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SARBAZ SEYAMAND SALIH

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SARBAZ SEYAMAND SALIH

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Supervisor

Prof. Dr. Metin BEDİR

Co-Supervisor

Asst. Prof. Dr.Mehmet Yakup HACIİBRAHİMOĞLU

by

Sarbaz Seyamand SALIH

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Approval of the Graduate School of Natural and Applied Sciences

Prof. Dr. A. Necmeddin YAZICI

Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Ramazan KOÇ

Head of Department

This is to certify that we have read this thesis and that in our consensus opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

Prof. Dr. Metin BEDIR — Supervisor

Asst. Prof. Dr. M. Yakup HACIİBRAHİMOĞLU — Co-Supervisor

Examining Committee Members: Signature

Prof. Dr. Metin BEDİR .....

Assoc. Prof. Dr. E. Vural KAFADAR .....

Asst. Prof. Dr. Rasim ÖZDEMIR .....

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Sarbaz Seyamand SALIH

ABSTRACT

A STUDY ON CORROSION CHARACTERISTICS OF AA2024 UNDER DIFFERENT CONDITIONS

SALIH, Sarbaz Seyamand
M. Sc. in Department of Engineering Physics
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Co-Supervisor: Asst. Prof. Dr. Mehmet Yakup HACIİBRAHİMOĞLU
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In this work the corrosion characteristics of bare aluminum based alloy (AA2024) and zinc coated AA2024 are studied in the aqueous solution having three different pH (2, 7 and 12). Apart from the traditional methods of aluminum coating (chromate conversion coating and zincating), this thesis suggests an alternative way to coat aluminum with a metal. A novel ionic liquid consisting of only cations and anions electrolyte is used for this purpose. AA2024 alloy in a deep eutectic solvent (DES) having zinc ions cannot be coated by zinc by applying anodic potential directly due to the typical characteristic of aluminium alloy which has Al_2O_3 thin layer occurring naturally on the aluminium surface. To electrodeposit zinc on aluminium alloy, an extreme anodic voltage (+1.65) is firstly applied for removing Al_2O_3 layer in Ethaline and then the cathodic potential (-1.5 V) is immediately applied in order to deposit zinc in-situ on newly prepared aluminium alloy surface which does not have Al_2O_3 anymore. Galvanised AA2024 displays the characteristic of an amorphous structure observed by SEM and XRD. Bare AA2024 has pitting corrosion at high potential in three aqueous medium use in this work (10 mM HCl, 0.5 M NaCl, 10 mM KOH). Zinc coated AA2024 has passivation behaviour in alkaline and acidic media. Corrosion resistance of zinc coated AA2024 alloy is almost as high as that of bare AA2024 in three different media. The work reported in this thesis presents that zinc coated AA2024 has more than six times higher corrosion resistance than bare Al2024 in alkaline medium (pH = 12).

Keywords: Electrodeposition; corrosion; AA2024; XRD; SEM; passivation.

ÖZET

FARKLI ORTAMLARDA AA2024 ALAŞIMININ KOROZYON KARAKTERİSKLERİ ÜZERİNEÇALIŞMA

SALIH, Sarbaz Seyamand
Yüksek Lisans Tezi
Fizik Mühendisliği Bölümü
Danışman: Prof. Dr. Metin BEDİR
Yardımcı Danışman: Yrd. Doç. Dr. Mehmet Yakup HACİİBRAHİMOĞLU
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Bu çalışmada kaplamasız ve çinko kaplamalı AA2024 alüminyum alaşımının sulu çözeltilerde (üç farklı pH da 2, 7, 12) korozyon karakteristikleri çalışılmıştır. Bu tez geleneksel alüminyum kaplama methodları dışında (kromlama, çinkolama) alüminyumu bir metalle kaplamak için alternatif bir yol teklif etmektedir. Bu amaç için sadece katyon ve anyon içeren yeni bir iyonik sıvı kullanılmıştır. Alüminyum alaşımının yüzeyindeki tabii olarak oluşmuş alüminyum oksit tabakadan dolayı çinko iyonları içeren derin öktektik solvent içinde AA2024 alaşımı çinkoyla direk kaplanamaz. Çinkoyu alüminyum alaşımının yüzeyine Elekro-kaplama ile kaplayabilmek adına öncelikle yüzeydeki Al_2O_3 tabakayı sökmek için Ethaline içinde aşırı değer olan +1.65V anodik voltaj uygulanır. Hemen akabinde yüzeyinde artık alüminyum oksit tabaka olmayana AA2024 alaşımına yerinde kaplama için katodik -1.5V uygulanır. SEM ve XRD yardımıyla galvanize edilmiş AA2024 in amorf yapıda olduğu gözlemlenmiştir. Yüksek potansiyelde üç sulu çözeltide(10 mM HCl, 0.5 M NaCl, 10 mM KOH) kaplamasız AA2024 alaşımının yüzeyi çukurcuklara sahiptir. Asidik ve bazik ortam içerisinde çinko kaplanmış AA2024 alaşımı pasivasyon davranışına sahiptir. Çinko kaplı AA2024 alaşımın korozyon direnci hemen hemen kaplamasız AA2024 alaşımının korozyon direnci kadar yüksek çıkmıştır. Bu tezde rapor edilen çalışmada bazik ortamda(pH=12) çinko kaplamalı AA2024 alaşımının korozyon direncinin kaplamasız AA2024 alaşıma göre altı kat daha fazla olduğu sunulmuştur.

Anahtar Kelimeler: Elektro depolama; Korozyon; AA2024; XRD; SEM; pasivasyon

To my lovely parents

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LIST OF SYMBOLS/ ABBREVIATIONS

AA 2024-T3	Aluminum Alloy
Ag	Silver
AgCl	Silver Chloride
Al	Aluminum
CCC	Central Cinema Campaign
Ce(dpp)3)	Cerium Diphenyl phosphate
ChCl	Choline Chloride
Cl	Choler
CP	Cooling Spraying
Cr (VI)	Hexavalent Chromium
Cu	Copper
$CuSO_4$	Copper Sulfate
CV	Cyclic Voltammetry
DES	Deep eutectic Solvent
EDP	Electro Deposition
EDX	Energy Depresive X-ray
EG	Ethylene Glycol
EIS	Electron Impedance Spectroscopy
Fe	Iron
FFC	Filiform Corrosion
FHWA	Federal Highway Agenceis
FSIMS	Time of Flight Secondary Iron Mass Spectroscopy
Gmd	Grams per Square Meter per day
GNP	Gross National Product
H	Hydrogen
HCl	Hydrochloric Acid
Hg	Mercury

H_2SO_4	Sulfric Acide
IL	Ionic Liquids
Ipy	Inch per year
JCPDS	Joint Committee Powder Diffraction Standard
K	Potassium
KCl	Potassium Chloride
Ksi	Kilopound per square inch
KOH	Potassium Hydroxide
LSV	Linear Sweep Voltammetry
Mg	Magnesium
Mn	Manganes
Mpa	Megapascal
Na	Sodium
NaCl	Sodium chloride
NH_4	Ammonium
NIST	National institute of standard and technology
O_2	Oxygen
pH	Power of hydrogen
SCE	Micro scale electrochemistry
SEM	Scanning electron microscopy
Si	Silicon
SKPFM	Scanning Kelvin probe Force Microscopy
Sn	Tin
SO_4	Sulfate ion
TEM	Transmission Electron Microscopy
Ti	Titanium
XRD	X-ray Diffraction
Zn	Zinic
ZnO	Zinc oxide
$ZnSO_4$	Znic sulfate

CHAPTER ONE

INTRODUCTION

1.1 Introduction

The Corrosion is process or act of reactions to the material surrounds. The materials that are subject to corrosion included polymers, ceramics and metals. The majority example of metals corrosion relates to its attraction with oxygen or water. The corrosion most refers to the oxidation of metals by electrochemical or chemical procedures. Rusting of steel due to exposure to water or humid air is known well as example of electrochemical corrosion. The metal is reacting with water or oxygen and forms iron oxide [1].The corrosion resistance of Al alloys was relate to the formation of an oxidation passive film, which naturally developed on the alloy surface under normal atmospheric conditions oxide film was form on the aluminium alloy surface is not uniform, thin and not coherent. Therefore, its importance certain levels of protections under normal conditions [2]. Corrosion is explained in the some typical ways and the common interpreted to the statement is attacking on materials by reacting with environmental. The conception of corrosion also, can be utilized in broader sense, where this contains attacking on non-metallic materials [3].

The growth of three importance industrial development in the late 19^{th} century and early 20^{th} century would, by material demand a characteristic consistency with unequalled the quality of aluminium alloy, great benefit development in the productions and have used of the new metals. The first of this was the institution of the first internal combustions engines powered vehicles. Aluminium working a role as self-propelled vehicles materials of increases engineering values. Secondly, electrification would be required to massive quantity of light weight m conductivity of metal for long distance transmissions and for constructions of the tower was need to be supported over the head network cables hat

to conducting electrical energy from sites of powers generations. Along with few decades third significant application was made possible to the inventions of the airplane by the Wright brothers. that That gave the birth to the entire new manufacturing which as growth in partnership with the aluminium industry development of structural reliable, strong, and fracture resistant parts for airframe, engine and ultimate, for fuel cells, missiles body and satellites components [4].

1.2 Literature survey for the corrosion of aluminium alloy

The corrosion of a metal in watery settings results from the metal oxidation, but is not necessarily due to the oxygen dissolved in water [5]. The oxidation can also occur when other chemical species, especially aggressive ions are existing. Corrosion is an electrochemical incident and any approach to corrosion can only be led within the scope of an electrochemical impersonification of the processes involved [6]. Though the laws of the electrochemistry are similar to all materials, their functional behaviour is nevertheless different and depends very often on their chemical composition and environment.

Although a lot of distinct kinds of metallic corrosion exist (e.g. pitting, galvanic, stress) most of them start at the surface, and the responses are often mentioned as taking place at the interface between the metal and its setting. The method of gathering alloying metals to modify the surface properties and therefore increase the corrosion impedance is famous and implemented for over a hundred years. However, adding the alloying element to the total bulk of the material is prospectively profuse, and considering that many of the principal alloying elements might be found only in few districts in the world, modern approaches that emphasize conservation, as well as commercial usefulness, must be found [7].

Processed of the AA 2024 and alloy were most significant to apply in industry especially in the aircraft technologies due to their outstanding physically and mechanically possessions. Hence, AA 2024 and alloy were most ready to corrosion. traditionally, subtreatments (chromatic coating) utilizing Cr (VI) mixtures as corrosion inhibitive, had been used widely to maintain the AA 2024-T3 corrosion because of the tough oxidase property of Cr (VI). Inappropriately, also the excellent oxide of Cr (VI) makes dangerous healthiness difficulties to human and known

chemical hazardous (carcinogen). Therefore, the pre-treatment uses depended on (VI) Cr is step-by-step be controlled to the safety and healthy reason with the environmental protections [8].

Some works have showed in the literatures concerning computer programming of in effect continuing corrosion inhibitors basis upon chemistry sol gel for the preservation of aluminium alloy. Some other study had showed to products a (Nano-structural) artificial lake in the sol and gel, matrix for the storing and manageable released of the corrosion inhibitors [9, 10]. Nevertheless, this coating needed temp. cure over to 120^0C. Farther more, continuing corrosion resistant is evaluating only in the very environment kind.

The 5xxx and 6xxx series aluminium alloys are commonly used in marine applications where low-density materials, good mechanical properties and better resistance to corrosion are desired [2, 4]. The corrosion resistance of these alloys is related to the formation of an oxide (passive) film, which naturally develops on the alloy surface under normal atmospheric conditions [11]. The oxide film formed on the aluminium alloy surface is non-uniform, thin and non-coherent. Therefore, it imparts a certain level of protection under normal conditions. When exposed to environments containing halide ions, of which the chloride (Cl^-) is the most frequently encountered in service, the oxide film breaks down at specific points leading to the formation of pits on the aluminium surface [2].

The defence of Al alloy as of corrosion pitting when resisted to a destructive environmental is a tremendously tough problematic, regulating the diversity of useful usage of the alloy. The numerous environmental and circumstances airplane are exposed to, associate with the exact necessities of armed airplane coating, resultant in the actual inspiring difficulty of the corrosion preservation of Al structural to the armed airplane. The increasing accomplishment of destructive electrolytic, gradient temp. And mechanically pressure can cause corrosion persuaded mechanic exhaustion. Positive application of the corrosion preservation methods depend on innovative naturally acquiescent coatings structures and corrosion preventer will rely on creating a major empathy of corrosion beginning and following pit construction. When a pit, designed because of corrosions, positions at a place which proves

mechanical strains, the pit will behave as a stress centre to begin exhaustion cracking [12]. By empathy pit morphologies and its influence on the cracking start and by prominently decreasing or getting rid of happening of pit creation, there will be a straight enhancement of the mechanics dependability and facility life of the armed airplane.

The individually pitting corrosion shape propose, the pitting of interested was treatment as the cracking on face of the example and the kinetic pit were applied to explain rate development [13]. Though, because of absence of quantifiable indication, these replicas could not be completely acceptable [14]. Consequently, to gathering more of this required indication in a practical quantity of the time, the corrosion pitting should be produced artificial in a monitored environmental. Those examples could then endure weariness examination to determination the typical of pitting that initiate a cracking [15].

Aluminium alloy was constantly used in the manufacture of the distinct weapon. However, the alloy is sensitive to corrosion loss and corrosion loss is important fatigue crack nucleation sites. The impact of corrosion on the exhaustion action of aluminium structures is of prominent significance in assessing of the basic totality of elder weapon. There has not been yet, totally constructive model available to forecast the regulation of corrosion damage evolution. Comprehending and forecasting of corrosion damage are vital for the structural unity of aircraft materials and structures [16].

Aluminium alloys were extensively applied in the aeronautical industrial and marine engineering due to their light mass and advantageous mechanical properties. However, these alloys have a low resistance against corrosion because of the attendance of alloying fundamentals which can locally break down the passive film and allow the attack of aggressive ions like chloride ions that can initiate pitting or crevice corrosion [12, 17]. Generally, localized corrosion can be prevented and corrosion degree can be decreased by using corrosion inhibitors that can shape a resistant oxidation films on the metallic face to prevent aggressive ions. The number of corrosion inhibitors had growth for this aim. Chromates, which are passivizing preventers, are known as being very well-organized to prevent the corrosion of Al

and Al alloy [18, 19]. The functions of this inhibitor are related to the interaction of chromate with the passive film and the formation of an unsolvable oxide chromatic Cr_2O_3 that can repair the defects of passive film [20, 21]. But the strong oxidizing properties of Cr (VI) and its carcinogenesis make chromates harmful to the environment, thus it is essential to earn a new corrosion inhibitor for aluminium and its alloys to replace chromates. Cerium has been proved to be a viable replacement for chromates [22, 23]. Cerium acts as a cathodic inhibitor by forming a cerium rich layer to inhibit the cathodic reaction [24]. Phosphate is another inorganic corrosion inhibitor replacement of chromates [25]. It is usually used in conversion coating baths to form the insoluble phosphate-aluminium layer and reduce significantly the hydration rate of A1 oxide [26].

For several years, chromate transformation coatings have been extensively used for corrosion protection of aluminium alloys utilized in aircraft. The benefits of chromate transformation coatings are their self-healing nature, ease of application and electric conductivity [27]. However, the carcinogenic effect of chromate has generated serious safety problems [28]. The utilization of chromate generates costs related to worker's safety and the treatment and disposal of hazardous materials. Due to intense boundaries on its usage, trading, academic and governmental facilities need collaboration to find alternatives for protection of aluminium alloys [29, 30]. Currently, an urgent task for the innovative conversion coating is to investigate for actual, low cost, naturally compliant coating matrix and non-chromate corrosion inhibitors [31, 32].

In recent years, there has been an updated importance in pitting of aluminium alloys in the existence of chloride species. The majority of these researches have centred on comprehending centralized corrosion at and in the zone of impact of isolated intermetallic (IM) particles and, accordingly, a larger comprehending of the contribution to the corrosion on alloys such as AA2024-T3 has appeared [33].

Jingyi Yue, showed that the corrosion resistance of selected aluminium alloys with various combinations of commercial coatings was searched by means of the Tafel electrochemical method in water and simulated salt water environments. The combination of an environmentally friendly electrodeposited ceramic coating with an

undercoat and surcoat, which results in a chromium-free coating, exhibited a higher polarization resistance and a poorer-rate of corrosion than the customary chromate conversion coating combination [34].

Tracey A. Markley, studied the corrosion preservation technical methods for aluminium alloy utilizing chromatic are environments broking and very poisonous. This reported offerings the initial inspection through infrequent plant phosphate as innovative situationally kind corrosion inhibitive. Completed submersion weight loss tested, cycle potentiodynamic polarization quantities, with applied the R. spectroscopy to the corrosion protection technologies for aluminium alloys. Results show cerium diphenyl phosphate ($Ce(dpp)_3$) acts as a cathodic inhibitor, decreasing cathodic existing solidity and *E*corr by passivating cathodic intermetallic particles on the alloy surface [35].

Jun Zhao, confirmed the actions of chromate transformation coated on armed airplane alloy of the Al 2024 was inspected by some kinds of experimentations, applying Raman spectroscopy as an initial method. First, Raman spectra of the films make from the economical featured typical of Cr(VI) which was separate of pure $Cr_2O_7^{-2}$, CrO_4^{-2} in the Raman's band. Secondly, the Raman-spectroscopy has applied to display immigration of chromatic sorts from film of the CCC to a primarily natural alloyed example. Creation of the Raman's noticeable Cr (VI) including fast deposition inside or close to pitting from alloys which is not treated example, so a deposited is spectroscopic of the CCC films in an uninterested unique. A chromatic migrate is electively put at activate places of corrosion, either by making an unsolvable aluminium chromatic is electively put at energetic corrosion locations, precipitated or adsorbed of corrosion form in the late time [36].

