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M.Sc. in Engineering Physics

ZEYNEP DOĞAN

REPUBLIC OF TURKEY

GAZİANTEP UNIVERSITY

GRADUATE SCHOOL OF NATURAL & APPLIED SCIENCES

STRUCTURE, COMPOSITION AND CORROSION STUDIES OF Zn, Cu, Sn AND THEIR ALLOYS ELECTRODEPOSITED FROM A DEEP EUTECTIC SOLVENT

M.Sc. THESIS

IN

ENGINEERING PHYSICS

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Supervisor

Prof. Dr. Ömer Faruk BAKKALOĞLU

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Asst. Prof. Dr. Abdulcabbar YAVUZ

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Zeynep DOĞAN

ABSTRACT

STRUCTURE, COMPOSITION AND CORROSION STUDIES OF Zn, Cu, Sn AND THEIR ALLOYS ELECTRODEPOSITED FROM A DEEP EUTECTIC SOLVENT

DOĞAN, ZEYNEP

M.Sc. Thesis in Engineering Physics

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In this thesis, platinum and steel were coated with metals (Cu, Zn and Sn), binary alloys (Cu-Zn, Cu-Sn and Zn-Sn) and a triple alloy (Cu-Zn-Sn) by electrochemical method. The corrosion behaviour of these films were investigated in 3.5% NaCl solution. Chlorine chloride-ethylene glycol based ionic liquid was used for electrodeposition of metals and alloys. The plating process was carried out on platinum and steel by a three electrode system by applying constant potential. As metals/alloys were electrodeposited potentiostatically, chronoamperometric graphs of deposition were obtained. The resulting coated samples were analyzed by SEM, XRD/EDAX and optical microscope. Potentiodynamic polarization (Tafel Plot) was applied to understand the corrosion mechanism of uncoated and coated samples in 3.5% NaCl. Corrosion current of Zn is lower than the other two metals and among these three metals zinc has passivation behaviour. Corrosion behaviours of binary alloys (Cu-Zn, Cu-Sn and Zn-Sn) and ternary Cu-Zn-Sn were examined. Generally, corrosion resistivity of binary alloys on Pt is higher than that of metals on Pt. It could be said that Zn dominates corrosion current of alloys deposited from a deep eutectic solvent. Corrosion resistivity of binary alloys on steel is close to each other. Corrosion current density of binary alloys on Pt is approximately 10 times more resistive than bare steel. The polarisation curve of the ternary alloy of Corrosion resistivity of ternary alloy (Cu-Zn-Sn) on Pt is eight times greater than bare steel. Alloys could be electrodeposited on steel to prevent corrosion

Key Words: Electrodeposition, Corrosion, Steel, Ionic Liquids, Alloys.

ÖZET

DERİN ÖTEKTİK ÇÖZÜNCÜDEN ELEKTRODEPOLAMANMIŞ ZN, Cu, Sn VE ALAŞIMLARININ YAPISI, BİLEŞİMİ VE KOROZYON ÇALIŞMALARI

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Bu tezde, platin ve çelik metaller (Cu, Zn ve Sn), ikili alaşımlar (Cu-Zn, Cu-Sn ve Zn-Sn) ve üçlü bir alaşım (Cu-Zn-Sn) elektrokimyasal yöntem ile kaplanmıştır. Bu filmlerin korozyon davranışı % 3.5'lük NaCl çözeltisi içinde incelenmiştir. Metallerin ve alaşımların elektrodepozisyonu için kolin klorür-etilen glikol temelli iyonik sıvı kullanıldı. Kaplama işlemi, sabit potansiyel uygulanarak üç elektrotlu bir sistemle platin ve çelik üzerinde gerçekleştirildi. Metaller/alaşımlar potansiyostatik olarak elektrodepozitlendiğinden, kronoamperometre grafikleri elde edildi. Elde edilen kaplanmış örnekler SEM, XRD/EDAX ve optik mikroskop ile analiz edildi. Kaplanmamış ve kaplanmış numunelerin korozyon mekanizmasını % 3.5'lük NaCl'de anlamak için potansiyodinamik polarizasyon (Tafel grafiği) uygulandı.Çinkonun korozyon akımı (i_{corr}) diğer iki metalden (bakır ve kalay kaplamasından) daha düşüktür ve bu üç metal arasında çinko pasivasyon davranışlarına sahiptir. İkili alaşımların (Cu-Zn, Cu-Sn ve Zn-Sn) ve üçlü Cu-Zn-Sn'nin korozyon davranışları incelenmiştir. Genel olarak, Pt üzerindeki ikili alaşımların korozyon direnci, Pt üzerindeki metallerden daha yüksektir. Zn'nin derin ötektik çözücüden biriken alaşımlarının korozyon akımını domine ettiği söylenebilir. Çelik üzerindeki ikili alaşımların korozyon direnci birbirine yakındır. Pt üzerindeki ikili alaşımların korozyon akımı yoğunluğu, çıplak çelikten yaklaşık 10 kat daha dirençlidir. Kolin klorür ve etilen glikolden elektrodepolamayla elde edilen üçlü Cu-Zn-Sn alaşımının polarizasyon eğrisi incelenmiştir. Üçlü alaşımın Pt üzerindeki korozyon direnci, çıplak çelikten sekiz kat daha fazladır. Korozyonu önlemek için alaşımlar çelik üzerine elektrokaplamayla elde edilebilir.

Anahtar Kelimeler: Elektrodepolama, Korozyon, Çelik, İyonik sıvılar, Alaşımlar.

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TABLE OF CONTENTS

Page

LIST OF TABLES

Page

LIST OF FIGURES

Page

LIST OF SYMBOLS

Cu	Copper
Zn	Zinc
Sn	Tin
XRD	X-Ray Diffraction
Pt	Platinium
RTIL	Room Temperature Ionic Liquids
SEM	Scanning Electron Microscopy
DES	Deep Eutectic Solvent
EDAX	Energy Dispersive X-Ray Spectroscopy

CHAPTER 1

INTRODUCTION AND AIM

Steel is a material widely used in many industrial areas such as bridges, towers, heating, and cooling systems, oil and natural gas transportation pipes. The reasons why steel is widely used are that steel is economical and has high strength, durability, elasticity, ductility [1]. While steel is widely used in numerous areas, it has some disadvantages such as its density which is not as low as other engineering alloys (aluminium and magnesium) and its corrosion susceptibility.

Metals are commonly used in daily life and a world without metals could not be imagined. Besides that corrosion is a weak point for metals. Corrosion which is a natural phenomena is destructive. The unwanted phenomenon of corrosion which destroys the appearance and strength of the object. As structure of metals/alloys are chaged due to corrosion, product lifetime could decrease [2]. The term corrosion has been described in many cases. It is the surface damage that occurs when metals are affected by the environment. It is the deterioration of materials due to chemical or biological factors or electrochemical reaction [2].

The corrosion has been defined only for metals/alloys up to around the 1960s. At the present time, corrosion is used in various materials including nanomaterials and biometals. Therefore, it is not limited to just metals/alloys [2].

Corrosion cannot be explained without the influence of the environment. These environmental impacts can be listed as follows: dampness, marine water, salt, gas, acids, and chemical compositions, atmospheric and industrial conditions [2]. For example, a metal pier piling is corroded because of seawater, temperature and humidity, thus corrosion occurs by reacting with environmental conditions [3].

A large portion of steel can be unusable every year due to corrosion. Corroded steel reduces the efficiency of steel. The corroded steel can also lose its physical

properties and this reduces the lifetime of steel. Corrosion occurs in various steel applications including steel building, bridges, poles, steel pipes, tanks, ships and guardrails. These structures become unusable at a short time in the presence of corrosion. In order to have initial properties of steel, corroded steel should be renewed. Changing corroded steel with new one inevitably increases the cost and effects the economy of a country. Therefore, corrosion is aimed to be prevented. Material degradation and deterioration can cause safety problems. Safety is an important factor for human life and the environment. It is known that corrosion is one of the biggest cause of material degradation. Therefore, corrosion prevention is an effective step to create a healthier public and cleaner environment.

Metals/alloys could become unusable at the short time due to corrosion. The main objective of corrosion control is to maintain integrity with the durability of the structure. Corrosion control methods such as protective coatings could reduce the premature deterioration of materials and protect both the people and the environment [4].

Common methods generally used to control corrosion are coatings and linings, cathodic protection, materials section and corrosion inhibitors. Coatings are principal tools for conservation against corrosion. Among these methods, the coating is the most convenient technique due to these substances are often applied for improving corrosion and erosion resistance, increase conductivity and decorative appearance [5].

Corrosion prevention is used to stop the oxidising effect of air, water, and soil. Corrosion phenomena are important for human life. Corrosion is a danger to the environment as water could be poisoned by corrosion product and unsuitable for consumption. Chirurgical implants must have high corrosion resistance due to the corrosive nature of human blood [2].

In this thesis, platinum and steel were coated with Cu, Zn, Sn, Cu-Zn, Cu-Sn, Zn-Sn and triple alloy (Cu-Zn-Sn) based coatings by electrochemical method. Corrosion behaviour of these films were investigated in 3.5% NaCl solution. The first objective of this research is to examine whether zinc, copper and tin based metals and their alloys could be electrodeposited from a deep eutectic solvent electrolyte. The second objective is to characterise Cu, Zn, Sn, Cu-Zn, Cu-Sn, Zn-Sn and triple alloy (Cu-Zn-

Sn) based coatings in terms of structural and surface behaviour. The morphologies of the electrodes electrodeposited from Ethaline ionic liquids were also explored and all of them were compared with each other. The third aim is to calculate the contents of alloys. Tafel graphs were used for all the films obtained on Pt and low carbon steel to elucidate the corrosion behavior (passivation or pitting process) in NaCl solution. The last objective is to examine the effect of corrosion behaviour of coated and uncoated substrate by means of microscopic and macroscopic imaging.

CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

2.1. Corrosion

Corrosion is a major issue not just for humanity, also ecosystem and economy [2]. The effects of corrosion could be observed in daily life. Corrosion effects could be observed everywehere such as home, company or school. For instance corrosion could effect car parts, panels, metal wares, garden furniture, grill, stair railing [3].

Depending on global research carried out by Battle Columbus Laboratories, (NIST, USA), corrosion cost was calculated to be 4-5% of the GDP of a developed country. For example the cost of corrositon is guessed to be 5258 trillion Yen per year in Japan. The average cost value is 3.5 – 4.5% of the GDP for most industrialized nations [2].

In the USA, corrosion cost of transmission pipelines is over the limit of seven billion US dollars. More than 8% of aircraft restore cost is paid on corrosion prevention. In the UK, £350 million for transport, £180 million for chemical industries, £280 million for marine applications and £250 million for building and construction are spent due to corrosion. 23.4 billion US dollars are used to compensate corrosion effect in automotive industry of USA every year [2].

These information illustrates how corrosion could cause serious damages. Engineers and scientists have studied this problem for ages. Some new methods, solutions and processes have been generated for this issue. [2] In 1946, Corrosion lectures were first studied in three USA Universities. Over time, they have participated in major and famous universities in the UK, Europe, Southeast Asia and Africa [2].

A few reasons can be listed to cause corrosion to work. First of all, corrosion protection and engineering can downsize the negative effect of corrosion. Corrosion is also a danger in the health field. It puts human health at risk. For instance, implants

must be corrosion resistant. Corrosion affects the environment. The American Water Works Association needs 325 billion dollars for modernize of the system in the next twenty years [2].

2.1.1. Corrosion Mechanism

An electrochemical battery mechanism is the same as the mechanism of aqueous environment corrosion in all circumstance. The anode and cathode reactions of the corrosion reaction in the electrochemical battery mechanism should be considered separately. In accordance with Faraday's law, the amount of metal dissolve in the anode caould be calculated. Thermodynamically the kinetics of corrosion reactions should be investigated. As a result of thermodynamic investigations, in the immunity of metal, the corrosion reaction does not occur thermodynamically. If thermodynamic investigations of the metal in active conditions observe, corrosion occurs and corrosion rate could be measured and the corrosion rate can be large [6].

A metal placed in a corrosive environment can act in three ways; firstly it can be corroded, secondly, corrosion may not be affected by the solution or thirdly it can be passive. If corrosion occurs, the metal will pass through the solution. In the second scenario, the metal potential is low enough to prevent the metal from passing into the solution. The passivation (the third scenario) causes a protective film layer on the metal/alloy to prevent metal from corrosion as this protective film prevents direct contact with the environment [7].

Corrosion has two types of species and classified according to the occurrence. These are chemical and electrochemical corrosion. The corrosion of the metal material due to ionization as a result of electron exchange with the elements that will cause corrosion is called chemical corrosion. Chemical corrosion is caused by oxygen. An oxide layer is formed on metal materials which are combined with oxygen. Electrochemical corrosion is an electrolysis occurrence. A metal surface in atmospheric and humid environments, electrochemical corrosion is coated with an oxide layer. The surfaces of iron materials which are ionized due to the effect of air and water, form rust and corrode [8].

The electrochemical process is the displacement of electric charges that occur between an electrolyte and an electrode. Two types of reaction occur in this process. One of these is the reduction and the other one is the oxidation reaction. The reaction

that occurs when a molecule or atom gives an electron around it is called oxidation and the reactions it performs by taking an electron from its surroundings are called reduction reactions [9].

Corrosion mechanism is the three types according to corrosion types. They are physical, electrochemical and chemical corrosion. Physical corrosion is a type of corrosion caused by organic liquids or molten metals. This is the result of physical dissolution or solid state change. Corrosion caused by the reaction of metal materials directly with the environment is chemical corrosion. As chemical corrosion occurs at high temperatures, it can also be called high temperature corrosion. Degradation of metals/alloys in the aqueous environment is called electrochemical corrosion. The electron exchange occurs at the interface in the electrochemical corrosion procedure. It is necessary to have an electrolyte in which the potential difference is found in the same environment and electron flow can be ensured [10].

There are basically two types of corrosion, both atmospheric and electrolytic, depending on the type of reaction that leads to corrosion. In atmospheric corrosion, the environment is cathode, the metal-oxide interface is the anode and an oxide layer that provides ionic conductivity is an electrolyte. In electrolytic corrosion, the noble metal is the cathode (in which reduction occurs) and the active metal is the anode (where oxidation occurs). Ions in the solution form the electrolyte solution in which the metal is immersed [11].

2.1.2. Corrosion Types

2.1.2.1. General Corrosion

The complete surface of metals/alloys could be corroded. Equally damaged on a surface by chemical and electrochemical corrosion is a type of general corrosion [12] .This type of corrosion occurs as a result of atmospheric environments. General corrosion is more common to see in chemical environments and aqueous media. The color of the steel turns of a colour which is an indicator of the corrosion. This colour is generally redish brown in steel and silver becomes black when it is corroded [13].

General corrosion is the most basic type of corrosion. As a general corrosion effect, metals become unusable over time [10]. Homogeneous corrosion is a kind of electrochemical corrosion. Corrosion on the surface is uniformly distributed in a

specific pattern. At the microscopic scale, the reduction and oxidation reactions occur randomly on the surface. Corrosion of steel and iron is the most general example. In addition, the darkening of silver is an example. The least exceptionable is the type of corrosion. It can be predictable and designed [14].

2.1.2.2. Erosion Corrosion

The degradation of a metal/alloy because of mechanical corrosion in the corrosive environment is called erosion corrosion. Erosion corrosion results in cavities and grooves on the metal surface. The material is coated or the corrosive medium is changed to minimize erosion-corrosion damage [12].

Erosive corrosion may occur in devices exposed to moving fluids. Pipes, pumps, propellers, condensers and mixers could have this type of corrosion. The speed of the fluid influence the rate of erosion corrosion. The flow rate of the fluid also affects the corrosion. Solid ingredient in the fluid affects the severity of corrosion [15].

This type of corrosion could occur between a metal/alloy and their media. Surface thickness decreases because of erosion corrosion. This type of corrosion takes place by combining mechanical action and chemical reactions. Chosen correct designs and coating can be prevented from erosion corrosion [13].

It is a kind of damage that is caused by chemical action and mechanical corrosion as a result of liquid movement. All metals may be exposed to this type of corrosion. The metal abrades the protective film on the surface so that the metal could be exposed to corrosive effect. The character of the liquid and the flow rate are directly proportional to the corrosion rate. The presence of gas bubbles and solid particles in the liquid could accelerate corrosion damage [14].

2.1.2.3. Pitting Corrosion

Holes and cavities could be produced locally on the surface of a material due to corrosion which is called pitting corrosion. It is generally considered to be more dangerous than general (uniform) corrosion as they cannot be easily detectable. Corrosion usually cover the pits. The region in the pit of metal surface is the anode (oxidation process); the area around the pit is the cathode (reduction). It is a severe corrosion because it causes the metal to be punctured [12]. Seawater containing

sodium chloride and oxygen provides a suitable environment for the corrosion of the metal [15].

This type of corrosion causes little mass loss in the metal. It is very difficult to notice because the damage is small on the surface. Corrosion of metal can be prevented when the environment and design are changed. [10] This corrosion is more visible in metals such as stainless steel and aluminium [16].

Small cavities and pits are formed in pitting corrosion and corrosion is proceeded from the surface of the metal to inward. Corrosion will not be determined until material damage occurs because the material losses are small. Pitting corrosion mechanisms with crevice corrosion mechanisms are identical. Pitting corrosion especially in stainless steels and aluminium alloys could be commonly observed. The corrosion resistance of the material can be improved with alloying methods for example by addition of 2% molybdenum [14].

