of Fe-Ni-Cr alloy coatings by using direct and pulse current electrodeposition,” *J Alloys Compd*, vol. 476, no. 1–2, pp. 234–237, 2009.
- [39] R. Özdemir, İ. H. Karahan, and O. Karabulut, “A Study on the Electrodeposited Cu-Zn Alloy Thin Films,” *Metall Mater Trans A Phys Metall Mater Sci*, vol. 47, no. 11, pp. 5609–5617, 2016.
- [40] I. H. Karahan and H. S. Güder, “Electrodeposition and properties of Zn, Zn-Ni, Zn-Fe and Zn-Fe-Ni alloys from acidic chloride-sulphate electrolytes,” *Transactions of the Institute of Metal Finishing*, vol. 87, no. 3, pp. 155–158, 2009.
- [41] I. H. Karahan, “Effects of pH value of the electrolyte and glycine additive on formation and properties of electrodeposited Zn-Fe coatings,” *The Scientific World Journal*, vol. 2013, 2013.
- [42] C. Jiang, M. Feng, M. Chen, K. Chen, S. Geng, and F. Wang, “Corrosion behaviour of iron and nickel aluminide coatings under the synergistic effect of NaCl and water vapour,” *Corros Sci*, vol. 187, no. December 2020, p. 109484, 2021.
- [43] I. El-Hallag, S. Elsharkawy, and S. Hammad, “Electrodeposition of Ni nanoparticles from deep eutectic solvent and aqueous solution as electrocatalyst for methanol oxidation in acidic media,” *Int J Hydrogen Energy*, vol. 46, no. 29, pp. 15442–15453, 2021.
- [44] J. Kruger and S. Begum, “Corrosion of Metals: Overview,” *Reference Module in Materials Science and Materials Engineering*, no. July 2015, pp. 1–10, 2016.
- [45] T. W. Neal., *Maintenance Issues and Alternate Corrosion Protection Methods for Exposed Bridge Steel*. 1998.

- [46] G.-S. F. Corvo, T. Pèrez, J. Reyes, L. Dzib, *Atmospheric Corrosion in Tropical Humid Climates*. 2009.
- [47] Z. AHMAD, *Principles of Corrosion Engineering and Corrosion Control*. 2006.
- [48] Z. AHMAD, *Principles of Corrosion Engineering and Corrosion Control*. 2006.
- [49] R. Hienonen and R. Lahtinen, *Corrosion and climatic effects in electronics*, no. 626. 2007.
- [50] T. Marlaud, B. Malki, A. Deschamps, and B. Baroux, “Electrochemical aspects of exfoliation corrosion of aluminium alloys: The effects of heat treatment,” *Corros Sci*, vol. 53, no. 4, pp. 1394–1400, 2011.
- [51] S. P. Knight, M. Salazaras, A. M. Wythe, F. De Carlo, A. J. Davenport, and A. R. Trueman, “In situ X-ray tomography of intergranular corrosion of 2024 and 7050 aluminium alloys,” *Corros Sci*, vol. 52, no. 12, pp. 3855–3860, 2010.
- [52] D. W. Hoepfner and C. A. Arriscorreta, “Exfoliation corrosion and pitting corrosion and their role in fatigue predictive modeling: State-of-the-art review,” *International Journal of Aerospace Engineering*, vol. 2012, 2012.
- [53] S. Madhavarao, R. V. Penmetsa, G. S. V. S. Kumar, C. R. Raju, and K. T. Kumar, “Investigation on mechanical properties of friction stir welded Aa7075 and Aa6061 joints,” *Mater Today Proc*, vol. 18, pp. 2288–2297, 2019.
- [54] S. Karabay, M. Zeren, and M. Yilmaz, “Investigation extrusion ratio effect on mechanical behaviour of extruded alloy AA-6063,” *J Mater Process Technol*, vol. 135, no. 1, pp. 101–108, 2003.
- [55] X. Zhao and G. S. Frankel, “Quantitative study of exfoliation corrosion: Exfoliation of slices in humidity technique,” *Corros Sci*, vol. 49, no. 2, pp. 920–938, 2007.
- [56] M. Bobby Kannan, P. Bala Srinivasan, and V. S. Raja, “Stress corrosion cracking (SCC) of aluminium alloys,” *Stress corrosion cracking: Theory and practice*, pp. 307–340, 2011.
- [57] B. R. N. Parkins, “Parkins : Stress-Oorrosion Oracking,” vol. 9, no. 35, 1964.
- [58] V. V. Bolotin and A. A. Shipkov, “Mechanical aspects of corrosion fatigue and stress corrosion cracking,” *Int J Solids Struct*, vol. 38, no. 40–41, pp. 7297–7318, 2001.