Jana Vander Kloet was studied the face effect of behaviours to the surface features of Al alloys 2024-T3 before the presence of filiform corrosion (FFC). The nature of the surface earlier to coating and beginning of FFC, with specific regard to the intermetallic is searched in this study. The SKPFM (Scanning Kelvin Probe Force Microscopy), To F-SIMS (Time of Flight Secondary Ion Mass Spectroscopy), XPS (X-Ray Photo Electron Spectroscopy) and SEM (Scanning Electron Microscopy) surface examination mechanism were utilized to depict polished

AA2024-T3 before and after etching. The etching pre-treatment is planned to eliminate surface intermetallic and boost the oxide layer thickness. By the way, the treatment was incompletely positive: some, of the particles were removed from the surface and the oxide thickness boosted by about 25% [37].

C.W. Ziemian, showed that the impact of a cooling sprayed coatings and substance surfaces arrangement on cracking beginning under load cycle had considered on the alloys specimen of AA 2024. Substance specimen has arranged by face gritted attacking or peen proceeding to coatings. An exhaustion behaviours of both uncoated and coated samples were then examined under rotational benders circumstances at two strain stages. The outcomes designate that a fatigued powerfulness is importantly enhanced on the total, until fifty percent at 180 MPa and until thirty eight percent at 210 MPa, by the admission of the cooling spraying CP aluminium coating. Coated samples first arranged by the crystal droplet gritted attacking practiced the prevalent average boost in exhaustion life over bared specimen. The consequences parade a robust reliance of a fatigued starch on a faces preparative and parameter of cooling sprayed [38].

P.L. Cabot was showed that the oxidation and free corrosion of hydroxide-etched high-purity aluminium in deaerated HCl media at attentions in the range 0.6-2.4 M by means of the potentiodynamic and Galvano-static transient mechanisms has been tested. Pitting possibilities were selected from cyclic polarization curves. The stationary E_{corr} values lay 200-100 mV more damaging than the consistent pitting potentials for the attentiveness range calculated. The evolution of the electrode surface was studied by visual microscopy. For low existing concentrations, the anodic galvanostatic curves display a primary area of persistent possibility by means of particular low charges and a following potential slowly increases over to as though non-moving circumstances. When an existing densities boosts, the conforming time to like an primary regions reduces, screening the potential increase quickly and eventually, to the existing density around (0.3 mA cm^{-2}) primary found the maximum sharps. The cathode and anode Tafel's slope to the potential ($\pm$70 mV) about E_{corr} corresponding with the errors of experiment, exist (92RT/F). The prospective ascent founded at somewhat highest existing density resembles for hydroxides creation in struggle with chloride attacking. From the confident potential amount, the pitting is

nucleate, which spread from stable circumstances of the curve of Galvano statics. When existing practical increase, the attack metal is further restricted. Prospective decreases founded after the early maximum, for up-to-date density about (0.3 mA cm^{-2}) with highest, are imputed to pitting nucleated, the following area of stability corresponded to the pitting propagation [39].

In recent years, excessive energies had made appropriate to discover and to improve naturally approachable alternates to the (Cr^{6+}) early processing implemented on aluminium alloy applied in an airplane manufacturing. The further working examines of the corrosion prevent behaviour of silica nano-particle implemented on the substrate of AA 2024-T3 alloys. Corrosion behaviour is examined from (0.1 M NaCl solutions with d.c. polarizations and EIS. related angle capacities and XPS are utilized to evaluate data on a chemical of a silane pre-treatment surface. The consequences had revealed that the primer of additional develops the corrosion protections possession of a compound of silicon layers [40].

Brettc. M. A., et. al. showed that the inhibition of the corrosion of pure aluminium by nitrite and chromate anions in nearby neutral aqueous chloride solution has been searched by electrochemical resistance spectroscopy, maintaining the ionic powerfulness constant by totalling of potassium sulphate electrolyte. Negative of the chloride pitting potential resistance spectra display that both anions are fruitful in reducing corrosion through adsorption, nitrite more than chromate. Positive of this value, nitrite becomes useless; whereas chromate stays adsorbed and goes on to deprive pitting corrosion, probably through its capability to fix flaws in the oxide film. Resistance mechanisms effectively display the qualitative and quantitative distinction between the two inhibitors [41].

The creation of chromate-fluoride alteration coatings is searched to the dual aluminium Cu alloys and Al 2014-T6 Al alloys so that to realize the effects of Cu on coatings progress. Cu is revealed to division factor of the coatings layers after special coatings time. The separation time was reducing with boost in the concentrated of Cu in the solid solutions in the separate alloys areas. The fact of occur following enrichments of Cu from alloys in the primary phases of the coatings creation, from the principal hydrated chromia layers of flaking near to the face alloys. It's

recommended that is conduct is interrelated for the incorporated of microscopic particle of Cu from the coatings [42].

The aluminium alloys have less magnesium and high amount of copper magnesium with mass ratio 3.7 had characterized to offer contribution information for micro scales and corrosion macro scales representations. The alloy aluminium 2024 microstructural have important attendance of Nano-scales dispersion and micro scales Al-Cu-Fe-Mn-Si second face inter-metals particle, but the small population of micro scales S phase Al_2CuMg and h phase Al_2Cu inter-metals particle. Micro scales electrochemistry information show that pitted probable (SCE) standards for second stage, S phases. The localized corrosions vulnerability is impacted by S and nonhomogeneous second stage atoms. To the more decades the aircraft manufacture have utilized aluminium 2024- T3 or 2024-T351 alloys for design of aerospace which had optimized for mechanically toughness. In the techniques of aerospace manufactures and long condition uses, it is significant to illustrate corrosions origination contrivances of aluminium 2024 alloys [43].

M. Iannuzzi's and the G.S. Frankel's studied the instruments of corrosions inhibitors of Al 2024 by the vanadinite were calculated by means curves of the chronoamperometric, polarizations and adhesion of atom lines. The electrochemistry conduct of pure solution comprising meta-vanadinite and orange solution comprising deca-vanadinites was obviously different. Meta-vanadinites reduce the kinetic of oxygen reductions to the same chromatic point. Corrosion inhibitor of the aluminium 2024 by meta-vanadinite was so fast and it may happen by the creation of adsorption layers. The reduced of obvious metavanadinite solutions were too slow. About thirty five minutes were obligatory to grow the mono-layers of reduction vanadinite classes. The adsorbed of inhibition expectedly jammed responsive places on inter-metals particle, depressing the oxygen reductions response. Adsorbed of the inhibitors on aluminium matrix also could transfer Cl ion, boosting the steadiness of the inactive films and reduced failure of S-phase particle [44].

Aluminium and aluminium alloys offer themselves to a lot of engineering implementations due to their slightness joining with power, their high corrosion confrontation, their thermal and electrical conductivity and low cost. The principal

implementations of these ingredients are in aeronautical, motorized and food industries. Compared to pure aluminium, its alloys are gifted with better automated possessions but with lower corrosion resistance.

J.W. Silva's, showed that It has been utilized a fresh copy inspections way, according to division by form parameter, for the pitting morphologies inspection from aluminium 2024 Al Cu alloys in HCl watery solutions. Corrosions behaviours of these alloyed in natural aeration of 3.5% NaCl solutions had examined into the potential assessments of opened circuits. Then, pitting has been categorized by images analysed take densities and size assessments in the corrosion surface. Morphological examination has been done for profile, cut related from mean face plane, and detected into lights microscopies. The Image analysed information can prove that pitting is broader than the intense, evaluated for unequal forms [45].

CHAPTER TWO

THEORY

2.1 Corrosion types

In the further discussion, we mention the general metals loss as general corrosion and localized corrosion. There are different types of corrosion, some are very commons and it could be seen in every days of the life, while there others are rarely seen except in very specific combination of materials and environment. The studies of corrosion involve such detailed knowledge of specific forms and their specific environments. To better understand corrosions and then to find the right mitigation and controlling method we need to know the different environment for different types of corrosion.

2.1.1 Uniform, or General, Corrosion

If we put aluminium in a soda solution or a piece of zinc in a hydrochloric acid solution. Uniform diminish of the metal's thickness will be observed. If we put a piece of carbon steel in a furnace at high temperature, we will observe the formation of even iron oxides film on the steel surfaces. Uniform, or general, corrosion is a type of corrosion attacking uniformly distribute over a metal surfaces. General corrosion is commonly recognized as rust of iron, or tarnishing of silver or fogging of nickel. The rate of uniform attacked is reported in different units. the most accept terminology in penetrates of corrosion is mil per year, millimetre per year (mm/year), or inch per year (ipy), and in terms of weight loss measure, it was report in grams per square meter per day (gmd) (a mil is a thousandth of an inch [0.001 in] and is equivalent to 0.0254 mm).

Examples of the average time, general corrosion rate values for steel corrosion in a seawater environment are showed shown as 0.13 mm/year, (mm per year) or 0.005 ipy (inch per year). R.W. Revie and N.D.Greene, concluded that the

corrosion magnitude is greater in the initial stages; hence, the period time of exposure should always be reported. Extrapolation data is not always safe in this regard.

In the corrosion rate, metal density also plays a significant role; hence, knowledge of metal density is essential for correct reporting of corrosion rate in ipy or mm/year. The weight loss given per unit area for light metal signifies a much greater actual loss than the same weight loss of a heavy metal.

For general corrosion purposes, the rate of corrosion is variously classified by different writers, but NACE in its corrosion data survey reports four levels, as follows:

- Less than 2 mils (0.05 mm)/year
- Less than 20 mils (0.508 mm)/year
- 20-50 mils (0.508-1.27 mm)/year
- Greater than 50 mils (1.27 mm)/year

Uhlig and Revie, describe the rate of corrosion in the various stages which as 0.15 mm/year (0.005 ipy or 5.9 mil): Metals in this category have a good corrosion resistance to the extent that they are suitable for critical parts (e.g., valve seats, pumps shafts, and impellors). From 0.15-1.5 mm/year (0.005-0.05 ipy or 5.9-59 mil): Metals in this category have a satisfactory performance, if a higher rate of corrosion can be tolerated (e.g., tanks, piping, valve bodies, and bolt heads). From 1.5 mm/year (0.05 ipy or 59 mil): Metals usually are not satisfactory in this category [46].

Common techniques applied for corrosion protective and control which are based on the general corrosion rate. The corrosion protection principle is to provide an electrical barrier between the cathode and anode for example to the coating and passivation of the surface.

2.1.2 Localized Corrosion

The uniform general corrosion is spread of corrosion over a large surface area in the form of 'rusting' or tarnish. In contrast, localized corrosion of the metal surface occurred on specific sites and in specific environmental conditions. Corrosion activities on these specific sites might be start and stop with a change of the environment. The surround area of the corrosion sites are often not affected by corrosion. In localized corrosion, the rate of corrosion on the same material is greater in some areas than others. Many different types of localized corrosion that are very specific to the environment and metal include:

- Pitting.
- Fretting.
- Crevice.
- Filiform
- Cavitation.

2.1.2.1. Pitting

Pitting is a narrow deep having the tendency to cause of carrion attack which often rapid penetration of the substrate. Pitting is localized as the surround metal remains unaffectedly. The initial activities start with a "flaw" in the metal surfaces that have different potentials than the surrounded metal surfaces. A flaw may be caused by a break-down of passive layers, such as coating rests, stainless steels, change in the structure of metals, or microbiological attacks caused by bacteria.

Pitting involves of the continuum mechanism, a cell between the interior of the pit and the external surface. The interiorly of the pit often contains tendency corrosion acids and hydrolysed salts. The anode has established inside the pit and the surround surfaces have become the cathode, a corrosion cell initially between inside of the pit and the external surface. The pitting is a deep depth of the pit was concentrating in a few area of metal that is arrack as anode for example; the corrosion of a stainless steel immersed in seawater shows deep pitting. Conversely,

shoal pitting is a depth of the pit dispersed over a larger area for example; the corrosion of an iron pipe buried in soil shows shoal pitting. Pitting factor is the ratio of depth metal penetrating to mean metal penetration determined by weight loss at the specimen. The corrosion pitting appears in different phases, these phases can be identified as:

- **Initiation:** pitting starts at the defect sites or imperfections in protective coating or at the locally loss of passive films as in the stainless steels. Once the initiation begins the corrosion activity is rapid.

- **Propagation:** Corrosion is driven by the difference of potential between the anode pitting and surface external of the surround metals. The environment, often acts with the pitting like an electrolyte and the cathodic area outside at the pitting edge completing all the elements that required for sustaining a corrosion cell.

- **Termination:** A pitting could terminate, if the internal of the pits have stopped being an anode for example; by the pit filling with corrosion production pitting or by the corrosive environment removals.

- **Reinitiating:** The pitting can start again, if the termination pitting was rewarded or corrosion productions have removed.

2.1.2.2. Fretting

Fretting is phenomenon of localized corrosion that has is caused by mechanical stress. It is the result of slight relative motion or as in vibration of two substances at least one of them is a metal, that are in contact and were not intended to have relative motion in that mode. Fretting manifests itself as a series of pits at the metal surface. Usually metal oxide scrap fills the pitting mask the pits, unless the corrosion product is removed. Such damage has appears from the interface between two surfaces which can move with respect to each other. The surfaces are free of any corrosion products and appear glossy. That could be result in oxidation of the surfaces or galling, fatigue, or seizing, eventually the materials cracking involved.

2.1.2.3. Cavitation

Cavitation erosion results from the formation and collapse of vapour bubbles at a dynamic metal-liquid interface. This collapse of bubbles causes pits, and often cavitation appears as a honeycomb of relatively deep fissures. An example of this type of corrosion can be found on the rotors of a pump or on the trailing edges of ships 'propellers.

2.1.2.4. Filiform

Filiform is happening by the specific oxygen cell appearing under the organic or metals coating on materials. Its occurring as a fine random network thread of the corrosion production developed under the coating material. Beneath of relative humidity in excessive of sixty percent (60%), filiform mostly occur on surfaces at lower level of the coatings. The corrosion mechanism for filiform is same to the crevice corrosion, that has determined by the difference in potential between the advancing head of attack and the surrounding areas of it. This form of corrosion advances in a filaments of about 0.1mm (0.01 cm) wide, where the head of the filaments become to the anode, as comparison to the sweeping cathodic area. The pH of the area immediately at the rear head of the filament is very low, also with notable absence of oxygen. The corrosion follows to the cathode as it chases the anode head. Metal oxidations are formed as a corrosion production.

2.1.2.5. Crevice

Crevice corrosion is happening by the difference in potential from the concentration of materials outside and inside the crevice, often as the result of a design 'flaw' that restriction of the free flow from the environment between the surfaces. The crevice corrosion is a form of corrosion which as the sites of the corrosion has restricted access to the environment surrounds. The crevices appear at the common boundary region and metal or metal and non-metal. The crevice corrosion mechanism may due to either metal ion concentration cells or oxygen concentration cells. Oxygen concentration cells are occurring by segment junctions, crevices, insulation. Below different conditions, oxygen work for as the anode while, areas that are reveal to oxygen are contemplated as cathode. The most common reaction of this typical reduction of the oxygen or water in one of the following modes, in which oxygen is the reactant.

$$2H_2O + O_2 + 4e^- \rightarrow (4OH^-) \text{ Water reduction} \quad (2.1)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \text{ Oxygen reduction} \quad (2.2)$$

The basic principle is that an increase from the concentration of reactants will further drive the reaction, implying, in turn, that a building up of reaction production will stifle the reaction. In other words, the build-up of corrosion production will stifle the corrosion process in the crevice.

2.1.3 Galvanic corrosion

This form of corrosion is taking place due to the potential difference between two metals or between metals and conductor of non-metals, when they are electrically connected in an electrolyte environment. Act of this configuration of materials forms, an electrochemical cell. The electrical connectivity may be direct or through any external path conduction. The impacted of the non-metals in galvanic corrosion is revealed by the conduction of non-metals, such as the presence of carbon and graphite in the plastics and corrosion production such as magnetite (Fe_3O_4) and sulphides that are often cathodic with respect to most metals. Ions of more outstanding metals maybe reduced on the surface of a more reactive metal, the resulting deposit reacts as a cathodic site potentially generate of more galvanic corrosion cells on the surface of the more reactive metals. Often galvanic corrosion can be recognized by one of the other two below conditions.

- By increasing corrosion of anodic material
- By decreasing corrosion of the cathodic material.

The corrosion reaction is more conspicuous, where different materials are placed instantly adjoining to each other in a corrosive environment. The earlier stated of the galvanic corrosion is an electrochemical cell reaction. For necessary elements that required occurring the galvanic corrosion are (anode, cathode, metallic path and electrolyte).

The electrons flow through a metallic path from anodic to cathodic sites in the existence of an electrolyte, which allow the ions to flow. In most galvanic

corrosion plots, all four essential elements are readily available. The metallic path, anode, and cathode are present in the metals [46].

2.2 Cost of corrosion

The study of corrosion cost conduction jointed by C. C. Technologies Inc., U.s. Federal Highway Agencies (FHWA), U.s and National Association of Corrosion Engineer, the direct corrosion cost was estimated to be around 276 billion U.s dollars, approximate to 3.1% of the national gross domestic product. Based on an extensivation pre-survey conduction by Battelle Columbus Laboratories' Columbus, Ohio, united states of America (USA) and National Institute of Standards and Technology (NIST), in 1975, the estimated cost was to 82 billion American dollars, which would have transcend 350 billion American dollars in-view of rising price over the last twenty-five years. Because of the long-time involved, in conduction cost structure, it's not possible to updating the information every-year. However, both studies view that corrosion costs are staggering and a figure of about 350 billion American dollars develop to be a sensible estimated for another two to three years. At least thirty five percent of the above amount may have been kept by taking proper measuring of the corrosion control. In the United Kingdom the cost of corrosion estimated to be 4–5% of the GNP. From the Japan country, amount of the corrosion cost has estimated to 5258 trillion Japan's Yen per year. For most industrial field, the average cost of corrosion is 3.5–4.5% of the GNP.

