ELECTROPLATING OF IRON ON AZ31 MAGNESIUM ALLOY FOR CORONARY STENT APPLICATIONS

A Thesis by

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The following faculty members have examined the final copy of this thesis for form and content, and recommend that it be accepted in partial fulfillment of the requirement for the degree of Master of Science with a major in Industrial and Manufacturing Engineering.

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ABSTRACT

Drawbacks with permanent metal stents led to the investigation of alternative biodegradable stent materials. Potential biodegradable polymers for stents lack the mechanical strength as compared to metals used for stents. Magnesium (Mg) based materials are being investigated as a potential biodegradable metallic stent materials because of its biocompatibility and high strength to weight ratio. Magnesium possesses poor corrosion resistance in physiological environments, thus surface modification strategies on magnesium are needed. Challenges with surface coating on magnesium exist due to the high reactivity of magnesium. The objective of this thesis was to electroplate iron on AZ31 magnesium alloy. Iron being a part of human body and a major component of 316 L stainless steel, which is considered to be the gold standard of arterial stent was electroplated onto the surface of the AZ31 magnesium alloy. Iron was electroplated with an intermediate copper layer to prevent its interaction with the electrolyte and compared with the iron coating without an intermediate copper layer. The electroplated sample was characterized using SEM-EDX, XRD, XPS and roughness measurements. EDX analysis proved the presence of 40% iron by atomic weight. XRD analysis proved the presence of iron in magnetite form and XPS confirmed the presence of iron. The thickness of the sample was measured by SEM which was found to be 30.8µm. Roughness of the sample was measured using a digital microscope with surface analyzer using which the roughness was found to be 10.4776µm. Accelerated corrosion tests conducted in PBS proved that iron coated magnesium samples had better corrosion resistance than bare Mg. The corrosion rate of coated Mg was 1.373632mm/yr and the corrosion rate of bare Mg was 40.4114 mm/yr. This proves that iron coated Mg can be expected to stay longer in the body compared to the uncoated ones.

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CHAPTER 1

1. INTRODUCTION

1.1 Medical Implants

A medical implant is a device used to replace a missing biological structure (Buddy D Ratner, 2013). Bone implants, arterial stents and ear implants etc are some of the most common types of implants used(Namnoum, Largent, Kaplan, Oefelein, & Brown, 2013). Implants are pictured to be very sturdy with very low corrosion rate, but there are some implants like bone screws, plates and arterial stents which needs to be removed surgically in the future if complications arise (Namnoum et al., 2013).

1.2 Biodegradable Implants

Some disadvantages associated with permanent implants are loosening of implant, metal ion dissolution and inflammation. There are some implants which are not justified in the human body beyond their functional duration. There are some cases where complications arise due to the presence of implants beyond its functional period, which in turn will require a surgery to remove it. In order to eliminate all of these disadvantages biodegradable implants were introduced. Biodegradable implants can be made of polymers, ceramics and metals. Polymeric implants were initially investigated for orthopedic, dental and soft tissue applications(Pihlajamäki, Kinnunen, & Böstman, 1997). Biodegradable ceramics are used as bone screws, bone spacers etc. Polymers are currently being used for drug delivery and scaffolding applications. Polymers have very high degradation rate and low strength. Hence they cannot be used for high strength applications. Mismatch of properties between metals and biodegradable polymers led to the investigation of biodegradable metals.(Pietrzak, Sarver, & Verstynen, 1996). Iron and magnesium was found to be the most eligible candidates based on biocompatibility tests. Iron and magnesium are being considered because they are a part of the human body and they are biocompatible.

1.3 Heart Diseases and Arterial Stents

Coronary artery disease (CAD) is the most common type of heart disease which causes the heart attack. This is caused by plaque building up on the walls of an artery. The plaque causes narrowing of artery which in turn reduces the blood flow this condition is termed as arthrosclerosis(Zachariah et al., 2013). Arthrosclerosis is treated by a process called angioplasty. In this process the doctor inserts a thin narrow tube (catheter) into the blocked artery. Another catheter with a deflated balloon at its tip is inserted into the narrowed area in the artery(Blumenthal, Cohn, & Schulman, 2000). The balloon is inflated which compresses the deposits against the arterial walls. A mesh like tube (stent) is left in the artery which keeps the artery open.

316-L stainless steel is regarded as the gold standard of stents because of its superior resistance to corrosion and very less metal ion dissolution. Initially polymers were considered as possible stent materials but its low strength lead to the development of biodegradable metallic stents(H. Hermawan, Dubé, & Mantovani, 2010). Magnesium can be considered as an ideal candidate for stent applications because of its high strength to weight ratio and its biocompatibility. Corrosion rate of magnesium is very high which requires some coating on it to lower the corrosion rate.

1.4 Surface Modification of Magnesium

Most common way to reduce the rate of magnesium corrosion is by alloying with nobler metals or rare earth metals. Rare earth metals like Li, Zr, Y can be used for increasing the corrosion resistance of magnesium (Gu & Zheng, 2010). Li-Magnesium can be specially used for treating maniac depressive psychoses, but the presence of even 2-4ng of Li causes nervous disorders and reduce kidney function(Zhou, Zheng, Leeflang, & Zhou, 2013). Presence of some rare earth metals causes hepatotoxicity (Horsmans, Lannes, Pessayre, & Larrey, 1994). The most common metals being considered are Ca, Zn, Mn, Si and Al. Zn, Mn are trace elements present in different enzymes, whereas Ca is one of the most abundant metal present in teeth and bone.

The degradation rate of Ca as high as 1.3mmol/l causes kidney stones and presence of high amounts of Zn and Mn causes neurotoxicity (Gu & Zheng, 2010). Higher aluminum content increases the strength of magnesium alloys and offers better corrosion resistance than pure magnesium, but high aluminum content causes neurotoxicity and accumulates in the human bone(Gu & Zheng, 2010). So magnesium alloy with low Al concentration like AZ31 is preferred for most biocompatibility tests. The corrosion rate of AZ31 magnesium alloy is higher than pure magnesium(Habibnejad-Korayem, Mahmudi, Ghasemi, & Poole, 2010).

Another possible useful procedure to reduce the rate of corrosion is surface modification which include alkaline heat treatment, micro arc oxidation, phosphatizing treatment, electroplating and polymer coating(Gu & Zheng, 2010). Alkaline heat treatment test was conducted in a Mg-Ca alloy. The test was carried out for 24 hrs in sodium carbonate, disodium phosphate and sodium bicarbonate and was subsequently heat treated for 12hrs at 773K(Gu & Zheng, 2010). In vitro tests in simulated body fluid depicted, lower corrosion rates and cytotoxicity evaluation showed presence of no toxicity.

Polymer coatings haven been researched on magnesium on a large scale. Polylactic acid (PLA) is one of the most researched polymers(Raquez, Habibi, Murariu, & Dubois, 2013). Most of the polymer coatings are dip coatings. Electrochemical impedance spectroscopy tests were conducted for PLA coated magnesium and pure magnesium in simulated body fluid which has a high concentration of chloride ions. PLA coated samples offered better corrosion resistance than bare sample(Raquez et al., 2013). But the corrosion resistance offered is less compared with metal coated magnesium samples(Arrabal et al., 2012). Different coating techniques like vapor deposition and electroplating can be used to obtain better corrosion resistance(Yamamoto, Watanabe, Sugahara, Tsubakino, & Fukumoto, 2001).

Vapor deposition is divided into physical and chemical vapor deposition which involves coating of a metal film on the surface of substrate by passing a gas. Most of these processes are done in high temperature and vacuum, whereas electroplating can be done at room temperature(Raquez et al., 2013). The major problem with the vapor deposition procedures is its high capital cost.

Electroplating is the cheapest metal deposition method available. It just requires two electrodes, electrolyte and a D.C power source. Aluminum has been successfully deposited on magnesium and corrosion results showed that it offered better corrosion resistance compared to bare magnesium alloy(C.C Yang 1993). On similar lines this metals which are nontoxic can be coated onto magnesium so that they can be used as possible medical implants. Some common examples are Ti, hydroxyapatite for orthopedic applications and Fe for arterial stent applications.

1.5 Research Objective

The objective of this thesis is to reduce biodegradation of magnesium inside the human body so that it can be used as possible arterial stents. Iron is proposed to be electroplated on the surface of magnesium because iron is the major part of 316-L stainless steel. Iron is also a part of human body and it is biocompatible.

1.6 Thesis outline

This thesis is divided into five chapters. Chapter 2 presents the literature review of previous work done on permanent stents and ways to control corrosion of magnesium based materials. Chapter 3 talks about the technique to electroplate iron on magnesium at a very low pH. Chapter 4 discusses about the results that proves the iron coating on the magnesium surface and compares the corrosion resistance of intermediate copper coated magnesium and one without a copper coating. In Chapter 5, conclusion and future research directions are discussed.

CHAPTER 2

2. LITERATURE REVIEW

2.1 Introduction

This chapter discusses the previous research on permanent biomedical implants and biodegradable implants. Section 2.2 reviews about the basics of biomaterials. Section 2.3 depicts about basic functions, properties of biomaterials and its response to living cells when placed in the body. Section 2.4 discusses about the different types of biomaterials. Section 2.5 talks about biomaterials. Section 2.6 talks heart diseases and angioplasty. Section 2.7 talks about disadvantages of permanent stents. Section 2.8 talks about biodegradable iron stents and section 2.9 talks about biodegradable magnesium stents. Section 2.10 talks about the types of corrosion of magnesium and its alloys in physiological media. Section 2.11 talks about chemical vapor deposition. Section 2.12 talks about sputtering. Section 2.13 talks about electroplating. Section 2.14 depicts the research motivation.

2.2 Biomaterial

A medical implant is a device used to replace a missing biological structure (Buddy D Ratner, 2013). Bone screws, bone spacers, bone plates and stents are some of the common types of implants used. Implants are pictured to be very sturdy with very low corrosion rate, but there are some implants like bone screws, plates, pedicle plates and arterial stents which needs to be removed because there some cases where unnecessary complications arise after surgery due to the presence of implants(Bartlett, 2007).

A medical implant has two functional requirements biocompatibility and functional performance. The implant when placed in the human body must not be toxic on its interaction with the tissues. When placed in the human body the biodegradable medical implants must not degrade in their properties within the body. Some common classification of biomaterials is metals, polymers, composites and ceramics.

2.3 Functions and Properties of a Biomaterial

Biomaterials are materials intended to interface with biological systems to evaluate, treat, augment or replace any tissue organ or function of the body(Grainger et al., 2013). Primary qualifications for a material to be used as a biomaterial are its biocompatibility and its functional performance. The biocompatibility of a material can be evaluated based on its end application. An implant when placed in the human body must not degrade within its properties when placed in the body. An implant placed in the human body must provide adequate mechanical strength and stiffness which depends on the type of application(Imwinkelried, Beck, Iizuka, & Schaller, 2013).

A medical implant manufactured from a biomaterial must not have any delirious changes or harmful side effects on its interaction with the living tissue. A medical implant needs to have a balance between physical and mechanical properties of the implant and must perform as expected(Celenza, 2012). The device under consideration must be easier to manufacture and conform to all technical and biological requirements. Human body has 3 different types of interaction with a foreign body they are 1) implant is toxic, and the surrounding tissue dies 2) implant is non-toxic and permits tissue growth 3) implant is non-toxic and accelerates tissue growth.

Most of the implants are subjected to either static or repetitive loading, which requires a combination of strength and ductility. This characteristic is found in metals, which sets it apart from polymers and ceramics. Lane first introduced the metal plate for bone fracture fixation (Hendra Hermawan, 2011). In the early stages, corrosion and strength were two factors influencing further design. After the introduction of stainless steel, the implant industry faced vast development because of its properties. The properties of 316-L stainless steel is regarded as the gold standard of stents.

2.4 Common Types of Biomaterials

There are two types of biomaterials which can be considered are 1) polymers 2) metals 3) Ceramics

2.4.1 Polymers

Polymers have been used in medicine for quite a long time they have been used as catheters, syringes, tissue regeneration and cell encapsulation. Based on their backbone reactivity they can be broadly classified into degradable and non-degradable (Shastri, 2003). The polymer backbone depends on the monomer and the linkages between the monomer. Particulate matter arising due to erosion of polyethylene overtime has long term health effects. Recycling and disposal of these polymers is also difficult. In contrast, biodegradable polymers are broken down by the human body. Some of these polymers are made up of starch, lactic acid and cellulose; these chemicals are taken from the nature and returned back to them (Richard. A. Gross, 2002). Biodegradable polymers can be used for drug delivery and scaffolding applications(Langer, 1991) but not for skeletal reconstruction owing to its poor strength in comparison with metals

2.4.2 Metals

Metals have been used in the history of implants for the last 100 years(Hendra Hermawan, 2011). In the early stages, of implant development corrosion was a major issue but after the introduction of 316-L stainless steel the problem of corrosion was eliminated. Some advantages of metal implants are better wear resistance, high loading capacity and excellent toughness. Some metals commonly being considered for stents are 316-L stainless steel, cobalt chromium and Ti alloys(Hendra Hermawan, 2011). 316-L stainless steel is regarded as the gold standard of stents.