2.1.2.4. Intergranular Corrosion

Intergranular corrosion occurs along the boundary line of the grains in the crystal structure of a metal/alloy. The boundaries of an internal structure of a metal can be eroded, and the abrasion of the metals could be observed especially after a heat treatment. As this type of corrosion is more common in the welded area, this process is called weld decay. This type of corrosion is seen in stainless steel generally [12].

The reason for the deterioration is the macro galvanic reaction due to the difference in phase and impurity in grain boundaries [13]. It is a kind of corrosion that occurs between grains in some alloys and environmental conditions. When heated at 500 and 800 degrees, stainless steels become damaged by grain boundaries. During this process, chromium and carbon form of a precipitate occurs at the boundary. Thus, it becomes susceptible to corrosion because chromium could diffuse to the grain boundaries. Protection against corrosion can be listed as follows: (1) high-temperature heat treatment of the sensitized material, (2) carbon control, (3) alloying of stainless steel with another metal such as niobium or titanium [14].

2.1.2.5. Laminar Corrosion

Laminar corrosion is a type of corrosion proceeding from initiation sites along planes which is parallel to the surface. This type of corrosion occurs in industrial

environments. It is similar to intergranular corrosion. This corrosion is observed due to humidity between two metals layers. Cold-worked Al and its alloys are susceptible to this corrosion. The grain boundaries are damaged and the layers are separated [10].

2.1.2.6. Crevice Corrosion

The crack on the metal surface becomes the anode (oxidation process); the circumference of the crack is the cathode (reduction process) in crevice corrosion. Corrosion develops within the fracture. Crevice corrosion occurs in aqueous solutions and the chlorinated waters increases corrosion rate [16].

Crevice corrosion is a kind of electrochemical corrosion. It is the result of concentration differences between the two regions of the same metal part. Corrosion occurs in the area with low concentration. When oxygen is exhausted in the crack, the oxidation of the metal occurs in this direction. The electrons in the electrochemical reaction are consumed by reducing the metal to the adjacent outer regions. Precautions can be listed as follows; frequent exit of accumulated water, liquids inside the storage areas must be completely drained away and should not contain static zones, choice of welded joints where bolt rivet screw is used [14].

2.1.2.7. High Temperature Corrosion

This type of corrosion occurs due to the high temperature. The material can protect from corrosion with three factors. First of all, this can be difficult to change the environment. Other factors are material exchange and material surface protection [9].

2.1.2.8. Atmospheric Corrosion

Material loss caused by atmospheric corrosion is greater than other corrosion types. The frequency of atmospheric corrosion could be differend depending on the geographical regions. The speed of corrosion depends on industrial pollution and atmospheric environments [17].

2.1.2.9. Corrosion on Galvanized Sheets

There are two types of corrosion in galvanized sheets. They are white rust and red rust. White rust is caused by seawater, humidity and temperature also red rust is caused by corrosive factors. Zinc provides cathodic protection [10].

Two metals with different potentials form a galvanic battery between them when they are in contact with each other. Reactive metal in a corrosive environment causes

corrosion. Corrosion is observed at the joint made in steel materials. The anode which has a lower electrode potential (standart redox potential) is more susceptible to corrosion. Metal with a high potential of electrodes is less likely to be corroded. The corrosion rate depends on the current density, the current of the corrosion surface in the unit area. Isolating the electrical connection of different metals may reduce the effect of galvanic corrosion. The large area of the anode can be another method for reducing the effect of galvanic corrosion. Electrically connect one of the three anodic metals to the other two could prevent corrosion [14].

2.1.2.10. Hydrogen Embrittlement

Metal and alloys could have a significant reduction in tensile strength and ductility when hydrogen atoms are introduced into the material. Cracks of hydrogen origin passing through the grains cause cracks between the grains. Exposure of the material to hydrogen during high-temperature exposure will be a problem. Hydrogen embrittlement will lead to breakage of materials, just like stressed corrosion. Cathodic protection is one of the methods to prevent stress corrosion. However, hydrogen embrittlement will lead to progression of corrosion. Lowering the tensile strength by heat treatment will cause the hydrogen embrittlement to be reduced. It is also possible to remove the dissolved hydrogen by heat treatment [14].

2.1.2.11. Selective Leaching

This type of corrosion occurs in solid melt alloys. This is the case where one of the elements or phases in the alloy is preferentially reduced. Zinc in zinc-copper alloy degrades by preferential corrosion. Copper remains in the back porous structure. The color of the brass alloy changes to copper colour. Mechanical properties are also damaged. Aluminum, iron, cobalt are chromium are sensitive to this kind of corrosion [14].

2.1.2.12. Stress Corrosion

It is a kind of damage caused by the tensile stresses and corrosive environment that the material is exposed. Firstly, small cracks occur on the surface. These cracks grow in the direction of stretching and ruptures occur. Many alloys are susceptible to corrosion when subjected to a certain level of stress. Stainless steels undergo stress corrosion in solutions containing chloride ions. Sudden temperature changes can also

cause stress corrosion. The action to be taken to reduce this type of corrosion is to reduce stress [14].

2.1.3. Protection against Corrosion

It is normally difficult to stop the corrosion process. However, negative effects of corrosion can be reduced. Protection and deceleration can be carried out with several methods depending on electrodes (metals and alloys) and environment (electrolyte, temperature). One of the most important step to decrease corrosion rate is material design. The causes of corrosion must be examined to examine the effect of corrosion [11].

Various types of corrosion which are explained in Section 2.1.2. are seen in the industrial field. Corrosion makes materials unusable. For instance; tank, store, guard board, ship and pipe could be affected negatively by corrosion. Methods for corrosion protection have been developed. A few of them are as follows: materials selection, coating, anodic protection, cathodic protection, environmental change, design and inhibitor [18].

2.2. Coating of Steel (Coating of Metal)

Metals/alloys could be protected with surface coating. It is known that corrosion can start on a surface and advances into the interior with time. Coated surfaces could prevent corrosion progression. Electrodeposition and chemical coating methods could be applied to metals for protection and change their appearance. This coating could protect the metal/alloy from the atmospheric environment. One of the precautions taken against corrosion is the metal coating with another metal [19].

The coating in metals could prevent the formation of corrosion. For example zinc plating is commonly used for corrosion prevention. Zinc is not only used for protection purposes, it can also change the colour of the surface. Therefore, coating could be applied for aesthetic purposes as well. When metals are corroded they lose their function and strength and it can cause economic loss [20].

Some of common metals used for surface coating are as follows: copper, tin, chromium, zinc, silver and gold. In this thesis electrodeposition of tin, copper, zinc and their alloys are electrodeposited on low carbon steel. Tin could have high

resistance against oxidation depending on media. The copper has high heat, electrical conductivity and has easy processing properties. Zinc is also deposited on metals/alloys for corrosion protection because zinc has a high corrosion resistance in atmospheric conditions. The cost of zinc alloy is relatively low [21, 22, 23].

2.3. Electrodeposition of Metals and Alloys on Steel

Zankana et. al. studied electrodeposition of metals/alloys by using different ionic liquids based on choline chlorides. In their work; Sn, Zn, and Zn-Sn alloys were electrodeposited. Elemental analysis and the elemental characteristic feature have been obtained by energy dispersive X-ray Spectroscopy (EDX). Scanning electron microscopy (SEM) was used for structural analysis. They illustrated that composition and morphology of the Sn-Zn electrodes are different when deep eutectic solvents are used as electrolyte instead of aqueous bathing solution [5].

Taktakoğlu obtained the ZnO by electrodeposition technique and characterized them. Electrical properties and optical transmittance were analysed. These results show that an easy production technique at low temperature with low cost has been developed in the laboratory for ZnO production [24]. Lehmberg studied electrodeposition of nickel-iron and nickel-zinc alloys by using XRD, optical microscope, EDX, regarding thickness [25]. Ghosh studied the electrodeposition of copper, tin and tin-copper alloy from a choline chloride based deep eutectic solvent. Material characteristics of the film including crystalline structure, grain size, deposition morphology, and chemical composition were studied by using XRD, optical microscope and SEM. The measurement showed that density and viscosity decrease and conductivity of electrolytes with and without metal ions increase upon increasing temperature. The reduction of tin and copper metal was found to be mass transfer control and limiting current for metal deposition was found [26].

Karahan investigated that Zn-Fe-Ni films were obtained under potentiostatic deposition conditions on aluminium and steel plates. Their structure, corrosion characteristics and construction were analyzed in terms of $FeSO_4$ concentration in the bath. Cyclic voltammetry of the deposition conditions was studied. SEM was used to study the morphology of the coatings. The study shows that Zn-Fe-Ni alloys can be manufactured with adhesive and anticorrosive characteristics, and all films have similar crystallographic structure as zinc, but with diverse crystallographic

orientations [27]. Giridhar et al. studied that the ionic liquid could be used as a deposition electrolyte in order to electrodeposite nanocrystalline Fe metal and Fe-Al alloys. XRD, SEM, CV, and magnetic measurements of modified electrodes were presented [28].

Page et. al. reported that shape memory alloys of Cu-Zn alloys can be obtained from a pyrophosphate electrolyte containing copper and zinc salts with KNO_3 and $K_4P_2O_7$. Brass contains 30-50 wt% Cu consisting of α and β phases [29]. Bajat et. al. studied electrodeposition of Zn–Fe alloy on steel under various deposition conditions. As a result, the uniform and regular Fe-Zn alloys were deposited electrochemically on steel by applying different current densities and their corrosion behaviours were tested [30].

2.4. Ionic Liquids and Deep Eutectic Solvents

2.4.1. Ionic Liquids

Organic reactions are usually carried out in a solvent media. These solvents are mostly liquid at room temperature. However, there is a new class of liquid consisting only ions at room temperature which are called room temperature ionic liquids. They have remarkable properties such as low vapour pressures, high thermal stability, chemical stability, and wide electrochemical windows. It is used in applications such as organic synthesis, enzymatic catalysis, separation processes and electrochemical processes. Ionic liquids can be reused in reactions and reduce the cost of a process. It has been used in various reactions as described in the literature and it has been observed that the reactions increase the efficiency, selectivity and decrease the amount of waste. Recently the usage of ionic liquids have been studied widely [31].

Kalsen et. al. explained the general characteristics of ionic liquids. Literature analysis was presented to understand the usability of ionic liquids in hydrometallurgy. It is a new type of solvent that starts to replace traditional solvents. Low melting points of them increase the usability of ionic liquids in electrochemical reactions. Ionic liquids have dissolved inorganic and organic compounds. This is important for solving different combinations of reagents in the same phase. Ionic liquids are expected to replace organic solvents in the near future due to their properties [32]. Uygun investigated that local structures of metals with the ionic liquid by using integral equation theory [33].

2.4.2. Deep Eutectic Solvents

Smith et. al. showed that physical properties of DESs are similar to these of ionic liquids. The terms deep eutectic solvent and ionic liquid are interchangeably used. However, it is essential to emphasize that DES and RTIL are actually two different types of solvent. It is showed that the physical properties of deep eutectic solvents are similar to these of ionic liquids. Deep eutectic solvents involve non-symmetric and large ions having decrease lattice energy and therefore high vapour pressure. There are four types of deep eutectic solvents. Research related to deep eutectic solvents has grown considerably in the last 15 years. Studies regarding deep eutectic solvents have commonly focused on their application in metal final treatment and various synthetic applications. There are only several deep eutectic solvents so far. However, various types of salts and hydrogen bond donors forming deep eutectic solvents are potential components which could be used in numerous applications of these solvents [34].

2.5. Electrodeposition from Deep Eutectic Solvents

Abbott et. al. studied the electrodeposition of Zn in different ionic liquids. Their research shows that components of electrolytes influence the physical characteristic of coatings. It is specified that the morphology of Zn modified electrodes was affected by deep eutectic solvents depending on hydrogen bond donors. Mass transport behaviours and the nucleation of zinc was investigated and components of ionic liquids effects metal growth mechanism. It was shown that increasing the concentration of $ZnCl_2$ decreased the viscosity of deep eutectic solvent electrolytes. It denoted that the physical properties of electrodes did not change just due to speciation because both ionic liquids have mainly $ZnCl_4^{-2}$. The study of nucleation mechanisms was examined in both deep eutectic solvent media. It is recommended that mechanism was different because of the adsorption of ions, probably Cl^-, on the substrate surface which blocked the growth on some crystal face [35].

Pereira et. al. researched the effect of electrolyte for the electrodeposition of Sn–Zn alloys. Additives were added into deep eutectic solvents and Sn-Zn film was electrodeposited. The morphological and physical characteristics of the Zn-Sn electrodes were analysed. The voltammetric behaviour of zinc and tin in the electrolytes were studied. The morphology of resulting coatings was checked. The

composition and structure of the Sn-Zn deposits were majorly changed by adding the additives. Compositional and morphological characterization of the electrodes that Idranal VII formed a homogeneous zinc-rich film. In spite of that, HEDTA caused a nonuniform electrodeposition which appears to be produced only by polyhedral form crystals [36].

Vijayakumar et. al. studied that the electrocoating of Co-Ni-Sn alloy was obtained at from the ethylene glycol and chlorine chloride based deep eutectic solvent room temperature. Sn-Ni and Sn-Co alloys were also electrodeposited using the same electrolyte to compare their properties. Microstructure, the mechanism of deposition, and electrochemical behaviours of the electrode in alkaline electrolyte were studied. The deposition of Co, Sn, Ni, Sn-Ni, Sn-Co and Ni-Sn-Co on the platinum substrate was also investigated by cyclic voltammetry. The cyclic voltammetry results indicated the formation of alloys. Nickle based binary and ternary alloys were characterized by TEM and XRD. The potentiodynamic polarization analysis illustrated that the Ni-Sn-Co alloy is more consistent in the anodic region [37].

Fashu et. al. investigated the electrodeposition of Zn-Mn and characterized the morphological, compositional, and corrosion behivour of alloy electrodes from a DES on copper substrates. Corrosion behavior of the electrodes was measured by linear sweep voltammetry in a 3.5 % NaCl electolyte. The characterization results have shown that

When Mn ratio in the Mn-Zn alloys increased, electrodeposition potential of the alloy also increased. The SEM analyses show that the morphology of the modified electrodes becomes thin and hard at higher electrodeposition voltage and with large concentrations of Mn(II) electrolyte. The crystal structure of Mn-Zn films have both hexagonal close-packed Mn-Zn and zinc at low electrodeposition voltage applied and low concentration of Mn^{2+} electrolyte. However, the crystal structure has only hexagonal close-packed Mn-Zn at high potential and with high concentration of Mn^{2+} electrolyte. The corrosion measurement of the specimens illustrated that modified electrodes have a passivation behaviours and their degradation performance can be controlled by altering their chemical and phase compound and also their morphology. The Mn-Zn films deposited at -1.8 V illustrates higher corrosion

resistance and this was connected to an enough high Mn raito in the alloy, a regular morphology and its phase structure [38].

Zhang et. al. studied that Sn-Co alloy coatings are electrodeposited from ethylene glycol and choline chloride based deep eutectic solvent electrolyte and deposited Co-Sn alloys were analysed to elucidate their corrosion performance. It is understood that the structures and chemical composition of the alloy electrodes generally depend on voltage applied to electrodeposite and temperatures of the electrolyte in the coating process. Cyclic voltammetry illustrates that Sn and Co electrodeposition are possible because of the reduction potentials of tin and cobalt salts in the electrolyte. Thickness of Co-Sn film was about 400 nm and corrosion behaviour of alloy was compared with the single metal electrodes in aqueous 3.5 wt.% NaCl bath. The electrodeposition of metals/alloys in a deep eutectic solvent media is a simple and practical method to apply alloy coatings for enhanced corrosion resistance [39].

Abbott et. al. showed that the deposition behavior of tin-copper alloy has been researched in a deep eutectic solvent by using electrochemical techniques. Surface analysis of resulting films were analysed. The phase behaviour of the electrodes were characterized by using X-ray diffraction depending on current density and solution composition. EQCM was used for mass change of the alloys. The method was not as successful as for Sn-rich alloys where surface morphologies are smooth as it is a limitation of quartz crystal microbalance. It is the first study that copper was deposited with brighteners in both aqueous solution and non- aqueous (a deep eutectic solvent). Generally using brighteners in an aqueous solution and a DES to obtain copper is an effective method [40].

Wang et.al explained the the mechanism of electrodeposition Cu-Ni electrodes from a choline chloride–urea based deep eutectic ionic liquid containing nickel and copper chloride salts. Corrosion resistance of Cu-Ni electrodes on copper substrate was analyzed. Cyclic voltammetry proves that codeposition of Cu-Ni is simply obtained in 1:2 ratio part of choline chloride and urea without complexing agents. The chronoamperometric data showed that Cu-Ni deposition has the 3D instantaneous nucleation mechanism, during solid solution formation. Potentiodynamic polarization analyses showed that the films involving around 17 % copper is appropriate against corrosion due to its crack-free structure and intensive [41].

Abbott et. al. showed that the electrodeposition of Sn, Zn and Sn-Zn alloys from two different deep eutectic solvent (urea/choline chloride and ethylene glycol/choline chloride) based ionic liquids including metal chloride salts. Morphological/elemental, compositional and electrochemical behaviours were characterized by SEM/EDAX, X-ray diffraction and cyclic voltammetry techniques. According to the result the morphological and compositional characteristics of alloys could be altered by tailoring the components of the DESs. Metals with a ceramic (such as Al_2O_3) can be deposited as a composite material in a deep eutectic solvent media. All coating obtained from deep eutectic solvent based electrolytes could be used to prevent corrosion of an appropriate substrate [42].