The estimated cost of corrosion to the gases and liquids transmittance pipelines in United States of America transcend seven billion American dollars. The image for the countries that producing oil in the Gulf region unknown however, the cost of corrosion is considered to be very high because of biggest corrosive environment in the region .The corrosion, free-life of the automobiles in the coastal regions of Arabian Gulf countries are only about six months. Near to ninety five percentage damage concretion in the Arabian Gulf countries in coastal region was caused by increased corrosion and consequence rocking of concreted. That was estimated ten percentage from all aircraft field in United States of America that is spent on corrosion resistance. Disadvantage of annually corrosion to the uniform cost approximately are three hundred fifty million pound in transportation and two

hundred eighty million pound in marine. The other more cost which are two hundred fifty million pound in construction and buildings, and one hundred million pound in in chemical and oil fields, have been reported in United Kingdom. These are non-correct image in 1971. In the united stated of America about one hundred twenty billion dollars are spent for conservation of aging and deterioration in (e.g. buildings, roads, power supplies) from United States of America [47]. The annually cost of corrosion in car industrials 23.4 billion American dollars from united stated of America.

2.3. Basic Introduction of Aluminium Alloys

More than 110 years past Charles Martin Hall's, an US, and Paul Heroult. The Frenchman's individually development the procedure which allowable the commercial producing of aluminium by electrolyze from a fuse salt baths. Though Al is a 'latecomer ', it have caused it replaced more orders, many steady material, thus now it is uses, on the volumetric based, further all not ferrous metal collected, included lead, zinc and copper [48]. The Al was lightly, malleable have a suitable thermal conductivities and electrical and could be created solid by alloys. The beneficial organic properties of aluminium are it is reactive with (O_2) which causes the thick layers foundation of Al_2O_3 on the face this protects the basis metals from farther environment fundamental interactions.

Table 2.1 Aluminium Alloy Designation System [49].

wrought alloys	
Alloy Series	**Principal Alloying Element**
1xxx	99 % Minimum Aluminium
2xxx	Copper
3xxx	Manganese
4xxx	Silicon
5xxx	Magnesium
6xxx	Magnesium and Silicon
7xxx	Zinc
8xxx	Other elements
Cast alloys	
Alloy Series	**Principal Alloying Element**
1xxx	99 % minimum Aluminium
2xxx	Copper
3xxx	Silicon Plus Copper and/or Magnesium
4xxx	Silicon
5xxx	Magnesium
6xxx	Unused Series
7xxx	Zinc
8xxx	Tin
9xxx	Other Elements

On the other hand, problem is realized if the layers are problem, for the instance by second phase, malleable distortion which fracture the protection layers, or by brushing chemical reactions. The four digits mathematical numbers are used for identification of Al and alloy. The system are used for the shaped alloy is some dissimilar from used to the casting alloy and both were showed in the Table 2.1 [49]. To the wrought alloy first mathematical signs assembly alloys which is estimated by main alloying element. Other last two digits recognizing the Al alloys or view purify of aluminium. Modifications of the originals alloys or impurities limits are showed by the next numeral.

First digit sign, which use for cast alloying and founding a block of metal also identification the group alloys by main alloying element. However, the alloy of Al or purify of Al is identified by second two digits. The last digit, followed by a point numbers, shows the producing form (for example '.0' to the cast and '.1 ' to a block of metal). A series letter before the numeric designated indication modify of the originally alloys or impurities limit. The serial signs are set alphabetical, but

removing ‘T’.”0”, “Q “. And/or 'X '. An X can be kept for the purpose of experimentally alloy.

The tempering designated system is conducted to the all form of wrought and/or east Al and Al alloying excepted ingots, which is based on the progression of basic treatable, aimed to create the various temper. The tempering designated goes after the alloy designations, a hyphen separate the two. Basic temper designations comprise of letters: F-as fabrication. O-annealed. H-tension hardness (wrought products only). Wsolution heat-treatable, and T-them ally treatment to produced stable tempering another than F. O. or II. Other division of the basic tempering, where requirement, are indication by one or many digit letters.

Microstructure possesses a proper influenced upon numbers of design-critically mechanic properties, which are labelled in Table1.2 [50].

Table 2.2 Property-microstructure relationships in aluminium alloys [50]

properties	**microstructure features**	**feature function**
Yield strengh	uniform dispersion of fine hard	inhibitor dislocation motion
Toughness	no constitent particles. Clean boundaries of grain	encourage plasticity inhibitor aginst develop
Ductility	low dislocation clean bounderies of grain no constituent particles	encourage plasticity inhibitor aginst develop
Creep	thermally stable particles. On grain boundaries. Large grain	inhibitor grain boundary sliding
Fatigue crack initiation	no shearable particles. well grain	limit magnitude of slip step at
Fatigue crack develop	no shearable particles. No abodic phases or interconnected	encourage crack closure. Branching. Deflection and slip reversibility
pitting	no anodic phases	prevent preferential dissolution of second phases particles
stress corrosion cracking hydrogen embrittlement	no anodic phases or interconnected hydrogen traps	prevent crack propagation due to anodic dissolution or hydrogen embrittlement
thermal electric conductivity	no particles with elastic strain field. Low solute concentration. Low dislocation density	limit scattering sites for electron migration

Along with desirability microstructural feature and their function. The appropriate microstructure for an aluminium alloys applications able to identification after the designer clarifies what the properties would be critically in the designation of the element. First standard sign may include tensile and yield starch, the fracturing strength, loss of the resistance strength, or conductivity of thermal electrical, only to

few name. The concept using of microstructural designing, the primary stage is to identification the basic properties of interest. Secondly, microstructural features allows each of the aims to be accomplish or identified. In the final stage optimize the microstructure is determined to provide a possible balance of the importance properties.

The concept affects in the metallurgical engineering of aluminium alloys contained the effected of the structure the mechanical working, or with heating treatments on physical or mechanicals properties. In this properties condition, starch determination of major object in the plan of aluminium alloys because of the low tough of the pure aluminium is about a 10 MPa. or 1.5 ksi. Tensile yield tough in the cooling condition, it has limit commercial benefits. The metallic that have most common presented in commercialized of aluminium alloying for provided increased toughness, particular when coupling and strained toughness by cooled working or with heating treatment or both of them are Cu, Mg, Mn, Si, and Zn. the classification of Aluminium alloys are heat treatable and have not heat treatable. Non-heat treatable of aluminium alloy constitution group of alloy that trust exclusive cooling working and solid solution starchiness for their toughness property.

Aluminium series which are 1000, 3000, 5000 and some of the 8000 series alloy have not heat-treatable. But the 2000, 6000, 7000 and some 8000 series alloys have consider as heat-treatment “precipitation hardening”. Those alloys containing element that decreased insolubility with decreased temperature, with in the strength of the solution that in the important manner pass to their equilibriums solid dissolution at room and mildly high temperatures[4].

2.4 Corrosion of the aluminium

Al is the second most plenteous metal component on the plant [51]. Because of the low strength of pure aluminium (about a l0Mpa, or 1.5 Ksi, tensile yield strength in the annealed condition), it is alloyed with small amounts of other constituents, such as copper (Cu), zinc (Zn), magnesium (Mg), manganese (Mn), iron (Fe), or silicon (Si). Aluminium alloys have very important applications in the aerospace, architecture, transportation and manufacturing industries.

Aluminium is a thermodynamically reactive metal based on its position in the electromotive force series; among structural metals, only beryllium and magnesium are more reactive. However, aluminium has excellent resistance to corrosion in most environments, which is attributed to the passivity produced by a protective oxide film. This film is strongly bonded to the surface of aluminium, and if damaged reforms almost immediately [51].

Unlike pure aluminium with a homogeneous solid solution phase, aluminium alloys are composed of a solid solution phase - the aluminium matrix - and another phase consisting of either pure alloying ingredients or the intermetallic components. “Because the permanence of the protective oxide film on the surface is affected by the microstructure of the metal, and in particular, by the presence and volume fraction of second-phase particles, the electrochemical properties, and corrosion resistance are strongly affected accordingly”. Composition of hard solution and added stages, in addition to quantities and spatial divisions of the additional phases, can affect both the type and extent of corrosion. Because the second-phase particles have different potentials from that of the aluminium matrix, the localized galvanic cell can be formed between second-phase particles and the aluminium matrix, and localized corrosion occurs at weak points on the protective oxide film in contact with an electrolyte. In the local corrosion cell, aluminium matrix frequently becomes oxidized and dissolved. Pitting corrosion is the most common corrosion form of aluminium and aluminium alloys [52].

For corrosion of a metal to take place, four conditions need to be satisfied. The first process is an oxidation or anodic reaction. The second is a reduction or cathodic reaction and the third is ionic transport for which a conductive electrolyte is required, such as water, seawater, or an acidic or basic solution. Finally, the fourth process is electron transport between the anode and cathode. If one of these processes is not present, corrosion will not occur. If these alloys are left untreated, they will corrode at a rate depending on the alloys composition and local environment. Generally, aluminium is resistant to most environments due to a layer of oxide film, which forms on the surface and reforms rapidly if damaged. However, this film is an insufficient barrier for relatively long term corrosion protection. This is because aluminium is able to react both as a base or an acid, which means its oxide

film is stable in neutral conditions but soluble in acidic and alkaline environments. This relationship is expressed by the diagram, which shows the relationship between potential and the solution pH. (Figure 2.1) is the diagram for aluminium, which specifies the conditions which Al shall view corrosion. The resistant of Al to corrosion be contingent significantly on it purify and microstructure. Pure aluminium is more resistant than any of its alloys. The most common form of aluminium corrosion is pitting, which is a localized corrosion form. It has been attributed to the breakdown of the natural passive film on the metal. The resistance to pitting corrosion is then determined by the electrochemical stability of the protective passive film. The tendency for pitting for a given metal electrolyte system is defined by the pitting potential (Ep), which is the potential above which pits will initiate and below which they will not. For aluminium, pitting corrosion is most commonly produced by halide ions, of which the chloride (Cl^-) is the most frequently found. The presence of chlorides can construct native corrosion potential drops between the metal surface and the obstructed region at which the chloride is accumulated. Chlorides facilitate the breakdown of the oxide film by forming $AlCl_3$. When aluminium ions migrate away from the pits, alumina precipitates as a membrane, which further isolates local acidity and pitting of the metal results. Pitting can be separated into two different stages, namely pit initiation and pit growth. While the growth mechanism is well understood, the initiation mechanism is not very clear. However, pitting has been viewed to pledge at fundamental elements, which are also anode or cathode relative to the matrix. Local connections among the atoms and the matrix improve the rates of pit development.

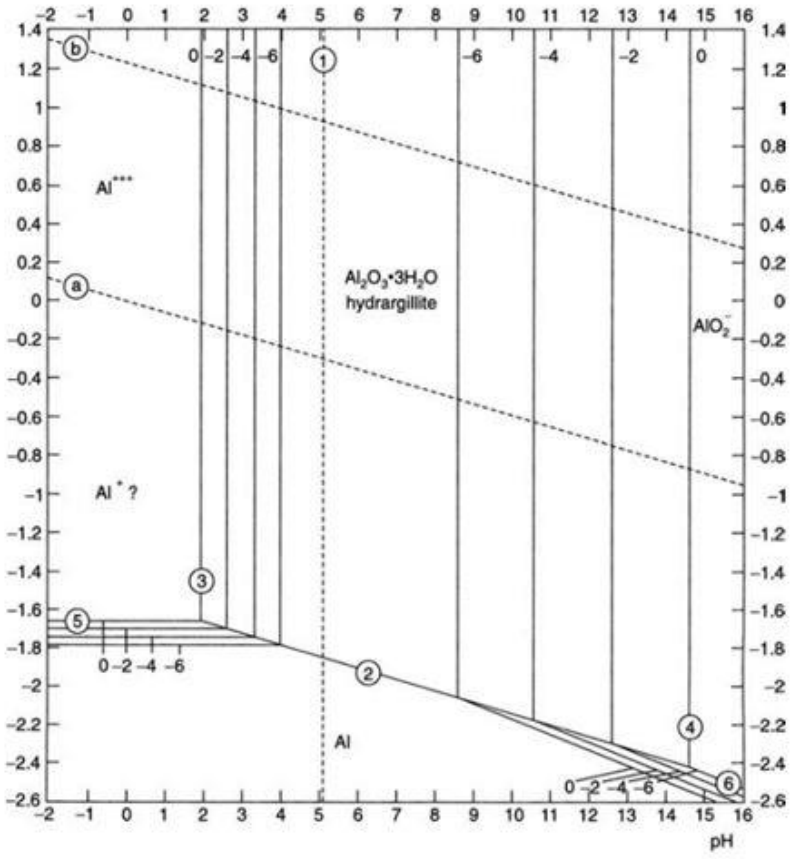


Figure 2.1 Pourbaix diagram for Aluminium [52].

2.5 Coatings

There can be two ways to protect Aluminium which are by formal plating or by electroless. Al and Al alloy could be acting as sacrifice anodic in the shape of Al clad tray or as coating practical or long for period time sacrifice anode on term that did not passivation in the particular mediums. The aluminium alloy could be preserved by cathodic protection or by more of active metal. Aluminium as a protective coating can be used for metallic powder application. The magnesium can be useful as initial colour for painting coatings systems which as include organic and metals coatings, were used in the more industrial works as essential need to provided protection of environmental corrosives and result in extending life-time of the protection structures. However, both of coating metals and organic coating utilized to protecting of most coating metals, usually can perform as the sacrifice anodic in a substrates couples of coating like to zinc coatings on steel metal and the Al clade layers on Al alloy, although the organic coating give main protects into the properties

of the film structure. From the some industrial technology like “aircraft industrial” the other coatings productions and corrosion prevents compound (CPC) were also used to give protections to the internal surfaces.

The system of organic coatings made up of a primer modification coatings and a prime coating. Occasionally, inhibit like a chromate is embodied through the organic coatings to farther inhibitor corrosion. The other researchers were operating on enhancing a professional coatings system into inhibitor could be received to corrode sites as need [53].

The protections provided by main organic coating was taken into consideration through the isolations in the violence environments, by adhesions against corrosions start from interface of the metallic coatings, and during the occurring coating the change structure taking place [54].

Hence, more times coatings are better choices when they have good barrier properties for separating the corrosion environments from the protection structural, however more times having a porosity coatings is necessary in order that the penetration electrolytes could precipitate the inhibit activity of the colouring from the coatings[55]. Hence the corrosion is possible to begin if rough specimen and water are transferred from the defect in coatings and affect the substrates coatings interfaces. The identification of initiation of failure corrosions coating, commonly could be with an inspected visual because the failure of protected in the organics coating are generally to the formations of bubble and delaminate area. Hence, the failure generally could not be verified till the late corrosion stage. Many time is required to recognize corrosions at ~~a~~ further stages to decrease impacted corrosion and to reducing over-all maintenances that was needed. Hence, it is highly important for the corrosion engineer to monitor coating degradation continuously during the process.

2.5.1 Convention Plate and Electroless Plating of Aluminium

The use of Electroplating of Al alloy is sometimes to give resistant to the corrosions while other anode treatment use of phase modification and provide prevent corrosion efficient. Hence, the use of electrolyte coating metals is to achieve

appearance metal certain, that improve friction properties, increase electric conductivity, and determine solvability. Electroplating Al base alloy is harder to process due to high passivated aluminium oxidation shaped on a surface. The metal is more generous than the alloys and any against, discontinuing, and scratching able to leading localize corrosion. The most established plating method seems to be electroplating with the nickel copper and is presently taken benefit in aircraft industrial and electronics technology application. Nickel is chemical plate on parts of aluminium with complex shape, for instance, integration electronics circuit. The different numbers to reduced agent is used recently in operate electrodeposition nickel bath like a sodium borohydride, sodium hypophosphite, amino borane and hydrazine. The sodium hypophosphite bath is currently being used. The advantage fundamental is lower cost [4]. Aluminium become possible to be plated by the using pre-treatment zincate in order to removing aluminium oxide films. By using a pre-treatment of zincate, the homogeneous of a zincate films is able to be increased. This involves strip of the first deposit sheet and perform second treat for homogeneous of a zincate films. The commercially hypophosphite nickel electroless layers could be aimed to bumps. The value of power hydrogen pH was 4.5 and bathing is processed at 90 ^{0}C. The metal plating rates of (twenty five mm/hour) is achieved. The electroless of this electrolytic contained ten percent phosphorus. The deposits Nickel deposition on Aluminium Integrate Circuit deposit plating are the electrocatalyte operation similar to the chemical reductions of metallic ion on the substrates in watery solutions. The depositions develop essential linear with the time and completely heavy deposition could be resulted in producing analog to this produce by conventional plating. Hence, electroless plating is able to create a uniform thickness and layer while the non-uniform current distribution in the plating cell was avoid [56].

2.5.2 Sacrificial Protection by Aluminium Alloys

The alloy of aluminium clad are build wrought production, its shapes are in the sheets forms, and tubing, hence, has cores of aluminium alloys and a coating on one or both side of Al alloys. The claddings on the each side are from 2 to 5 percent of total thickness. The metallurgical coatings and heavy adhesions to the substance. Usually the coatings are considered to be anodic the substance alloys in several

nature environment and would galvanic protection the substance, where reveal from edge cut, scrapes or stud hole. The aluminium cladded alloy could be even-more resist penetrative by the neutral solution than any other Al alloy. The both prevention and reduction of corrosion can happen by the clad with corrosions resistance alloys, to the occurrence of high aluminium purities, the one percent of zinc alloy and or few alloys of silicon magnesium. Often of those cladded materials are working to provide corrosion resistance to the Al 2xxx and 7xxx series alloy [57].

For the cathodic protecting of steels in seawater, sacrificial aluminium anodes were used. The most Al sacrificed anodes are casting alloys of AlZnIn, AlZnSn or and AlZnHg containing around 94 to 95% of Al and 3.5 to 5% of Zn. The additional of gallium which is from 0.01 to 0.1% or mercury 0.05% have been used for sacrificed anode against passivating prevention. The alloys of aluminium zinc alloys with very little of Sn (tin) which is 0.01% in commercial rank Al is make darkness surfaces on cooling and increasing to corrosion susceptibleness, which due to move of Sn (tin) to surfaces. The small additions of copper (0.2%) may reduce such an impact. These alloys could work in environments only where aluminium is still active [57].