Most of the stent implants are subjected to both compressive loads and erosion due to vigorous conditions in the human body. Most metallic biomaterials are exploited due to their inertness and structural functions(Hendra Hermawan, 2011). In order to prevent any complication after surgery and maintain the same compressive strength similar to permanent implants biodegradable metallic implants are being researched(Peuster et al., 2006).

2.4.3 Ceramics

Ceramics are commonly used in bone and dental applications. Some common types of ceramics are alumina, zirconia and calcium phosphate(Hayashi, Inadome, Tsumura, Mashima, & Sugioka, 1993). The ceramics are divided into 3 types they are 1) Inert 2) Bioactive 3) Degradable. Alumina and zirconia are inert ceramics and are most commonly used in hip replacement implants. Bio glass is an example for a bioactive ceramic and it is most commonly used as a coating. Hydroxyapatite a form of calcium phosphate is a degradable ceramic and it is also used as a coating on other metals or ceramics. Hydroxyapatite has chemical and structural properties similar to bone minerals. Nanostructured hydroxy apatite is found to have better bioactivity compared to coarse ones(Hayashi et al., 1993). Most modern hip replacement implants are coated with hydroxy apatite to promote cell growth. Coral skeletons can be converted into hydroxy apatite by heating it up. At high temperatures the porous structures allows rapid ingrowth at the expense of mechanical strength. Porous hydroxyl apatite is used for local drug delivery in bones(Kundu et al., 2010)

2.5 Biodegradable Implants

Some implants in the human body are not justified beyond their functional period. Possible ways to remove the implant is by second surgery. Biodegradable implants degrade over a period of time. The major idea of biodegradable implant is to dissolve after the specified functional period with no harmful effects to the human body. The rate of degradation needs to match the tissue healing rate. Biodegradable polymers, metals and ceramics are considered for biodegradable implants. According to (Y. Wang & Grayson, 2012) polymers can be used for drug delivery application owing to their low mechanical strength. (Wildemann, Sander, Schwabe, Lucke, & Stöckle, 2005) suggested that polymers can also be used for orthopedic applications. According to (Wildemann, Sander, Schwabe, & Lucke, 2005) and(Middleton & Tipton, 2000) poly-l-lactide can be used in fracture fixation devices. Calcium phosphate based hydroxyl apatite can be used as a biodegradable implant owing to its osteoinductive properties. They have properties similar to human bone and the nano-pores permit growth. Metals are also considered for biodegradable implants, some of the metals which are being considered for biodegradable stents are iron and magnesium. The degradation rate of iron is 10 years which is too high and it is as good as having a permanent stent in the body. The biodegradable stents are justified in the body for only 2 years which is the restinosis period. Rate of degradation of iron can be increased by alloying with lesser nobler metals there by inducing intergranular corrosion. Degradation rate of magnesium is very high, magnesium is found to degrade in 30 days in human body conditions(Willumeit, Feyerabend, & Huber, 2013). The degradation rate can be slowed down by selective alloying or surface coating. Alloying magnesium with nobler metals increases corrosion resistance.

2.6 Heart Diseases

A human heart has four chambers. The top two chambers are called atria and bottom two chambers are called ventricles. The job of the ventricles is to pump blood and atria when the atrium fills with blood. The atria and the ventricles work together. Left and right side of the heart is separated by a muscle called septum. Heart contracts to pump blood into the body and relaxes to let the chambers fill up. The human heart has valves which makes sure that the blood flows in the correct direction. The heart valve opens and closes during each cardiac cycle which is approximately 40 million times in one year and 3 billion times during a life span of 75 years(Buddy D Ratner, 2013).

Disorders in heart valve can cause stenosis (i.e., obstruction to blood flow) or regurgitation (i.e., reverse blood flow across the valve) (Buddy D Ratner, 2013). In some cases, both stenosis and regurgitation might occur in the same valve. Infective endocarditis is a form of heart valve disease which causes heart valve failure(Helms & Bach, 2013). This leads to abrupt heart failure and death. Heart valve diseases are of several types the most common ones involve failure of mitral valve and aortic valve. The only option to this is valve replacement. Most common disease which leads to valve replacement is due to obstruction at the aortic valve secondary to age related calcification of cusps of a valve that was previously anatomically normal(Buddy D Ratner, 2013). According to (Fernandes et al., 2013) and (Helms & Bach, 2013)Symptoms of this disease occur approximately during 7th-8th decades of life. This essentially takes decades to develop.

Several hundred designs for valve replacement have been developed to replace diseased heart valves. Most of them have been abandoned owing to flaws in design and material that surface only during clinical use (Buddy D Ratner, 2013). Valvular replacement is divided into types they are mechanical valves and biological tissue valves. Mechanical heart valves are ones which are made of non-physiological matter and composed of only biomaterials. Mechanical heart valves employ rigid, mobile occluders in a metallic cage which are usually made up of cobalt-chrome and titanium alloys(Buddy D Ratner, 2013). Nowadays all mechanical replacements are done using pyrolytic carbons which has high strength and wear resistance(Camilleri et al., 2001). Patients with mechanical valves need to take anticoagulants all their life to reduce the risk of thrombosis. Tissue valves are most frequently derived from pigs and cows. The valves are treated with glutaraldehyde which fixes the tissue and decreases its immunological reactivity(Buddy D Ratner, 2013). Another heart disease which is very prevalent is atherosclerosis. Some basics idea of atherosclerosis and the method to treat it is mentioned in section 2.6.

2.6 Arterial Stents

Atherosclerosis is a disease where a plaque builds up on the walls of the artery(Ibrahimi et al., 2013). The plaque is made up of fat, cholesterol, calcium and other substances which are present in the blood. Arteries are blood vessels which carry pure blood and the plaque which forms on the walls of the artery prevents blood flow to organs and other parts of the body(Ibrahimi et al., 2013). Atherosclerosis can cause stroke, heart attack or even death. Plaque developing on the arteries of the heart prevents blood flow to heart muscle(Ibrahimi et al., 2013). It is the most common type of disease in both male and female. A procedure called angioplasty is used to treat narrowed arteries.

Angioplasty is the process of placing a stent in the human body. Stents are narrow mesh like tubes used to treat narrowed blood vessels. Fig 2.1 shows an image of a stent. They are used to keep the arteries open for treating coronary heart diseases.(So et al., 2010). Stents reduce pain and they ensure survivability in the event of an acute myocardial infarction. For a stent to be placed in the heart, the doctor will make a small hole in the arm, neck or groin. Through this hole the doctors will insert a small flexible tube called a catheter with a balloon in its tip. A stent is placed around the deflated balloon.

Fig.2.1 Schematic view of an arterial stent- (Buddy D Ratner, 2013).

During the process a thin catheter tube with a balloon at the tip is threaded through the blood vessel to the affected artery. Once the balloon is in place it is inflated to compress the plaque against the walls of the artery. This ensures better blood flow through the artery. Baloon is deflated and pulled out. Fig 2.2 shows the various stages of inserting a stent during angioplasty.

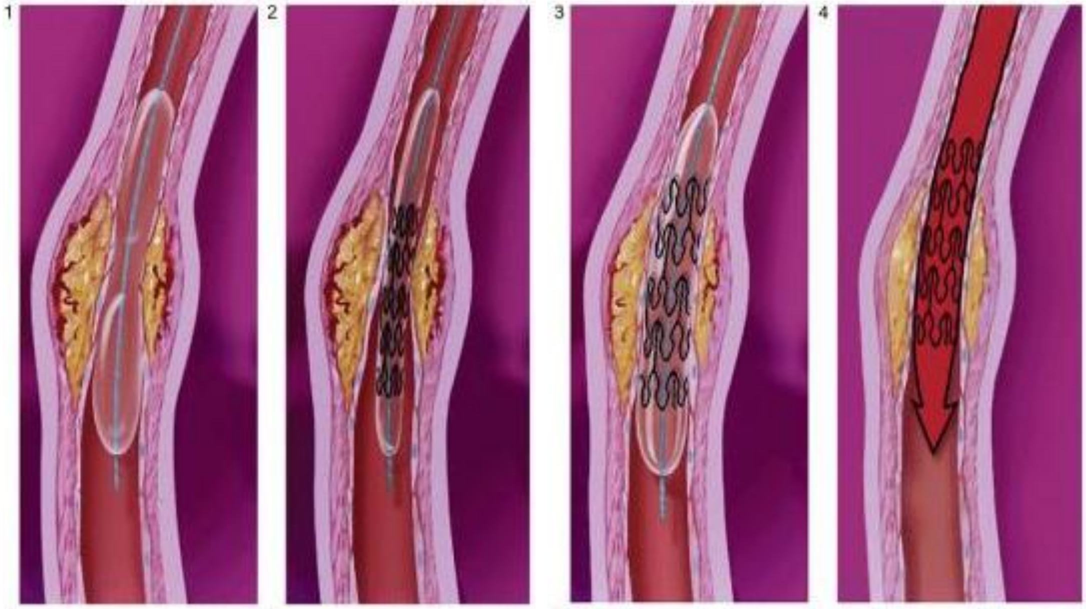


Fig.2.2 Various stages in inserting a stent- (Buddy D Ratner, 2013).

2.7 Disadvantages of Permanent Stents

Despite all the benefits of permanent stents there are some disadvantages associated with it. In case of blockage in the same artery insertion of another stent in that artery is also difficult. (Garg & Serruys, 2010) says that stent thrombosis associated with permanent stent is a major problem associated with stents. The average restinosis period is 12-18 months and the presence of a stent is not justified beyond that duration. Presence of a permanent fixture in an artery over a longer time periods can cause inflammation to the surrounding tissues. As a result of which biodegradable stents are being researched. Polymers and metals are being investigated for possible biodegradable stents. Polymers lack the mechanical strength compared to metals so biodegradable metals like magnesium and iron are being investigated.

Magnesium and iron are the most commonly researched biodegradable metals. Magnesium has high strength to weight ratio and the degradation products of magnesium are biocompatible. Degradation rate of magnesium is higher when compared with iron making it a suitable candidate for stent applications. Peuster et al found out that it takes around 10 years for a pure iron stent to degrade (Peuster et al, 2006). Metallic biomaterials are widely used because of their fracture toughness and mechanical properties (Wong et al., 2010).

2.8 Iron as Biodegradable Stent

Iron has been investigated for stents over the last decade. The symbol of iron is Fe. It is the 4th most abundant metal on the earth. Iron has been used since ancient times through copper alloys, which have lower melting points. The color of iron is silvery grey but it starts oxidizing when exposed to the atmosphere. It forms a layer of iron oxide on it. It is commonly called rust. It is a D-block metal. Iron is the most common metal on the surface of earth and it is also a part of the human body. Iron is biocompatible and degradation of iron does not produce any toxins.

Iron is a transition metal. Pure iron is very soft and amount of carbon content in iron changes its hardness. Iron is an allotropic metal, it exsist in 4 allotropic forms. Iron exists in 6 different oxidation states, ferrous and ferric being the most common ones. Iron in human body takes around 10 years to degrade in a simulated body fluid. Stent in the artery is not justified beyond 12 to18 months. (Hendra Hermawan, Purnama, Dube, Couet, & Mantovani, 2010) and (Kathuria, 2006) suggested that the rate of corrosion of iron alloyed stents can be increases with lesser noble metals which will increase its rate of degradation. Since the rate of degradation is very less magnesium is being evaluated because of its high degradation rate and biocompatible properties.

2.9 Magnesium as Biodegradable Stent

Magnesium is the 12th element in the periodic table. Symbol of magnesium is Mg. It is an alkaline earth metal. The common oxidation state of magnesium is +2. Magnesium forms around 2.7% of the entire earth's crust(L.-p. Wu, Zhao, Xie, & Yang, 2010). It is the 8th most abundant metal on the earth's crust. Magnesium is highly soluble in seawater from where most of it magnesium is obtained. Magnesium is not found free in nature it is available in minerals like Magnesite and Dolomite. The metal was first produced by Sir Humphry Davy discovered magnesium oxide and concluded that it was an oxide of a new metal. Magnesium is the lightest of all metals.