Mandroyan et. al. investigated the reduction of Cu in a DES including choline chloride and ethylene glycol called Ethaline. Copper (II) chloride salts were dissolved to obtain copper (II) oxide (CuO) or copper (I) chloride CuCl. The high chloride concentration of a deep eutectic solvent increase oxidation degree. Kinetic parameters were qualified for the copper (II) chloride mixture. One-step deposition mechanism was unchangeable. Temperature increasing from room temperature to more than 75 °C increase the coefficient of mass transfer and heterogeneous rate constant. Accordingly, the diffusion-limiting current was calculated in potential range in which the reaction is five times greater. Viscosity of electrolyte decreases because of temperature. According to a study of aqueous solutions, ultrasound mixing was known to induce nearly the same rise. It is less productive than temperature activation, showing that the intense viscosity of the solution is the main delimiting kinetic factor. However, the combination of ultrasound and higher temperature cause to increase the reduction limiting current 10 times compared with beginning conditions, because ultrasonic mixing is more effective in lower viscosity fluid. These results may be acceptable for copper recovery using ultrasound. Thus, ultrasound will provide copper reduction by combining temperature [43].

Popescu et. al. investigated the electrochemical behaviour $CuCl_2$ on Pt electrode in urea and choline chloride based deep eutectic solvent. Electrochemical measurements (impedance spectroscopy and cyclic voltammetry) were used for redox analyses. Choline chloride and urea in the ratio of 1 to 2 in which the $CuCl_2$ (anhydrous) salt was dissolved, was used in that work. Deposition behaviours of choline chlorine-urea based deep eutectic solvent including CuCl or $CuCl_2$ salt was

investigated by cyclic voltammetry. Cyclic voltammogram results demonstrate that Cu^{2+} ions in choline chloride and urea based ionic liquid could be the electrochemical reduction to Cu^{0}. The impedance spectroscopy analysis was conducted as well for the deposition of copper at negative potentials. This study presents a different option to classical copper electrode deposition in choline chloride-based ionic liquids rather than using aqueous solutions. The electrodeposition process explains in the choline chlorine -urea deep eutectic solvent can be applied for the recycling of non-ferrous metals containing copper or copper compounds in the metallurgical industry [44].

Abbott et. al. reported the electrochemical reduction of $ZnCl_2$ in a DES by mixing urea or ethylene glycol with choline chloride. Mass transport and charge transfer mechanisms were elucidated by using electrochemical quartz crystal microbalance (EQCM) and cyclic voltammogram techniques. Their results showed that the two different liquids cause opposite behaviours with nucleation and growth rates of the film. Nucleation in the urea and chloine chloride based liquid is rapid but the growth of bulk is late, however, nucleation in the ethylene glycol based liquid is severe but the growth of bulk is fast. EQCM results illustrated that surface adsorption behavior is similar for these two DESs when nucleation is transformed to bulk growth [45].

Xie et. al. have been studied Zn and Cu–Zn alloy electrodeposition from choline chloride-urea based DES. Cyclic voltammetry analysis indicated two electrons (Zn^{2+} to Zn in one step) are spent with a diffusional-controlled mechnism. The chronoamperometric studies showed that the electrodeposition of zinc on a copper electrode generally includes 3D nucleation with diffusional controlled process. This study shows that micro and nanostructured of Zn electrodes can be controlled by altering temperature and potential. Zinc films could be deposited with positive potentials and moderate temperatures. These films could have high corrosion resistance in NaCl electrolyte. This investigates that copper and zinc alloy electrodes had been deposited electrochemically from copper oxide and zinc oxide in choline chloride and urea based deep eutectic solvent. The XRD analysis shows that the composition the Zn-Cu alloys can be toilared by altering deposition potential [46].

Ibrahim et. al. demonstrated the effect of organic contribution and current mode for grain size and film morphology of zinc electrodes obtained from a deep eutectic

solvent (mixture of choline chloride and urea). Potentiodynamic voltammetry results showed that the Zn electrodeposition was reversible. The additives also changed zinc reduction kinetics and the cyclic voltammogram data. The efficiency of the Zn deposition was significantly reduced due to additive adsorption on the cathode surface. The morphology analysis showed that Zn deposits were generally non-homogeneous and had a clearly visible difference. The pulsed current produced uniform morphology with fine particles. Besides, by applying the pulsed current in the ionic liquids containing acetonitrile, a brighter Zn surface having fine particles of about 500 nm was produced [47].

Vieira et. al. showed that zinc electrodeposition on different electrode material from choline chloride and ethylene glycol based DES. The substrates used are gold, copper, platinium, glassy carbon, zinc and stainless steel substrates. Cyclic voltammetry results showed a cathodic peak in the reduction side on copper, gold, zinc and platinium. Stainless steel and glassy carbon substrated illustrated a cathodic peak when zinc is electrodeposited in the negative scanning. The voltammetric reduction of the bath had hydrogen reduction, as the reduction potential of zinc and hydrogen are close to each other. The morphology of Zn on copper substrate was analyzed by an electron microscopy. Cu_4Zn phase was determined by X-ray diffraction [48].

Abbot et. al. studied zinc–tin alloys deposited potentiostatically from deep eutectic solvents having choline chloride. They researched the electrochemical stripping mechanism using cyclic voltammetry. SEM and X-ray diffraction were used to characterize resulting coatings. Tin and zinc could be deposited from these liquids either individually or as an alloy. [39] Abbott et. al. also elucidated the electrodeposition mechanism of copper and its composites from either urea based or ethylene glycol based deep eutectic solvents having metal chloride salt. The mechanism of Cu nucleation was examined by chronoamperometric data. Spontaneous nucleation mechanism caused a nano-structured electrode with bright surrface. Instantaneous nucleation causes a full deposit with low copper concentrations, They investigated that the current performance for copper deposition was quickly reached to 100% in both liquids. Composites of copper with Al_2O_3 and SiC had been obtained [49].

Vieira et. al. had studied the Zn electrodeposition from a choline chloride and ethylene glycol based deep eutectic solvent. Cyclic voltammetry on glassy carbon electrodes in a deep eutectic solvent (containing choline chloride and ethylene glycol) having $ZnCl_2$ shows an cathodic peak around −0.8 V. The same voltammetric behavior was observed at high temperature. They recommended in this investigation that active regions on the carbon were inhibited by ion adsoption such as choline or ethylene glycol at low potentials. The viscosity of the solution differed by adding sodium ethoxide to the deep eutectic solvent. It also simplify Zn deposition. The cathodic peak of zinc deposition was determined at the same potential which does not have ethoxide in the cathodic and anodic scanning. The treatment of zinc electrodeposition with sodium ethoxide cause a complex of zinc (II) in a deep eutectic solvent. The absence of a constant current limit in a rotating disk electrode voltammetry occurred due to blocking adsorbed ions on the electrode. The electrochemical of zinc in choline chloride based deep eutectic solvent bath is studied not only for the zinc reduction mechanism bu also to understand the interfacial structure of electrode and electrolyte and aldo the influences of the electrochemical reactions [50].

Pereira et. al. characterized the electrodeposition mechanism of zinc in terms of the effect of the tartrate ion. Resulting morphology of the deposits were analysed as well. Voltammetric results indicated the importance of tartrate on zinc electrodeposition. The addition of potassium hydrogen tartrate did not have major changes in the voltammetric behavior of zinc in solution, on the other hand, the oxidation peaks were changed. After the addition of tartaric acid, the main modifications in the voltammetric profile reduced the intensity of the voltammetric peaks, bringing the reduction peak to more positive values. The oxidative scan results demonstrated no proof of alloying between the electrode material and the zinc deposited. The first stages of the electrodeposition of zinc in the existences of tartaric acid consist of 2D progressive nucleation/growth mechanism and along the electrodeposition process, the growth process variances to the 3D progressive mechanism. The use of tartaric acid suggests a more dramatic alteration [51]. The usage of deep eutectic solvents for metal electrodeposition has been studied recently. The usage of different metals/alloys for electrodeposition of alloys (metals) from DESs for corrosion

prevention of steel has not been undiscovered on a low carbon steel yet. In this study, corrosion the effect of metals/alloys on steel has been investigated.

2.6. Corrosion Resistance of Alloys Coatings from Deep Eutectic Solvent

Bajat et. al. were electrochemically deposited Zn-Fe alloys on a steel under various deposition conditions for corrosion resistance. As a result that the uniform and regular Zn–Fe alloys were electrodeposited on steel at different current densities. The plating of Zn–Fe effect current density in alloys electrodeposition and the corrosion resistance of these alloys has lower corrosion rate [52].

Karahan studied the electrodeposition of Zn-Fe-Ni films on aluminum and steel substrates by potentiostatic deposition. Their structure, corrosion characteristics, and composition were analyzed as a function of the $FeSO_4$ concentration in the electrolyte. Cyclic voltammetry of each metal was explained. SEM technique was also used to study the efficiency of electrocoating process of the films. The study shows that Zn-Fe-Ni alloys can be manufactured with good adhesive and anticorrosive characteristics, and all films have the same crystallographic structure as zinc, but with diverse crystallographic orientations. The alloy of the $Zn_{88}Fe_{10}Ni_2$ has high corrosion resistance [53].

Tsurtsumia et. al. obtained Mn-Cu-Zn alloy with electrodeposition method from sulfate bath. Deposition parameters of films depending on the characterization of Mn-Cu-Zn alloys, cathodic current efficiency, and structural and electrochemical features could be used for optimization of a probable electrode. Deposited alloys were polarized in aerated 3.5% NaCl solution. Tafel polarization curves of Mn-Cu-Zn alloy coating in aerated 3.5% NaCl solution did not show a typical passivation characteristic. Consequentially, electroplating studies complete a successfully cathodic conservation coating for a steel product [54].

Assaf et. al. studied the electrodepositin of Zn-Ni-Mn alloy on steel from sulfate bath and characterization of them. A homogeneous surface of Zn–Ni–Mn film was investigated at a higher current density. The depositions explained higher corrosion strength due to normal deposition and for the highest studied current densities regarding to the thickness and the surface morphology. According to the data obtained, Zn-Ni-Mn alloys with higher Ni capacity presented higher resistance to corrosion and higher cathodic current efficiency [55].

Bhat et. al. studied the electrodeposition of Zn-Fe alloy coated on the mild steel in chloride bath. They have investigated the effect of current density and temperature on depositional features such as corrosion resistance, hardness, thickness and cathode current efficiency. Potentiodynamic polarization and electrochemical impedance spectroscopic methods were used to assess the corrosion behaviours of the films. Surface morphology of coatings was examined using scanning electron microscopy. Corrosion resistance occurs due to the barrier effect of the oxide layer [56].

Kharmachi et. al. explained that Ni-Co alloys were electrodeposited on carbon steel from an electrolyte containing Ni^{2+} ions. Compositional, morphological and electrochemical characteristics of the films were examined by XRD, SEM and EIS. Ni-Co alloy was corroded in 3% NaCl solution by using linear sweep voltammogram. According to the results of the Tafel plots, coating with an important amount of nickel components on a carbon steel has higher corrosion resistivity [57].

Karahan et. al. deposited Zinc–iron alloy (Zn-Fe) on AISI 4140 steel. Zn-Fe film was characterized by scanning electron microscopy and X-ray diffraction method. The corrosion of Zn-Fe alloy deposited on carbon steel electrodes with and without PANI film in 3.5% NaCl solution was analyzed with Tafel plot [58]. Ramanauskas et.al electrodeposited Zn and Zn alloy (Zn, Zn-Co, Zn-Fe and Zn-Ni) coatings from alkaline baths. After corroded of the films, they were characterised in aerated chloride solutions (in 0.9 NaCl solution) and in neutral salt spray tests. Similar corrosion resistance of Zn and Zn-Fe, indicates that Fe in the Zn coating form does not have an important influence on its corrosion reaction compated with Zn deposition. The addition of Co or Ni appears to increase the coating corrosion resistivity [59].

2.7. Introduction of Theory

This chapter contributes to fundamental electrochemical concepts. The combination of electrochemical and the Tafel plots method is given in this chapter as well.

2.8. Electrochemistry Concepts

2.8.1. Fundamentals

The electrochemical reaction can be expressed as:

$$\text{Reduced form} \leftrightarrow \text{Oxidized form} + e^-$$

$$M \leftrightarrow M^{n+} + ne^-$$

where reduction and oxidation indicate the oxidised and reduced redox respectively. The kinetics of reaction identify the current response which potential is applied to a conducting electrode.

2.8.2. Diffusion

The spontaneous movement of ions and molecules is called diffusion. Diffusion movement depends on the consantration gradient. It moves from a high concentration zone to a low concentration zone until a homogeneous of the chemicals in the system is reached. The diffusion occurring takes place in all electrode reactions, as predicted, because the concentration of the compound is reduced. Product concentration is increased by electron transfer on the surface.

2.8.3. Migration

The action of ions due to the impact of a potential gradient is called migration. Migration happens in the surroundings of the electrode and electrolyte interface. It is not an important phenomenon of mass transport for electrode reactions compound and product because of the effect of migration is reduced by using excessively of an inert electrolyte. The average of the counter electrolyte decreases the field strength on the target surface to just close the electrode surface. Ionic liquids do not need supporting electrolyte for the migration.

2.8.4. Convection

The formation of chemical movement of ions due to mechanical effect is called convection. It is a treatment taking place intentionally by stirring the solution or moving the electrode. Natural convection may occur in the unmixed solution due to small density gradients resulting from the concentration or temperature around the electrode resulting from the electron transition reaction at the electrode surface [60].

2.9. Electrodeposition

In electrochemical deposition systems, nucleation of electrochemically adsorbed atoms on a substrate and crystal growth can be expressed by electrocrystallization. The electroactive species in the solution to the surface of the electrode by diffusion, as a result of electron transfer, electrocrystallization is called solid phase formation

on the surface. Electrocrystallization stages are first of all adsorption of electroactive species atoms after that electron transfer result of adsorbed atoms coming together to form a stable crystal phase and then the growth of these nuclei. The interaction forces between the adsorbed atom and the substrate atom and the adsorbed atoms are important parameters in describing the subsequent steps of electrocrystallization. Electrochemical deposition techniques have the advantages of being economical, easy to apply, working under atmospheric conditions, not requiring maintenance systems such as very high vacuum, and being able to control at the atomic level. However, there are also disadvantages of electrodeposition. Factors such as nucleation and growth in the electrodeposition, adsorption-desorption and diffusion in electrochemical deposition can cause the formation of unwanted compound in polycrystalline form. The structure of the electrochemically deposited material changes depending on the addition of the supporting electrolyte and the substrate surface crystal structure. Important factors in thin film by electrodeposition are deposition potential, pH of solution, current density and electrolyte temperature. In addition, the concentrations of metal ions in the electrolyte, the presence of the chemical substances or the presence of things that break the purity and whether the current is a continuous or pulse current are important variables in electrodeposition [61].

2.10. Corrosion Reaction

Corrosion can be defined as the transfer of electrons from the metallic form to the ionic form. The anodic and cathodic reactions occurring on a metal surface occur in different places on the metal surface depending on the heterogeneous properties of the metal. In addition, anodic and cathodic reactions can change their appearance on the metal surface. This can lead to corrosion on the metal surface, such as pitting corrosion, crack corrosion, intergranular corrosion, or galvanic corrosion. In most conditions, the reduction reaction in the cathodic region is generally carried out not in the metal surface but in the water phase. Two important reduction reactions in aqueous environments can be observed in corrosion. Corrosion reactions tend to occur at the most reactive sites on a surface. An ordered list of increased reactivity may be: crystal folds, emerging dislocations, high indexed grain faces, impurities, grain boundaries, inclusions, particles, second phases, crevices and cracks. Corrosion reactions tend to occur at the most reactive points on a surface. Anodic and cathodic

reactions take place in separate places, but these regions can be very close. There must be a potential difference for the current to pass from the cathode to the anode. If the anodes and cathodes are very close, the potential difference will be very small. The corrosion process progresses due to the small changes in surface reactivity. If the local anodic and cathodic regions are continuously moving along the surface, uniform corrosion will occur. If the position of the anodic reaction does not move continuously, but remains in localized areas, the attack pattern will be localized [62].

2.11. Tafel Extrapolation Method

Corrosion reactions consist of anodic reaction formed by dissolution of metal and cathodic reaction formed by reduction of oxygen or hydrogen ions [63]. It is the overvoltage that provides the deviation from the external potential balance applied to a corroded electrode. Tafel polarization method for corroded metal anodic and cathodic Tafel plots are obtained [64].

The semi-logarithmic flow-potential curves drawn from the corrosion potential in anodic or cathodic direction are known as Tafel curves, and the linear parts of the Tafel curves intersect the corrosion potential when extrapolated backwards. The current corrosion current at which the point where they intersect at the corrosion potential is determined. [63] With the intersection of these curves, there is i_{corr} (corrosion rate) and E_{corr} (corrosion potential) [64].

CHAPTER 3

MATERIALS AND METHODS

3.1. Materials

3.1.1. Electrodes

Coating were electrodeposited on a platinum (1 cm^2) and low carbon steel sample (AISI 4140) which were used as working electrodes. Corrosion resistance of metals/alloys on platinum and steel was measured. The diameter of steel surface was 1 cm.