The aluminium as sacrificed anodes to structure of steel will show potential to non-alloyed of metal which is 99.5% pure metal in a range of 0.6 to 0.8 and various with the environments, since the Al alloy exhibiting various of potential both of them sufficient active to be used as cladded material for other noble alloys. The copper have an efficient effects on the anodic alloys and it has been suggested a minimum of 0.025 of mercuries was need to the reasonably anodes activities. When copper and iron are in the low levels, the good performance could be obtained with 0.04% of mercury and 0.4% of zinc. Zinc in high level is advantageous in anaerobe mud. Another alloys develop groups are all of general tension, as used indium from 0.005 to 0.03 wt % which the Principe alloy metals. Generally with high purities of Al and some of Zn, the anodic capacity was high and it works near to ninety percent efficiencies, it show that drive force is higher than the anodic mercury, usually from the 0.3 V to the protect steel or 1.10 Volt to Ag,AgCl and KCl electrical conductor.

The sacrificed Aluminium spray coating, the spraying of Al is a current function to coating less of resistance alloy. For the some composition, galvanic action controls the corrosion behaviours between the reinforce materials and Al matrix. The thermal spray of aluminium was a successful technique of protection for non-continuous silicon carbides Al composition which has been reported recently; to the continue Al graphite or silicon carbide Al composition, H_2SO_4 anodize has provide protective, which has organic coating or iron vapours deposit Al [52]. Even more recently works on the corrosion protection of aluminium alloy was done for aircraft technology application by spraying sacrificed coating have been reported. That could be apply in locate maintenances. In one studied, the coatings 125 mm thickness is enough while single 12.5 mm were used period 1000 hrs of immersed by the alloys coated disturbed and treated 3.5% solution of chloride sodium at 25 ^oC. The Al 5 Mg sprayed mixture of metals offer similarity protect which another sacrificed coating bases on aluminium, zinc, aluminium zinc or zinc 15 magnesium, though it provides the least sacrificed currents. Those coatings are able to provide good performances in alkaline environment while Mg suggestion good resistant than Al to corrosion of cathode. Those coatings are able to stop corrosion stress crack; nevertheless, when it comes to pitting's corrosions it's not too effective while potential pitting was lowest than the mix-potential of a coatings and the substrates. Although pitting, retarder, able to leading to trans-granular break and the corrosion tiredness break. Also, it has been demonstrated corrosion medium is able to infiltration into the tiny holes of the coated for alloys coatings user interface like to that observation with clades alloy [58].

Steady, Al Anode for impressing cathode protects system more local water installing has been kept used impressing cathode current system. The characteristic system takes advantages of the anodic aluminium to make protection for internal surfaces of steel artificial lake and pipes. The fundamental attractions are:

In the anodic:

$$\mathbf{Al \rightarrow Al^{3+} + 2e^{-}} \tag{1.3}$$

$$\mathbf{Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^{+}} \tag{2.4}$$

In the cathodic:

$$\mathbf{Al^{3+} + 2e^{-} \rightarrow Al} \quad (2.5)$$

The anodic reaction causes to create hydroxide aluminium in a colloid shape since the cathode one devours oxygens. Hydroxide Al shaped, on the order of (0.1 to 0.2 mm) thickness, acting as a layer protection for internal cathode surfaces of the lake that could be created of steel, copper and or galvanize steel. The power hydrogen pH of the water must be set up among 6 and 8.5, as the passivate region of anodic aluminium. Steel or aluminium could be path to using as expendable anodic in seawater for protective cathode impressing system currents. Both work at highly efficiency than in refresh water, the steel being efficient around 90 to 100% since Al was about 50 to 90%. Nevertheless, permanently anodic producing from the leading alloy or platen films electrode were the two most possible [58].

2.5.3 The Aluminum alloy by using Cathodic Protection

The cathode prevention needed smart controlling to assure that sufficient prevention is obtained except excessive protection, which could cause cathode corrosion. Aluminium cladded alloy may show as have a self- containing prevention of cathode system [58].

Buried Al pipelines are always persevered by sacrificed anode zinc for coating line and magnesium for non-coating line. The impressing current detector system is not used to protecting Al pipes [57]. The parts of aluminium alloys in some applications, structural assembly and pipeline were protection cathodic. Shifting the potential is suggestion practically at 0.15 Volt but not further value of 1.20 Volt opposite a saturate copper $CuSo_4$ the references electrolyte. The high current of the cathode could solve adequately alkaline to serve corrosion of important cathode. In a some soil, potential as lowest –1.4 Volte had been come across except substantial cathode corrosions.

2.5.4 Conversion Coating

The conversion coating is the most famous techniques to pre-paint treating procedure for metallic substance. The conversion layer are able to modifying

surfaces of Al to have good adhesion, the free surfaces of contaminant, or the coating layers that contained activate corrosion inhibitive. Conversion coatings are chosen ~~base~~ based on the corrosion prevention function and colored treatment. Corrosion protection, at the least partly, could be maintained throughout passivate of a metal based of the aluminium, by producing a block avoid wetness, by the oxygen and another rupture factor, by the electro chemicals insulations, and by prevention opposite mechanically eroding [58].The united stated aircraft technology highly recommends coatings to be used for painting or repainting existing aircraft fleets.

There are three individual coating layers in a standard coating system. The conversion coating of first layer was creating substance treatments. Usually, conversion coating was very thinness which is from 10 to 60 nm inorganic layers that gives corrosion prevention and developed adhesive among substance and primers of a second layer to a coated system. The usage thickness of the primers could be varied 5-200 mm though the thickness of 25 mm was typical intended due to having weight constraint on an aircraft. The priming was primary principle of the prevention corrosion. The principal widely known conversions layer were from electrochemical anodic, plasma extirpation, and chromatic converse coating [29].

2.5.5 Anodizing

Anodizing is an electrochemical method in which it can convert aluminium to oxidation aluminium at the surface of pieces of aluminium. Anodizing Al surface endure corrosion and also enhance the corrosion resistant of the alloys to weather and other corrosion conditional. Anodized can be used in every location where Al item were produce. The anodized was use for Al more except the metals element, like to magnesium with titanium. For a film sample from 5 to 7.6 mm thickness was normal specified for brightness automobile trimness and from 17 to 30 mm for architecture production finish [58]. An electrolytic oxidation is a process of anodizing in which the surfaces of the alloys become the anodic and was transformed through aluminium oxidation amorphous, thickness from 3 to 30 mm layers, bounders as tenacious to the alloys as the nature oxidation films. Anode coating, particular these apply in the sulphur acid electrolytic and suitable seals high powerful in preserve discolour or surfaces stained of the aluminium alloy mentioned in the previous. Moreover, the use

of aluminium alloys architecture were ready clean of atmosphere contaminant if they had been anodic ally coating. However, anodized is not give Needed Protected alone if alloy themselves were not suitably for the environmental to which they were exposes. Anodize coating were perfect coating base [52]. Chromate acid anodized includes the electrochemically development of an oxidation layers where the thin, non-porous oxidation layers was formulation with the thickness porousness layers on above of it. The thicker of anodizing layers depends on the applying voltages period time of film development, but usually 0.05–0.1mil thick. Introducing chromates will be in the end stages of anodizing by seals the porousness layers with chromatic acidic (H_2CrO_4). The contempt super corrosive prevention served by anodizing, the conversion coating were preference using because of financial advantages [80]. The most anodized process were softness. Currently softness type of anodized was processed in sulphuric or chromatic acidic bath, and was using about ninety percent of produced with oxidation layer from 5 to 18 mm production. The chromate acid anodized made possible bases for coating, almost the sulphuric and phosphorate acids are recommended to have environmentally acceptable anodizing solutions. Hard coating is a way better to resist and was using when wearing resistant was request and sometimes for corrosive resistant in many parts of aircraft and food instruments. The hard kind of anodized sulphuric acids baths alone or with some other additional production the thicker on an order of 51 mm [59]. In the hardness coatings, the section phase was oxidation and oxygen which as anodic specified if the coating develop was on the order of 50 mm, 25 mm was down the origin phase. Significantly penetration must be on a same order which that of external development (Figure 2.2). Mag-oxide coating was the ceramic like surface prevention coating. The anode aluminium film was normally formulated of two layer [59].The control films is special morphology corresponded to the hexagonal cells structures. The kind porousness anode oxidation films shown in (Figure 2.3) and could be achieved by anodization in acidic solutions.

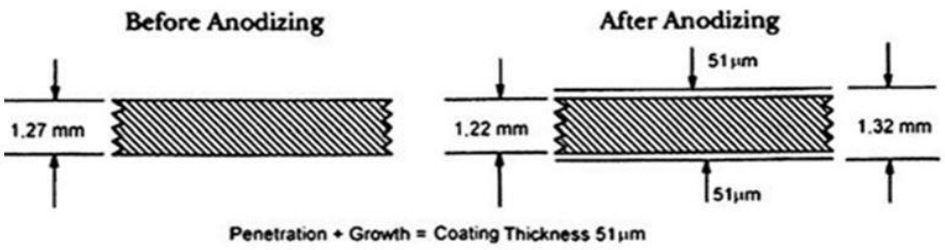


Figure 2.2 Schemata presenting of effective anodic hardness on the thickness development and penetrated consideration as special sample[59].

The characterization of external layers was closed packed arrange of columned hexagonally cell that were perpended on the metallic surfaces and each cells have centre tiny holes that was regular to the surface of substance. At the base of metallic oxidation interfaces, there was the thin hemi-spherical obstacle layers [60].

The morphologies of anodizing oxidation film could be observed by TEM and SEM. In the transmission electron microscopy oxide film is cleaned off at the metallic substance and a thin piece of vertical parts of oxide film is achieved by ultrathin technical parts. Figure 2.4 shown the vertical part of a type of tiny holes oxidation film is formulated on the Al in the medium of acidic [83]. The property of oxide layers could obtain on Al in the mixed electrolytic of the oxalic sulphuric acid is optimizing used experiment designs. To this aim, a four various Doehlert designs baths temperatures, current density of anode, acid-sulphuric and oxalic acid concentration were designed. In order to maximizing the amount of development and micro-hardness of anode oxidation layers and to minimized the effective of this speed on chemical and abrasive resistant of the anodizing surfaces, a multi-criteria improvement use desirableness works was done. The using of dissolve amount of oxidation in phosphor acidic chromic solutions "B680-80 of ASTM" is to show, it is chemical resistant. Below the determination optimum anodized condition. (C_{ox} = 12.6 gL^{-1}, 10 ^0C, 2.6 Adm^{-2}, C_{sul} 183.6 $g.L^{-1}$), approximation reaction value are 0.730 μm min^{-1}, 4.38 gm^{-2} min^{-1} 481 of HV, and 53.3 gm^{-2} for development rates, dissolve rates, micro-hardness, and weight-loss after abrasive, incidentally. The highest abrasive and chemical resistant of optimal anode layers have correlativity connection with it is morphology reveal by scanning electron microscopy observation.

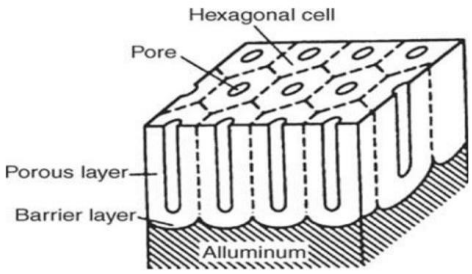


Figure 2.3 Structural of tiny holes type anode oxidation films formed on the aluminium in acidic solution [60]

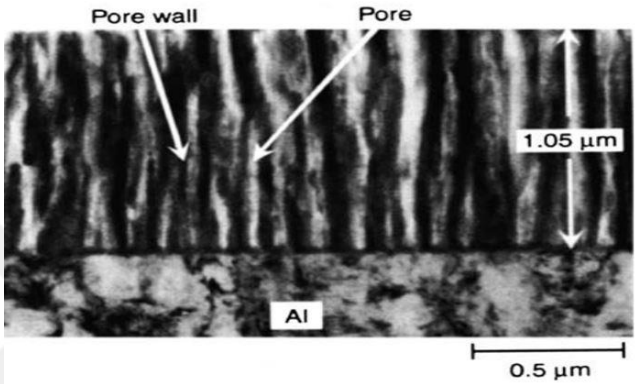


Figure 2.4 Al upright part of anodize Al phase in 0.16 M oxalic acidic by transmission scanning microscopy showed the tiny holes and it is wall after one hour of immersion at open circuit potential in same anodize solutions [61].

Value ratio among 7 to 10 nm for optimizing sheet. The few porousness structural of optimized anode Al sheet was verify by higher ratio of a coatings rate (R = 1.71) when it comparing for the non-optimal example (1.26 and 1.50) [62].

2.5.6 Coating including Metal More Active than of Aluminium

The Mg by taking advantages of a pigment could offer the possibility option to sacrificed preservation of alloy aluminium. The concept basis on magnesium basis primer to preservation of structural aluminium has been improved with examined. The perfect acting of the aluminium board sprays with rich magnesium priming in process test had determined. This rich modern metallic class priming could be form for alloy of aluminium preservation in similarity for luxuries zinc priming invented for steel preservation. The luxuries magnesium priming is producing use to make stable particular of magnesium from 30 to 40 µm in the averages sized, produced by

(Non Ferrum-Metallpulver) Salzburg Austria. The particular comprises of protecting magnesium covered with the thin sheet of MgO, desired to taking controlled for reaction of magnesium, hence avoid farther oxide under non wet condition. Dispersive is making used silane modified multi-layers IPN matrix polymers [63].

Magnesium atomic metals in priming can provide sacrificial protection, when it is in electrode with the substance and so, with each other's. The luxuries magnesium priming formulation at fifty percent of PVC, approximate close to the important colored substance density size of coatings. The behaviour of electrochemical of the luxuries magnesium priming on the Al 7075 and Al 2024 have investigated through the EIS, the potential of opened circuit, and dynamic of measuring device tendencies. The electrochemical methods survey have complement by the SEM. The majority of electrochemical examine consisted of 0.1 wt% NaCl purify water. The vivid experiment have done in the solution of Dilute Harrison, which imitate rain acid and consisting from the 0.05 wt % NaCl in purified water and 0.35 wt % $(NH_4)_2SO_4$.

In the Result, it concluded that the luxuries magnesium priming gives sacrificed preservation to aluminium substance by the mechanisms of two stages. At first level, cathodic polarization prevented of aluminium corrosions, since from the later level the precipitate of the porousness obstacle layers of the oxide Mg was monitored. Mg have high potential negativity, compare to the alloys of aluminium, corrosion was fast and simultaneously seeing visible bubbling on the surface well as. With measure the power of hydrogen PH as which approximately eleven, from the surface of magnesium can assess a high ratio of the reaction of cathodic [64].

2.5.7 Electrodeposited Coatings

Electrodeposition (EDP) is a coating system which a range condition of the industrial process especially in car technology and it is organic rosin. at first patenting had been supplied for the Ford motor (automaker) company in the 1960, and the electrodeposited system had been economically availed from that day forwarded.

The unique use of EDP was a thickness (over to several mm) coatings could be easy deposit on the conductor substance with fine the thickness control. The half similar and continue films can be achieved with outstanding interface adhesive obtained, even areas is fewer nearby that is because of applying in the height casting power of the technique. The deposited progress can be adjusted to endure, also anode or cathode deposited based on the rosin operationally. Currently deposition of cathode was mainly taken benefit to the application of corrosion due to about essential disadvantaged of the anode progress. And cathode electrodepositions, oxides of rosin and electrochemically dissolve of a metallic turn into insignificance characteristics. Many kind of rosin were recommended properly to use for e-coating of material strike. Those materials strike involve alkyd, acrylic, epoxies, polyester, polyurethane and polyamide. Another use of Electrochemical evaluation of e-coating system is to illustrate that is perfect barricade possessions. Twit with Bierwagen's introduce information viewing the larger barricade protected performance of polyurethanes and obstructed isocyanides e-coating on alloy of aluminium alloy through and short of the chromatic conversional coatings pre-treatments. Enhanced sit out from Prohesiony disclosure showed that the conversional coatings were need to protecting broken parts, but then again the coating improved perfect barricade material goods past the broken part. It is extremely able to production adequately thickness coating which let e-coatings to be used as the basic coverage or one system of coating. Other frequently they remain consumed as basic coverage because of having poor weather ability of resins that bring about disadvantages of polish and pigment. On the other hand, more or less epoxies basis (obstructed isocyanides) resin because of their good weather ability can be used quite extensively as standalone coatings [29].

The EDP advantages are appropriate technique for use the coatings protection of the metals. The specific reaction can controller the thick and homogeneity of a coating properly perfectly into the Faradaic equivalence for the complete passed electrical charges, permitting for the slightly incompetence. This allows the face quality of precious materials like to tin and nickel to be brought to the metal of the low values, like steel, by using them as actual thinness coatings. Frequently the coatings are desired to have mutually protecting rate and artistic entreaty and from these cases there was farther budget in using EDP for the reason that is typically

probable to producing brightness attractive surfaces that required no posteriority dealing. In addition, the flexibility of EDP commendable, this one for the widely varieties of application rang of bunch coating of slight part to going on coating of stripe emergent rapidly from steel crushers [65].

2.6 Scientifics attention on aluminium alloys

As mentioned before, the aluminium 2024 T3 alloys are generally used for practical applications of aerospace. Their mechanical starch was obtained through additional copper alloy and magnesium alloy. Table 2.1 viewed the chemical compositions of this alloys. The copper additions are particularly deleterious to the corrosion resistance [23, 66]. The arrangement of alloy aluminium was wrapped from a protect natural passivity oxidation film which a corrosion resistance. The additional alloys lead the shaping of big component composed two or more metals particle while casting. That was favour site of cathode reduction oxygen and sequel corrosion developing specially localized pettings.

Table: 2.3 The Aluminium alloy 2024 T3 chemical composition (in weight %).