- [59] R. Baboian, J. Schully, and R. Gangloff, "Chapter 26—Environmental Cracking-Corrosion Fatigue," *Corrosion Tests and Standards: Application and Interpretation—Second Edition*, pp. 302–302–20, 2009.
- [60] W. Zhang and H. Yuan, "Corrosion fatigue effects on life estimation of deteriorated bridges under vehicle impacts," *Eng Struct*, vol. 71, pp. 128–136, 2014.
- [61] K. J. Bundy, *Biomaterials and the chemical environment of the body*. Woodhead Publishing Limited, 2008.
- [62] N. R. Cerulia, *Gas and Oil Reliability Engineering Modeling and Analysis Second Edition Gas and Oil Reliability Engineering Modeling and Analysis*.
- [63] A. Gopichand *et al.*, "Analysis and Estimation of Attenuation Coefficient of Aging EN-19 Steel," vol. 2, no. 1, pp. 590–595, 2012.
- [64] V. R. Rathi, S. D. Nirmal, and S. J. Kokate, "Journal of Chemical and Pharmaceutical Research" vol. 2, no. 2, pp. 97–100, 2010.
- [65] S. Frick *et al.*, "Geochemical and Process Engineering Challenges for Geothermal Power Generation," no. 12, pp. 2093–2104, 2011.
- [66] R. M. Stratt and M. Maroncelli, "Nonreactive Dynamics in Solution: The Emerging Molecular View of Solvation Dynamics and Vibrational Relaxation," 1996.
- [67] D. S. Jayakrishnan, "Corrosion Protection and Control Using Nanomaterials," in *Corrosion Protection and Control Using Nanomaterials*, pp. 86–125, 2012
- [68] E. Prinsip and A. D. A. N. Kaedah, "Electrodeposition: principles, applications and methods," pp. 1–5, 2011.
- [69] F. Béron, L. Carignan, D. Ménard, and A. Yelon, "Extracting Individual Properties from Global Behaviour : First-order Reversal Curve Method Applied to Magnetic Nanowire Arrays," no. February, 2010.
- [70] C. Chukwuka and K. A. Folly, "Batteries and super-capacitors," *IEEE Power and Energy Society Conference and Exposition in Africa: Intelligent Grid Integration of Renewable Energy Resources, PowerAfrica 2012*, no. July, pp. 9–13, 2012.
- [71] R. W. Lashway and G. Editor, "Fuel Cells : The Next Evolution," vol. 30, no. August, pp. 581–586, 2005.
- [72] N. Bhalla, P. Jolly, N. Formisano, and P. Estrela, "Introduction to biosensors,"

Essays Biochem, vol. 60, no. 1, pp. 1–8, 2016.

- [73] M. S. Halper and J. C. Ellenbogen, “Supercapacitors: A brief overview,” *MITRE Nanosystems Group*, 2006.
- [74] G. D. Sulka, *Introduction to anodization of metals*. INC, 2020.
- [75] G. Yang, B. Wang, K. Tawfiq, H. Wei, S. Zhou, and G. Chen, “Electropolishing of surfaces: theory and applications,” *Surface Engineering*, vol. 33, no. 2, pp. 149–166, 2017.
- [76] G. S. and Q. Z. Biao Geng¹, Wenxuan Hu¹, Xing Wu¹, Miao Du¹, “NiCoAl Ternary Metal Hydroxides Prepared by Fluorine Ion Assisted Electrodeposition Process for Long Lifespan Supercapacitor Electrodes,” *J Electrochem Soc*, vol. 169, no. 8, 2022.
- [77] F. Wu, C. M. Chamchoumis, and R. P. Thummel, “Bidentate ligands that contain pyrrole in place of pyridine,” *Inorg Chem*, vol. 39, no. 3, pp. 584–590, Feb. 2000.
- [78] Y. Li and M. Bowker, “Acetate formation, stabilisation and surface explosion on Rh(111),” 1993.
- [79] J.-C. Berthet, P. Thuéry, and M. Ephritikhine, “Advances in f-element cyanide chemistry,” *Dalton Transactions*, vol. 44, p. 7727, 2015.
- [80] Y. Konda *et al.*, “An Efficient Synthesis of (Pyrrolidin-2-ylidene)Glycinate Using Intramolecular 1, 3-Dipolar Cycloaddition of Azide and Olefin,” 1999.
- [81] I. Jabin, G. Revial, N. Monnier-Benoit, and P. Netchitaïlo, “Reaction of cyclohexanone benzylimines with ethylidenemalonate diesters. Diphenyl 2-ethylidenemalonate: A highly electrophilic synthetic equivalent of crotonic esters,” *Journal of Organic Chemistry*, vol. 66, no. 1, pp. 256–261, Jan. 2001.
- [82] P. Barpanda, S. I. Nishimura, and A. Yamada, “High-voltage pyrophosphate cathodes,” *Advanced Energy Materials*, vol. 2, no. 7, pp. 841–859, Jul. 2012.
- [83] D. Fernández, E. Boix, I. Pallarès, F. X. Avilés, and J. Vendrell, “Structural and functional analysis of the complex between citrate and the zinc peptidase carboxypeptidase A,” *Enzyme Res*, vol. 2011.
- [84] H. Matsumoto, “Review: Ionic liquids as a potential electrolyte for energy devices,” *2014 IEEE International Nanoelectronics Conference, INEC 2014*, pp. 1–4, 2016.
- [85] P. Sun and D. W. Armstrong, “Ionic liquids in analytical chemistry,” *Analytica*