Free magnesium is highly reactive and burns with a bright white light. This property is commonly used in flares. Magnesium is obtained by electrolysis of magnesium salts obtained from brine(L.-p. Wu et al., 2010). Magnesium is commonly used as an alloying agent with aluminum. Since magnesium is lighter than aluminum they can be alloyed and these alloys are known for their lightness and strength. In the human body, magnesium is the eleventh most abundant element by mass in the human body. Magnesium is essential to all living cells.

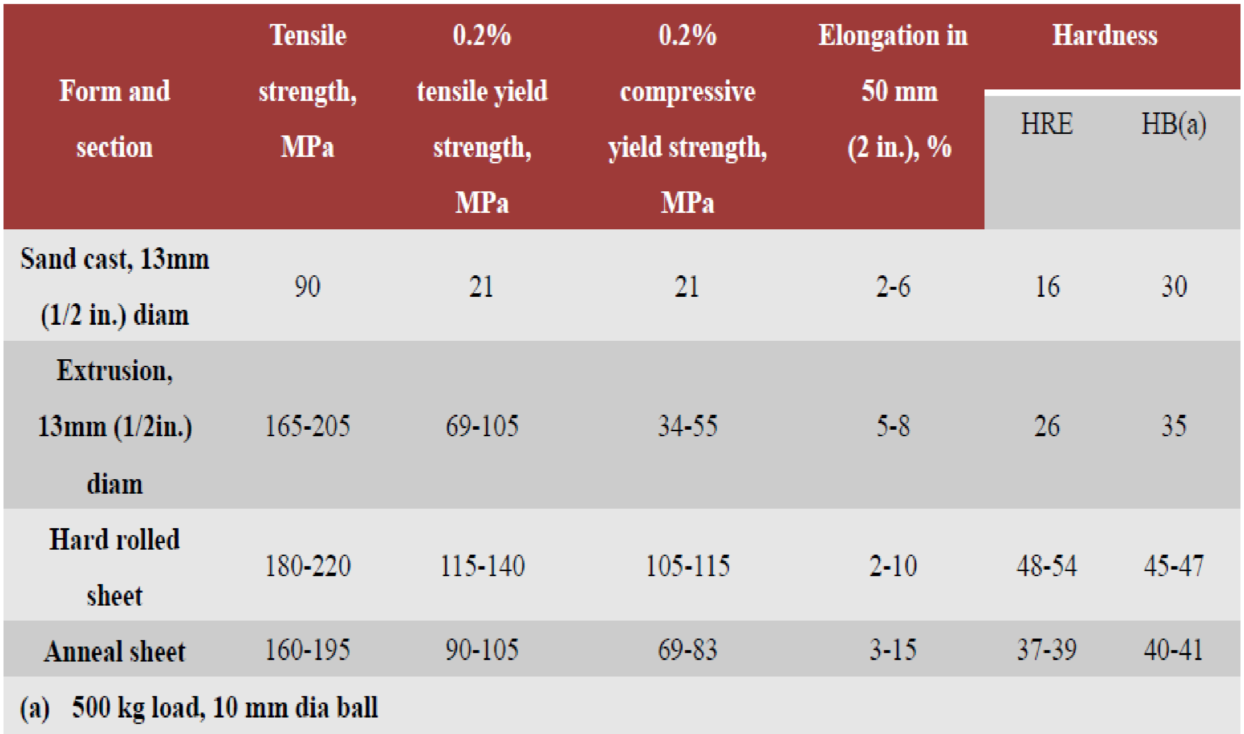
Magnesium plays a major role in manipulating biological polyphosphates compounds. Some common properties of magnesium are given in the table 2.1 below

Table 2.1 Properties of magnesium

Atomic mass	24.305±0.0006u
Atomic number	12
Density (g/cc)	1.738
Atomic radius(pm)	160
Atomic volume(cc/mol)	14.0
Melting point,^{0}C	650
Boiling point,^{0}C	1,091
Electron configuration	Ne 3s2
Specific heat capacity(25^{0}C), J/g^{0}C	1.020
Thermal conductivity (25^{0}C),W/(m.K)	156

Pure magnesium is rarely used in bio applications because of its reactivity and low corrosion resistance. Corrosion is the major problem of magnesium. Typical mechanical properties of unalloyed magnesium are shown in table 2.2. Magnesium corrodes rapidly in a chloride atmosphere and in low pH containing acidic solution. Corrosion of magnesium in human body is due to high chloride concentration in blood and varying human body temperature(Blumenthal et al., 2000). The next section talks about the different ways in which magnesium undergoes corrosion and possible ways to reduce the rate of corrosion.

Table 2.2. Typical mechanical properties of unalloyed magnesium. (L.-p. Wu et al., 2010)



Form and section	Tensile strength, MPa	0.2% tensile yield strength, MPa	0.2% compressive yield strength, MPa	Elongation in 50 mm (2 in.), %	Hardness	
					HRE	HB(a)
Sand cast, 13mm (1/2 in.) diam	90	21	21	2-6	16	30
Extrusion, 13mm (1/2in.) diam	165-205	69-105	34-55	5-8	26	35
Hard rolled sheet	180-220	115-140	105-115	2-10	48-54	45-47
Anneal sheet	160-195	90-105	69-83	3-15	37-39	40-41

(a) 500 kg load, 10 mm dia ball

2.10 Types of Corrosion of Magnesium and its Alloys in Physiological Media

Some common types of corrosion of magnesium alloys in physiological media are 1) galvanic corrosion 2) Stress corrosion 3) pitting corrosion and 4) fretting corrosion

Galvanic corrosion is the one which takes place when two metals are electrically in contact through an electrolyte. A galvanic cell consists of a cathode, anode, electrical contact and an electrolyte (Guo, 2010). In most of the cases magnesium acts a sacrificial anode. Alloying doesn't necessarily reduce galvanic corrosion since it causes internal galvanic corrosion between the grain boundaries. Probable ways to reduce galvanic corrosion is by minimizing the potential difference between magnesium and other metals and by maximizing circuit resistance(Guo, 2010).

Stress corrosion is the occurrence of cracks in a corrosive environment. Stress corrosion can lead to sudden failure of metals. Stress corrosion is divided into discontinuous crack propagation under the effect of mechanical failures and discontinuous propagation due to anodic dissolution(Guo, 2010). The propagation of cracks can be intergranular or transgranular. Transgranular crack propagation is bound to have severe cracking with several secondary cracks. Stress cracking is caused when there is a long term stress above the critical level, a susceptible alloy and a stress cracking inducing environment(Guo, 2010). A stress cracking inducing environment involves NaCl + K_2CrO_4, H_2SO_4, HNO_3, NaOH, NaCl, KF, KCl etc (Guo, 2010).

Pitting corrosion is the most the common form of corrosion found in magnesium and its alloys. This is a form of localized corrosion. Pitting takes place when magnesium is exposed to chloride or acidic medium. Pitting is accelerated in the human body due to changes in temperature. In pitting corrosion the pit acts as the anode and the entire surface of the metal acts as cathode(Han et al., 2012). When there is a change of potential surface erosion takes place. When two pieces of metals which are in contact are pressed by an external force and one of metal piece gets displaced. If the displacement is less than 0.03 inch it is termed as fretting corrosion. Fretting is common only in orthopedic applications.

Some common ways to reduce corrosion is alloying and surface coating. Magnesium can be alloyed with metals like aluminum, steel, zinc, manganese, silicon, copper, rare earth metals and zirconium to form strong alloys. AZ31 contains 3% aluminum, 1% zinc and 0.3% manganese(Xue-Nan Gu, 2010). AZ31 is being explored for possible bio applications but aluminum ion dissolution as low as 2.1-4.8 µg leads to neurotoxicity(Xue-Nan Gu, 2010). Since some of the alloys cause toxicity alternate methods like surface coatings are being researched to increase corrosion resistance. This thesis deals with electroplating which is economical compared with other commonly used processes. A few commonly used processes other than electroplating are 1) Chemical Vapor deposition and 2) Sputtering.

2.11 Chemical Vapor Deposition

Chemical vapor deposition (CVD) involves depositing a solid material onto the substrate from a gaseous phase(Ishizaki, Hieda, Saito, Saito, & Takai, 2010). The process involves passage of a carrier gas with the gaseous material through a reaction chamber, as the gas passes over the heated substrate they decompose forming a solid phase and is deposited onto the substrate. CVD process is divided into Low pressure CVD, atmospheric CVD, and ultra high vacuum CVD(Ishizaki et al., 2010). CVD process is always carried out at a very high temperature which is highly critical for a good deposition(Ishizaki et al., 2010).

The metals used for coating must be volatile so that it is converted into gas easily and it must be stable in the reactor(Ishizaki et al., 2010). The carrier gases which are commonly used inert gases. Parts of a CVD machine are 1) gas delivery system 2) reactor chamber 3) substrate loading mechanism 4) Vacuum system 5) Exhaust system 6) Exhaust gas treatment system 7) process control equipment(X. Wang, Zeng, Wu, Yao, & Lai, 2007). Induction heating or laser heating can be used as energy sources for heating up the substrate(X. Wang et al., 2007). The coatings obtained are fine grained, impervious and have high purity(Ishizaki et al., 2010). Typical precursor materials are metals alkyls ($Ti(CH_2tBu)_4$), metal alkoxides ($Ti(OiPr)_4$), metal dialylamides ($Ti(NMe_2)_4$), metal diketonates ($Cu(acac)_2$), metal carbonyls ($Ni(CO)_4$)(Ishizaki et al., 2010). Titanium coated Mg alloys can be used for bone applications. They provide very high corrosion resistance. By products of the CVD processes are volatile gases which are toxic, flammable and they must be treated properly(X. Wang et al., 2007). CVD setup is very expensive and the melting point of magnesium is 650^0C most CVD processes are carried out at a temperature higher than 1000^0C.

2.12 Sputtering

Sputtering is one of the most commonly used techniques to deposit a thin film onto the surface of magnesium. It is done by creating gaseous plasma and accelerating ions from this plasma onto the target material(G.-s. Wu et al., 2008b). The source ions are ejected from the substrate and they travel in straight lines. When a wafer is placed on the path of these ions they get coated. The free electrons will induce a negative charge to the substrate and these accelerated ions collide with the neutral gas atoms and knock off the electrons in the outer most shell leaving the atom unbalanced and it becomes a positively charged atom(G.-s. Wu et al., 2008b). This positively charged atom is accelerated and it is made to strike the substrate ejecting out the target material, which is deposited on the substrate. By law of energy conservation the electrons are restored back to the gas atom and the process continues(G.-s. Wu et al., 2008a). Electroplating is preferred over sputtering because of the high initial setup cost.

2.13 Electroplating

Electroplating is the process of depositing a coating having a desirable form by means of electrolysis (Liu & Ma, 2010; Tang, Chan, & Shih). Its primary purpose is to alter the surface characteristics of the surface so as to provide better corrosion resistance to abrasion and corrosive agents(Liu & Ma, 2010). To complete an electric circuit the following are required which consists of an anode, cathode, electrolyte and an electric power source. The process of electrolysis is governed by two laws of electrolysis. First law of electrolysis states that the amount of chemical change produced is proportional to the amount of electricity passed. Second law of electrolysis states that amount of substance deposited by passage of a given amount electricity is proportional to the chemical weight of substance.

There are two kinds of reaction taking place in an electrolytic bath. Reduction reaction take place at the cathode and oxidation takes place at the anode(Liu & Ma, 2010). During the process of plating cations ions from solution and from the counter electrode (anode) gets reduced at the working electrode (cathode). Acids having the same anion as the electrolyte are used to lower the pH. For example concentrated nitric acid in silver nitrate bath. Most of the electroplating process is carried in a very low pH. Reactions governing electroplating process are given as follows

Cathode: $Cu^{2+} + 2e^{-} \rightarrow Cu$ (Reduction)

Anode: $Cu \rightarrow 2e^{-} + Cu^{2+}$ (Oxidation)

There is another alternate process in electrolysis called electroless plating. This process is slower compared to traditional electroplating process(Sirianuntapiboon, 2013). In this process the counter electrode or the anode is an inert electrode. Some examples of inert electrodes are platinum and graphite. Source of cations is only from the electrolytic bath. The cations move through the electrolyte and get reduced at the cathode. The process used in this thesis the traditional electroplating process.