	Cu	Mg	Si	Fe	Mn	Cr	Ti	Al
Al 2024 T3	**4.6**	**1.2**	**0.1**	**0.1**	**0.6**	**0.06**	**0.04**	**Bal.**

A typical cathodic reaction, e.g. oxygen reduction, leads to a local pH increase, which can dissolve the matrix and lead to accumulation of copper at its surface. The copper is cathodic alloy active and can supply currents required for localized corrosion. It is therefore clear that the copper is critical in controlling the corrosion behaviour of this alloy, both for bare surfaces and for those that have been treated with coatings.

For this reason, various researchers have investigated the copper on the surface of A1 2024. As early as in 1983, Mazurkiewicz and Piotrowski [67] observed the deposition of copper both from the copper electrolyte solution and solid copper particles, and considered that this is the result of the selective dissolution of

aluminium matrix or the dissolution of particles. Chen, et al [14]. also suggested the reduction of Cu^{2+} dissolved in the solution and observed the copper deposition on the Al, Cu, Fe, Mn including particles by energy dispersive X-ray spectrometry (EDS). They considered that the Al.Cu.Mg including atoms enactment in anode area misplace Mg with Al in the solubility of the primary stages of the corrosion with come much cathode as Cu is leaving in rear with collection.

Guillaumin and Mankowski [68] confirmed the selective dissolutive of the aluminium and magnesium from Aluminium copper magnesium containing particles and the enrichment of Cu on these particles using EDS, electron probe microchemical analysis (EPMA), and XPS. Paez, et al., [69] found a narrow layer of Cu enrichment at the alloy/film interface in Al-Cu alloys using TEM. Dimitrov, et al. [70] developed a new quantitative electrochemical technique for measuring the copper redistribution occurring during corrosion and pre-treatment of high-strength aluminium alloys. They also confirmed the enrichment of elemental Cu on the 2024 T3 surface after immersing in the '0.1 M NaOH' or '0.5 M NaCl' solution. Other investigations [71, 72] were mainly in relation to surface microstructure and understanding localized corrosion. It is widely reported that the alloy microstructure exhibits two primary classes of course, copper-containing intermetallic particles, one class containing (Al, Cu, Fe, and R Mn θ-phase) and the other containing (Al, Cu and Mg or Al_2CuMg, S phase). The former cathode with consideration matrix of the Al and the latter anode in the direction of the matrix Al. Studies by Buchheit et al., have indicated the composition of the predominant particles, in decreasing order of population density, to be S-phase Al_2CuMg, Al_6(Cu, Fe, Mn) and Al_7Cu_2Fe. (Figure 2.5) showed with uniforms divided into the sub phase's particle of Al 2024 T3 matrix. That location was choosing randomly on the recently shiny surfaces alloy.

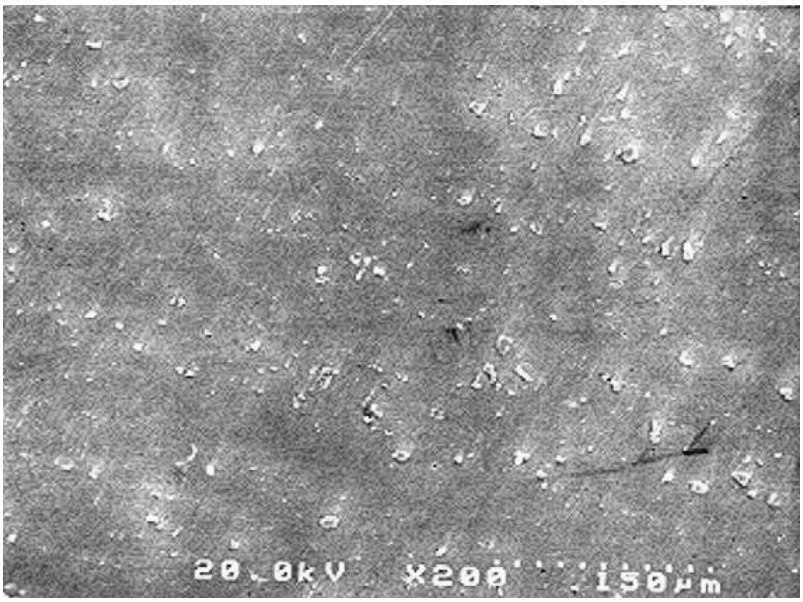


Figure 2.5 The Al 2024 T3 matrix particles divided on the secondary phase [73].

Buchheit also discussed the pitting corrosion mechanisms associate with S surface particle in Al 2024-T3. In the additional AL 2024T3 corrosion initiation of the anode de-alloy, S surface particle which outcome of the galvanic corrosion impelled by the matrix Al anode with cathode Cu-rich S stage leftover have established. That will be leading to other galvanism corrosions solubility of edging matrix of Al. In short, the dealloying process results in Cu-rich remnants that induces pitting around their periphery. A related discovery is the copper redistribution mechanism during corrosion of Al 2024 T3 [74]. This process is triggered by very small copper particles (tens of nanometres in size) that become mechanically disconnected from dealloyed S-phase intermetallic particles. Then these copper-rich particles can redistribute onto the alloy surface and initiate corrosion. But there will be no copper dissolution and redistribution if the copper stays mechanically and electrical connected to the substrate. Both of the anode galvanized S stage, Al_2CuMg with cathode matrix of Al. As de-alloying proceeds remain S stage occurs productive Cu with final become cathode in the direction of the close to matrix of Al. resulting against couples of galvanized.

2.7 Ionic liquids

An ionic liquid is a salt which solvents being liquid below arbitrary temperature such as 100°C, also known as molten salts at room temperature. Ionic liquids commonly consist of a large organic cation and an organic or inorganic anion. Commonly, selection of cation and anion has widely effective on their properties.

In recent decades, ionic liquids have been very important for manufacturing applications comparison to evaporate organic solvents. There are about 600 conventional solvents used in industry, however, related to 10^6 simple ionic liquids can be easily prepared in a laboratory. The change structural of ionic liquids can be prepared either to the cation, anion, or to the substituents on the anion or cation, in order that nearly unlimited numbers of ionic liquids are possible. The physical and chemical properties may be tailored by selecting suitable cation and anion groups for synthesis. They are studied for a large spectrum of applications, including their uses as solvent for organic synthesis and biological reactions refer to their low volatilities, which decrease the risk of atmospheric pollution and reduce associated health concerns [75]. One significant application related to electrochemistry is electrodeposition. The key advantages of ionic liquids are wide potential windows, wide liquid range, low vapour pressure, high solubility of metallic salts, and reduced germination of hydrogen evolution refer to low water content in these systems and relatively higher conductivity compared to other non-aqueous solvents. In additional common properties of ionic liquids are include melting point, density, hydrophobicity, viscosity, solubility etc.

Compared with conventional ionic liquids, deep eutectic solvents may represent a “green alternative” for metallic and alloys electrodeposition. Ionic liquids became one of the more significant major of solvent systems. Initially, the applications of aluminium chloride based ionic liquids were limited, because of their highly hygroscopic nature. Additionally, they were not inert towards various organic mixtures. They consist of eutectic compounds of quaternary ammonium salt such as choline chloride with a hydrogen bond donor species such as amides, glycols or carboxylic acids [76].

Choline chloride describes an organic mixture and a quaternary ammonium salt, which has a choline cation with chloride anion. The main reason behind Choline chloride being such a beneficial quaternary ammonium salt is to do with the fact it is an asymmetric quaternary ammonium salt with a polar functional group, but is also small. The asymmetric nature of this molecule reduces the freezing point of the ionic-molecular liquid, as dose polar functional group. By consolidating these two mixtures in a ratio of 1:2 (ChCl: urea), the product formed has a freezing point of 12 °C. In additional, used for many years primarily as a chicken feed additive so is very cheap to buy. With the current economic and industrial.

2.8. Electrochemical measurements

2.8.1 Cyclic Voltammetry

Cyclic voltammetry has become a most common electrochemical technique of the new systems and have used for the inspection and achieving information about the electrochemical cell reaction. It has given beneficial information about the characteristic and properties of electrochemical reactions and it is progressively used to calculate the effective of ligand on the depletion and oxidation potential of the mean metallic ion in system and multinuclear bunches [77].

In the technique, the potential submitted to the working electrode is linearly sweep, back and forth, between two chosen values, the swapping potentials. To achieve a CV, the current reaction is designed as a purpose of the submitted potential. The current be contingent on two steps to total procedure, the motion of the electroactive type to the exterior of the electrode and the electron transmission response. The significant stricture of a CV is the magnitude of the current peak, ipa and i_{pa}, and the potential from the peaks happen, E_{pa} and E_{pc} and the half potential $E_{1/2}$ located exactly central among E_{pa} and E_{pc}.

The short reduction reaction pair in which equally species transfer electrons with the working electrode is expression an electrochemical reverse pair. Of the kind couple able to intent on from a CV by calculating the potential change among the two tip potentials. Eq. (2.6) Submitted to a scheme that was both electrochemical and chemical reversed:

$$E_{pa} - E_{pc} = 0.058/n \quad (2.6)$$

Where n is the exchange electron number and Epa and E_{pc} are difference peak potentials of anode and cathode, individually, in volts. The change in peak potentials is affected by the exchange potential [78], and need to be not dependent of concentration and scanning rate [79].

One significant application of Cv is to inspection the differences in the reducing potential that a metallic ion go through above composition with dissimilar ligand that steady one oxidation state in predilection to another, as well as the result of a ligands on the depletion potential of ion of dissimilar metals [80].see figure 2.6

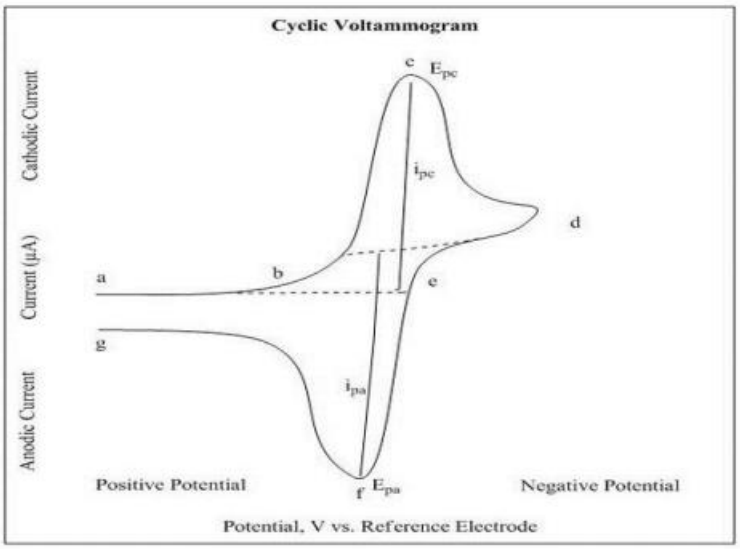


Figure 2.6 In the above plot showed the Cyclic voltammetry [81]

2.8.2 Linear Sweep Voltammetry

All of the techniques accessible in study electrode procedures, the sweep potential technique is possibly widely applied technique. It consisted of the incessant timing various potential to the electrode working versus a non-varying reference electrodes in the presentation. The linear sweep method is actively used with stationary electrodes. Its application is applied in diagnostic mechanics of electrochemistry reaction, for documentation of type's presence in mixture and for the semi measurable investigation of the reacted rates [82]. It is used to compare to

infrared in terms of “fingerprinting” nature. In linear sweep voltammetry the potential scan can be completed in only one direction. The scanning directional could be negative or positive, in standard; the rate sweep able to have any value in general. The voltage ramp is applied to an immersed electrode in a quiescent electrolyte and the resultant current is measured as unction of time (see Figure 2.7) [83].

$$E = E_i - vt \tag{2.7}$$

Where E; is the initial potential of the electrode (selected so that no reaction takes place) and (volts/sec) is the potential scan rate.

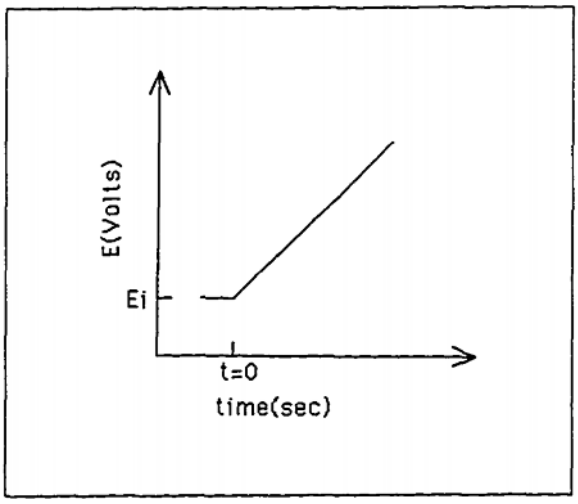


Figure 2.7 Linear sweep voltammetry, voltage vs. time signal [83].

The form of the current-time curve response or current-potential and its dependence on reactant concentrations and scan rate characterize the electrode process kinetics. The curve shape of the obtained can be understood as follows (see Figure 2.8) when the potential where the electrode reaction beginning is to be reached, the current rises until reach maximum value of current (peak current) is observed. If the potential is continually swept, the supply of electroactive species to the electrodes begin to fall. This is the result of consumption of electroactive species and concentration gradients in the reaction. When the certain value just after the peak current is reach, the current begins to decay following a profile proportional to $\mathbf{t^{1/2}}$

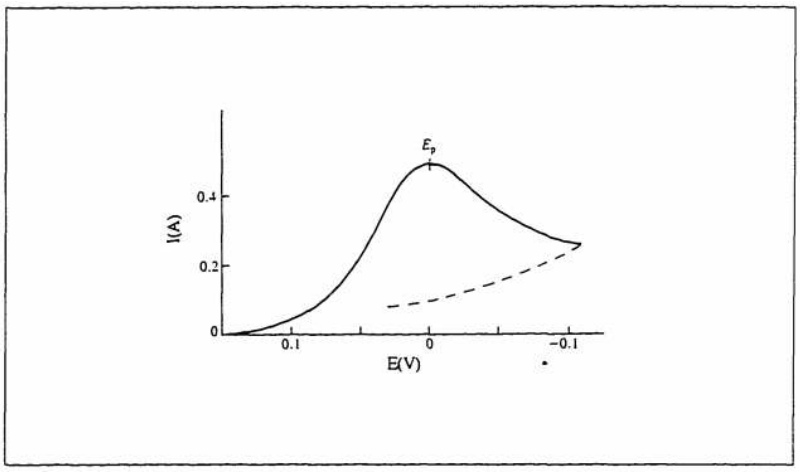


Figure 2.8 Linear sweep voltammetry for a reversible reduction process [82]

The two significant parameters of a linear voltammogram are the peak potential (E_p) and the magnitudes of the peak current (i_p) [84], The top current to the a reversibly scheme is defined by the R. Sevcik's equations for the first cyclic of forward sweep

$$i_p = 268{,}600\, n^{3/2}\, AD^{1/2}\, Cv^{1/2} \tag{2.8}$$

Where,
i_p: is the current (Am).
n : electron number
A : is conductor area (cm^2)
D : is the coefficient diffusion ($cm^{2/s}$)
C : is the concentration in ($mole/cm^3$)
v : scan rate (V/s)

Based on the equation in (2.8), by $v^{1/2}$ i_p increases and is straight perpendicular to the reactant concentration. The rate of scan concentration and dependence on concentration are mainly significant in systematic applications and in the electrode appliances studies.

2.9 Three electrode measurement methods.

In the electrochemical, the electrode is an electronically conductors in connection with the ionic metal conductors. The electrode should be metallic, electronic mixed, ionic electrode or a semiconductor. The ionic conductors is a solution of electrolytic, conversely, electrolytic solids and dissolves ionic could be

apply as good. The electrode duration was using in the practical sentiency, which mean that the electron conductivity. If this is not quantified, the mean stretch of electrode. In the simple method the ionic conductor is a metallic conductor which is submerged in the solution of electrolyte. On the surface of electrode, the dissolving electro-active charge atoms are changing them particles by exchanging one more electron in a conductor. In the electrochemistry attraction both oxidized and reduced ion are remaining in the mixture, since the conductors are chemical add and work for as the sources and electron drops. The practical conditions of the conductors generally contain all the mechanically supportive conductor parts (for example static mercury drop conductor or a rotating disk conductor). Farther more, was included all physical and chemical variations of the electrode, or it is face (for example, a mercury film electrodes, a carbon paste electrodes and an enzyme electrodes). Nevertheless, this condition will not support electrolyte mixtures and ionic section of double layers at the interface of conductor mixtures. Ionic electrodes, in which apply from potentiometric. Practical and theoretical facet of the conductor is supported in other references and articles [85, 86].

One of the most mutual investigational arrangements to record CV consists of the electrochemistry cells ~~that~~ having three conductors which are working electrode (W), reference electrode (R) and counter electrode (C), and all put into the liquid and with connecting to the system [87]. The system allows the potential differences between working electrode and the reference to be controlling with minimum intervention of the *IR* (ohmic) put. In this arrangement, the current that is allowing into the reference electrode, so could be minimized there by preventing polarization of a reference electrodes and then saving the submitted potential to distribute among the stable of reference and working electrode [88]. See figure (2.9).

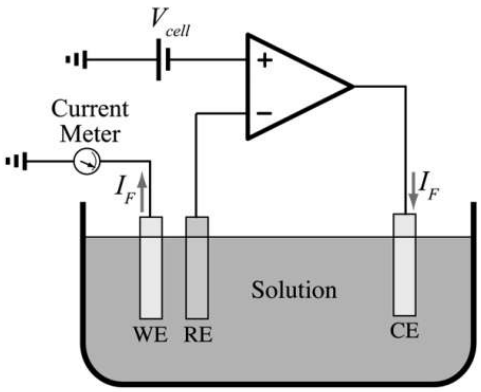


Figure 2.9 The drawing of a three-electrode amperometry electrochemical sensor and a potentiostat [89].