Platinum coated titanium mesh electrode was used as a counter electrode. Ag wire reference electrode was used in deep eutectic solvent deposition electrolyte as this electrolyte does not have water. However, Ag/AgCl electrode (saturated KCl) was used as a reference electrode in the aqueous solutions and Pt wire was used for corrosion resistance measurements (in NaCl electrolyte).

3.1.2. Deep Eutectic Solvent

Ethylene glycol (liquid) shown in Figure 3.1a was added to choline chloride in a 1:2 molar ratio to obtain a deep eutectic solvent (Ethaline). This mixture was heated in a beaker on a hotplate at 50°C and stirred (Figure 3.1b) up to a colourless and homogeneous liquid phase (approximately 30 minutes), as phographed in Figure 3.1s, was formed.

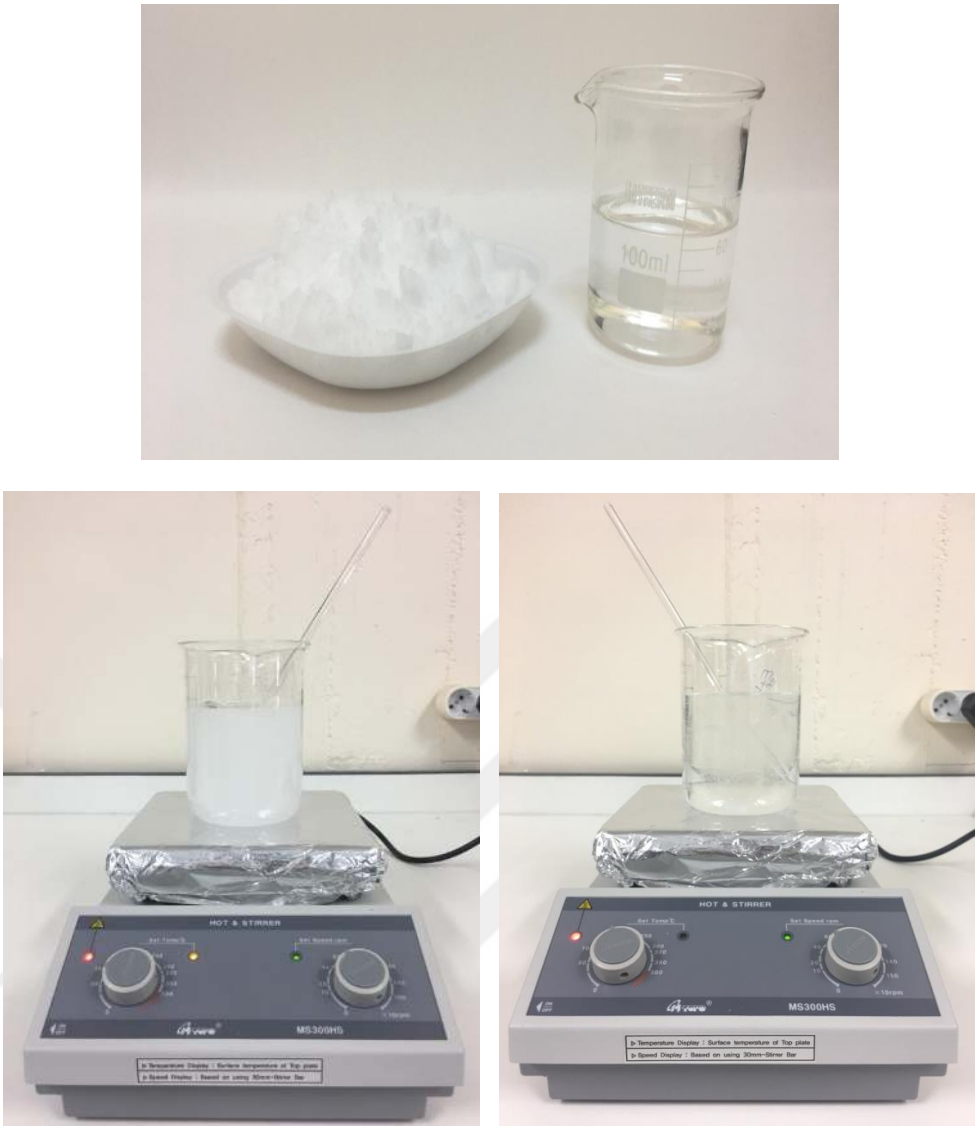


Figure 3.1 The process of the preparation of ethylene glycol and choline chloride based deep eutectic solvent. a) Choline chloride (solid) and ethylene glycol (liquid; b) stirring and heating of the mixture on a hotplate (50°C); c)the formation of homogeneous and colourless Ethaline.

3.2. Procedure

Coarse and fine sandpapers (from 180 to 3000 grits) were used to grind and polish the surface of AISI 4140 steel. If it is not cleaned well, oil and dirt could affect the coating quality. Rinsing and drying processes were performed. Platinum electrode cleaned with saturated nitric acid (HNO_3) to remove all contaminations.

After the required chemicals were weighed in a sensitive balance, they were prepared by mixing in a magnetic stirrer heater using pure water. Prepared solutions shown in Figure 3.2 are just 100 mM $CuCl_2$, just 100 mM $SnCl_2$, just 100mM $ZnCl_2$, 50 mM $ZnCl_2$ + $SnCl_2$, 50 mM $CuCl_2$ + 50 mM $SnCl_2$, 50mM $CuCl_2$ + 50 mM $ZnCl_2$ and

33mM $CuCl_2$ + 33 mM $ZnCl_2$ + 33 mM $SnCl_2$. The electrodeposition process and corrosion studies were performed using Princeton Applied Research mark VersaSTAT potentiostat with three-electrode cell system presented in Figure 3.3. As it was explained counter electrode is platinum coated titanium electrode and working electrode is either steel or platinum flag electrode. Reference electrode is Pt wire electrode (for non-aqueous electrolyte). All deposition experiments were carried out at 65° C. Therefore, ionic liquids having salt for electrodeposition was heated up to 65° C. Applied potentials for electrodeposition were -1.5 V for electrolyte having zinc salt. All other deposition potentials were -1.0 V. All potentials were applied for 360 seconds.

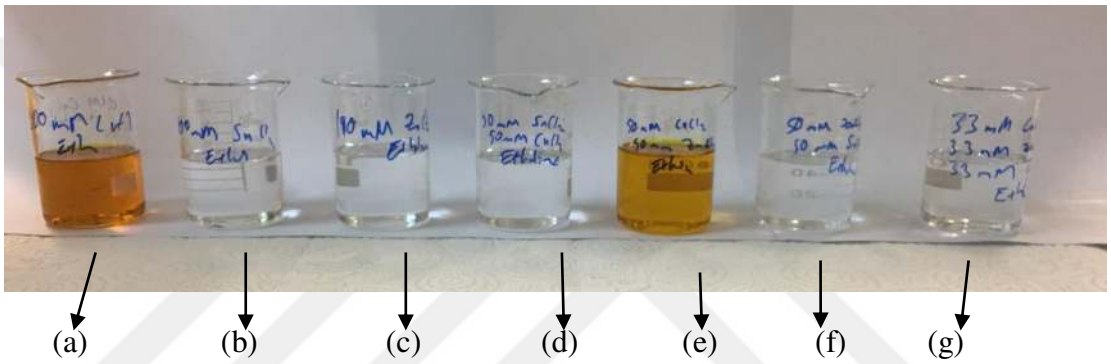


Figure 3.2 (a) 100mM just $CuCl_2$, (b) 100mM just $SnCl_2$, (c) 100mM just $ZnCl_2$, (d) 50mM $CuCl_2$ + $SnCl_2$, (e) 50mM $CuCl_2$ + $ZnCl_2$, (f) 50mM $ZnCl_2$ + $SnCl_2$, (g) 33mM $CuCl_2$ + $ZnCl_2$ + $SnCl_2$

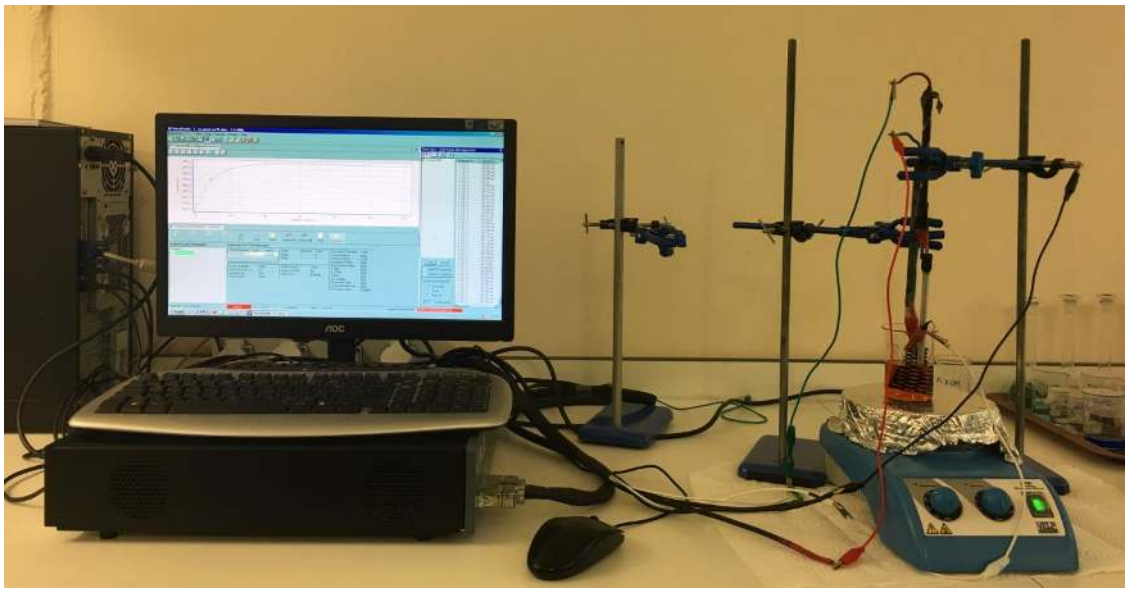


Figure 3.3 Film growth on a substrate (either steel or Pt) by three-electrode cell system in a deep eutectic solvent by means of a potentiostat connected to a computer.

3.3. Characterization

3.3.1. Electrochemical

3.5 wt.% NaCl solution was used to test the corrosion behaviour of coated and uncoated AISI 4140 and platinium substrates. Corrosion resistance of the electrodes was examined by using a three-electrode cell system. NaCl solution was placed in a 250 ml beaker. Metal/alloy coated (or uncoated) working electrodes, Pt wire reference electrode and platinium coated titanium counter electrode were immersed into the NaCl electrolyte for linear sweep voltammetry. Different coatings on AISI 4140 and platinum electrodes was investigated in 3.5% NaCl for corrosion behavior shown in Figure 3.4. The samples used in corrosion tests were not exposed to any heat treatment before or after coating.

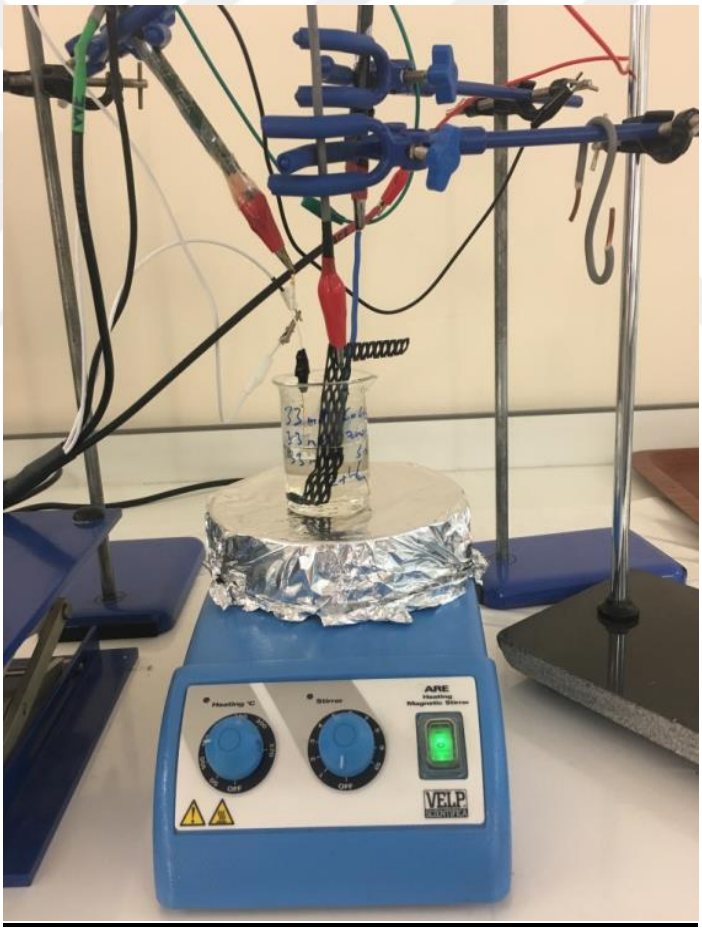


Figure 3.4 Three-electrode cell system in beaker

The coating process was performed using Princeton Applied Research VersaSTAT machine with three-electrode cell system in a deep eutectic solvent media. Coated electrodes were transferred into NaCl solution for corrosion study. All corrosion

experiments were carried out at a room temperature. The scan rate of 20 mV/s was applied for corrosion experiments for consistency. Bare platinum working electrode was corroded in NaCl of 3.5% between -0.8 and 1 V. Cu, Zn, Sn, Cu-Zn, Cu-Sn, Sn-Zn and Cu-Zn-Sn coated Pt electrodes were also scanned from negative potential to positive potential in NaCl bath. The same experiment was conducted for uncoated and coated steel as well. Corrosion behaviour of coatings was investigated with potentiodynamic polarization (Tafel Plot). Corrosion behaviours of uncoated and coated substrates were compared with each other.

3.3.2. Non-Electrochemical

Metals (Cu, Zn, Sn) and alloys Cu-Zn, Cu-Sn, Sn-Zn and Cu-Zn-Sn) were coated on steel (presented in Figure 3.5) by means of Princeton Applied Research mark VersaSTAT. SEM and XRD analysis was used to characterize resulting films. All experiments were carried out at a room temperature.

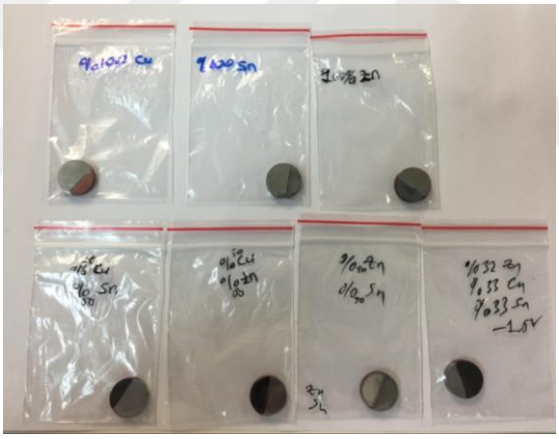


Figure 3.5 Photographs of steels electrodeposited by Cu, Sn, Zn, Cu-Sn, Cu-Zn, Zn-Sn, Cu-Zn-Sn; respectively

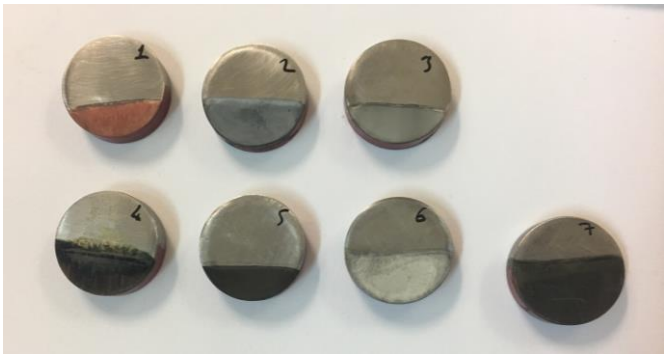


Figure 3.6 Photographs of steels electrodeposited by 1) Cu; 2) Zn; 3) Sn, 4) Cu-Zn; 5) Cu-Sn; 6) Zn-Sn; 7) Cu-Zn-Sn

The optical misroscopy images were obtained in refracting mode with a Nikon LV150NL trinocular microscope operated by the ToupTekToupView software.