2.14 Research Motivation

Polymers were initially considered for biodegradable stent applications. Natural polymers like polylactic acid are biocompatible and its degradation products are not toxic. But these polymers lack heavily in strength so there was need to develop metals which are biodegradable and at the same time have high strength. Iron can be used as a possible solution and electroformed iron is being researched as coronary stents(Moravej, Purnama, Fiset, Couet, & Mantovani, 2010). It offered less corrosion resistance than that of pure iron considered for stents. Iron is a major component of human blood and it is biocompatible(Bajaj, Malhotra, & Choi, 2010). But iron usually takes 10 years to degrade in a human body environment, whereas the actual stent duration is 12-18 months. Magnesium was investigated because of its high strength to weight ratio(Zeng et al., 2006) and magnesium is biocompatible but the corrosion rate of magnesium is very high and it is highly susceptible to corrosion in chloride based media. Corrosion rate of magnesium can be overcome by alloying or coating.

Metals which can be alloyed with magnesium needs to be biocompatible. AZ31 was investigated since it contains 3% Al, 1% Zn and rest magnesium. AZ91 (9% Al, 1% Zn) offers better corrosion resistance than AZ31 but higher aluminum content is neurotoxic. Electroplating was selected based on the lower capital cost. The objective of this thesis is to electroplate iron on magnesium and improve the corrosion resistance of bare magnesium substrate and ultimately reduce biodegradation of magnesium. To the best of my knowledge I could not find any reports on electroplating iron on magnesium.

CHAPTER 3

3. EXPERIMENTAL PROCEDURE

3.1 Materials Used

The substrate material was magnesium AZ31 alloy with a size of 35 × 35 mm size purchased from Goodfellow Cambridge Limited. The counter electrode was an iron rod of length 100mm and diameter 16mm purchased from Goodfellow Cambridge Limited. Copper plates were bought from Goodfellow Cambridge Limited. All the other chemicals were bought from Sigma Aldrich.

3.2 Selection of Ionic Liquid

An ionic is liquid is a salt in which the ions are poorly coordinated. They remain in solvent phase at a temperature less than 1000^0C(Kamiński, Krawczyk, Augustyniak, Weatherley, & Petera, 2014). Any salt which melts without decomposing or vaporizing gives an ionic liquid. Ordinary liquids like water and gasoline are made up of neutral molecules whereas ionic liquids are made up of ions or short lived pairs. When an ionic liquid is cooled it forms an ionic solid. These ions help in conduction of electricity. Ionic liquids are commonly used as electrolytes and powerful solvents(Kamiński et al., 2014). Ionic liquids were introduced to replace acidic baths commonly used in electroplating processes to lower the pH. Primary reason behind this invention was to make sure that electrolytic baths are environment friendly.

A mass loss test was conducted among a set of 6 ionic liquids to determine which least corroded the magnesium surface owing to the fact that most electrolytic baths are acidic. Mass loss analysis is the one in which the percentage loss in mass is found based on the initial and final mass of the substrate after an immersion time. Mass loss analysis does not give the degradation rate but gives the percentage mass loss before and after immersion. The percentage mass lost is given by the formula ((Initial mass-Final mass)/Initial mass)*100.

The 6 ionic liquids taken into consideration are 1) 1-Butyl- 2,3 dimethyIimidazolium tetrafluoborate 2) 1-Butyl Virdinium Chloride 3) Trimethyl phenyl ammonium bromide 4) Cholene Chloride 5) Cholene Hydroxide + ethylene Glycol 6) 1-ethyl-3 methylimidazolium chloride . The samples taken for this analysis is a 0.25mm AZ31 magnesium alloy. The test was carried out in a 1M solution of the corresponding ionic liquid for a time interval of 2hrs, 4hrs, 6hrs and 8hrs. At the end of each time interval the samples were taken out of the ionic liquid, rinsed in DI water and finally air dried. After selecting the ionic liquid an electrolyte was prepared with ferrous ammonium sulfate salt. Ferrous ammonium sulfate was selected because sulfate ions does not affect the magnesium surface unlike chloride ions.

3.3 Iron Plating

Iron was electroplated directly on the surface of AZ31 magnesium alloy. The ionic liquid was selected based on the ionic liquid test conducted. 1-Butyl- 2,3 dimethyIimidazolium tetrafluoborate was the ionic liquid used. The entire electrolytic bath consisted of 1M 1-Butyl- 2,3 dimethyIimidazolium tetrafluoborate and 350g/l of ferrous ammonium sulfate(Liu & Ma, 2010). The anode used was a pure iron rod and the cathode used was an AZ31 magnesium alloy sample. The electrodes were connected to a D.C power and source and immersed in the electrolyte to complete a circuit. The entire experiment was carried out in a glass beaker. The experiment was carried out a current density of $4Adm^{-2}$ for 20 minutes and the pH was maintained at 2. Table 3.1 shows the parameters of the iron plating process.

Table 3.1 Contents and parameters for electroplating iron directly on AZ31 magnesium

Anode	Pure iron rod
Cathode	AZ31 Magnesium Alloy
Ionic Liquid	1-Butyl- 2,3 dimethylimidazolium tetrafluoborate
Electrolyte	Ferrous Ammonium Sulfate
Current Density	$4Adm^{-2}$
Time	20 minutes
pH	2

3.4 Iron Plating with an Intermediate Layer

Iron was electroplated on the surface on the surface of magnesium by depositing a set of intermediate layers on the magnesium surface. The major reason for the intermediate layers is to prevent magnesium interaction with the electrolyte. The electroplating process in done in 5 steps they are 1) Ultrasonication 2) Chemical pickling 3) Zinc immersion 4) Copper plating 5) Iron plating. The steps involved are given in the Fig 3.1.

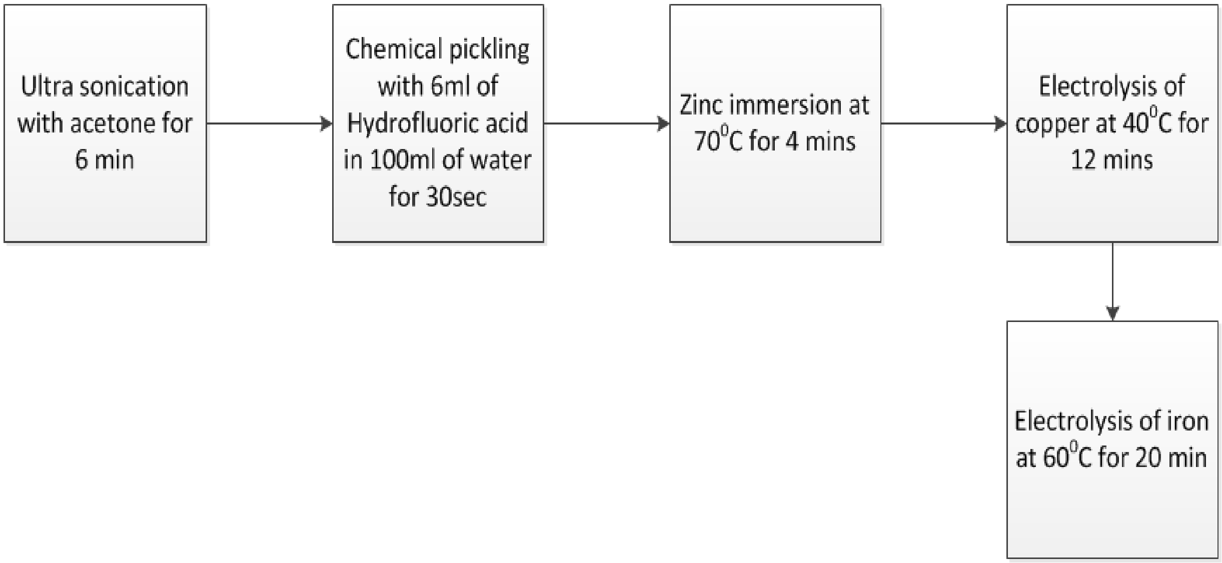


Fig. 3.1 Steps for electroplating iron on AZ31 magnesium alloy with an intermediate copper layer

3.4.1 Ultrasonic cleaning

Ultra sonication process is carried out in an ultra sonication instrument which produces sound waves with an appropriate solvent to clean the surface. The solvent usually depends on the type of the application. Cavitation bubbles induced by high frequency sound waves are used to agitate the cleaning solution. Most commonly used substrates are plastics, metals, glass, rubber and ceramics. Aim of this test if to remove dust, dirt, pigments, rust, grease and bacteria.

In this process acetone was used for cleaning. Acetone was selected because it is a good disinfectant, highly miscible with water and the flash point is much higher compared to other alcoholic solvents commonly used. The process was carried out for 6 min.

3.4.2 Chemical Pickling

Chemical pickling is a method used to dissolve oxide layer on the surface of substrate. A solution called pickling liquor is used for this process this commonly contains a strong acid. Some commonly used acids are hydrochloric, sulfuric and hydrofluoric acid. Hydrochloric acid was rejected because magnesium undergoes heavy corrosion in chloride based mediums(Yamamoto et al., 2001). Hydrofluoric acid was selected because magnesium corrodes comparatively less in fluoride based medium. Magnesium fluoride layer formed on the surface of AZ31 offered better corrosion resistance and helpful for growth of osteoblast cells. One disadvantage with hydrofluoric acid is that it cannot be stored in glass containers.

In this process a very dilute solution for etching was made. The solution consists of 6ml hydrofluoric acid in 100ml of water(S. Zhang et al., 2011). The samples were dipped in the solution for 30 seconds and rinsed in DI water.

3.4.3 Zinc Immersion

An adherent coating of zinc is obtained on the surface of magnesium only if it is activated by an acidic bath or an alkaline bath. An aqueous zinc immersion bath usually consists of a pyrophosphate, a zinc salt, a fluoride salt and some quantities of carbonate if needed to maintain the pH. The zinc immersion layer ensures better adhesion of electroplated copper on the surface of magnesium. Presence of this zinc layer ensures that the magnesium substrate does not interact with the copper electrolyte. The process starts by dissolving of zinc sulfate in DI water and then potassium pyrophosphate is added so that potassium complexes zinc to form potassium zincate. Formation of the complex compound is indicated by the chemicals dissolving in DI water. Then potassium is fluoride is added and then finally sodium carbonate is added.

The bath is operated at a pH of 10.0±2 and at a temperature of 70^{0}C. Time of immersion usually varies between 3.5 to 5 min. Zinc is part of human enzymes. So the issue of biocompatibility is taken out of consideration. Immersion times depend on the Al content of the alloy (Richard. A. Gross, 2002). Contents and conditions of the bath are given in table 3.2 as follows

Table 3.2 Contents and conditions of zinc immersion bath(L.-p. Wu et al., 2010)

Zinc sulfate heptahydrate	30g/l
Potassium Pyrophosphate	180g/l
Potassium Fluoride	5g/l
Sodium Carbonate	5g/l
pH	10.0±2
Temperature	70^{0}C

3.4.4 Copper Electroplating

A layer of copper was applied on to the surface of zinc coated magnesium by means of electrolysis for 12min. The bath is prepared by dissolving potassium pyrophosphate in DI water and copper pyrophosphate was dissolved in it forming a complex compound potassium cuprate. Finally ammonium citrate was added. Copper electroplating can be done from a variety of salts like copper sulfate, copper cyanide, copper fluroborate and copper pyrophosphate. Copper pyrophosphate was selected because the bath can be operated at an alkaline pH whereas copper sulfate and fluroborate cannot be operated at high pH. Conditions and parameters of the plating procedure is mentioned in the table 3.3 below

Table 3.3 Contents and conditions of copper electroplating bath(S. Zhang et al., 2011)

Copper Pyrophosphate	28g/l
Potassium Pyrophosphate	100-150g/l
Ammonium Citrate tribasic	60-70 g/l
Time of plating	12 min
Temperature	40^0C
Current Density	1.2A/dm^2
pH	8.2-8.8
Anode	Copper rod
Cathode	Zinc immersion coated magnesium

3.4.5 Iron Electroplating

A commonly used double salt, ferrous ammonium sulfate is used for electrolysis purpose. The bath can be operated from 25^0C to 60^0C, rate of deposition increases with increasing temperature but there is no change in rate beyond 60^0C (Liu & Ma, 2010). Addition of ammonia to ferrous sulfate can reduce the rate of oxidation and prevent formation of iron oxide in the bath. The entire set up consists of an anode which is an iron rod and cathode is copper coated magnesium. The current density was maintained at $4dm^{-2}$. The contents and conditions of iron electroplating process is shown in the table 3.4.