2.9.1 The Working Electrode

A working electrode consists of the electrode that makes examined procedures happen. The researcher is able to indicate one from the electrodes. The major principle is accessibility of probable window, in which the necessities of research could be obtained. Regularly, in the scope of constructive possibilities, gold, platin and carbon (glassy carbon, graphite) electrodes were utilized. The outsides of these ingredients should be incompletely oxidized in watery resolutions at this probable range. Thinning coats of oxides are made of platinum, gold, and distinct efficient sets, such as –OH and –C=O, are connected to the carbon ingredients. In the destructive probable scope, in watery resolutions and other protic solvents, mercury electrodes are always outstanding because of high over-potential of the reduced hydrogen. Moreover, numerous organic composites are powerfully adsorbing on mercury, which might confuse the exploration of voltammograms. In aprotic solvents, Au, Pt and C electrodes can be utilized in both aspects of advantages and disadvantages potential range. Electrodes are made of some principled metal, like Ag and Ir which are fewer often utilized. A solid electrode, in relationship to a drop mercury, regularly needs vigilance pre-treatments. The electrode surface ought to be fresh and refined on a complete wet pad to mirror glosses. This competed by means of abrasive powder (or their suspension in the water), such as alumina and diamond, of numerous sizes of particle. Relying on the definite states of the surface, the refining ought to begin with the suitable sizes of the abrasive materials, ensuing

refining with minor particles. Regularly, during finishing the process, 0.1 and 0.05 μm particles are utilized. After polishing, the electrode surface ought to be cautiously prepared (removing of abrasive materials) with go-ahead streams of water, and drying with, for example, methanol, if a non-aqueous solvent utilized in the tests. Water-based suspension of the diamond and alumina that is existing commercially. Oil-based suspension is not suggested for polishing, since they cause to lipophilic material goods of the polishing surface and this bounds considerably the application of the electrode. An investigative of the superiority of the electrode surface with a microscope ought to be performed before the polishing process and before the tests. Similarly, this assists to guarantee that the abrasive materials have been numerally erased from the surface. Tracings of alumina added to the electrode surfaces might vary, e.g. pH at the electrode/solution interface. For specific electrochemical objectives inexpensive one-use electrode is suggested to keep a good re-producibility of the measurement.

To gain obviously understandable voltammogram, it is imperative that the electroactive section of the electrodes is totally fixed into the electrode body. In other respects, the context for the voltammograms is habitually extreme and steep. Frequently, to earn reproducible curves/waves, the solid electrode requires electrochemical activation/regenerations. This is habitually finalized through cycling the potential in a suitable scope and protecting the electrode in a fitting resolution. There is no global scope of prospective and global resolution that employed for such activation. In the effort with Pt and Au an electrode, often the voltammetric cycling/activation is completed in a diluted sulphuric acid. Solid electrodes adapted with polymers or enclosed by gels, membranes, and numerous composite ingredients that is unable to be solved by polishing. The single method to make them be active correctly, capably and reproducibly is to implement a suitable training potential (or a sequence of potential) before the voltammetric tests. It is imperative that, before performing voltammetric tests analyses, the current potential window (range) is identified and that there are no peaks of unsolicited impurities in that range. The current potential window is showed by the streams of reduction/oxidation of the supportive electrolyte/solvent and, in the tests, one must avoid from ingoing potentials where these procedures clearly will happen. The produces formed at the potential boundaries might interfere the classification under examination and might

impact the electrode surface. After the usage, the functioning electrode ought to be thoroughly rinsed and dried to dodge crystallization of the substance on the face of conductors.

2.9.2 The Electrode Reference

The reference electrode describe as a critical in the voltammetry especially while the exact information on official potential of the both reduction under examining are required. Tradition electrodes based on Ag and Hg (Hg/HgCl, Hg/Hg_2SO_4, Ag/AgCl, could be constantly used. though; them concentrating electrolytic shall be completely divided from the mixture analysis. In other word, all things shall be performed to avoid leak of the solutions at the reference electrode cells, and reverted. Hence, initial of very good electrolyte bridges filled with analysed mixture and good covered with appropriated conductor stopper most be applied. Such good bridge to protects cell solution avoid leaking of unrequired expect ions as well to the reference electrode. Usually, this instructs to using similar solutions in the section cell with reference electrode. While the experiment has completed with both electrode systems, the current flow into are reference electrode. In their condition which potential of reference electrode might not be steady around during the period time. less the electrodes work a few amount risk of affect the potential of the reference electrode. From the work and microelectrode “conductors and the dimensional of them activate sections in a scope of micrometre or few” the work electrode using from two electrodes systems are justifications. So, If three electrodes systems have applied, reference conductor basically charge with amount of few current, in the pA scope the current. Such little current could not act well the activity of the specie that determines the potential of reference electrode. So, in react situation when the half wave potential voltammetry or potentials of peak have not known exactly and what really matter peak or wave length [90].

2.9.3 The Counter Electrode

The auxiliary or counter electrode was utilized only in the three of electrode system. At this system the currents are flowing between components of working electrode and counter electrode. Occasionally the piece of platinum tool or the titanium tool is working as source of counter electrode. Also, the carbon tools are

used. It's supported that area of a counter electrode considerably bigger than that of the working electrode [90].

2.10 Scanning Electron Microscope

SEM is a typical method used routinely in quality controlling of the film deposition usage physical vaporization deposited, regarding to other methods which included the beam of electron Lithography. From the process of SEM, beam of electrons is used for interaction with material because of the atom in material to reacting by emitted and production electron in the samples regards of the secondary electron. The scanning electron microscope based on addition the secondary electron[91].

2.11 Energy Dispersive X-rays

The Energy dispersive X-ray detectors (EDX) are developed since 1960s, at the first for atomic application" says Reed [92]. Energy dispersive x-rays analysis is measuring for determination and quantification ultimate compositing of the samples. The typical X-ray is producing while materials are bombarded with electrons from the instrument of beam electron. Like to the scanning electron microscope (SEM). Reflection of this x-ray is able to be accomplished by the energy dispersive spectrometer. That is a solid state device which ~~is~~ differentiates between X-ray energies. Detection and measurement of the energy are allowed for elemental analysis. When an incidence beam bouncing inside the samples creates second electron, which have leave the thousand holes and atom samples in the election shells. At from the secondary electron have located. If these holes have in the interior shells, the nucleases are in the unstable stated and to stabilize atoms, electrons from external shells would come into the interior shells. Since the external shells is at a higher energy state, the nuclease most lost some energy. The energy is liberated as a form of heat or X-rays. The characteristic in wavelength and energy to the parent atom elements which is emitted x-ray from the samples, the shells lose electron which shell replace them. The X-rays are formed by the electrons beam incident and act with the surface of samples. This action allows the scanning electron microscope to perform ultimate analysis in selecting a very small area. The X-ray is emitted from a depth electron same to how deeps are formed of the secondary electrons.

Depending on the density of sample and acceleration voltages of the incidence beams, usually this is from 0.5 to 2 micron in depth. Energy dispersive x-ray analysis also is able to quantify the detection elements. The analysis measurement is able to perform by a standard or standard less analysis. A standard less express analysis elements by calculation area under the peak of each determine element and after take accounting for the accelerate voltages of the beam to production the spectrum, execute calculations to creating sensitivity factor that is change the area under the peak into atomic percent or weight. Standards quantifications are performed by calculations of the area below the ultimate peak, the areas are comparing to standard data which is spectra of element would be quantifying acquire below the complete condition of the un-known spectrum. Since it requirements of these add spectra, this form of analysis is more times consummation and mainly is not much performing than a standard less determination except the X-ray peaks of the element would be fix overlap or the elements are in quantities of trace.

The samples prepared for the SEM analysis are first used to obtain the surface image and then obtain the EDX spectrum. Conditions of the samples are equal to those mentioned before for the SEM image acquisition. The spectra are performed on a high resolution area, where a single particle is analysed to obtain its elemental composition.

The detectors of the X-ray are able to use getting database from the energy of photons, which are able to provide details of the chemical component of a sample in the energy spectrum form. Along with the photons process of EDX, X-ray is emitted and comes into the sample. When the photon comes into the samples then it will eject a photoelectron, which will have the photon energy less than the activate energy. Have been produced x-rays must to reach the X-ray detector before they able to contributing to the spectrum, which able to then be match to an arrangement of chemical energy information. X-ray detector able to use to determination the counting rates of the ejected photoelectrons. The counting rate of small amount counting rate of the EDX detectors oblige to the sensitiveness and preciseness of the analysis. Chemical-elemental components are tested in further work using EDX.

2.12 X-Ray Diffraction

The purpose of XRD method which to verify material structure and for a crystalline material this mean verifying the unit cell structures, the unit cell proportion, and the accurate position of all of the particles or atoms in the unit cell. In broad terms, the size and proportion of the unit cell found by verifying the site of the Bragg peaks, while the nature of the foundation and the location of the atoms or particles within the cell control the Bragg peak concentrations. Depending on the surrounding, the crystalline material could also be in the shape of a single crystal or a powder.

Single crystal XRD permits determine the structures with additional confidence than powder XRD on because single crystal X-ray data stand for the three-dimensional mutual interplanetary, as opposite to powder diffraction, in which the three-dimensional mutual interplanetary is charted in one dimension. Hence, there is a severe intersection of Bragg reflections at the identical angle (2θ), in addition an operative intersection of reflection segregation by a narrow (2θ) growth, which is analytically not determined. Likewise, powder diffraction is subject to a sample that has a completely random scattering of crystallites of identical size. If the polycrystalline combined is constrained, there is a change from random dispersion texture, which influences the intensity of Bragg peaks and more significantly, the consistent peak form; this in sequence reasons an incorrect determination to crystal symmetry and unit cell coefficients. The subject of texture happening in the polycrystalline collective is not current in the distinct crystal specimen; refer to a distinct sample used [93].

The blasted affected on the microstructure of break the Al 2024 T3 sheet is tested by the method XRD. The sources of x-rays are perfected for measuring in sheet residually tension direction by transmissions of a beam into the samples [94]. The x-ray diffraction spectrums of the breach and non-breach sheets have taken at area near to the middle of the blasted. Both spectrums are showing the characteristics spectra of Al and displayed that the blasted did not created any new phase. However, in the XRD peaks with regard to the reference XRD peak have observed, indicated community distortion.

CHAPTER THREE

EXPERIMENTAL PROCEDURE

3.1 Introduction

The material, equipment and experimental procedures utilized in this work are described below. Here the experimental study is divided into two parts. The first one is about the measurements of corrosion parameters of bare and Zn coated substrates, second one is the surface and structural analyses of these substrates. After coating the specimen, parallel to the determination of kinetic parameters (E_{corr}, i_{corr}), morphological and structural analyses are examined. The whole steps are summarized in figure 3.1 as follows:

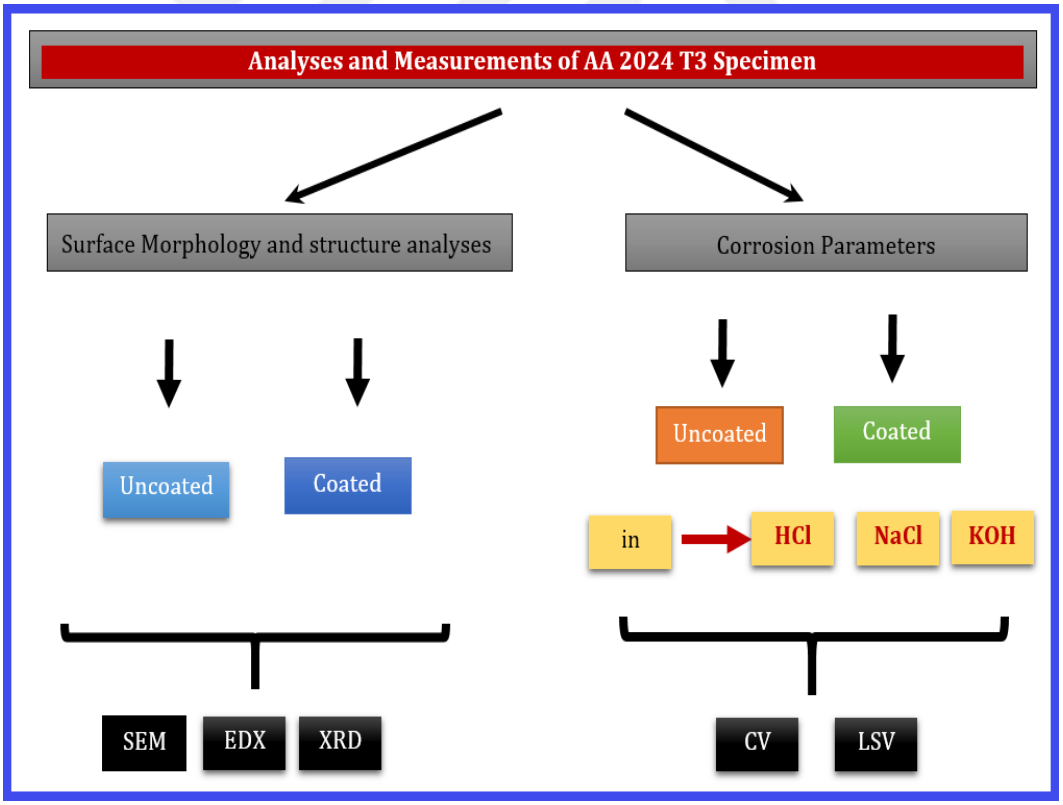


Figure3.1 Study protocol of specimen

3.2. The Properties and preparation of the research samples, AA-2024 T3 alloy

3.2.1. Content of the Samples

The surface of the provided sample has been investigated with the aid of SEM-EDX device about elemental analyse in detail. The compositions are listed as shown in the table 3.1.

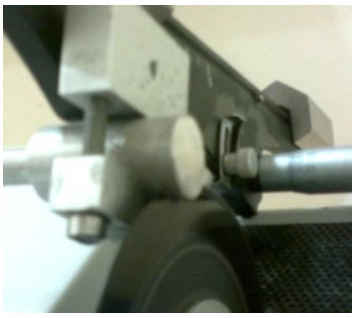
Table 3.1 The Content of the Alloy

AA-2024 T3 Alloy Composition			
Aluminium (Al)	90.8 to 94.7 %	Zinc (Zn)	0 to 0.25 %
Copper (Cu)	3.8 to 4.9 %	Zirconium (Zr)	0 to 0.2 %
Magnesium (Mg)	1.2 to 1.8 %	Residuals	0 to 0.15 %
Manganese (Mn)	0.3 to 0.9 %	Titanium (Ti)	0 to 0.15 %
Iron (Fe)	0 to 0.5 %	Chromium (Cr)	0 to 0.1 %
Silicon (Si)	0 to 0.5 %		

3.2.2. Preparation of the AA 2024 T3 Substrates

The specimen were cut into rectangular shape with 10x15 mm length of edges and then soldered with Cu-wire for an electrical connection and mounted onto the epoxy resin to have only one active flat surface exposed to the corrosive environment and were polished by ***Struers – LaboForce – 3 polishing set*** as they are shown below in the figures 3.2. (a), (b), (c) and (d) respectively.

a)



b)

c)

d)

Figure 3.2 (a) Cutting process, (b)The cutting machine, (c) Polishing process and (d) The polishing machine

3.2.3. Preparation of Chemical Solution for the Zn Coating with Electrodeposition System

The used analytical grade chemicals are supplied by Merck, Sigma, and Aldrich. The ChCl-EG ionic liquid (IL) namely ethaline was formed by mixing ChCl (0.36 mole) and EG (0.72 mole) with the molar ratio of 1:2 at 100°C until a homogeneous, colourless liquid (ethaline) was obtained. After Under the same condition $ZnCl_2$ solute is added for each different experiment part. The solution (electrolyte) has been used in coating process at the temperature of 50°C by using traditional three electrode system connected to a CHI 1100 potentiostat. The counter electrode was 0.3 mm diameter platinum strip, the reference electrode was Ti(titanium). The working electrode consisted of AA 2024 sample.

In this study we used an ionic liquid (IL) based on choline chloride (ChCl) and ethylene glycol (EG) eutectic mixtures as the Zn replacement deposition solution (type I) to replace conventional aqueous media. The ChCl-based IL, also known as deep eutectic solvent, is one of a relatively new class of ionic liquids developed by Abbott et al. [95]. The reason why we used ionic liquid is because ionic liquids have larger potential window than organic solvents. The wider potential window reduces

the possibility of any side reactions occurring that can affect the deposition of the metal onto the substrate, such as hydrogen evolution.

Prior to each experiment, the working electrode is polished gradually with a sequence of emery papers of different grades (400, 800, 1000, 1200, 1500, 2000 and 3000), washed with doubly distilled water, degreased with acetone. After this stage, the samples were then washed with distilled water and exposed to hot air until drying and used instantly for electrodeposition.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

Zinc (in deep eutectic solvent DES) is electrodeposited on “aluminium based alloy” (AA2024). Initially aqueous solutions ($ZnSO_4$ in acidic and alkaline aqueous bath) are used to deposit zinc on aluminium surface. No deposition of zinc on the surface is however observed with aqueous media. Deposition techniques such as pulse [96], potential step [97] are varied for zinc deposition, which do not coat as well. As the DESs consist of only ions and do not include water [98], they are chosen to study deposition of Zn on a Al alloy. Zn coated aluminium is then characterised by SEM and XRD given in section 4.2.2 and 4.2.3, respectively. As the main objective of this research is to improve the corrosion resistivity of aluminium based alloys, potentiodynamical study of zinc coated AA2024 substrate in different media is presented in section 4.3.

4.2. Zn deposition on Aluminium Alloy

Aluminium alloy AA2024 as working electrode is immersed in different eutectic based ionic liquids (Reline and Ethaline) in order to analyse their redox mechanisms. The aim is to analyse how a metal (Cu or Zn) could be electrodeposited on Al alloy surface. After the deposition conditions of a metal are decided, zinc contained deep eutectic solvent is used to obtain Zn coated Al alloy. All potentials given in this study is against Ag wire and Ag/AgCl (*sat.* KCl) reference electrodes for ionic liquid and aqueous solutions, respectively. The deposition of zinc in Ethaline is performed at 50 °C. This high temperature makes the probable trace of water in Ethaline to be evaporated and not to be considerable in the experiments.