- Chimica Acta*, vol. 661, no. 1. pp. 1–16, Feb. 19, 2010.
- [86] C. Chiappe and D. Pieraccini, “Ionic liquids: Solvent properties and organic reactivity,” *Journal of Physical Organic Chemistry*, vol. 18, no. 4. pp. 275–297, Apr. 2005.
 - [87] T. J. Smith and K. J. Stevenson, “Reference Electrodes,” 2007.
 - [88] K. C. Honeychurch, “Printed thick-film biosensors,” *Printed Films: Materials Science and Applications in Sensors, Electronics and Photonics*, pp. 366–409, 2012.
 - [89] C. Valero Vidal and A. Igual Muñoz, *Influence of protein adsorption on corrosion of biomedical alloys*. Woodhead Publishing Limited, 2013.
 - [90] A. K. Singh., *Engineered Nanoparticles Experimental Methodologies for the Characterization of Nanoparticles*. 2016.
 - [91] N. Mehrban and J. Bowen, “Monitoring biomineralization of biomaterials in vivo,” *Monitoring and Evaluation of Biomaterials and their Performance In Vivo*, pp. 81–110, 2017.
 - [92] L. Hanke, “Handbook of analytical methods for materials,” *Materials Evaluation and Engineering, Inc*, pp. 1–50, 2001.
 - [93] R. Kohli, *Methods for Monitoring and Measuring Cleanliness of Surfaces*, vol. 4. Elsevier, 2011.
 - [94] D. D. le Pevelen, *X-ray crystallography of small molecules: Theory and workflow*, 3rd ed., 3rd ed., Elsevier Ltd., 2016.
 - [95] J. A. Griffiths, P.; de Hasseth, *Fourier Transform Infrared Spectrometry*, 2nd ed., . 2nd ed., 2007.
 - [96] L. Kumar Puneet, Subir Kumar Chakraborty, “Infrared Radiation: Principles and Applications in Food Processing,” in *Thermal Food Engineering Operations*, M. K. G. Nitin Kumar, Anil Panghal, Ed., 1st ed., 2022.
 - [97] Dr. R. Paschotta, “RP Photonics Encyclopaedia,” *RP Photonics Encyclopaedia*. [Online]. Available: <https://www.rp-photonics.com/wavenumber.html>
 - [98] E. Hecht, “Optics,” 2nd ed., pp. 15–16, 1987
 - [99] B. H. Flowers, “21.2 Periodic functions,” in *an introduction to numerical methods in C++*, Cambridge University Press, p. 473, 2000.
 - [100] D. (Richard F. Lyon), *Plot of a sine wave, showing three pairs of corresponding points between which wavelength (lambda) can be measured*. 2009.

- [101] C. Lin *et al.*, “A comparative investigation of the effects of some alcohols on copper electrodeposition from pyrophosphate bath,” *Surfaces and Interfaces*, vol. 22, Feb. 2021.
- [102] A. Yavuz, P. Yilmaz Erdogan, and H. Zengin, “The use of polyaniline films on flexible tape for supercapacitor applications,” *Int J Energy Res*, vol. 44, no. 14, pp. 11941–11955, Nov. 2020.
- [103] M. Bedir, D. Korkmaz, O. F. Bakkaloglu, M. Oztas, I. H. Karahan, and M. Y. Hacıibrahimoglu, “Effect of pH values on the characterization of electrodeposited Zn-Mn coatings in chloride-based acidic environment,” *Int J Electrochem Sci*, vol. 10, no. 6, pp. 4513–4522, 2015.
- [104] I. H. Karahan, “A study on electrodeposited $Zn_{1-x}Fe_x$ alloys,” *J Mater Sci*, vol. 42, no. 24, pp. 10160–10163, 2007.
- [105] C. Instruments, “Model 700E Series Electrochemical Analyzer / Workstation User Manual,” vol. 2014.
- [106] D. Starosvetsky, R. Armon, J. Yahalom, and J. Starosvetsky, “Pitting corrosion of carbon steel caused by iron bacteria,” 2001.
- [107] R. G. Fratesi R, Lunazzi G, “Organic and inorganic coatings for corrosion prevention,” in *Organic and inorganic coatings for corrosion prevention*, B. P. Fedrizzi L, Ed., 20th ed., london: CRC Press, p. 130, 1997
- [108] I. H. Karahan, “A study on electrodeposited $Zn_{1-x}Fe_x$ alloys,” *J Mater Sci*, vol. 42, no. 24, pp. 10160–10163, 2007.
- [109] R. Ramanauskas, P. Quintana, L. Maldonado, R. Pomés, and M. A. Pech-Canul, “Corrosion resistance and microstructure of electrodeposited Zn and Zn alloy coatings,” *Surf Coat Technol*, vol. 92, no. 1–2, pp. 16–21, 1997.
- [110] I. Hakki Karahan, O. Karabulut, and U. Alver, “A study on electrodeposited Zn-Co alloys,” *Phys Scr*, vol. 79, no. 5, 2009.
- [111] D. Sylla, J. Creus, C. Savall, O. Roggy, M. Gadouleau, and P. Refait, “Electrodeposition of Zn-Mn alloys on steel from acidic Zn-Mn chloride solutions,” *Thin Solid Films*, vol. 424, no. 2, pp. 171–178, 2003.
- [112] I. Suzuki and M. Enjuzi, “The development of the corrosion resistance of an Fe-Zn alloy coating on the basis of the behaviour of the corrosion product,” *Corros Sci*, vol. 26, no. 5, pp. 349–355, 1986.
- [113] P. D. Ngo, “Energy Dispersive Spectroscopy,” 1999.