Table 3.4 Contents and conditions of iron electroplating process

Ferrous Ammonium Sulfate	350g/l
1-Butyl-2,3dimethylIimidazolium tetrafluoborate	12.5g/l
Temperature	50^0C
pH	2.5
Time	25 min
Current density	$4\text{-}10A/dm^2$
Anode	Iron rod
Cathode	Copper electroplated magnesium

3.4.6 Summary

The entire process parameters and conditions from beginning to end is summarized in the table 3.5

Table 3.5 Contents and conditions of the entire iron plating process

Process	Solution composition	Concentration	Conditions
Ultra sonic cleaning	Acetone		6 min RT
Pickling- Activation	HF(40%)	6ml/l	30s RT
Zinc immersion	$ZnsO_4.7H_20$ $K_4P_2O_7$ KF Na_2CO_3	30g/l 180g/l 5g/l 5g/l	4 min 70^0C pH 10.0±0.2
Copper plating	$Cu_2P_2O_7$ $K_4P_2O_7$ $(NH_4)_3C_6H_5O_7$	28g/l 150g/l 70g/l	12min 40^0C pH=8.2-8.8 J=1.2 A/dm^2
Iron plating	$(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$ $C_9H_{17}BF_4N_2$	350g/l 12.5g/l	25 min pH 2.5 50^0C J=4-10A/dm^2

3.5 Characterization Techniques

The surface morphology was characterized using by optical microscope, SEM-EDX, XRD, XPS, roughness evaluation and corrosion evaluation.

3.5.1 Optical Microscopy

The Leica Optical Microscopy connected with a digital camera and a computer was employed for viewing the surface of the coated samples. Leica Optical Microscope is shown in

Fig.3.2. In order to process the images Leica vision was installed on the computer. Depending on the demands of the experiment different magnifications can be obtained. An inverted microscope is normally used to view metal surface due to the absence of an inverted microscope a flash light was used to mimic an inverted microscope. Images were taken at 10x, 20x, 30x magnification.

Fig.3.2. Optical microscope apparatus(Bartlett, 2007)

3.5.1 SEM-EDX

The scanning electron microscope has a large vacuum tube in which electrons are produced by a heated filament and they are driven by high voltage finally the electrons are made to strike the sample which produces an image(Pihlajamäki et al., 1997). Mostly conductive materials can only be imaged if it is not conductive it can be made conductive by coating with a conductive material. This procedure enables higher magnification compared with optical microscope and the image obtained from a scanning electron microscope has a greater field depth. They have little features which can be imaged clearly. The SEM-EDX apparatus is shown in the Fig 3.3.

In addition to scanning electron microscopy, they generate x-rays which gives the elemental composition of the surface. EDX can be used in determining the elemental composition of metals heavier than boron not including hydrogen(Kathuria, 2006). The size of the sample which can be used for elemental detection is limited to a few cubic inches.

Fig.3.3. SEM-EDX apparatus(Pihlajamäki et al., 1997)

3.5.2 X-Ray Diffraction

X-ray diffraction is a method in which the atomic and molecular structure of a crystal can be determined. Different kinds of crystal can cause x-rays to deflect in a particular pattern. The kind of element can found out by comparing the peaks with the already present reference metals.(Kathuria, 2006) XRD used is divided into single crystal and poly crystalline. Since iron coated sample with an intermediate layer has more than one kind of element a polycrystalline XRD was preferred. The XRD set consists of a goniometer emitting x-rays, which is made to strike the sample at an angle(Kathuria, 2006). Fig 3.4 shows a bruker polycrystalline XRD machine. The reflection gives two dimensional images which is converted into 3 dimensional electron density, using the mathematical method of fourier transforms, combined with chemical data known for the sample, the patterns can be obtained.

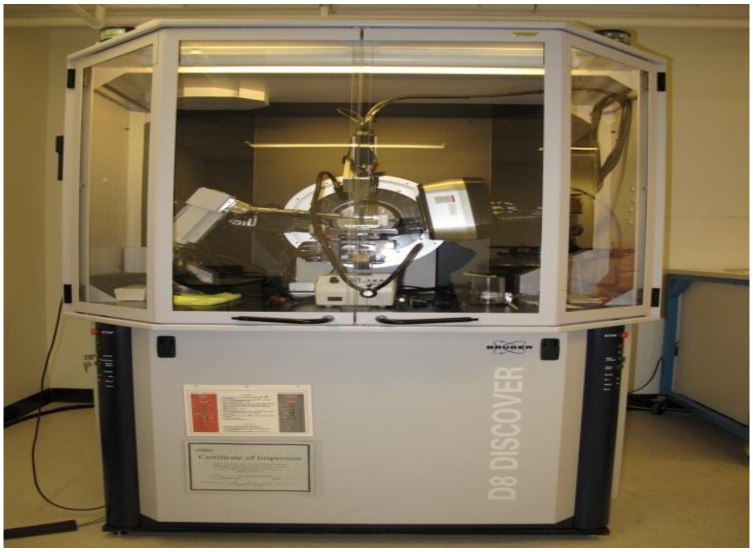


Fig.3.4. Polycrystalline Bruker D8 Discover X-Ray Diffraction Machine(Inoue & Hirasawa, 2013)

3.5.3 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a quantitative spectroscopic technique which calculates the elemental composition, empirical formula, chemical state and electronic state. In this case XPS was performed just for determining the elemental composition. It is a technique where the surface of the substrate can be analyzed. XPS detects all elements higher than lithium but it cannot detect hydrogen or helium. Detection limit for XPS is mostly in parts per thousand, detection in parts per million is obtained but it needs special conditions. XPS values are obtained by making the X-rays strike the surface of the substrate and measuring the kinetic energy and the number of electrons that escape from the top 1 to 10nm of the material. This process is done at ultra high vacuum. XPS analysis used was a large area mode (7*20mm) and the anode used was aluminum at 250W and the pass energy used was 20. Three scans were taken at 1eV/step. The Fig 3.5 shows a picture of a XPS machine.

Fig.3.5. X-ray photoelectron spectroscopy machine(Inoue & Hirasawa, 2013)

3.5.4 Roughness Evaluation

Roughness of the iron coated sample was evaluated using a VK-X100/X200. It is used to perform non-contact profile and roughness measurements on any metal. It is a combination of an SEM, microscope and roughness gauge. Poor resolution, shallow depth and traceability are some disadvantages with microscope(Gontijo, Machado, Miola, Casteletti, & Nascente, 2004). Monochrome, time consuming, limited sample size are SEM's disadvantages. This instrument is combination of all advantages all these instruments and eliminates all of their disadvantages. This instrument is similar to a non contact angle type profilometer. Line scans are performed all over the sample to find the corresponding surface roughness(Chen, Peng, & Bradshaw, 2013). The images were taken on the iron coated sample. All the images were taken at a magnification of 10X. The Fig 3.6 shows the picture of the VK-X100/X200 surface roughness analyzer.

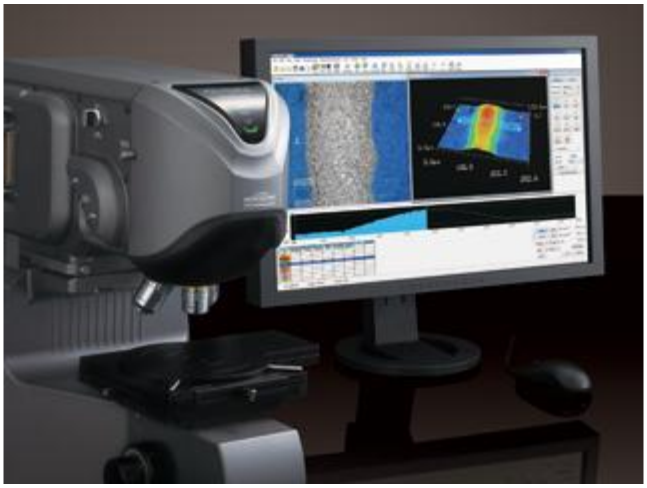


Fig.3.6. VK-X100/X200 apparatus for measuring the surface roughness(Lee, Kim, Yim, & Tönshoff, 1987)

3.5.5 Thickness Measurement

The thickness of the iron coated samples was evaluated using SEM. The sample used was a 0.25mm (250μm) thick AZ31 magnesium sample. The samples were dipped in liquid nitrogen; it makes the metal brittle to gives a clean break. A clean break is necessary to view the layers. The entire idea behind dipping the substrate in liquid nitrogen is to break the sample rather than shearing it.

3.5.6 Corrosion Evaluation

Corroding ability of iron coated AZ31 magnesium alloy was evaluated by evaluated by and less porous coatings yield better corrosion resistance(Song, Song, Shen, & Liu, 2012). Electrochemical methods give an idea of corrosion capability over a year. All the electrochemical tests were conducted in a Gamry Reference 600TM potentiostat/Galvenostat in phosphate buffered saline solution (PBS). PBS is a buffer solution which is commonly used in biological research. It is an aqueous solution containing salts like sodium chloride, sodium phosphate, potassium chloride and potassium phosphate. The ion concentrations of this solution match that of the human body. The electrochemical tests were conducted in a 3 electrode corrosion cell. The entire set up consisted of an anode, a cathode and a reference electrode which is a saturated calomel electrode. The voltage was swept between the reference electrode and the working electrode. The potentiodynamic curves and open circuit curves were obtained at a constant voltage scan rate of 10mV/s. The specimen area exposed was 0.9503 cm^2 with scan voltage ranging from 2 to -2 V. The open circuit voltage actually tells how much the given sample would corrode without passing any current through it. The experimental parameters for tafel and open circuit potential are given in table 3.6. The Fig 3.7 shows picture of the GAMRY 600 setup.

Table 3.6 Experimental parameters for tafel plot and open circuit potential

Initial Voltage	2.5 V vs. Eoc
Final Voltage	-2.5 V vs. Eoc
Scan Rate	10 mV/s
Sample Period	0.245 s
Specimen Area	0.9503cm^2