4.2.1. Electrochemical Study

Figure 4.1 presents the cyclic voltammogram of AA2024 in Ethaline in order to analyse the effect of potential direction.

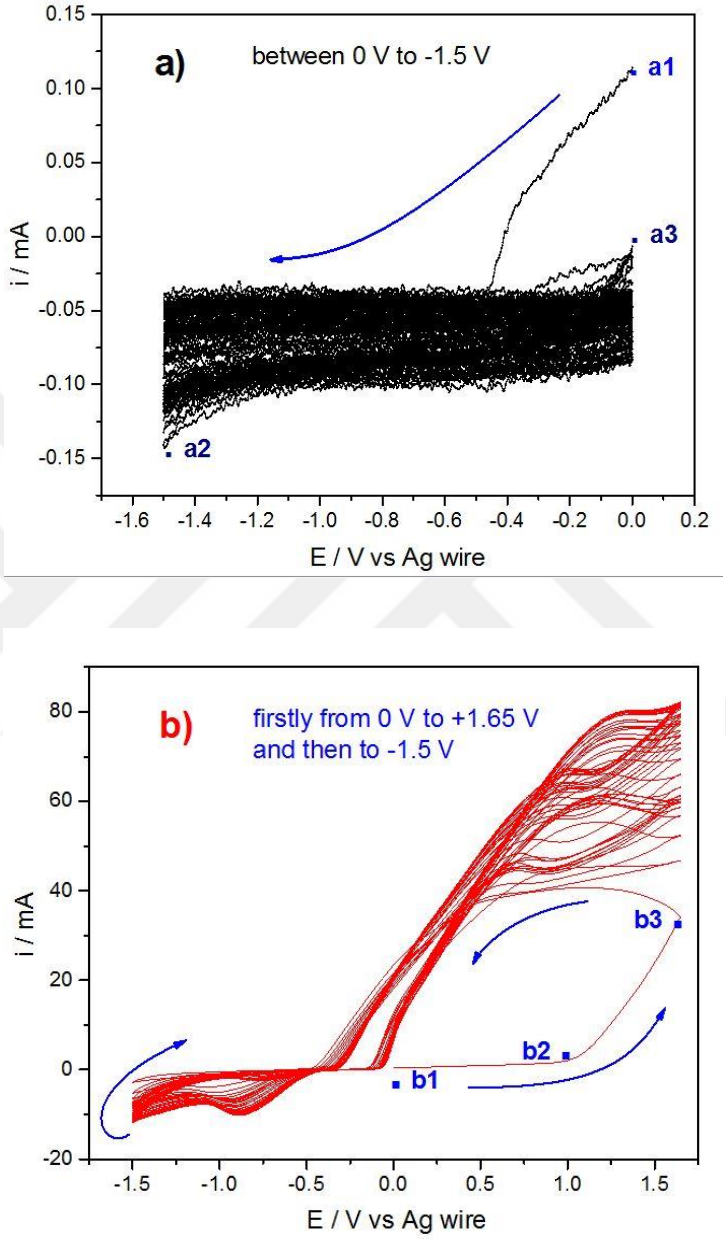


Figure 4.1 Consecutive cycling of Al working electrode in Zn containing electrolyte (0.1 M $ZnSO_4$ in Ethaline) at a sweep rate of 10 mV s^{-1}. The potential window is a) directly from 0 V to -1.5 V; b) starting from 0 V and going to the positive direction (+1.65 V) and then going to the negative direction (-1.5 V). The experiments were carried out at 50 °C.

Figure 4.1 is given to observe the effect of potential direction on Al alloy working electrode in a DES. In Figure 1a there is no redox reaction of Al based alloy in Ethaline between 0 V and -1.5 V. This means that Zn cannot be deposited on Al alloy surface as there is no redox peaks and current range is between 0.05 and 0.15 mA. This is a well-known behaviour of Al alloy surface. Zn is normally electrodeposited at -1.5 V as its standard reduction potential is -1.2 in Ethaline found for novel Pt working electrode [99]. Figure 4.1b presents the cyclic voltammetry data of Al alloy in Ethaline scanned from 0 V to the positive direction firstly (+1.65) and then to negative direction (-1.5 V). Although there is no reduction of Zn on Al alloy in Ethaline between 0 V and -1.5 V (Figure 4.1a), there is a reduction peak in Figure 4.1b commencing from around -0.6 V when Al alloy is firstly oxidised to 1.65 V and then cathodic potential is applied. This reduction peak is associated with zinc reduction on Al alloy surface. Current range of the cathodic side of -1.5 V shown in Figure 4.1b is around 11 mA which is 73 times greater than that of -1.5 V shown in Figure 4.1a (11 mA/0.15 mA = 73). This difference could be due to the hydrogen evaluation occurring at -1.5 V for wider potential window (form 0 V to firstly +1.65 V and then to -1.5). The cyclic voltammograms shown in Figure 4.1 are obtained at 50 °C. As it is known, Al alloy has passivated Al_2O_3 surface and there are limited methods to break up this Al_2O_3 surface and then have a different compound on Al alloy surface [100-102]. Passive Al_2O_3 surface which is about 4 nm [103] depending on alloy, preparation history and environments could be eliminated in zincate or chromium conversion system. Cyclic voltammogram shown in Figure 4.1b suggests that the passive Al_2O_3 surface could be disrupted by applying positive potential (up to +1.65 V). This makes the surface of Al alloy ready to have metal deposition. The critical point here whether or not the metal deposition on newly prepared Al alloy surface is well attached. There are several metal/alloy deposition on Al alloy surface (indeed on Al_2O_3 surface). These depositions are not however well adhesive on Al_2O_3 surface and removed when it is touched by a tissue. During deposition of some metals/alloys on Al_2O_3 surface is fallen off directly and quickly when particles of metals/alloys/compounds are formed in a deposition bath. Another interesting point worth to emphasize here is that the multiple cycle effect on different potential window. When the potential window is between 0 V and -1.5 V, the current approaches to a linear line shown in Figure 4.1a. However, the current peaks of

reduction increases with increasing the number of scans when the potential window lays between +1.6 V and -1.5 V. The same current trends for different potential windows were obtained for Ethaline electrolyte having 0.1 M $CuSO_4$, which is not presented in this work. The comparison between the first cycles of Figure 4.1a and 4.1b is presented in Figure 4.2a. Figure 4.2b is given to explain the analysis of the first two cycles of Figure 4.1b in detail.

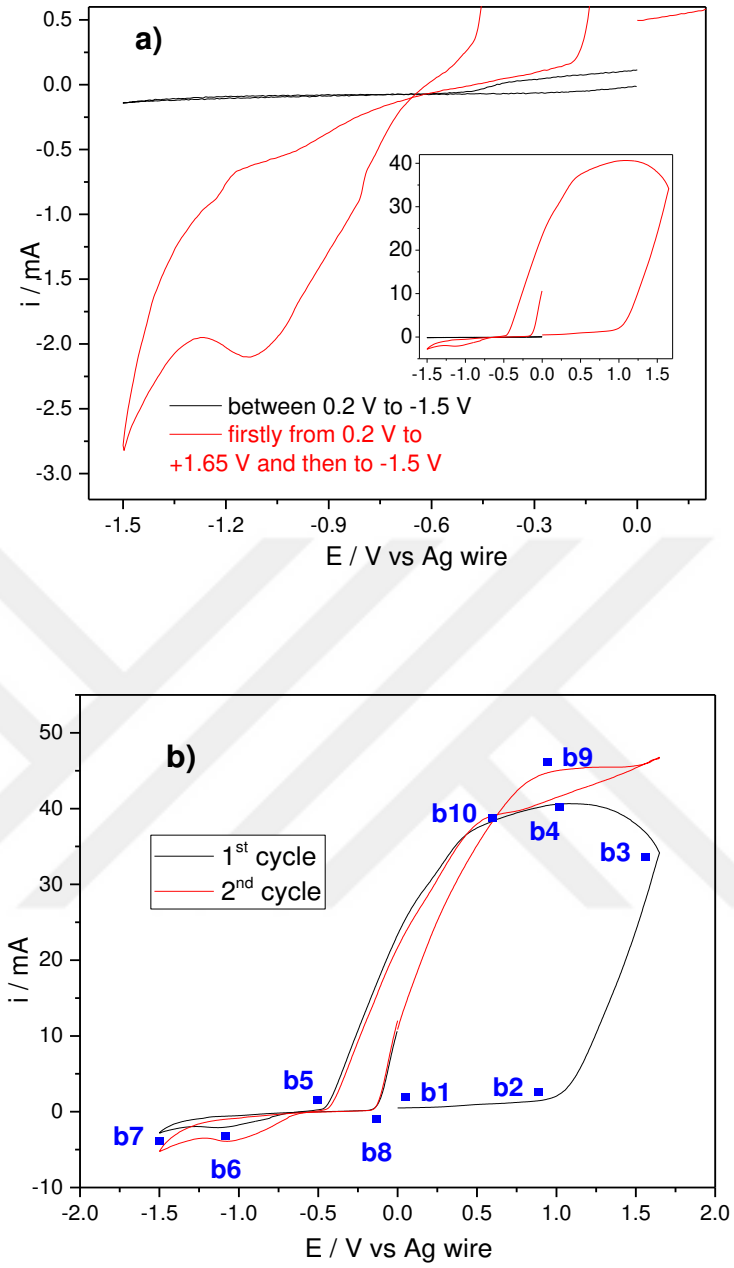


Figure 4.2 Cyclic voltammogram data of Al alloy working electrode in Zn containing electrolyte (0.1 M $ZnSO_4$ in Ethaline) at a sweep rate of 10 mV s^{-1}. a) potential window directly from 0 V to -1.5 V (black line) compared with the potential window starting from 0 V and going to the positive direction (+1.65 V) and then going to the negative direction (-1.5 V) (red line). The inlet is whole cycle. b) The first two cycles data of Al alloy working electrode in Zn containing electrolyte presented in Figure 1b. The experiments were conducted at 50 °C.

The detail of the first cycles of Figure 4.1a and 4.1b is given in Figure 4.2a and the whole first cycles of them are presented inlet of Figure 4.2a. When aluminium (indeed Al_2O_3) in Ethaline is scanned directly from 0 V to -1.5 V, the charge of reduction (area under the cyclic voltammogram) is only 3.4 mC which is shown in black line of Figure 4.2a. When firstly extreme anodic potential (+1.65 V) is applied to aluminium alloy having indeed Al_2O_3 surface in Ethaline DES and then extreme cathodic potential (-1.5 V) is applied, the cathodic charge between -0.6 V and -1.5 V is 65 mC (red line) which is 19 times greater than black line. This difference shows obviously that the Al_2O_3 surface (on aluminium alloy) is changed by applying of anodic potential. This applying anodic potential could be used to break up Al_2O_3 surface and then without losing time immediately a new surface of bulk aluminium could be coated.

To analyse cyclic voltammogram data obtained from Al alloy in DES applying anodic potential firstly, Figure 4.2b is presented. Point b1 is the starting potential (0 V) given in Figure 4.2b. There is no oxidation of Al alloy surface (Al_2O_3 surface indeed) until point b2 (1.0 V). The current starts to increase from point b2 until point b3, the reversing potential at +1.65 V. The current continues to increase from point b3 til point b4 (+0.8 V) on the reverse direction. After point b2, at the same time there is both the peeling of Al surface layer and the formation of bubbles on the surface of aluminium alloy which in turn causes a new surface of aluminium alloy. Although the mechanism of aluminium in Ethaline at high potential (around +1.65 V) could not be detected, Al_2O_3 surface could be broken up and dissociated into Ethaline. The new surface would be bare aluminium (not having Al_2O_3 layer on it) or a thin layer of Al_2O_3. As the current increases continuously from point b2 to point b4 and the peeling of aluminium alloy surface simultaneously occurs, the increase of current is not related to Ethaline oxidation because potential window of ethaline is between -1.4 and 1.5 on carbon working electrode. The current decreases from point b4 to point b5 (-0.5 V) of Figure 4.2b. It is shown that there is no reduction of zinc when the starting potential was 0 V (black line of Figure 4.2a). There are two reduction peaks here (point b6 and point b7 of Figure 4.2b) when Al_2O_3 surface is broken up and dissolved in Ethaline at extreme cathodic potential (after 1 V until +1.65 V). The first peak commencing at around -0.6 V is associated with Zn^{2+} to Zn^{+} and the second peak commencing at around -1.3 V is due to zinc deposition from Zn^{+}

to Zn^0. When +1.65 V is firstly applied potentiostatically for 400 seconds and then -1.5 V is applied potentiostatically for 800 seconds, there is a zinc coated aluminium alloy (see left image of Figure 4.3). However, application of -1.0 V for 800 seconds after the application of +1.65 V for 400 seconds, there is not any zinc deposition. This shows that the reduction peak of Zn^{2+}/Zn^{+} occurs before -1.0 V and the peak starting at around -0.6 V is due to reduction of Zn^{2+} to Zn^{+} (point b6 of Figure 4.2b). There is no oxidation peak after point b7 (-1.5 V) until point b8 (-0.2 V) because the current efficiency of zinc coating is very low compared to hydrogen evolution. The current increases significantly at point b8 due to the change of surface which is now probably bare Al alloy (not Al_2O_3 surface anymore). As point b8 is very different than b2, the formation of a new surface and dissolution of Al_2O_3 surface at higher potential (at +1.65 V) is proven. The direction of current increase is seen through point b9 and on the reverse direction b10. After point b10, the i-E curve shown in Figure 4.2b is similar.

4.2.2. Morphological Study

It is shown in section 3.1.1. that passive Al_2O_3 layer on bulk aluminium based alloys is broken up in a DES (ethaline) at high anodic potential (around +1.65 V) and zinc can be coated on this new bulk aluminium based alloy which does not have Al_2O_3 surface. Therefore, the cathodic potential of +1.65 V is firstly applied for 400 seconds to aluminium based alloy (AA2024) in Ethaline having zinc salt in order to eliminate Al_2O_3 layer and then the anodic potential of -1.5 is applied to deposit zinc on newly in-situ prepared aluminium surface. The images of uncoated and zinc coated aluminium alloy are shown in Figure 4.3.

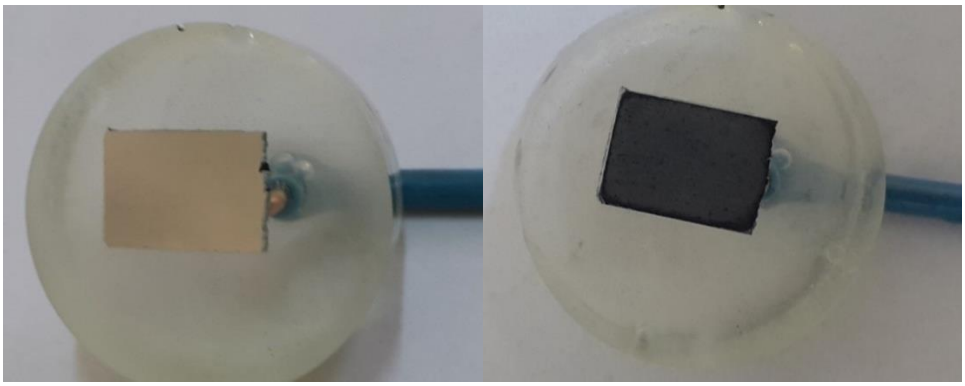


Figure 4.3. Images of uncoated and zinc coated aluminium alloy. Zinc coating on aluminium alloy was obtained by applying firstly +1.65 V for 400 seconds and then applying -1.5 V for 800 seconds in Ethaline at 50 °C.

Aluminium alloy is not taken out from Ethaline after the implementation of cathodic potential because newly prepared bare aluminium can form Al_2O_3 surface immediately when it is in contact with the atmosphere. As the formation of Al_2O_3 cannot be coated with zinc, aluminium alloy is not taken out from Ethaline electrolyte after the application of +1.65 V. A well attached zinc coated Al alloy is obtained and shown on the right side of Figure 4.3. This method is used for copper coating as well. As the focus of this research is the corrosion protection of aluminium in alkaline solution, copper coating is beyond to scope of this report and not shown here and it is the subject of a different work. The trace of air and water in Ethaline (around 1-2 percent [104]) do not restrain the formation of zinc coating. SEM graphs of uncoated and zinc coated aluminium alloys are presented in Figure 4.4.

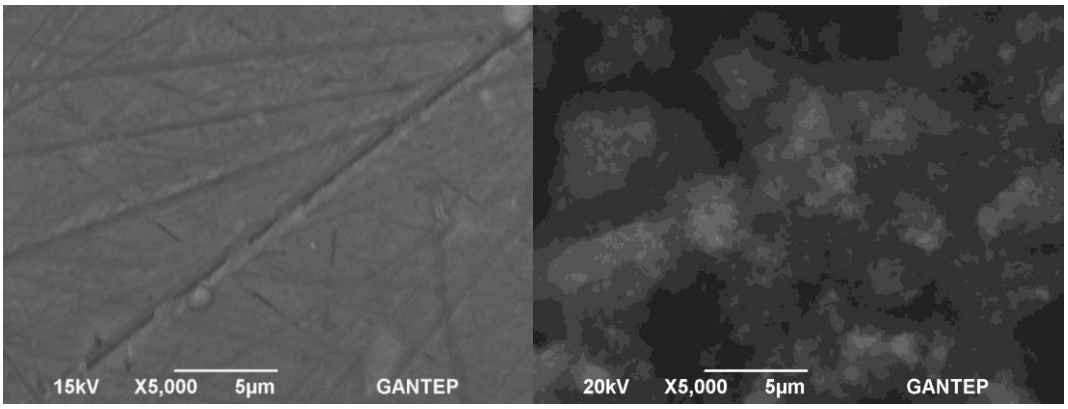


Figure 4.4. SEM images of a representative bare AA2024 aluminium alloy (left image); Zn-coated Al alloy (right image). Zinc coated aluminium alloy was obtained by applying firstly +1.65 V for 400 seconds and then applying -1.5 V for 800 seconds in Ethaline electrolyte at 50 °C.