- [114] C. Savall, C. Rebere, D. Sylla, M. Gadouleau, P. Refait, and J. Creus, "Morphological and structural characterisation of electrodeposited Zn-Mn alloys from acidic chloride bath," *Materials Science and Engineering A*, vol. 430, no. 1–2, pp. 165–171, 2006.
- [115] S. J. Lee, J. Han, S. Lee, S. H. Kang, S. M. Lee, and Y. K. Lee, "Design for Fe-high Mn alloy with an improved combination of strength and ductility," *Sci Rep*, vol. 7, no. 1, Dec. 2017.
- [116] I. H. Karahan, "Electrodeposition and Properties of ZnFeNi Alloys," *Chinese Journal of Physics*, vol. 46, p. 1, 2008.
- [117] R. L. Twite and G. P. Bierwagen, "Review of alternatives to chromate for corrosion protection of aluminum aerospace alloys," *Prog Org Coat*, vol. 33, no. 2, pp. 91–100, 1998.
- [118] Ö. Bedir and T. H. Doğan, "Comparison of catalytic activities of Ca-based catalysts from waste in biodiesel production," *Energy Sources, Part A: Recovery, Utilization and Environmental Effects*, vol. 00, no. 00, pp. 1–18, 2021.
- [119] A. S. W. D. Aryanto, T. Sudiro, "Correlations between Structural and Hardness of Fe-50%Al Coating Prepared by Mechanical Alloying," *PISTON Journal of Technical Engineering*, vol. 1, 2019.
- [120] R. J. Jadaa, A. N. Abd, and A. A. Khadom, "Polyacrylamide as a corrosion inhibitor for mild steel in 2 M phosphoric acid: experimental and theoretical studies," *Chemical Papers*, vol. 75, no. 10, pp. 5375–5386, 2021.
- [121] J. G. and Yungang L. Tao Ma, Huirong Li, "Corrosion Behaviour of Cu/Carbon Steel Gradient Material," *Crystals (Basel)*, 2021.

CURRICULUM VITAE (CV)

SURNAME, NAME: Cemil AKDOĞAN

EDUCATION

PhD Physics Engineering (2009-2023)

Gaziantep University, Türkiye

Thesis: Analysis of The Microstructure and Corrosion Behavior of Electrodeposited Fe and Fe Alloys.

Supervisor: Prof. Dr. Ömer F. BAKKALOĞLU

Co-Supervisor: Prof. Dr. Mustafa ÖZTAŞ

MS Physics Engineering (2002-2004)

Gaziantep University, Türkiye

Thesis: Optical and Electrical Characteristics of CdSe Thin Films Deposited by Spray Pyrolysis Method.

Supervisor: Asist. Prof. Dr. Mustafa ÖZTAŞ

BS Physics (1991-1997)

Gaziantep University, Türkiye

PUBLICATION

Article

Akdogan, C., Bakkaloglu, O. F., Bedir, M., Erdogan, P. Y., & Yavuz, A. (2022). Electrodeposition of Fe-Zn, Fe-Mn and Fe-Zn-Mn alloys on steel from ionic liquids. Digest Journal of Nanomaterials & Biostructures (DJNB), 17(2).

CONFERENCE

M.Bedir, Ö.F.Bakkaloğlu, M.Öztaş, D.Korkmaz and C.Akdoğan. (2014) International Semiconductor Science & Technology Conference.