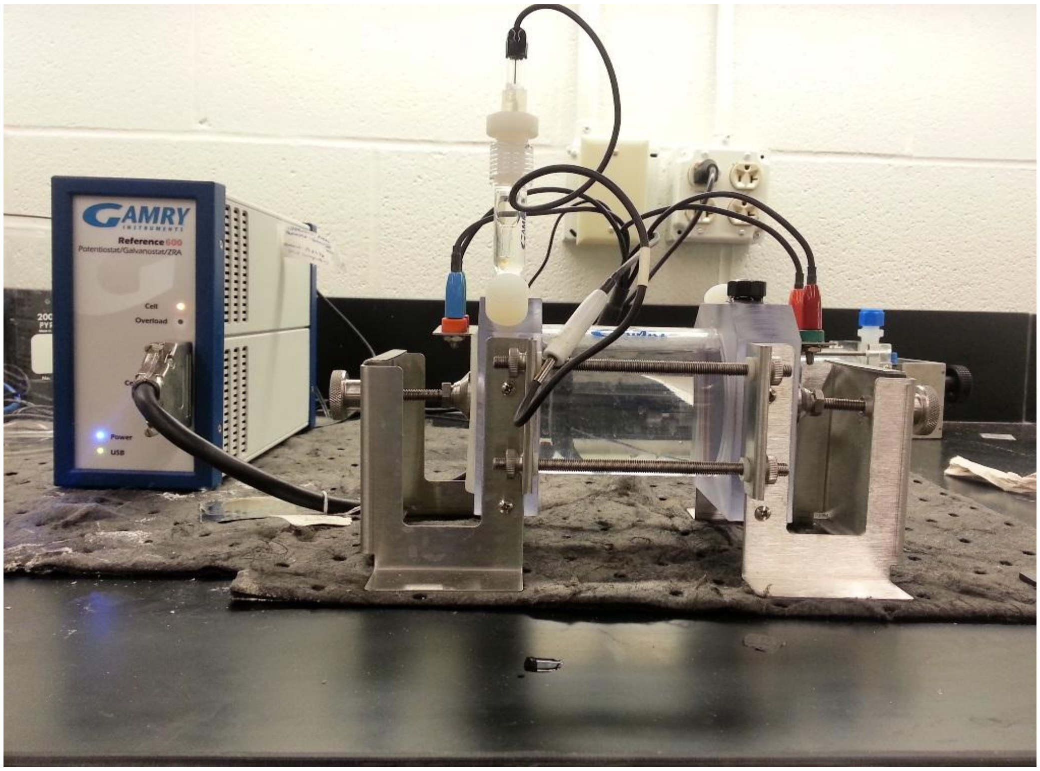


Fig.3.7 GAMRY reference 600™ setup for corrosion analysis

CHAPTER 4

4. RESULTS AND DISCUSSION

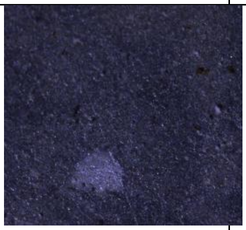
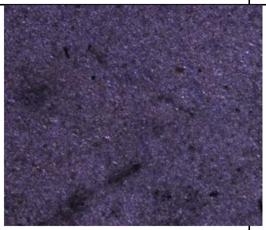
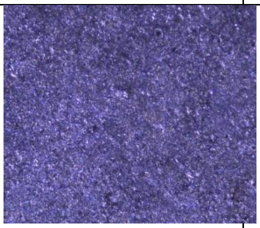
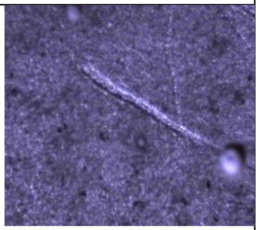
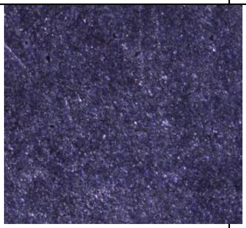
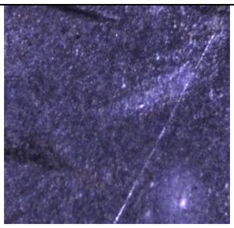
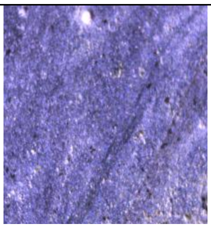
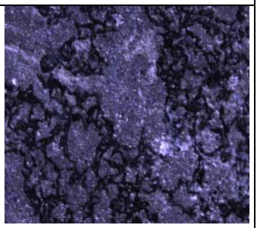
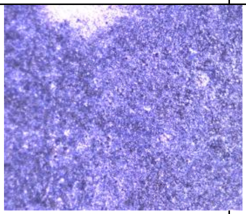
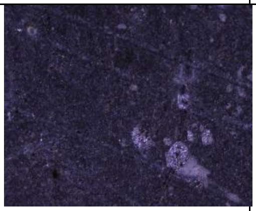
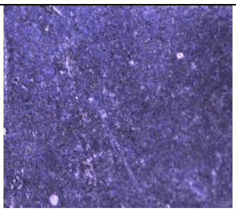
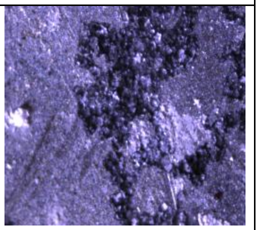
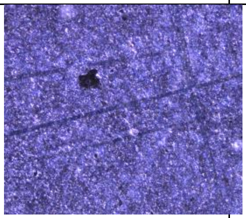
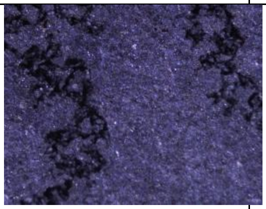
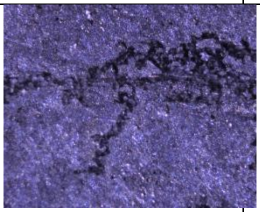
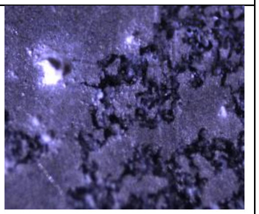
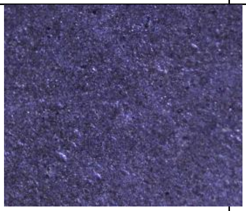
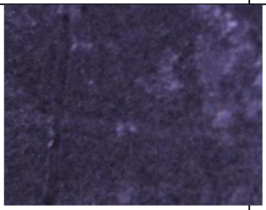
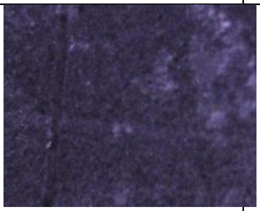
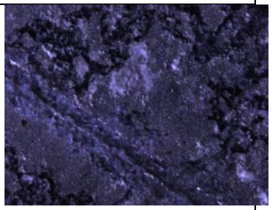
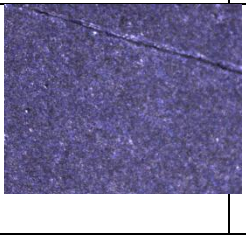
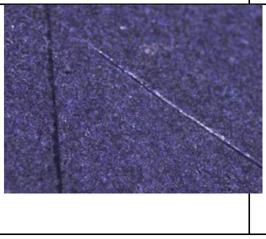
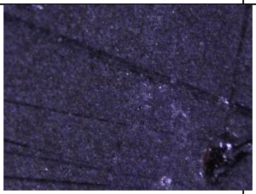
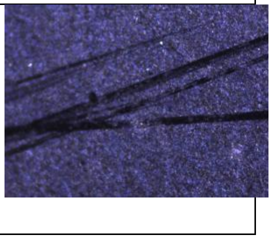
4.1 Ionic Liquid Test

The ionic liquid test was conducted as mentioned in the section 3.2. Based on the mass loss analysis tests conducted 1-Butyl-2,3 dimethyIimidazolium tetrafluoborate and cholene hydroxide +ethylene glycol was found to be best with lowest the lowest mass loss percentage. The table 4.1 shows the mass loss percentage of AZ31 magnesium in different ionic liquids. The table 4.2 shows the corrosion on the surface of the magnesium substrate for different ionic liquids. The samples dipped in 1-Butyl-2, 3 dimethyIimidazolium tetrafluoborate and cholen hydroxide was found to have the least corrosion. 1-Butyl-2, 3 dimethyIimidazolium tetrafluoborate was chosen among the two because cholene hydroxide +ethylene glycol mixture is highly basic and has a pH of 13 which drastically increases the pH of the electrolytic bath to 12 where iron precipitates as ferric hydroxide and lowers the throwing power of the bath.

Table 4.1 Mass loss analysis data of the ionic liquid test conducted

Ionic Liquid	0hrs Weight(g)	2hrs Weight(g)	4hrs Weight(g)	6hrs Weight(g)	8hrs Weight(g)	%mass loss
1-Butyl-2,3 dimethylImidazolium tetrafluoborate	0.1015	0.1015	0.1013	0.1017	0.1015	0
1-Butyl Virdinium Chloride	0.1165	0.1158	0.1133	0.1128	0.1125	3.5
Trimethyl phenyl ammonium bromide	0.113	0.1123	0.1111	0.1103	0.1106	0.63
Cholene Chloride	0.1168	0.1148	0.1143	0.1131	0.1140	2.3
1-ethyl-3 methylimidazolium chloride	0.1275	0.1260	0.1256	0.1252	0.1254	1.6
Cholene Hydroxide + ethylene Glycol	0.739	0.740	0.735	0.739	0.739	0

Table 4.2 Mass loss analysis images of ionic liquid test conducted

Ionic Liquid	2hrs	4hrs	6hrs	8hrs
1-Butyl-2,3 dimethyIimidazolium tetrafluoborate				
1-Butyl Virdinium Chloride				
Trimethyl phenyl ammonium bromide				
Cholene Chloride				
1-ethyl-3 methylimidazolium chloride				
Cholene Hydroxide + ethylene Glycol				

4.2 Iron Plating without an Intermediate Layer

Iron was electroplated directly on the surface of magnesium without an intermediate layer. Since magnesium is highly reactive it corrodes at a pH less than 10. Magnesium undergoes pitting corrosion and the primary corrosion product is magnesium hydroxide which increases the pH of the electrolyte and the pH increases from 2 to 4 during the plating time. Presence of hydroxide precipitates also lowers the throwing power of the bath which is its ability to plate without any pores (Liu & Ma, 2010). As a result of which magnesium reacts with ferrous ions in the solution and oxidize them to ferric ions thereby making the bath sludgy. The deposits obtained on the surface of magnesium are ferric and they are immersion deposits which stick to the magnesium surface due its reactivity. Besides that magnesium corrodes during the plating period. The coating obtained is very porous and it forms a galvanic cell which makes increases the rate of corrosion, in this case magnesium becomes the sacrificial anode and corrodes at a rate faster than usual. From fig.4.1 it is seen that the coating obtained is highly porous and highly oxidized which will be proved by EDX analysis.

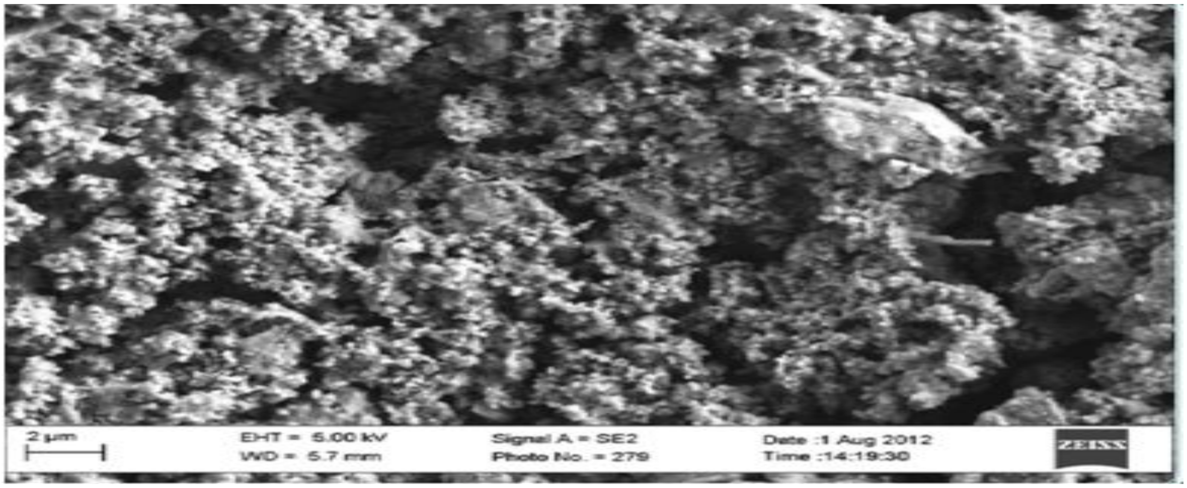


Fig. 4.1 Iron coated AZ31 Magnesium without an Intermediate Sublayer

4.3 Iron Plating with an Intermediate Layer

Iron was electroplated on the magnesium surface with an intermediate layer as mentioned in section 3.4. The results and discussion of each and every stage is mentioned below

4.3.1 Chemical Pickling

The AZ31 magnesium alloy consists of two phases α (Mg) and β phase ($Mg_{17}Al_{12}$)(L. Wu, Pan, Yang, Wu, & Liu, 2011). The α phase consists of pure magnesium and β phase consist of magnesium and aluminum. After HF activation potential difference between the α and β phase is reduced, which contributes to the lower chemical reactivity of AZ31 magnesium alloy(S. Zhang et al., 2011). After the initial HF activation for 30sec the surface of the specimen gets etched β and α interface. The activation step not only dissolves the oxide layer but also stalls fierce replacement of oxide layer to an extent which is necessary to plate smooth layers(S. Zhang et al., 2011).

4.3.2 Zinc Immersion

The zinc immersion technique was performed as mentioned in the methods section. The pyrophosphate added dissolves all oxides and hydroxides on the surface of the substrate to form water soluble complexes. Rate of deposition depends on the fluoride content, lower fluoride content causes high rate of deposition which produces a loose coating(L.-p. Wu et al., 2010). Amount of carbonate salt added depends on the pH. Water for preparing the bath needs to be free from iron deposits in order to get pore free deposits

The AZ31 magnesium alloy consists of two phases α (Mg) and β phase (MgAl)(L. Wu et al., 2011). A zinc immersion layer is coated on the surface of the HF pickled magnesium. EDX results show no concentration of Al and very high concentration of Zn. The β phase is gradually dissolved and covered by a Zn layer during the time of immersion. The Zn layer will gradually extend to α phase and reduce the chemical reactivity of substrate. The potential difference between α and β phase is reduced at the end of the immersion process which makes the substrate more stable than the HF activated zinc. Zn layer also helps better adhesion of the intermediate copper layer(Z. Zhang et al., 2009). Fig 4.2 shows the zinc immersion coated magnesium substrate.

Fig. 4.2 Camera image of zinc immersion coated AZ31 magnesium alloy

4.3.3 Copper Electroplating

After the zinc immersion layer, copper was electroplated on the surface of zinc. The zinc layer formed was resistant to any attacks in the electroplating bath but non-resistant to attacks by ferrous ammonium sulfate bath. Hence a layer of copper was deposited on to the zinc immersion coated magnesium(L.-p. Wu et al., 2010). Copper is an essential constituent for all living beings like zinc copper is also a part of enzymes. In enzymes it is involved in energy production. Copper plays a major role in storage, absorption and metabolism of iron. So biocompatibility is not an issue here. Intake of more than 10gm/day of copper causes effects like nausea and weakness(Chen et al., 2013) .