CHAPTER 4

RESULT AND DISCUSSIONS

4.1. Electrodeposition of Coatings

Cu, Zn and Sn films were electrodeposited potentiostatically onto a steel substrate from chlorine chloride ethylene glycol (called Ethaline) electrolyte including individually 100 mM $CuCl_2$, 100 mM $ZnCl_2$ or 100 mM $SnCl_2$, respectively. -1.0 V potential was applied for Cu and Sn deposition (Equation 1 and Equation 2) but -1.5 V was applied for Zn deposition (Equation 3) because Zn could be deposited at high potential. The potential was applied to all of the electrodes for 360 seconds at the temprature of 65 °C. Figure 4.1 shows the chronoamperometric results of the growth of metal and alloy films on Pt and steel working electrode. Cu-Zn, Cu-Sn and Zn-Sn alloys were electrodeposited from Ethaline having 50 mM $CuCl_2$ + 50 mM $ZnCl_2$, 50 mM $CuCl_2$ + 50 mM $SnCl_2$, 50 mM $ZnCl_2$ + 50 mM $SnCl_2$ salts as given in Equation 4, Equation 5 and Equation 6, respectively. Ternary alloy of Cu-Zn-Sn was deposited on steel from ionic liquid solution including 33 mM $CuCl_2$ + 33 mM $ZnCl_2$ + 50 mM $SnCl_2$ salts illustrated in Equation 7. Pt wire reference electrode was used. All the potential is given for metal and alloy growth were against this Pt wire reference electrode. Figure 4.1 generally illustrates a fluctuation of current because lower voltage could cause hydrogen evolution. During the deposition, hydrogen bubbles were not clearly monitored when Cu, Sn and Cu-Sn were electrodeposited. The equation for metal and alloy deposition can be given as:

$$CuCl_2 + 2e^- \xrightarrow{in\ Ethaline,-1\ V} Cu_{(s)} \tag{4.1}$$

$$SnCl_2 + 2e^- \xrightarrow{in\ Ethaline,-1\ V} Sn_{(s)} \tag{4.2}$$

$$ZnCl_2 + 2e^- \xrightarrow{in\ Ethaline,-1.5\ V} Zn_{(s)} \tag{4.3}$$

$$xCuCl_2 + (1-x)ZnCl_2 + 2e^- \xrightarrow{in\ Ethaline,-1.5\ V} CuZn_{(s)} \tag{4.4}$$

$$xCuCl_2 + (1-x)SnCl_2 + 2e^- \xrightarrow{in\ Ethaline,-1\ V} CuSn_{(s)} \quad (4.5)$$

$$xZnCl_2 + (1-x)SnCl_2 + 2e^- \xrightarrow{in\ Ethaline,-1.5\ V} ZnSn_{(s)} \quad (4.6)$$

$$xCuCl_2 + yZnCl_2 + (1-x-y)SnCl_2 + 2e^- \xrightarrow{in\ Ethaline,-1.5\ V} CuZnSn_{(s)} \quad (4.7)$$

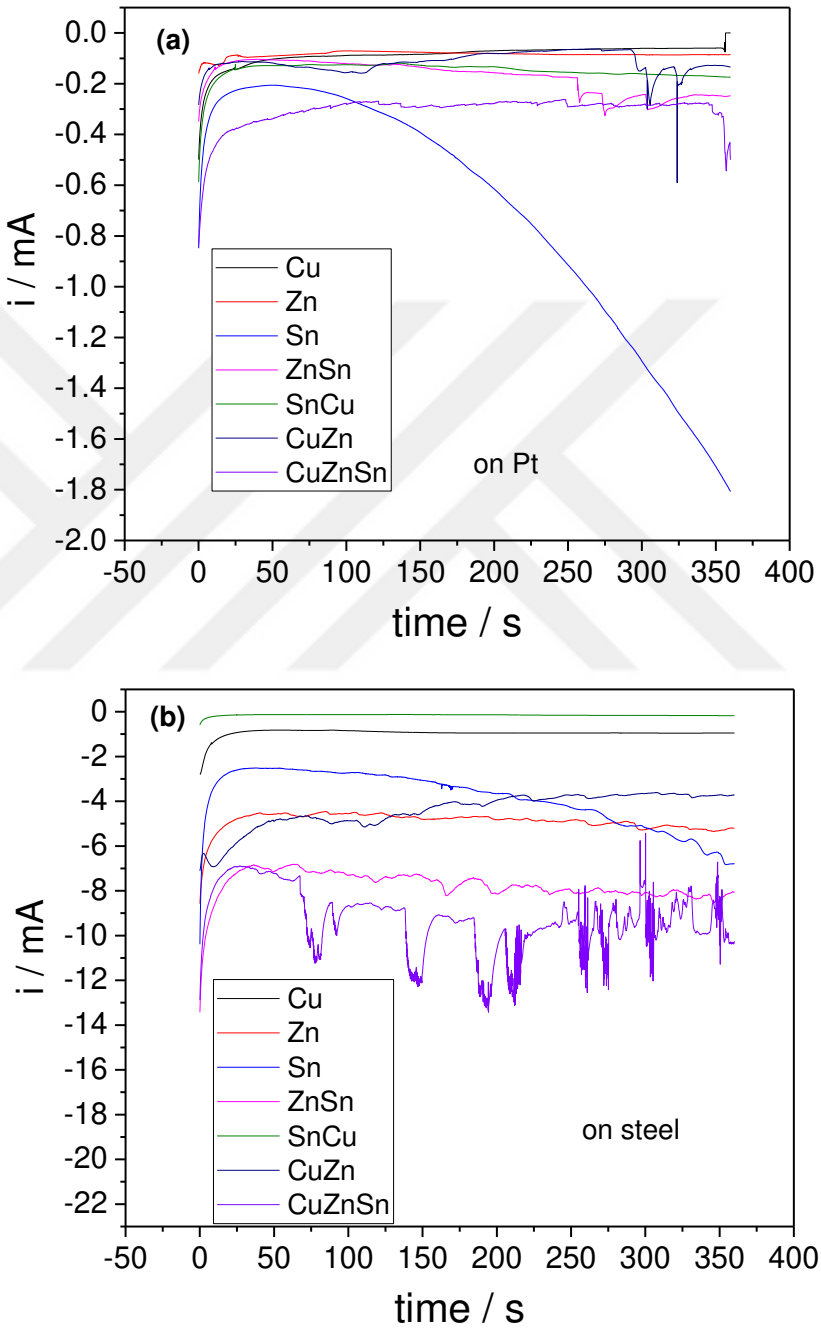


Figure 4.1 Chronoamperometric data obtained for metals/alloys growth on a) Pt electrode; b) steel electrode in Ethaline having metal chloride salts by applying -1.0 or -1.5 V for 360 seconds at 65 °C.

4.2. Characterization of Coatings

In this thesis, thin film coatings were produced by electrodeposition method. Compositional and structural analysis of the films were carried out by means of SEM, XRD and EDAX.

4.2.1. Scanning Electron Microscope

Steel was coated by metals and alloys from ionic liquid media and resulting images were obtained by means of scanning electron microscope presented in Figure 4.2 and Figure 4.3. Pure Cu, pure Zn and pure Sn coatings were deposited from 100 mM salt chloride solutions in the Ethaline electrolyte (100 mM $CuCl_2$ or 100 mM $ZnCl_2$ or 100 mM $SnCl_2$ individually in Ethaline). Binary alloys were electrodeposited from 50 mM salt chloride solutions in Ethaline for example to deposit Cu-Zn alloy, 50 mM CuCl2 and 50 mM $ZnCl_2$ in Ethaline was used. 33 mM $CuCl_2$, 33 mM $ZnCl_2$ and 33 mM $SnCl_2$ was added to Ethaline for Cu-Zn-Sn film. The potentials applied potentiostatically for 360 seconds was -1 V and -1.5 V. The potential applied to obtain Zn included electrodes was -1.5 V. The potential for coatings which did not have Zn was -1 V. The reason why -1.5 V was applied for zinc deposition is that zinc cannot be electrodeposited by applying -1 V. The films deposited electrochemically was washed by ethanol and dried by hot air.

Deposited electrodes were homogenous and well adherent to the steel surface and they were all crack free. Cu electrode consists of agglomerated microparticles with sizes of about 0.6-3 μm as seen in Figure 4.2a. Zinc film has hexagonal flakes structure and large surface of each particle is approximately 400-600 nm (see Figure 4.2b). Sn film presented in Figure 4.2c and Figure 4.3c is dense and their flakes are connected to each other. EDAX analysis is a common method used to explore the elemental composition on a sample. Composition of metal and alloy coatings presented in Figure 4.2 is tabulated in Table 4.1. EDAX results illustrates that electrodes deposited potentiostatically from individually $CuCl_2$, $ZnCl_2$ and SnCl solution have only their pure metallic deposition.

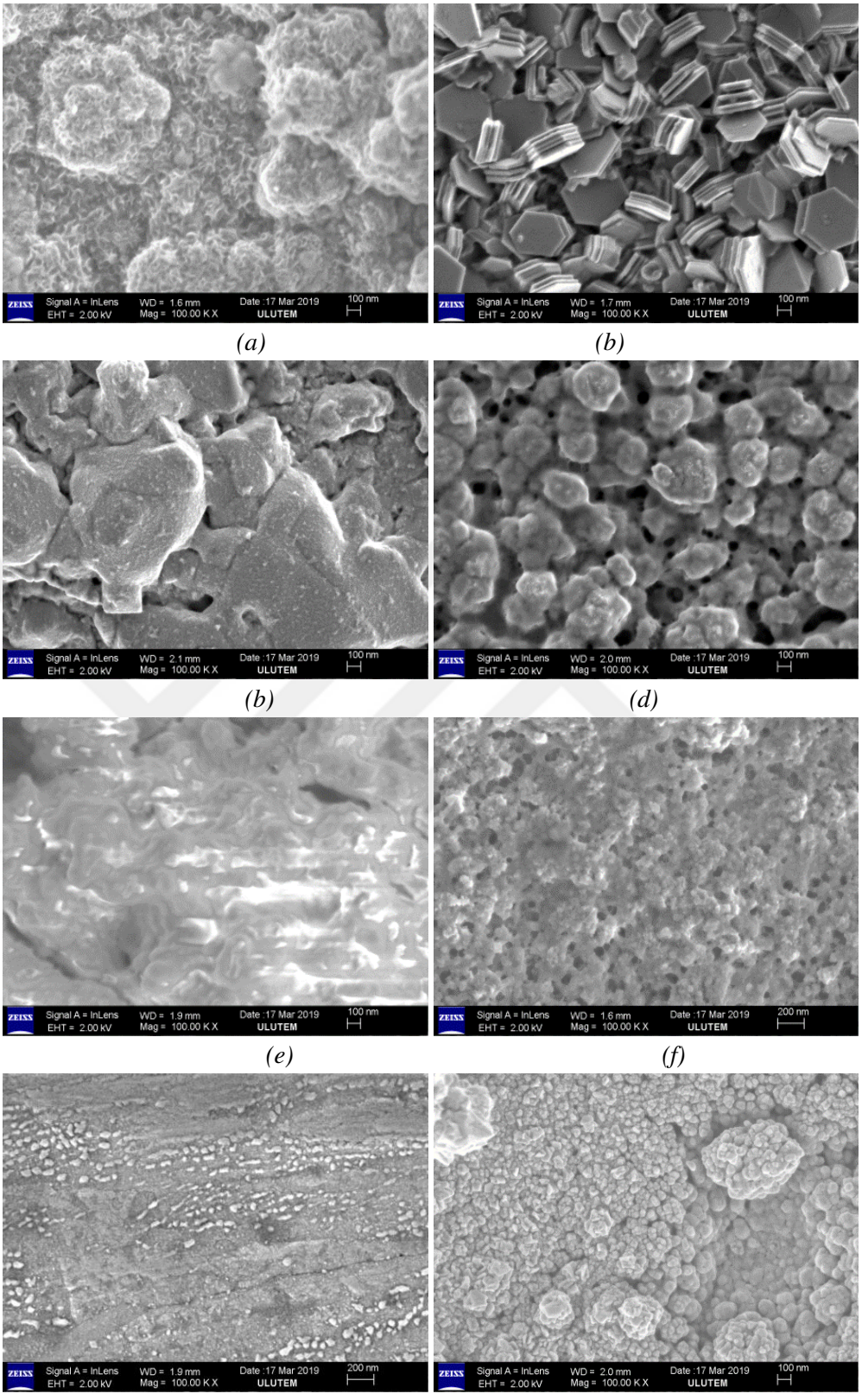


Figure 4.2 SEM images of (a) Cu; (b) Zn; (c) Sn; (d) Cu-Zn; (e) Cu-Sn; (f) Zn-Sn; (g) Bare Steel; and (h) ternarny Cu-Zn-Sn films. The magnification of each sample is 1 000 000×.

Binary alloys structure are different than monolithic metal coatings. Alloy structure of Cu-Zn is agglomerated microparticles (Figure 4.2d and Figure 4.3d) and surface coverage of Cu-Zn is less than pure copper (Figure 4.2a and Figure 4.3a). Cu-Zn structure is amorph than both metals. Cu-Sn coating (Figure 4.2e and Figure 4.3e) also has less surface area than copper film (Figure 4.2a and Figure 4.3a) and flaky structure of Sn film is disappeared (Figure 4.2c and Figure 4.3c). Zn-Sn film (Figure 4.2f and Figure 4.3f) has a sponge-like structure and completely different than pure Zn (Figure 4.2b and Figure 4.3b) and pure Sn (Figure 4.2c and Figure 4.3c). SEM images of uncoated steel (Figure 4.2g and Figure 4.3g) was flat by compastion with coated steel. The ternary alloy of Zn-Cu-Sn consists of particles ranging from nanometers to micrometres as presented in Figure 4.2h and Figure 4.3h.

Table 4.1 Percentage weight of Cu, Zn and Sn in film obtained from EDAX analysis of the sample given in Figure 4.2.

Coatings	wt% Cu in the coating	wt% Zn in the coating	wt% Sn in the coating
Cu	100	-	-
Zn	-	100	-
Sn	-	-	100
Cu-Zn	39	61	-
Cu-Sn	56	-	44
Zn-Sn	-	37	63
Cu-Zn-Sn	56	35	9

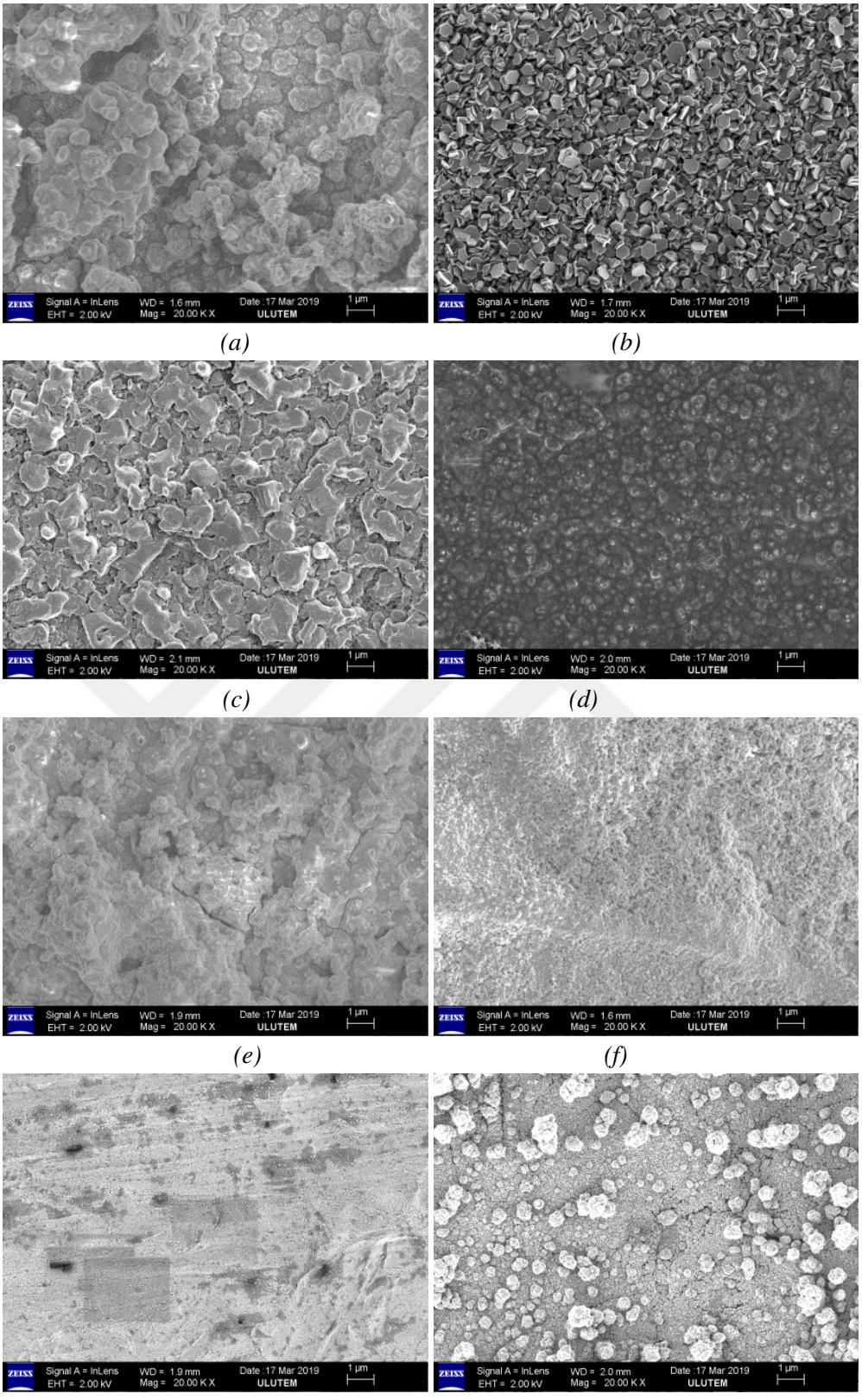


Figure 4.3 SEM images of (a) Cu; (b) Zn; (c) Sn; (d) Cu-Zn; (e) Cu-Sn; (f) Zn-Sn; (g) Bare Steel; and (h) ternarny Cu-Zn-Sn films. The magnification of each sample is 20 000×.

4.2.2. X-Ray Diffraction

XRD patterns recorded in the 2θ range from 10˚ to 80˚ for the films presented in Figure 4.2 are illustrated in Figure 4.4. All films given in this work show characteristic peaks with intensities which are narrow and sharp indicating good crystallinity. The XRD patterns of pure Cu, pure Zn and pure Sn are shown in Figure 4.4. They are indexed according to the Joint Committee on Powder Diffraction Standards as Cu (#85-1326), Zn (#65-3358) and Sn (#65-2631) as predicted.