Bare aluminium alloy presented in the left side of Figure 4.4 has some scratched as its surface is abraded with appropriate sandpapers roughly. Its surface is not polished well (see left side of Figure 4.3) in order to simulate a realistic aluminium alloy surface which could be found in industrial applications. Zinc coating of aluminium alloy surface has a dark grey colour (right side of Figure 4.3b). The scratches of bare AA2024 alloy are observed by SEM (left side of Figure 4.4). On the other hand, zinc coating is covered aluminium alloy surface presented in right side of Figure 4.4. Cracking or defect of zinc coting layer are not observed for any zinc coated aluminium alloy. Metal ratio of the coating is obtained by EDAX analysis. Zn coated Al has 68 % wt Zn and 32 wt % Al. The expectation was to obtain 100 wt Zn coating. There are two possibilities to explain the presence of Al in surface elemental analysis. It could be either a thin Zn film on Al surface showing Al contents in EDAX analysis or the formation of Al-Zn alloy on Al surface occurred due to deposition of Zn with Al ions which dissolved in Ethaline at high cathodic potential. Ethaline could not be changed during oxidation of Al_2O_3 surface and reduction of zinc because Al_2O_3 surface could be formed by itself when Al is in contact with the atmosphere. Zinc film has an amorphous-like structure shown in right side of Figure 4.4. The amorphous solid structure of zinc coating with other metals has a potential application of transistors [105-108]. Similar morphology of

zinc coating is seen before [109, 110]. The structural analysis by XRD is presented in next section.

4.2.3. Structural Study

Figure 4.5 shows typical X-ray diffraction patterns of bare aluminium and Zn deposited on aluminium alloy substrate obtained from an Ethaline electrolyte having 0.1 M ZnSO4 in potentiostatic two-step processes. The crystal planes (hkl) obtained experimentally are compared with expected phases reported in JCPDS.

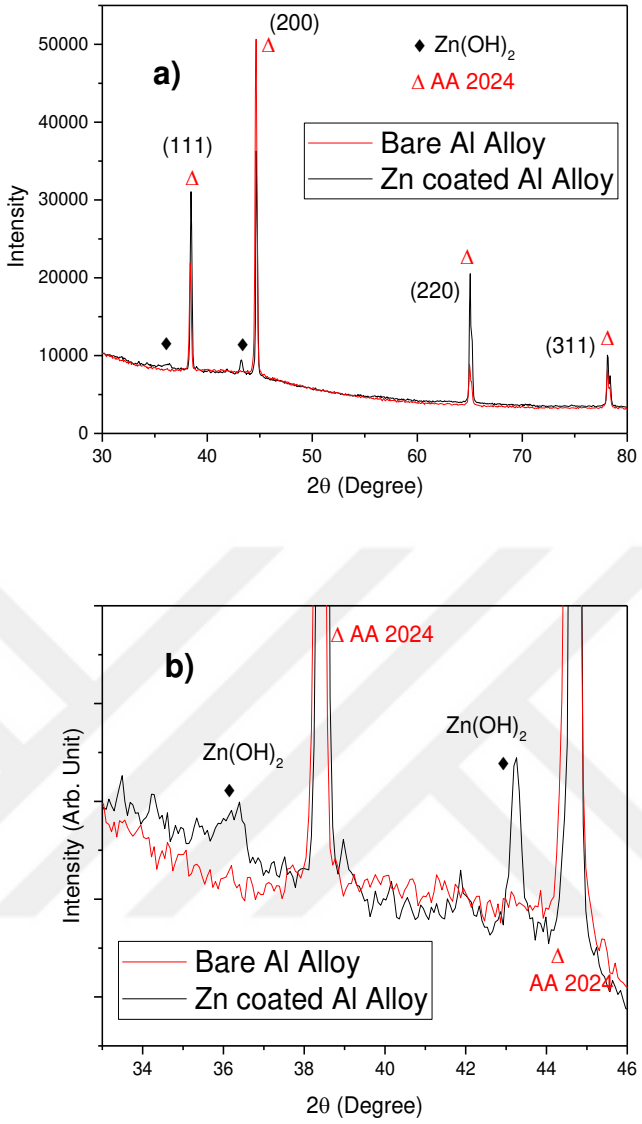


Figure 4.5 XRD pattern of uncoated aluminium alloy (red line) and Zn coated aluminium alloy (black line). The JCPDS X-ray file data (Ref. Code: 01-089-4037) is for face-centred cubic Al. The pattern for $Zn(OH)_2$ (JCPDS file no. 38-385) was reported. Zinc coated aluminium alloy was obtained by applying firstly +1.65 V for 400 seconds and then applying -1.5 V for 800 seconds in Ethaline electrolyte at 50 °C.

The crystal orientation of bare aluminium is reported in the literature in detail by The JCPDS X-ray file data (Ref. Code: 01-089-4037) [111, 112]. The peaks for bare aluminium (red line of Figure 4.5) are observed at 2θ values of 38.4°, 44.8°, 65.1° and 78.1° which are well indexed to the planes of face-centred cubic Al (111), (200),

(220) and (311), respectively. The crystal orientation obtained from the surface of zinc coated Al alloy is similar to that of bare Al alloy apart from two lower intensity peaks observed at 2θ values of 36.3° and 43.4°. The new observed peaks can be indexed to the diffraction of $Zn(OH)_2$ at 36.3 and 43.4 degree (JCPDS file no. 38-385) [113, 114]. The expectation from XRD results was to have only zinc based diffraction patterns. Several zinc coated aluminium alloys were characterised in terms of diffraction patterns and all of them were the same as the representative one shown in Figure 4.5. The diffraction similarity obtained from uncoated and Zn coated Al alloy can be linked to two possible scenarios. One is that the Zn film on Al alloy substrate is so thin that the EDAX analysis revealed aluminium contents in the film. The other one is that Zn coating on Al alloy has high amount of amorphous solid and hence it does not show high crystallinity and crystallinity of aluminium alloy dominates the diffraction pattern. The amorphous structure of Zn film was also observed in SEM analysis presented in section 3.1.2. As aluminium contents were found from EDAX analysis of Zn coated Al alloy, both scenarios must be also possible together. As a result, a thin amorphous solid of zinc coating is obtained by applying +1.65 V for 400 seconds in order to dissolve Al_2O_3 layer into Ethaline and then applying in-situ -1.5 V for 800 seconds in order to obtain electrodeposition of Zn on fresh Al alloy surface. This kind of films were obtained for corrosion in different aqueous media: acidic (pH = 2), neutral (pH = 7) and alkaline (pH = 12).

4.3 Corrosion Resistance Properties of Zn Coated Al Alloy

The polarisation behaviour of the bare and zinc coated AA2024 alloys is presented in Figure 6. Al_2O_3 layer formed on aluminium/aluminium alloys in atmosphere protects the bulk aluminium from corrosion. Although passive aluminium alloys is not required a coating in acidic or neutral environment as they have quite high corrosion resistivity, aluminium based alloys cannot be used in alkaline media as aluminium has a high reaction kinetic with OH- ions. As zinc is passivated especially in alkaline media, zinc metal was selected as coating to compare the corrosion resistivity of coated and uncoated aluminium in different aqueous media. As zinc and aluminium both have lower standard potential (around -1 V) than other metals and E_{corr} value is not important in corrosion rate, E_{corr} value is not considered in this study. The main focus here is to find out how difference the current density (i_{corr}) is and whether there

is passivation of the coatings. The bare Al alloy displays a low current density (18 μA cm^{-2}) than zinc coated Al alloy (49 μA cm^{-2}) in acidic media given in Figure 4.6a. An important improvement here is that zinc coated Al has passivation behaviour as current density of Zn coated Al decreases at around -0.4 V in acidic solution (pH = 2). After -0.5 V, both uncoated and zinc coated Al alloys have pitting corrosion in acidic media.

Uncoated and zinc coated aluminium in classical corrosion environment (3 wt % NaCl) solution have different polarization curves but their current densities are close to each other which are 1.6 μA cm^{-2} and 1.9 μA cm^{-2} respectively illustrated in Figure 4.6b. Zinc coating demonstrates no improvement of the corrosion resistivity of aluminium alloy in neutral solution (pH = 7).

Although bare AA2024 alloy has quite high current density in alkaline media (79 μA cm^{-2}), current density of zinc coated Al alloy is decreased to 12 μA cm^{-2} in the same media (shown in Figure 4.6c). The corrosion rate of bare aluminium alloy is therefore more than 6 times higher than that of zinc coated aluminium alloy. Passive current density was obtained that range from 10^{-4} to 10^{-5} A for zinc coating in alkaline media (Figure 4.6c). The Zinc coating could protect aluminium alloy against corrosion in alkaline media.

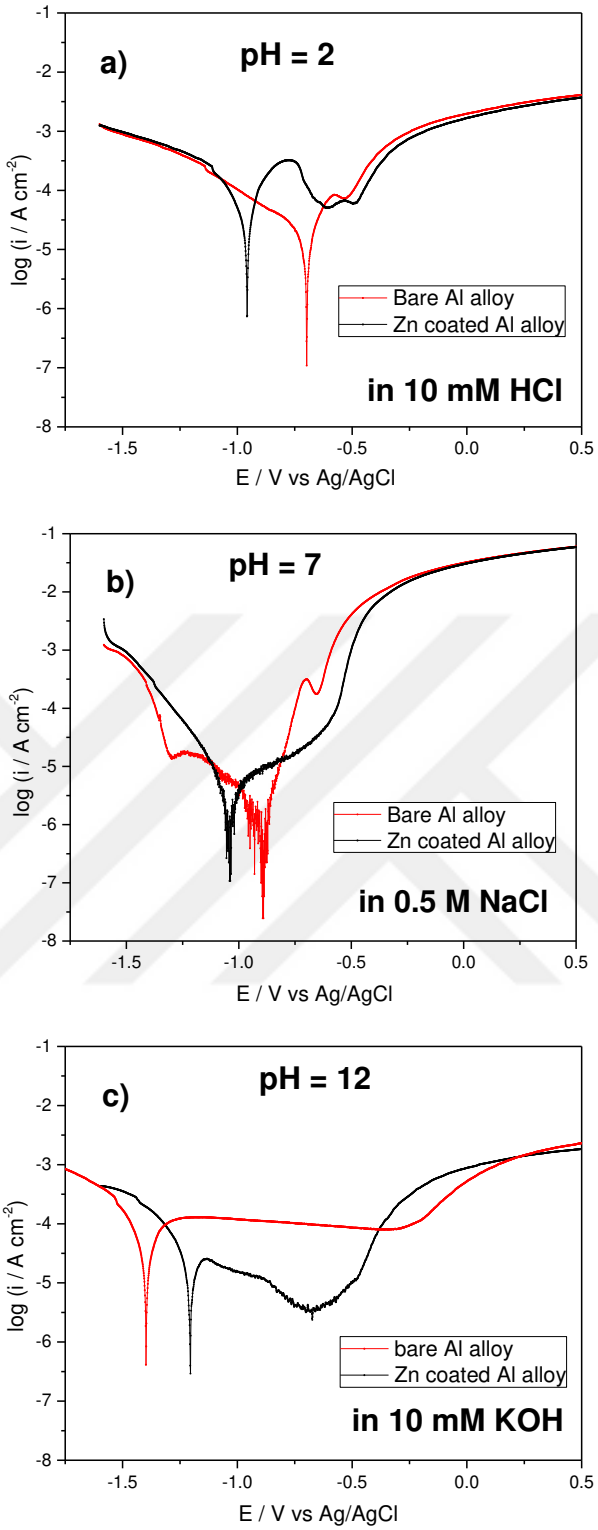


Figure 4.6 Polarization curves for bare AA2024 aluminium (red lines) and Zn coated aluminium alloy (black lines) in the aqueous electrolytes whose pH are respectively a)2; b) 7; c)12. The scan rate is 20 mV s^{-1}.

Zinc coating on aluminium alloy is a passive film and it protects aluminium alloy in alkaline corrosive media. The image of passive zinc is shown in Figure 4.7 (right side).

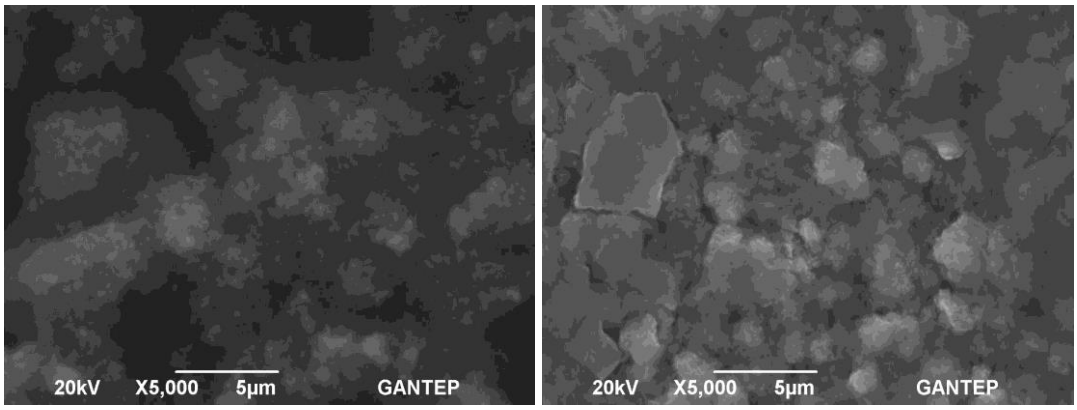


Figure 4.7 SEM images of Zn-coated Al alloy: a) before and b) after alkaline polarisation.

On the left side of Figure 4.7 there is an image of zinc coated aluminium alloy which is higher magnification of Figure 4.4 (right side). The right side of Figure 4.7 is the images of zinc coated aluminium alloy after treatment with alkaline solution. XRD results (in section 3.1.3) and SEM images showed that zinc coating is more likely in amorphous structure. A passive zinc oxide/hydroxide film however has more crystalline solid (Figure 4.7).

CHAPTER FIVE

CONCLUSION

In the present study, the AA 2024 alloy has been chosen to investigate the corrosion behaviour in an aqueous solution having various pH (2, 7 and 12). As it is known the coating of aluminium alloys is awkward. That is why after some experiments it is decided to use deep eutectic solvent as deposition electrolyte (Ethaline was prepared by mixing analytical grade choline chloride ($C_5H_{14}NOCl$) and ethylene glycol $C_2H_6O_2$ in 1:2 ratio). The reason to choose Ethaline is that Ethaline displays a wider potential window than aqueous solutions.

Immersing of AA2024 in Ethaline results in no redox reaction between 0V and -1.5V meaning that there is no possibility to coat Zn onto AA 2024 alloy in anodic potential. This is a typical characteristic of aluminium alloy due to the existing of Al_2O_3 thin layer occurring naturally on the aluminium surface which may hinder the formation of any metal coating on it. Therefore anodic voltage (positive potential) was firstly applied to remove this film (Al_2O_3). After that the cathodic potential was immediately applied to deposit zinc on aluminium alloy. After applying the anodic potential (+1.65 V) to aluminium alloy (Al_2O_3 surface) in Ethaline, the Al_2O_3 surface is deformed and become a different surface. Then immediately Zn coating was electrodeposited on the surface of bulk aluminium alloy by applying cathodic potential (-1.5 V). Applying start potential revealed that there was no zinc reduction at the beginning. Zn coating takes place at higher anodic potential (around +1.65V). The peeling of Al_2O_3 surface layer and the formation of bubbles on the surface of aluminium alloy occurred at high anodic potential between 1.00 V and 1.65 V during the deformation of Al_2O_3 surface and formation of a new surface of a bulk aluminium alloy. There was no reduction of zinc when the starting potential was 0 V. Two reduction peaks arose when Al_2O_3 surface was dissolved in Ethaline at extreme cathodic potential (between 1 V and +1.65 V) one of the peak at around -0.6 V is related to Zn^{2+} to Zn^{+} and the other at around -1.3 V is associated with zinc

deposition from Zn^{+} to Zn^{0}. The deposition of zinc and cyclic voltammograms experiments in Ethaline were carried out at 50 °C.

SEM and EDAX analysis prove that the Zn coating has been formed on the AA 2024 alloy. The ratio of Zn content on the film is 68% which may depend on either thickness of film having Al or the formation of Zn-Al alloy on the substrate surface due to dissolved aluminium ions taking place at high anodic potential. Zn film displays the characteristic of an amorphous structure. That is why there is a weak crystallinity of the film and the domination of crystalline patterns arising from the AA2024 substrate (indicated by XRD patterns).

Corrosion resistance properties have been examined in three different media (acidic, neutral and alkaline). In acidic medium (pH = 2) it has been seen that the Zn coated AA 2024 substrate shows the passivation behaviour. Bare AA2024 however has pitting corrosion at high potential in that medium (pH = 2). Although at the beginning of this research the expectation was to coat aluminium based alloy with Zn film in order to have galvanised aluminium in alkaline media, it is observed that zinc coated aluminium in acidic media has passive film.

Zn coating performs no improvement of corrosion resistance in neutral solution (pH = 7). On the other hand, the coated substrate presents more than six times higher corrosion resistance of zinc coated AA2024 than that of bare AA2024 in alkaline medium (pH = 12). Furthermore, zinc coated film in alkaline medium shows the passivation of the coating. SEM images reveal the change of coating structure during the potentiodynamic polarisation.

As it is well-known that the electrodeposition techniques- has some advantages such as ease of application, inexpensiveness and controllability. This allows the extended changing in the deposition conditions through changes of chemical conditions (such as pH, aqueous-non aqueous, contents), physical conditions (temperature, thickness) and selected electrochemical techniques (potential step, pulse). The preparation of desired films with specific properties is expected to be possible with extended work. The forthcoming study may be detailed experimental parts of coating different metals or alloys on aluminium based alloys with different deposition conditions such as variations of temperature, ionic liquid based electrolyte and electrodeposition parameters (time, controlled potential, controlled current).

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