Copper cyanide, copper pyrophosphate, copper sulfate was evaluated for copper electroplating process. Copper cyanide was rejected owing to its toxicity. Copper sulfate was rejected because it could be operated only at very low pH but the zinc layer could not with stand acidic attacks at a pH of 2. Copper pyrophosphate was selected because the bath operating pH is 8 and it is also not toxic.

The primary aim of the copper layer was to prevent attack in acidic medium. Since electroplating of iron is done at a very low pH there is a need to make the magnesium surface non-reactive at a very low pH. During electroplating a high current density of 3-4 A/dm^2 is applied for a period of 1min and then reduced to 1.2A/dm^2(L.-p. Wu et al., 2010). Care must be taken so that the process was not carried out at a high current density during the period which results in burnt and powdery deposits(Liu & Ma, 2010).

Gassing must be prevented during electroplating process which takes place when there is a high current flow when the part to be plated enters the bath. A voltage of 0.5 to 0.8V needs to be maintained initially to prevent gassing(L.-p. Wu et al., 2010). Having a very high initial current density causes burnt and powdery deposits. The size of the cathode must be atleast few times the size the anode(Liu & Ma, 2010). The Fig 4.3 shows the camera image of copper coated AZ31 magnesium substrate.

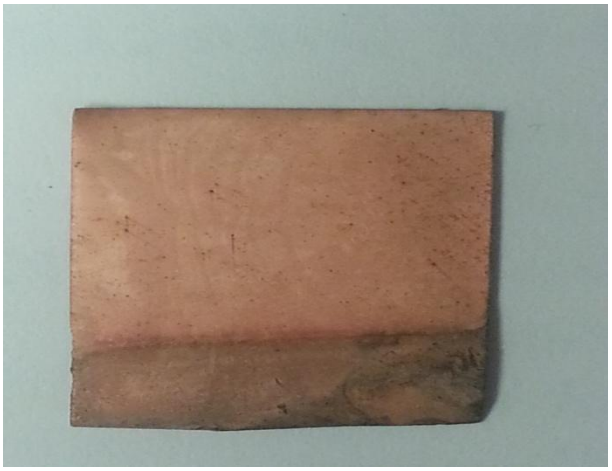


Fig. 4.3 Camera image of copper coated AZ31 magnesium alloy

4.3.4 Iron Electroplating

After a layer of copper was deposited on the surface of zinc immersed magnesium, iron was electroplated from a ferrous ammonium sulfate bath. Ferric chloride is considered to be the best bath for electroplating of iron but since magnesium undergoes corrosion in a chloride medium it was rejected. The electroplating was done as per the parameters mentioned in the methods sections. Fig. 4.4 shows the camera image of iron coating with an intermediate copper layer. The coating obtained was grey and shiny.

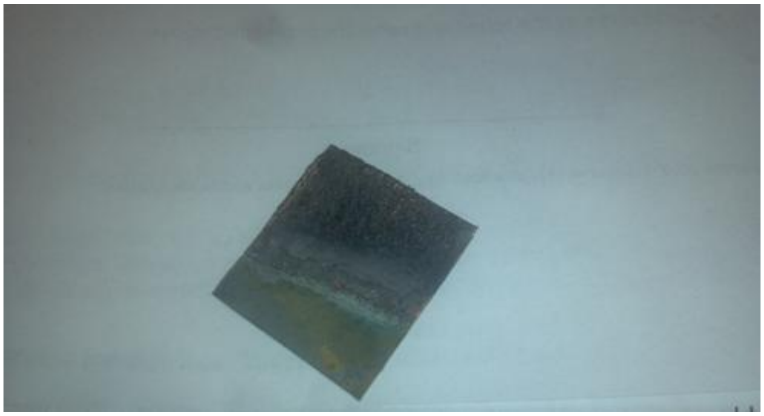


Fig. 4.4 Camera image of iron coated AZ31 magnesium alloy with an intermediate copper layer

4.4 Optical Microscopy

The optical microscope images were taken for each and every layer. The images are listed in different levels of magnification for different layers.

4.4.1 Zinc Immersion

The Fig 4.5 shows the optical microscope images of zinc immersion coated magnesium at different magnification. The magnesium surface was entirely covered and no pores were found on the surface of substrate.

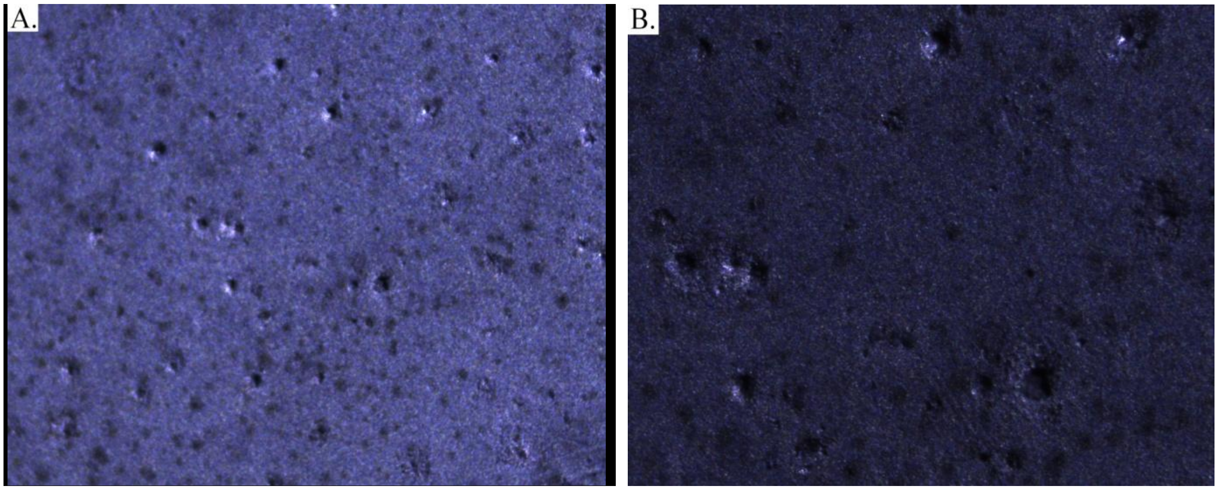


Fig.4.5 Optical microscope image of zinc immersion coated AZ31 magnesium alloy at a magnification of A)10X and B) 20X

4.4.2 Copper Electroplating

The Fig 4.6 shows the optical microscope image of copper plated AZ31 magnesium alloy at different magnification is shown. The coating was red and shiny. The coating had no pores on it.

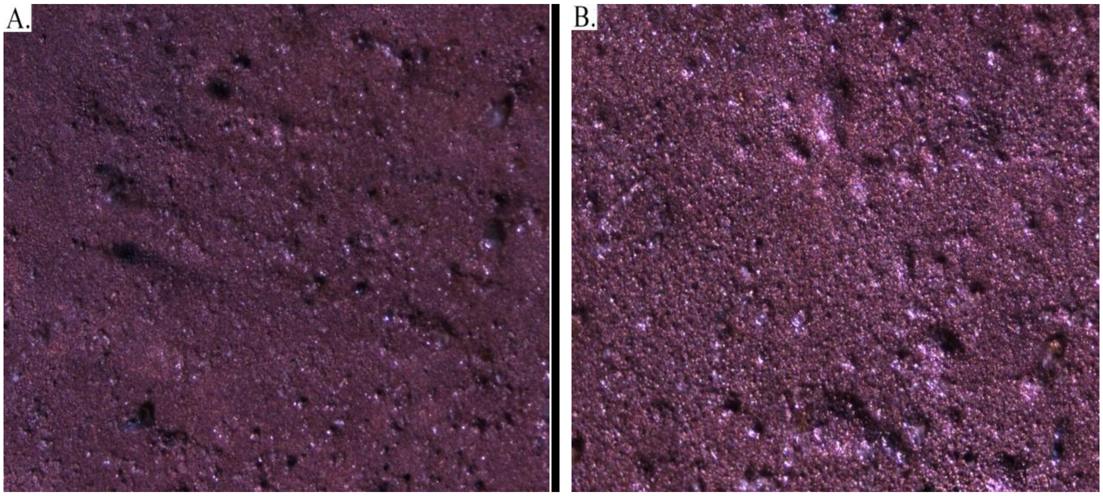


Fig.4.6 Optical microscope image of copper electroplated AZ31 magnesium alloy at a magnification of A)10X and B) 20X

4.4.3 Iron Electroplating

Iron was electroplated on the copper coated magnesium. The Fig 4.7 shows the optical microscope image of iron coated AZ31 substrate. The coating obtained was grey and shiny. The coating obtained was ferrous and the coating underwent less rusting compared to the iron coated magnesium without an intermediate sublayer.

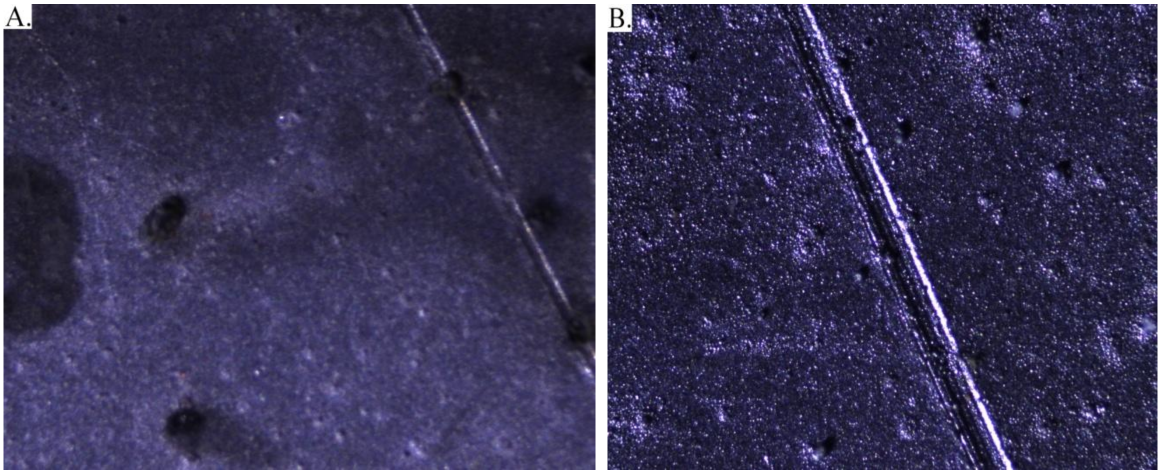


Fig.4.7 Optical microscope image of iron electroplated AZ31 magnesium alloy with an intermediate copper layer at a magnification of A)10X and B) 20X

4.5 SEM-EDX

SEM-EDX analysis was conducted using the equipment as mentioned in the methodology. EDX analysis proves the presence of each and every element during different stages of the coating.

4.5.1 Iron Plating without an Intermediate Layer

Fig.4.8 shows the SEM image of iron coated magnesium without an intermediate layer. Fig 4.8 shows that the coating is porous and further EDX analysis proved very less iron content and high oxygen content due to very high oxidation. The EDX analysis of iron coated AZ31 magnesium without an intermediate is shown in table 4.3.