The XRD figure for steel substrate indicates the peaks at 45 ° and 65 ° which are the chracteristic of the body centered cubic (BCC) structure having lattice planes of iron (110) and (200) (see black line of Figure 4.4). The XRD analysis confirms that the copper electrodeposited from Ethaline has the face-centred cubic (FCC) structure as the peaks at 43° and 51° observed which is red line of Figure 4.4. These peaks are well indexed to Cu(111) and Cu(200), respectively (#85-1326). The same results were reported in the literature [66]. XRD peaks of Cu film observed at 45° and 65° belongs to the steel substrate (black line of Figure 4.4) because film is thin. As all films have XRD peaks of iron presented Figure 4.4, there will not be indicated here. The highest peak of Zn film observed at 36, 38, 43, 55 and 72° could be assigned to (002), (100), (101), (102) and (103) (#65-3358). These are the characteristic peaks of zinc presented in the literature [67]. XRD peaks for Sn deposition are the same as the results found in the literature [68]. XRD pattern of Sn deposit on a AISI 4140 substrate electrodeposited from choline chloride and ethylene glycol based deep eutectic solvent [26] was also similar to pink line of Figure 4.4.

When Cu-Zn alloy is deposited, XRD peaks of Cu and Zn were disappeared, and one peak with low intensity appeared. As it was indicated in Section 4.1.1, Cu-Zn is amorphous-like structure. The XRD patterns of Cu-Sn illustrated two peaks at 43° and 44° which are different than both components. XRD peaks obtained from Zn-Sn alloy coating has two peaks at 31 and 33° which are the same as pure Sn coating. These results suggest that Zn-Sn film electrodeposited from choline chloride and ethylene glycol based deep eutectic solvent is partly coherent. Zn-Sn film was prepared from Ethaline by Beattie et. al. and they reported that the peak at 43° belongs to zinc rich alloy [69].

Ternary alloy of Cu-Zn-Sn has only one new wide peak observed at 44°. All other peaks belonging to pure metals were disseappered as a new alloy was formed.

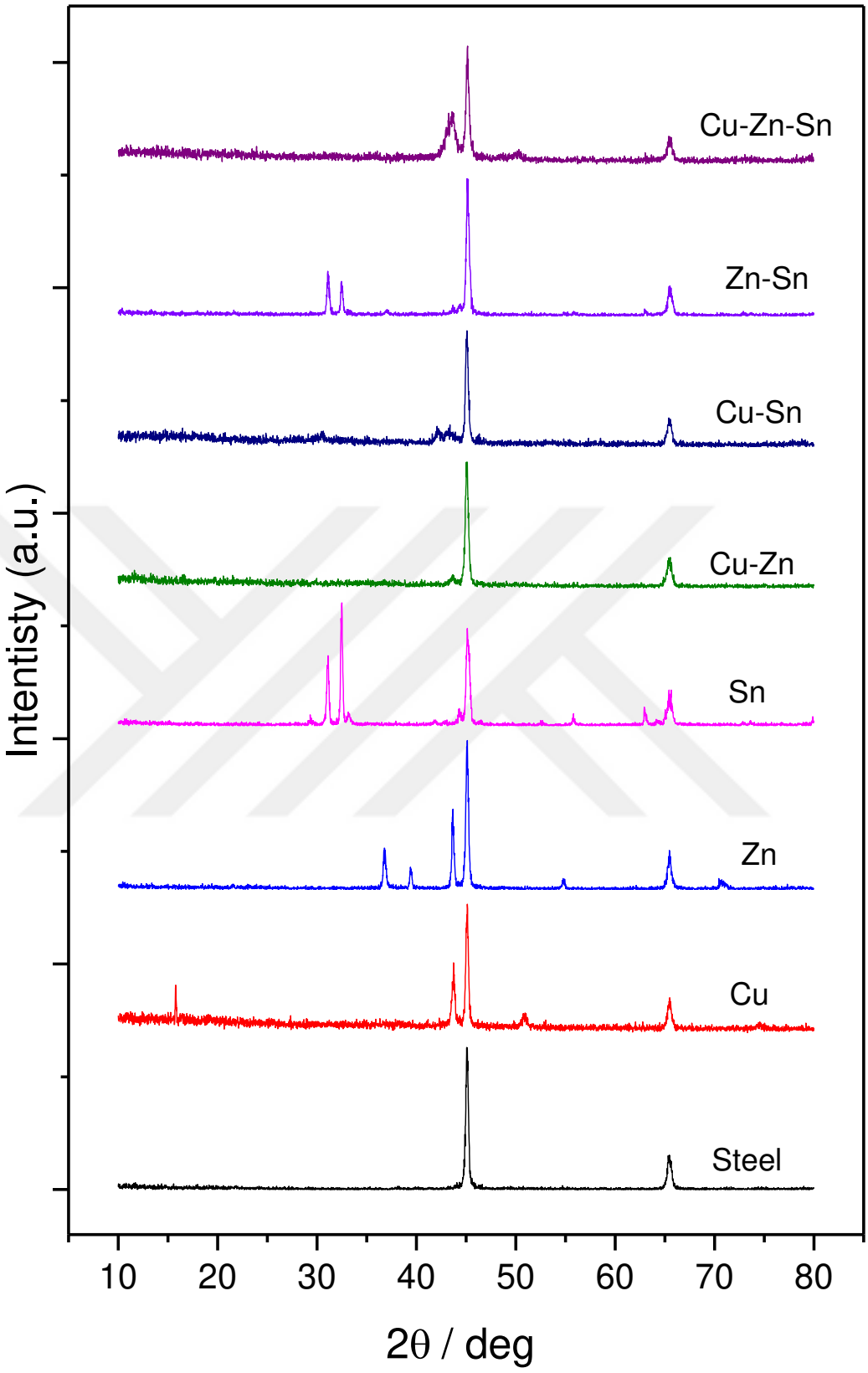


Figure 4.4 XRD patterns of uncoated steel and Cu, Zn, Sn, Cu–Zn, Cu-Sn, Zn-Sn and Cu-Zn-Sn films electrodeposited on the steel substrate from the Ethaline. Deposition conditions are given in the text.

4.3.Corrosion Behavior of Films

Low carbon steel was coated by monometals (Cu, Zn and Sn), binary alloys (Cu-Zn, Cu-Sn and Sn-Zn) and ternary alloy (Cu-Zn-Sn) from a Deep Eutectic Solvent (explained in Section 4.1.). XRD and SEM results of coated and uncoated steel electrode were examined in Section 4.2. This section presents the corrosion resistance of electrodes in 3.5% NaCl at the scan rate of 20 mV s^{-1} at room temperature.

4.3.1.Tafel Plot

As explained in Chapter 3, metals (Cu, Zn and Sn) and alloys (Cu-Zn, Cu-Sn, Sn-Zn and Cu-Zn-Sn) were electrodeposited in a deep eutectic solvent media at 65℃. The ionic liquids used in this study consist of two part ethylene glycol with one part choline chloride which is called Ethaline. The electrodes obtained in Ethaline were then transferred to NaCl electrolyte for corrosion test. All corrosion tests were conducted at room temperature of 20 ±2 °C. Working electrodes were AISI 4140, platinum and their coated forms. Working electrode was Cu, Zn, Sn, Cu-Zn, Cu-Sn, Sn-Zn and Cu-Zn-Sn coated steel obtained potentiostatically. Reference electrode was Ag/AgCl (sat. KCl) and counter electrode was Pt coated Ti mesh. Tafel curves were obtained by polarising the samples in NaCl media. After Tafel plots were obtained, E_{corr} and i_{corr} values of films were retrieved and tabulated.

Figure 4.5 illustrates the corrosion polarisation of coated and uncoated platinum in 3.5% NaCl and their E_{corr} and i_{corr} values are tabulated in Table 4.2. The reason why platium electrode was used is that Pt cannot give an interference reaction with metals/alloys used in this study. As corrosion current of bare Pt is lower (0.16 µA cm^{-2}) than all metals coated Pt (just Cu, just Zn and just Sn on Pt), corrosion resistivity of Pt is –as expected- better than all metal coatings obtained in this work. Even this current density is not realted to the corrosion of Pt. It is related to hydrogen evolution. Corrosion current of Zn is lower than other two metals and amoung these three metals zinc has passivation behaviours because the current of zinc polarisation decreases at -0.38 V. Passivation of zinc coating has been studied in detail.

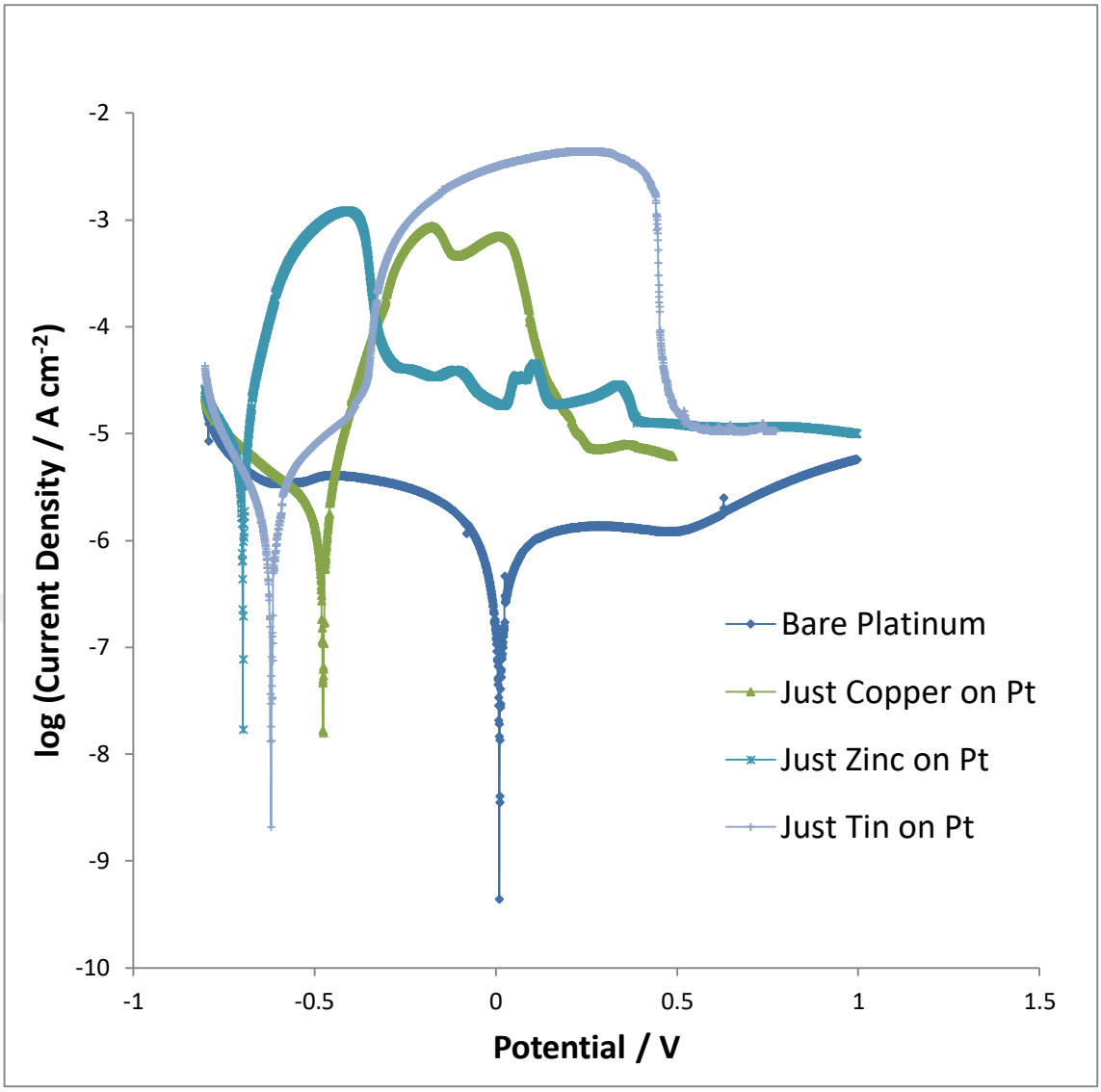


Figure 4.5 Potentiodynamic polarization of uncoated and coated platinum(just Cu, just Zn and just Sn on Pt) in 3.5% NaCl.

After corrosion behaviours of metals on Pt were tested, corrosion behaviours of binary alloys (Cu-Zn, Cu-Sn and Zn-Sn) were examined and their polarisaiton curves are given in Figure 4.6 E_{corr} and i_{corr} of binary alloys are tabulated in Table 4.2. Corrosion current of binary alloys are 0.40, 0.62 and 0.45 µA cm^{-2} for Cu-Zn, , Cu-Sn and Zn-Sn, respectively. Generally, corrosion resistivity of binary alloys on Pt are higher than that of metals on Pt. Corrosion potential of binary alloys presented in Figure 4.6 were shifted to different potential than metals.

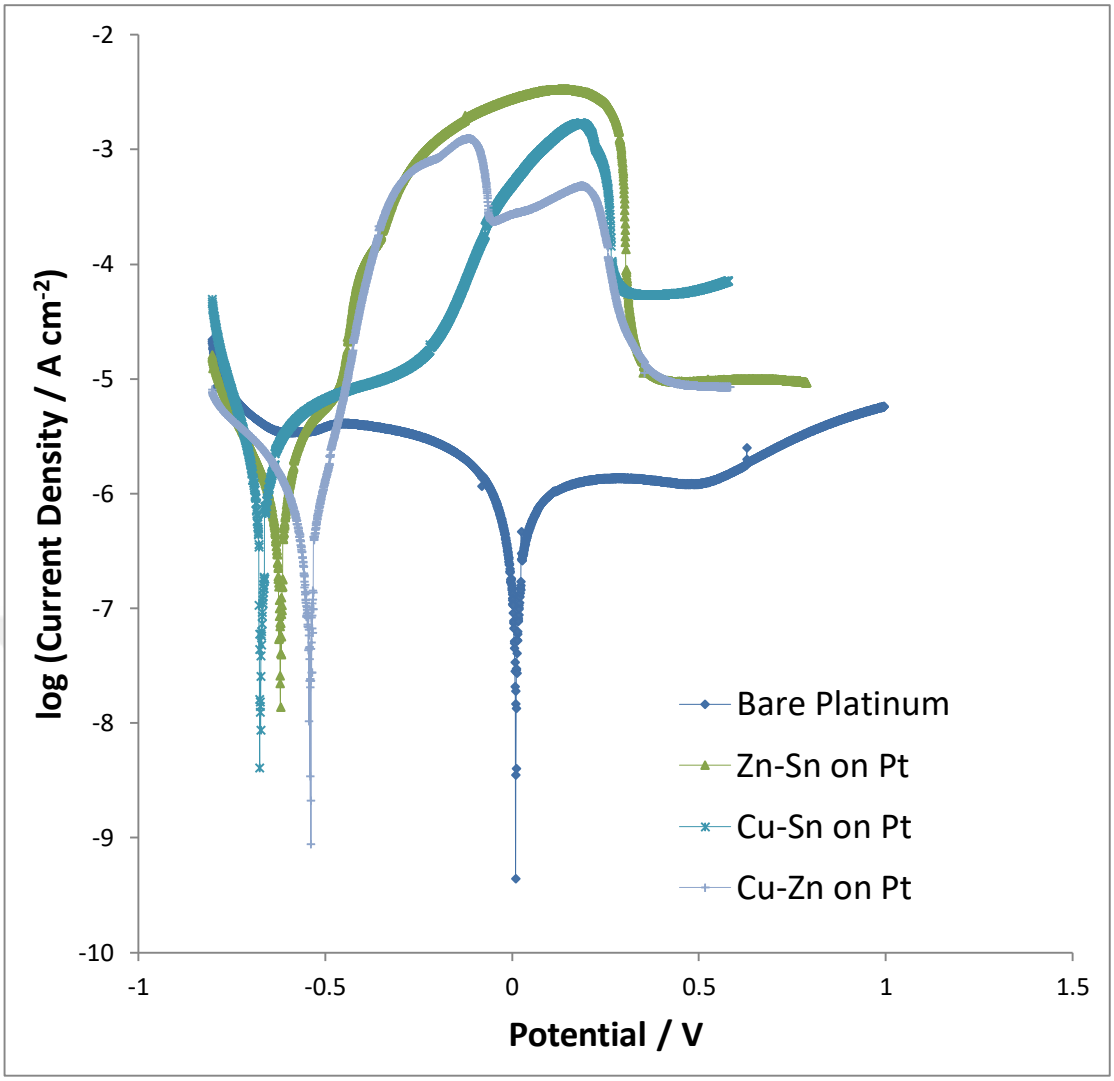


Figure 4.6 Potentiodynamic polarization of uncoated and coated platinum(Cu-Sn, Cu-Zn and Zn-Sn on Pt) in 3.5% NaCl.

Ternary alloy of Cu-Zn-Sn was also electrodeposited from choline chloride and eyhlyne glycol based deep eutectic solvent and its polarisation curve was obtained in NaCl media (see Figure 4.7). Corrosion current of ternary alloy (0.50 µA cm^{-2}) is approximately the same as zinc based binary alloys as Cu-Zn and Zn-Sn have corrosion current density of 0.45 and 0.62 µA cm^{-2}, respectively. Generally it could be said that Zn dominates corrosion current of alloys.

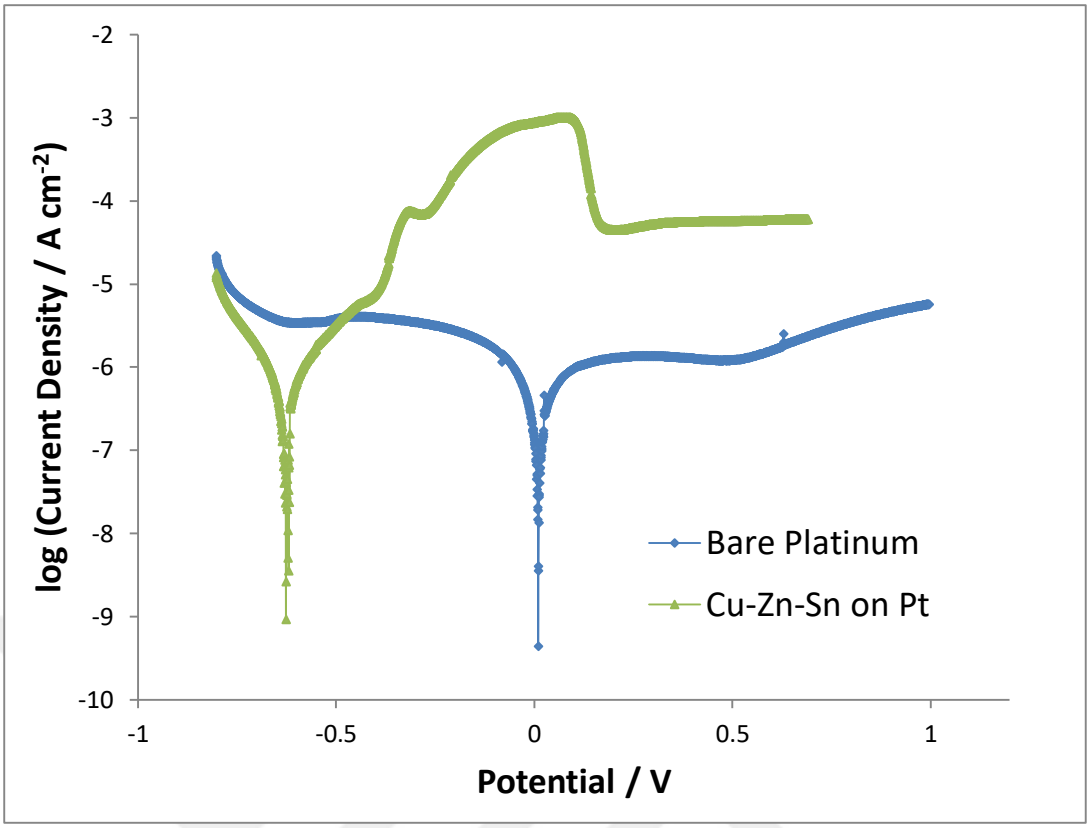


Figure 4.7 Potentiodynamic polarization of uncoated and coated platinum (Cu-Sn-Zn on Pt) in 3.5% NaCl.

Table 4.2 E_{corr} and i_{corr} values of uncoated and coated platinum in 3.5% NaCl medium. Data were retrieved from Figure 4.5, Figure 4.6 and Figure 4.7.

	İcorr (μA cm^{-2})	Ecorr (V)
Bare Pt	0.16	0.024
Just Cu on Pt	0.9	-0.41
Just Zn on Pt	0.5	-0.7
Just Sn on Pt	2.5	-0.61
Sn-Zn on Pt	0.45	-0.58
Sn-Cu on Pt	0.62	-0.62
Cu-Zn on Pt	0.4	-0.55
Sn-Cu-Zn on Pt	0.5	-0.52

Figure 4.8 illustrates the corrosion polarisation of coated and uncoated AISI 4140 in 3.5 wt. % NaCl and their E_{corr} and i_{corr} values are tabulated in Table 4.3. Corrosion current density of bare steel is higher (4.0 µA cm^{-2}) than copper coated steel. Therefore, copper coated steel has slightly higher corrosion resistivity than steel. Corrosion current density of Zn and Sn is higher than that of bare steel. It could be said that corrosion resistivity of bare steel is higher than Zn coated and Sn coated steel. However, classical passivation behavior of zinc occurs at 0.06 V in Figure 4.8 because polarization current decreases suddenly. At the same time pitting corrosion of steel started at 0.32 V shown in Figure 4.8. As zinc coated on steel could passivate itself, steel may be protected by zinc coating. It can be understood that steel substrate effects corrosion behavior of coatings. In order to observe the effect of only electrodes (without domination of steel), film coated Pt can be compared with bare steel. Corrosion current density of metal coatings (just Cu, just Zn and just Sn) – respectively 0.9, 0.5 and 2.5 µA cm^{-2} are lower than that of steel (4.0 µA cm^{-2}) meaning that steel is more readily to corrode than metals (Cu, Zn and Sn). Therefore, these metal could be coated on steel from Ethaline to protect steel against corrosion.

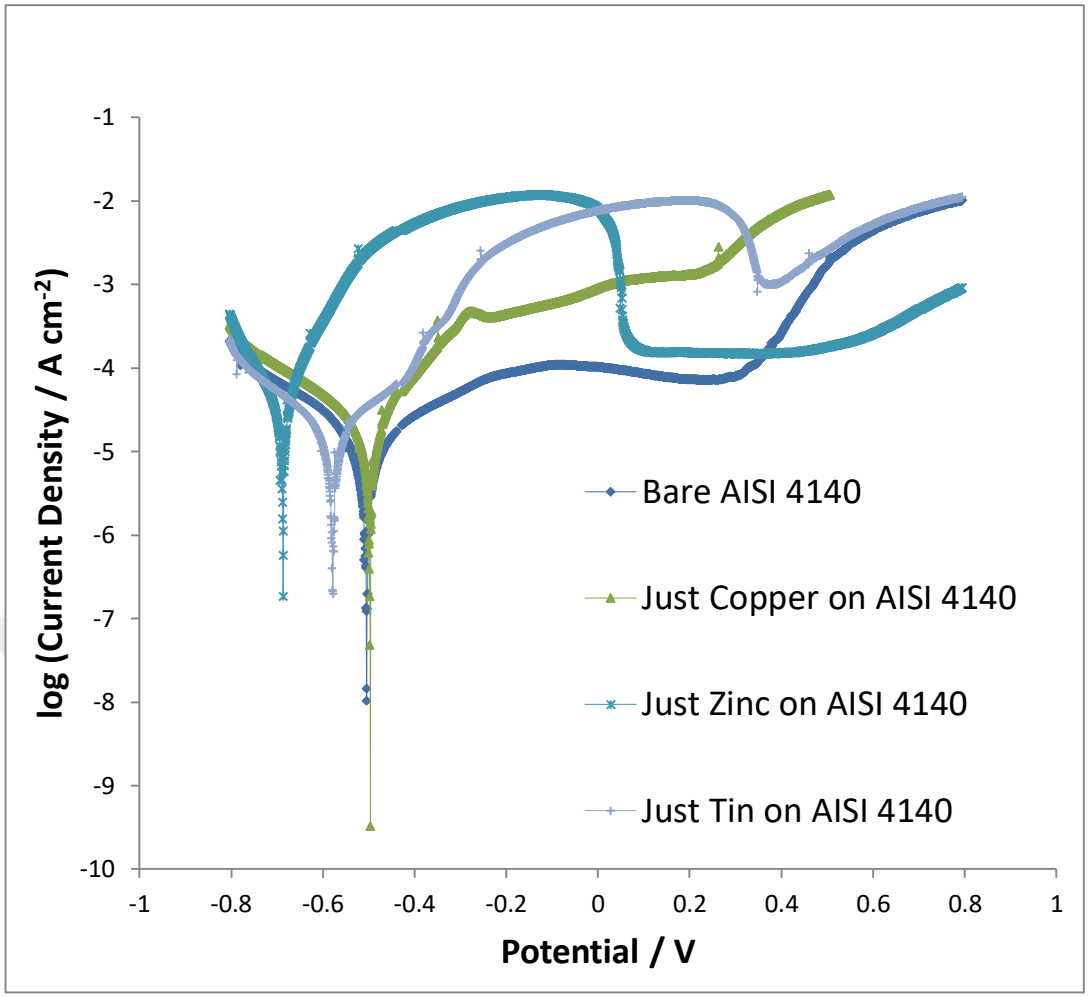


Figure 4.8 Potentiodynamic polarization of uncoated and coated AISI 4140 (just Cu, just Zn and just Sn on AISI 4140)in 3.5% NaCl.

After corrosion behaviours of metals on steel were tested, corrosion behaviours of binary alloys were examined and their data are given in Figure 4.9. E_{corr} and i_{corr} of binary alloys are tabulated in Table 4.3. Corrosion current of binary alloys is 5.4 and 5.6 and 5.0 µA cm^{-2} for Cu-Zn, Cu-Sn and Zn-Sn, respectively. Corrosion resistivity of binary alloys on steel is close to each other. Zn can be passivated with Cu as current density decreases suddenly at 0.08 V but Zn-Sn alloy is not passivated as current increases continuously until 0.75 V in Figure 4.9. As it is indicated above that the corrosion behavior of coated steel can be dominated by steel itself, corrosion resistivity of binary alloys on Pt can be compared with bare steel. Corrosion current density of binary alloys on Pt is around 0.5 µA cm^{-2} and it is approximately 10 times more resistive than bare steel (4.0 µA cm^{-2}).

Ramanauskas et.al. studied the crystallographic texture and lattice cell parameters for Zn, Zn-Co, Zn-Fe and Zn-Ni coatings, deposited from alkaline baths, and the the corrosion behaviour of the resulting films were analysed in aerated chloride solutions and in neutral salt spray tests. Electrochemical parameters for Zn on steel in aerated 0.9 M NaCl solution (pH 6.0) were obtained as 0.214 µA cm^{-2} i_{corr} and -1.074 V E_{corr}. In this thesis , Zn on steel (AISI 4140) corroded in 3.5% wt. NaCl solution (pH of natural) has 32 µA cm^{-2} i_{corr} value and -0.69 V E_{corr} value[70].

Zhang et.al. investigated that Co-Sn alloy coatings could be electrodeposited from a choline chloride/ethylene glycol eutectic-based electrolyte. XRD, SEM, TEM and corrosion analysis in the 3.5% NaCl aqueous solution were presened. Corrosion study results of pure Sn was revealed that its i_{corr} value was 0.42 µA cm^{-2} and E_{corr} value was -380 mV. In this thesis , Sn on steel (AISI 4140) corroded in 3.5% wt. NaCl solution was 12 µA cm^{-2} (i_{corr}) also Ecorr value is -0.58 V (E_{corr})[71].

Conway et.al. investigated the corrosion characterization of tin–lead and lead free solders in 3.5 wt.% NaCl solution through potentiodynamic polarisation. Sn-Cu corrosion current density was 0.178 µA cm^{-2} , 0.166 µA cm^{-2} and 0.661 µA cm^{-2} at the scan rate of 30 mV/min, 60 mV/min and 300 mV/min, respectively. In this study, corrosion current of Cu-Sn alloy was 5.6 µA cm^{-2} at the scan rate 20 mV/seconds[72].

Subramanian et.al. studied corrosion behaviour of Cu–Sn alloy coatings on mild steel substrates produced by the brush plating process. The corrosion protection study of brush plated Cu–Sn alloy on mild steel has been measured using saltwater submersion and electrochemical corrosion tests. The results represented a high charge transfer resistance and very low corrosion curent for the alloy system comparing with that of individual elements on the substrate and the mild steel substrate. Corrosion parameters obtained from polarization studies in 3.5% wt. NaCl were reported. Corrosion density of Sn on mild steel was 7.22 x 10^{-5} A/cm^2 and corrosion current density of Cu on mild steel was 5.59 x 10^{-5} A/cm^2. However, corrosion curren of Sn-Cu alloy on mild steel was 0.57 x 10^{-5} A/cm^2 . In this study corrosion current of just Cu coating, just Sn coating and Cu-Sn alloy coating were 3.2 , 12 and 5.6 µA cm^{-2}, respectively [73].

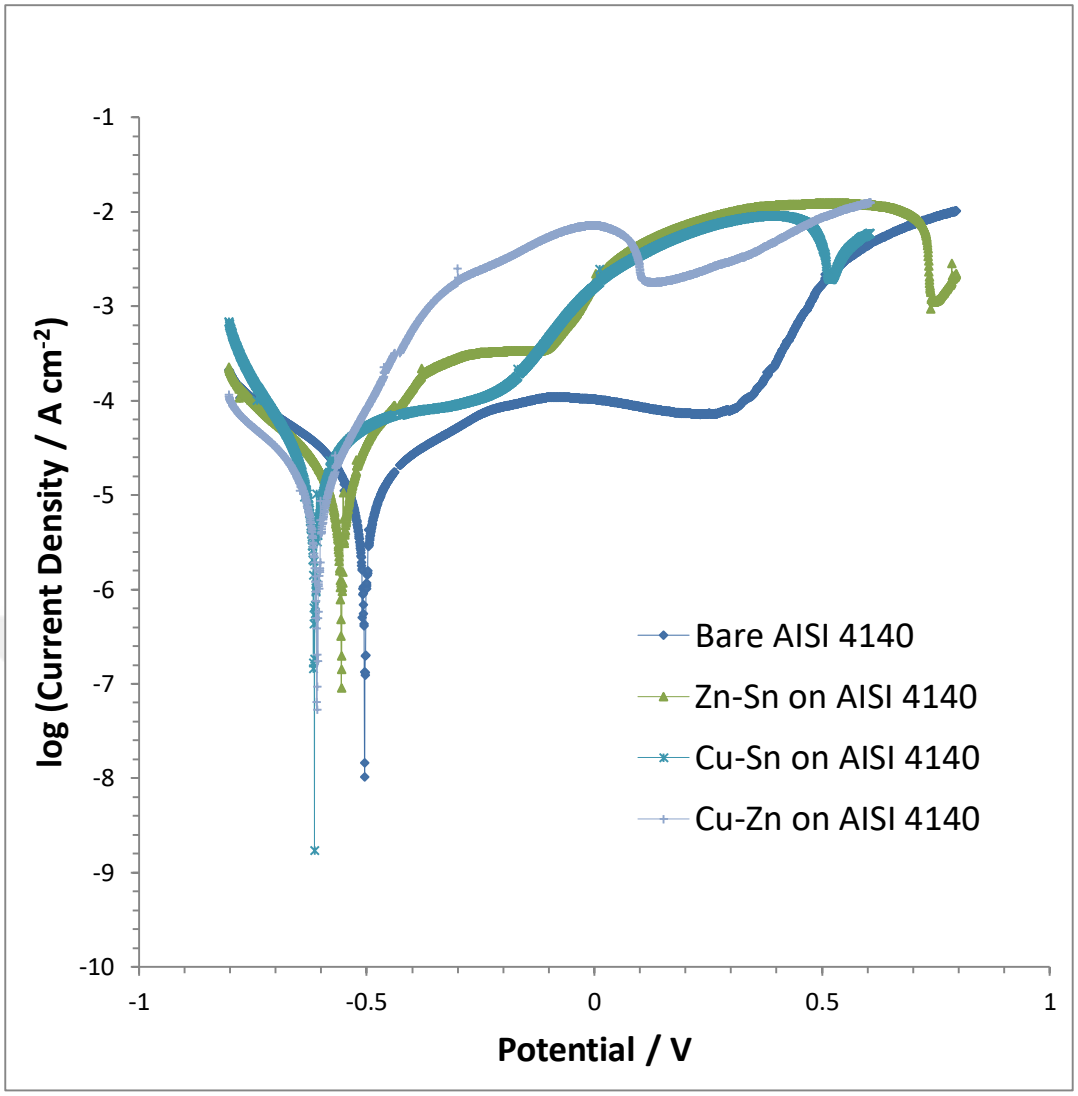


Figure 4.9 Potentiodynamic polarization of uncoated and coated AISI 4140 (Cu-Sn, Cu-Zn and Zn-Sn on AISI 4140) in 3.5% NaCl

Ternary alloy of Cu-Zn-Sn was also electrodeposited from choline chloride and eyhlyne glycol based deep eutectic solvent and its polarisation curve was obtained in NaCl media (see Figure 4.7). Corrosion current density of ternary alloy on steel (6.3 µA cm^{-2}) is approximately the same as zinc based binary alloys on steel as Cu-Zn , Cu-Sn and Zn-Sn have corrosion current of 5.4, 5.6 and 5.0 µA cm^{-2}, respectively. Generally it could be said that Zn dominates corrosion current of alloys. Corrosion resistiviy of ternary alloy on Pt is eight times greter than bare steel.

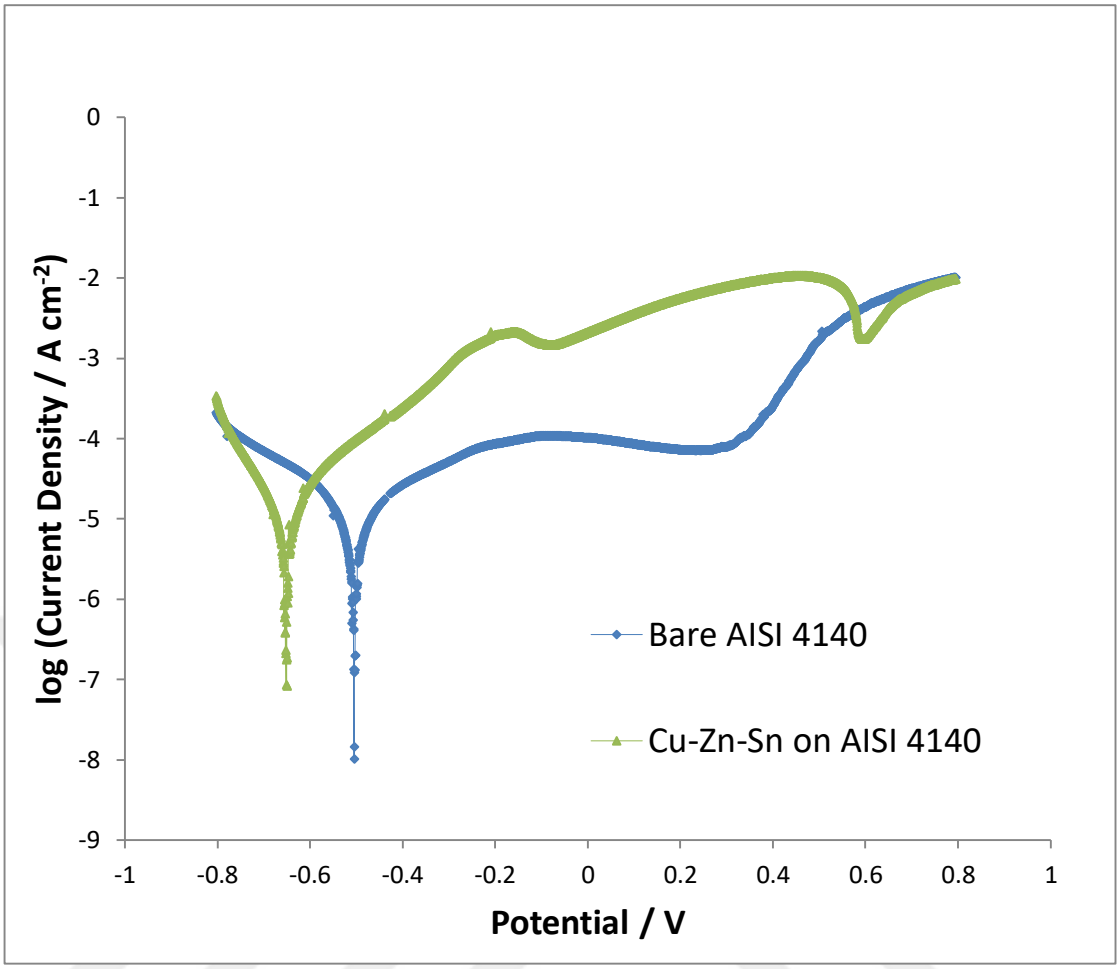


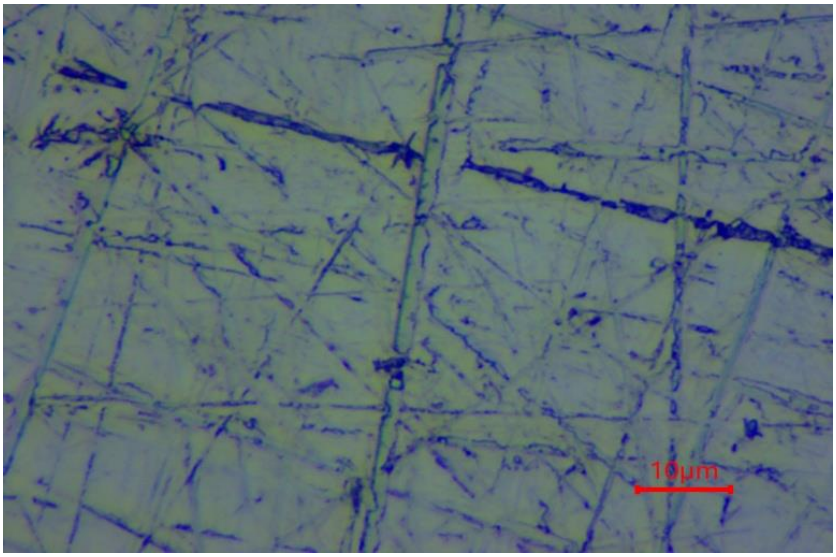
Figure 4.10 Potentiodynamic polarization of uncoated and coated platinum (Cu-Sn-Zn on AISI 4140) in 3.5% NaCl.

Table 4.3 Ecorr and icorr values of uncoated and coated AISI 4140 in 3.5% NaCl medium. Data were retrieved from Figure 4.8, Figure 4.9 and Figure 4.10

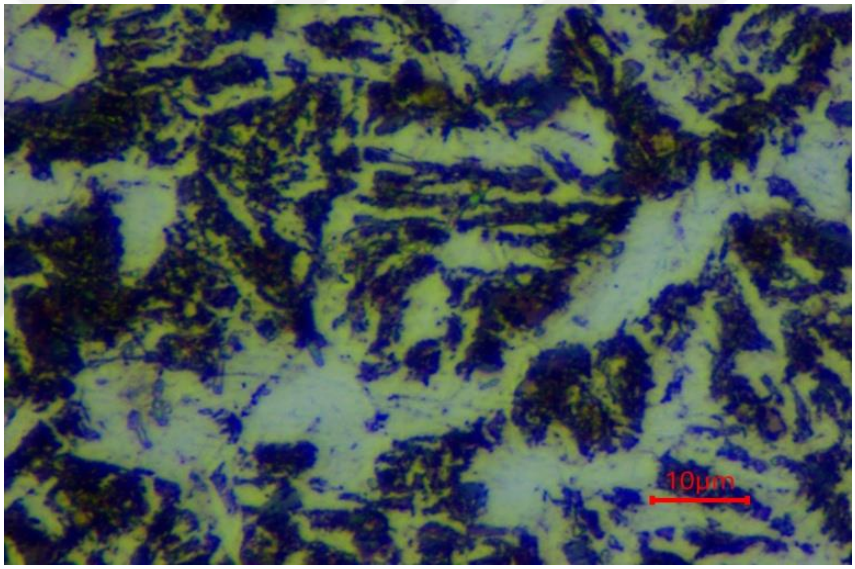
	İcorr ($\mu A\ cm^{-2}$)	Ecorr (V)
Bare AISI 4140	4.0	-0.50
Just Cu on AISI 4140	3.2	-0.49
Just Zn on AISI 4140	32	-0.69
Just Sn on AISI 4140	12	-0.58
Sn-Zn on AISI 4140	5.0	-0.56
Sn-Cu on AISI 4140	5.6	-0.61
Cu-Zn on AISI 4140	5.4	-0.62
Sn-Cu-Zn on AISI 4140	6.3	-0.65

4.3.2. Optical Microscope

Films obtained electrochemically from ionic liquid media and were polarised in 3.5 wt% NaCl electrolyte to test corrosion resistivity. Coated and uncoated steel were forced to corrode and their microstructure are observed by means of a microscope. This analysis was carried out to monitor the changes in the surface of the samples. Figure 4.11 illustrates the microstructures of bare steel before and after polarisation in NaCl electrolyte. Steel was ground by SiC sandpapers and there are scratches on steel surface presented in Figure 4.11a. Steel has pitting corrosion after polarisation in NaCl media (see Figure 4.11b).



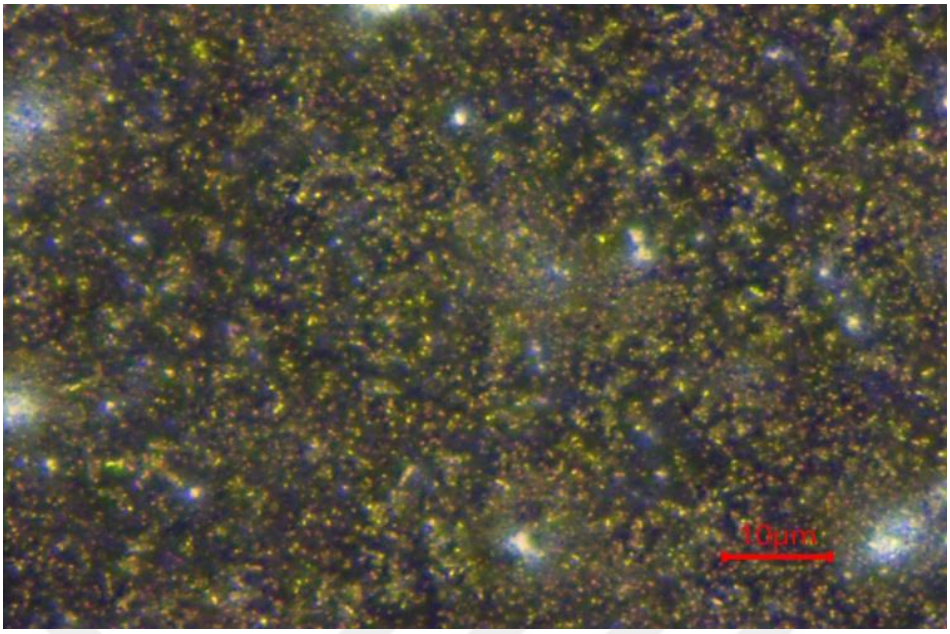
(a)



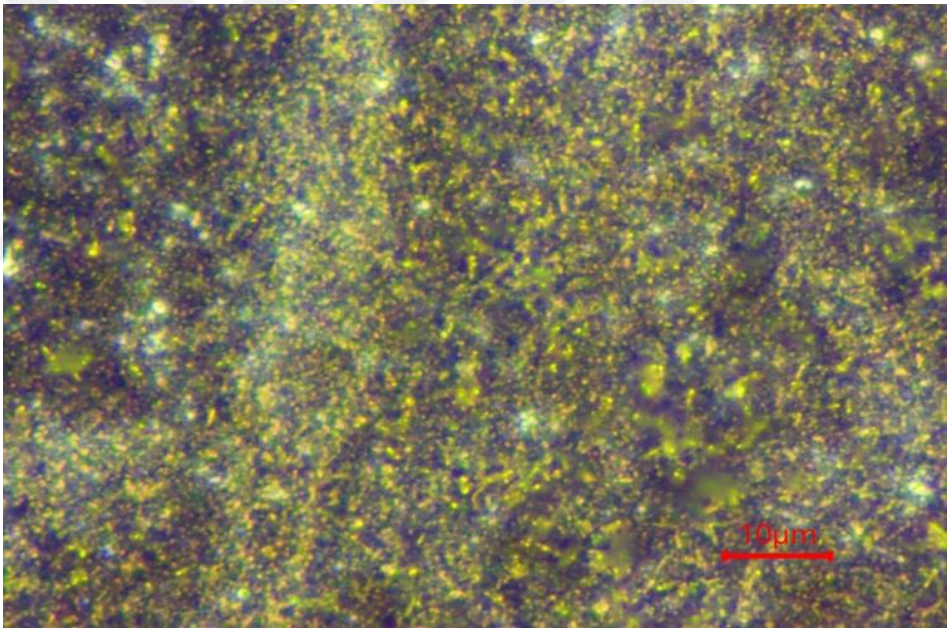
(b)

Figure 4.11 Micrographs of bare steel (a) before polarisation and (b) after polarisation in 3.5 wt% NaCl media.

Figure 4.12a illustrates the microstructure of Cu-Zn-Sn ternary alloy coated steel coated from Ethaline. Figure 4.12 (b) shows the film obtained after polarisation in NaCl. There is no clear differences between the micrographs of Cu-Zn-Sn ternary film on steel before and after polarisation in 3.5 wt% NaCl media. This means that the coating could be used effectively against corrosion of steel.



(a)



(b)

Figure 4.12 Micrographs of Cu-Zn-Sn ternary film on steel (a) before polarisation and (b) after polarisation in 3.5 wt% NaCl media.

CHAPTER 5

CONCLUSION AND FUTURE WORK

5.2. Conclusion

In this thesis; Cu, Zn, Sn, their binary alloys and thier ternary alloys based coatings were successfully produced potentiodynamically by electrochemical three-electrode methods from an ionic liquid. Ethylene glycol and choline chloride based deep eutectic solvent was used as deposition electrolyte. All coatings were obtained on steel and Pt electrode. Pt working electrode was used to examine corrosion behaviour of coatings because linear sweep voltammetry responses of metal/alloy coatings on steel in NaCl solution is overlapped by that of steel. The corrosion behaviour of the coatings was tested in 3.5 wt% NaCl solution.

The chronoamperometric results of the growth of metal and alloy films on Pt and steel working electrode were studied. Thin film coatings were produced by the electrodeposition method. Deposited electrodes were homogenous and well adherent to the steel surface and they were all crack free.

Compositional and structural analysis of the films were carried out by means of SEM, XRD and EDAX. Electrodes deposited potentiostatically from individual $CuCl_2$, $ZnCl_2$ and $SnCl_2$ solution have only their pure metallic deposition. Binary alloys structure is different than monolithic metal coatings. The ternary alloy of Zn-Cu-Sn consists of particles ranging from nanometers to micrometres.

Morphological analysis with XRD was found to be compatible with the literature. All films given in this research show characteristic peaks with intensities which are narrow and sharp indicating good crystallinity. The ternary alloy of Cu-Zn-Sn has only one new wide peak observed at 44°. All other peaks belonging to pure metals were disappeared as a new alloy was formed.

The corrosion polarisation of coated and uncoated platinum in 3.5% NaCl and their E_{corr} and i_{corr} values were calculated. As corrosion current of bare Pt is lower (0.16 µA cm^{-2}) than all metals coated Pt (just Cu, just Zn and just Sn on Pt), corrosion resistivity of Pt is –as expected- better than all metal coatings obtained in this work. Even this current density is not related to the corrosion of Pt. Corrosion current of Zn is lower than the other two metals and among these three metals zinc has passivation behaviours because the current of zinc polarisation decreases at -0.38 V. Passivation of zinc coating has been studied in detail. After corrosion behaviours of metals on Pt were tested, corrosion behaviours of binary alloys (Cu-Zn, Cu-Sn and Zn-Sn) were examined and their polarisation curves were analysed. E_{corr} and i_{corr} of binary alloys illustrated that corrosion resistivity of binary alloys on Pt is generally higher than that of metals on Pt. Corrosion potential of binary alloys was shifted to different potential than metals. The ternary alloy of Cu-Zn-Sn was also electrodeposited from choline chloride and ethylene glycol based deep eutectic solvent and its polarisation curve was obtained in NaCl media. Generally, it could be said that Zn dominates corrosion current of alloys.

The corrosion polarisation of coated and uncoated AISI 4140 in 3.5 wt.% NaCl and their E_{corr} and i_{corr} values are found. Corrosion current density of bare steel is higher than copper coated steel. Therefore, copper coated steel has slightly higher corrosion resistivity than steel. Corrosion current density of Zn and Sn is higher than that of bare steel. It could be said that corrosion resistivity of bare steel is higher than Zn coated and Sn coated steel. As zinc coated on steel could passivate itself, steel may be protected by zinc coating. It can be understood that steel substrate effects corrosion behaviour of coatings. In order to observe the effect of only electrodes (without domination of steel), film-coated Pt can be compared with bare steel. Therefore, these metal could be coated on steel from Ethaline to protect steel against corrosion. After corrosion behaviours of metals on steel were tested, corrosion behaviours of binary alloys were examined. Corrosion resistivity of binary alloys on steel is close to each other. As it is indicated above that the corrosion behaviour of coated steel can be dominated by steel itself, corrosion resistivity of binary alloys on Pt can be compared with bare steel. Corrosion current density of binary alloys on Pt is around 0.5 µA cm^{-2} and it is approximately 10 times more resistive than bare steel. The ternary alloy of Cu-Zn-Sn was also electrodeposited from choline chloride and

ethylene glycol based deep eutectic solvent and its polarisation curve was obtained in NaCl media. Corrosion current density of ternary alloy on steel is approximately the same as zinc-based binary alloys on steel as Cu-Zn, Cu-Sn and Zn-Sn have corrosion current of 5.4, 5.6 and 5.0 μA cm^{-2}, respectively. Generally, it could be said that Zn dominates corrosion current of alloys. Corrosion resistivity of ternary alloy on Pt is eight times greater than bare steel.

Coated and uncoated steel were forced to corrode and their microstructure was observed by means of an optical microscope. This analysis was carried out to monitor the changes in the surface of the samples. The microstructures of bare steel before and after polarisation in NaCl electrolyte were obtained and steel has pitting corrosion after polarisation in NaCl media. The microstructure of Cu-Zn-Sn ternary alloy coated steel electrodeposited from Ethaline was compared before and after polarisation. There were no clear differences between the micrographs of Cu-Zn-Sn ternary film on steel before and after polarisation in 3.5 wt% NaCl media. This means that the coating could be used effectively against corrosion of steel.

5.2 Future Work

Cyclic Voltammetry of metals/alloys can be performed to understand the mechanism of growth. Corrosion rate of coated and uncoated steel could be compared with another method. The effect of coating thickness can be elucidated. Corrosion behaviour of coatings can be tested in different electrolyte including acidic and alkaline solution. Corrosion studies can be carried out in different corrosive environments. The effect of temperature on corrosion of coated and uncoated steel can be tested for corrosion studies. Corrosion studies can be applied after heat treatment of the produced coatings.

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