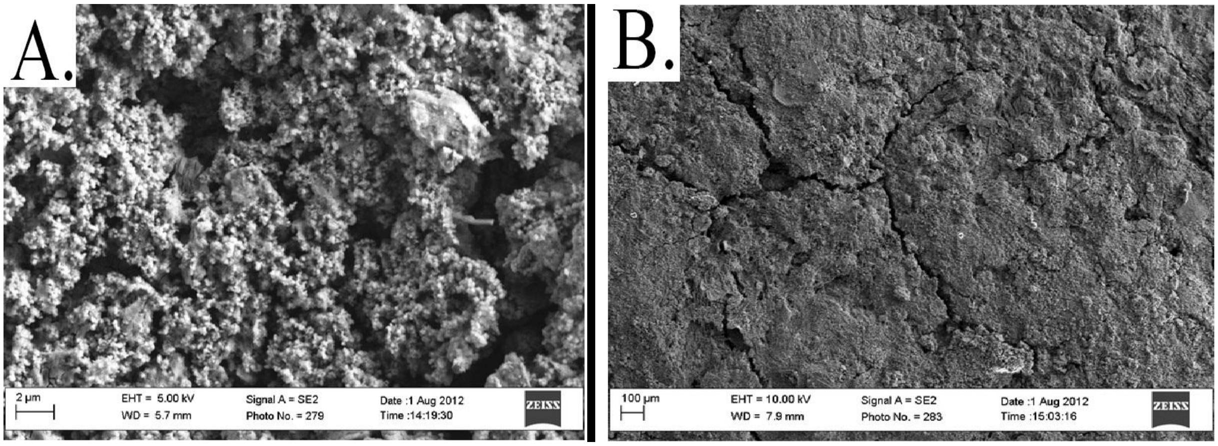


Fig.4.8 SEM image of iron coated AZ31 magnesium alloy without an intermediate sublayer at magnification of A) 2µm B) 100µm

Table 4.3 EDX analysis of iron coated AZ31 magnesium alloy without an intermediate layer

Element	Weight%	Atomic%
Carbon	16.12	28.79
Oxygen	34.89	46.52
Magnesium	4.09	3.61
Phosphorus	0.85	0.65
Sulfur	12.16	8.14
Iron	31.99	12.29
Total	100.00	100.00

4.5.2 Iron Coated Magnesium with an Intermediate Layer

The iron coated magnesium with an intermediate layer is done in three major steps. The SEM-EDX analysis of every step is given as follows.

4.5.2.1 Zinc Immersion

Fig 4.9 shows the SEM image of zinc coated magnesium shows a non porous image and the magnesium surface was fully covered with the zinc immersion coating. EDX analysis shows the presence of zinc with traces of oxygen. Table 4.4 shows the EDX analysis of zinc coated AZ31 magnesium substrate.

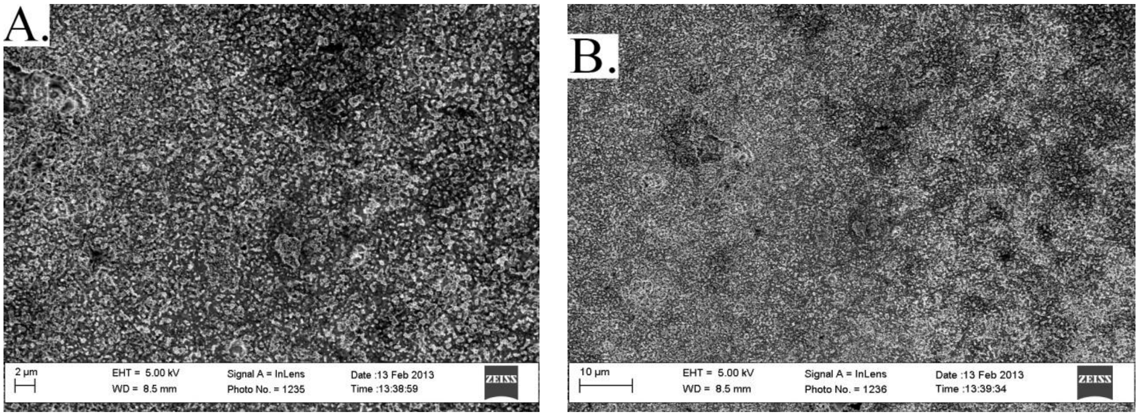


Fig.4.9 SEM image of zinc immersion coated AZ31 magnesium alloy at a magnification of A) 2µm B) 100µm

Table 4.4 EDX analysis of zinc coated AZ31 magnesium alloy substrate

Element	Atomic %	Weight%
Oxygen	4.34	14.37
Magnesium	4.96	10.80
Phosphorus	0.66	1.13
Potassium	1.46	1.97
Zinc	88.58	71.73

4.5.2.2 Copper Electroplating

Fig 4.10 shows the SEM image of copper coated magnesium shows a fully coated substrate with no pores and EDX analysis shows the presence of copper. Table 4.5 shows the EDX analysis of copper coated AZ31 magnesium substrate.

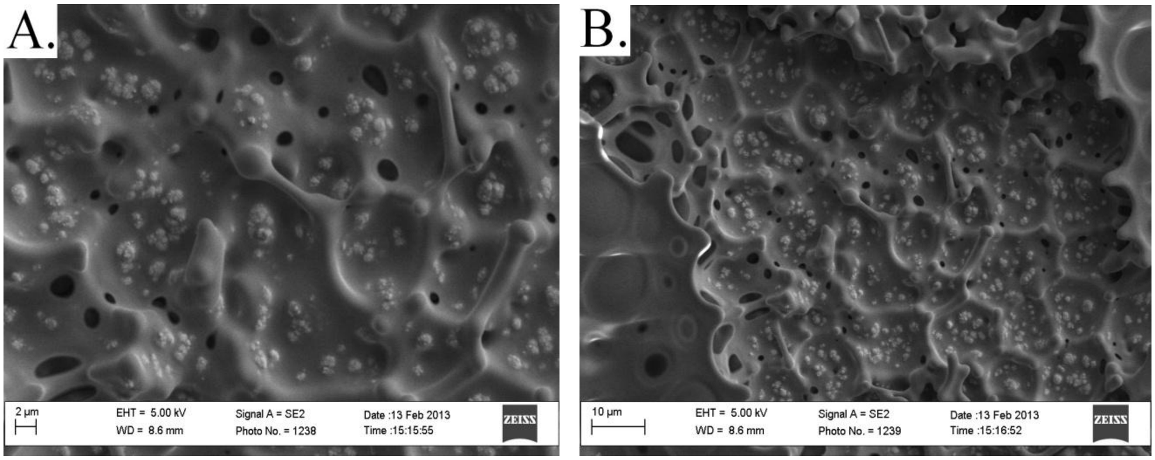


Fig.4.10 SEM image of copper coated AZ31 magnesium alloy at a magnification of A) 2µm B) 10µm

Table 4.5 EDX analysis of copper coated AZ31 magnesium alloy substrate

Element	Atomic%	Weight%
Carbon	4.15	15.98
Oxygen	5.88	16.97
Phosphorus	1.24	1.85
Potassium	1.50	1.77
Copper	87.23	63.43

4.5.2.3 Iron Electroplating

Iron was electroplated on the surface of copper coated AZ31 magnesium alloy. The Fig 4.11 shows that the coating was less porous compared to the coating without an intermediate layer. EDX analysis confirmed the presence of 40% iron by atomic weight. Table 4.6 shows the EDX analysis of iron coated AZ31 with an intermediate layer.

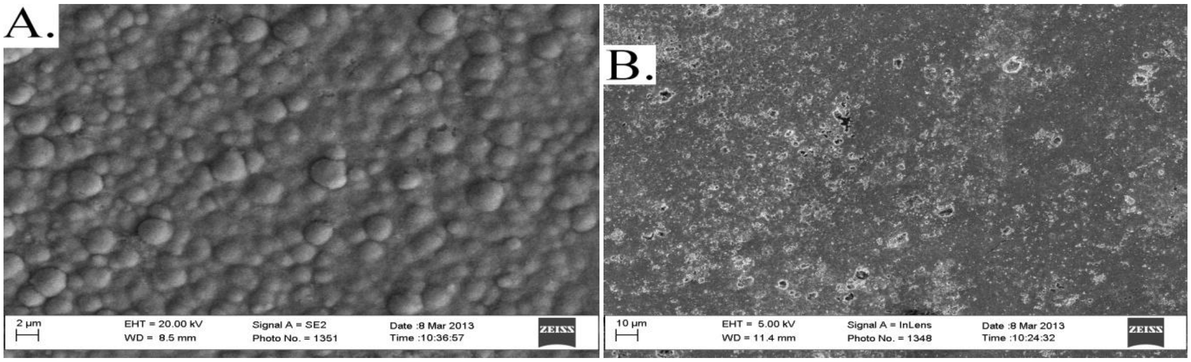


Fig.4.11 SEM image of iron coated AZ31 magnesium alloy with an intermediate at a magnification of A) 2µm B) 10µm

Table 4.6 EDX analysis of iron coated AZ31 magnesium alloy with an intermediate layer

Element	Weight %	Atomic %
Iron	37.89	40.97
Copper	62.11	59.03

4.6 X-Ray Diffraction

As mentioned section 3.5.2 the XRD data was collected using a bruker D8 discover system with a Cu X-ray tube. The samples were collected at 1600W. The data was smoothed and the kα2 peak stripped prior to library matching. The scan was done from 20 to 120 to check for all possible elements present. The XRD pattern in the figure 4.12 indicates the standard reference value of iron in magnetite form(Gurgul, Łątka, Hnat, Rynkowski, & Dzwigaj, 2013). The value obtained is 45^0, 65^0, 85^0 which confirms the presence of iron in Magnetite form (Gontijo et al., 2004). The peak shows the presence of the AZ31 magnesium substrate.

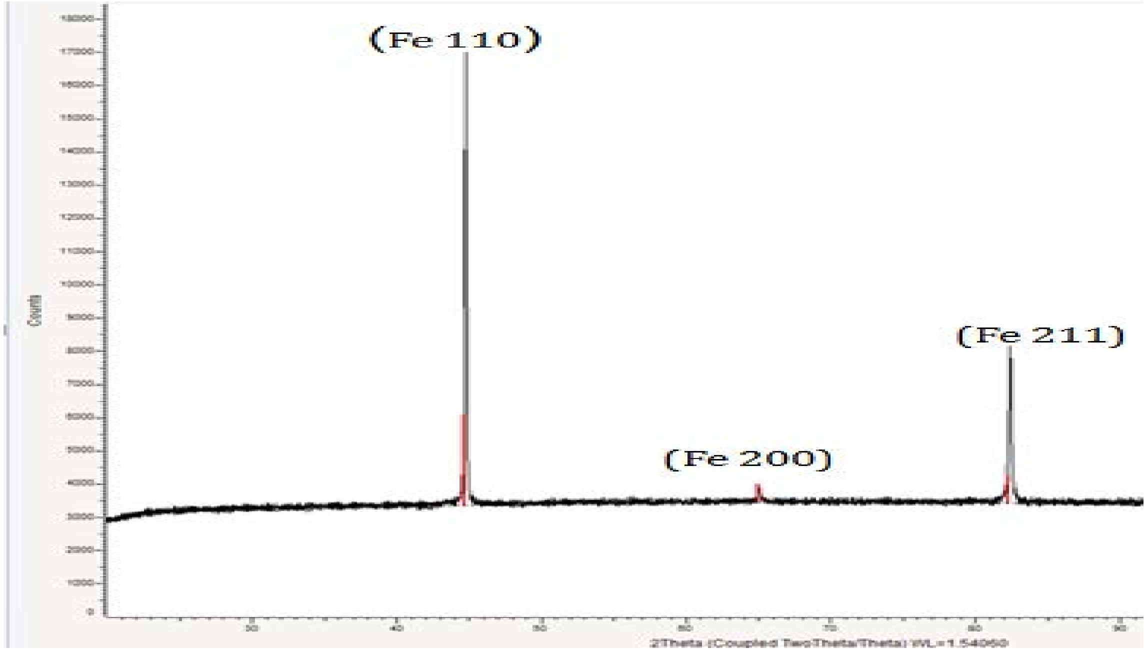


Fig.4.12 XRD pattern of iron coated AZ31 with Fe 113 peak and MgO peaks

4.7 X-Ray Photoelectron Spectroscopy

The basic idea of XPS is based on binding energy of each and every type of element. Binding energy is the least amount of energy required to keep the electron in the outer most orbit to be in its valance shell. Elemental composition is obtained based on when the electron escapes at the already found binding energy of each and every type of element. Fig 4.13 shows the full survey XPS scan of iron coated AZ31 magnesium with an intermediate layer. Fig 4.14(A) shows the magnified carbon peak, Fig 4.14(B) shows the magnified oxygen peak, Fig 4.14(C) shows magnified iron peak and Fig 4.14(D) shows the magnified magnesium peak. The Fe 2p region exhibits 2 moieties, with spin orbit splitting resulting in 4 peaks(Gurgul et al., 2013). The Mg region has peaks associated with the Fe 3s peak at 53eV. The Fig 4.14(C) shows the presence of two peaks for Fe 2p which is due to orbital spin common to P-sub shell. The peak on the left at a position of 727.291 is oxidized form of Fe and the peak on the right at 709.337 is the metallic Fe(Ohtsu, Oku, Satoh, & Wagatsuma, 2013). There are two sub peaks within the metallic peak on the right. The purple peak towards the right is the presence of iron in Fe^{2+} form (Ferrous) shown at position 722.703 and the pink peak shows the presence of iron in Fe^{3+} (Ferric) at peak position 712.754(Ohtsu et al., 2013). Peak position for all elements is mentioned in table 4.7.

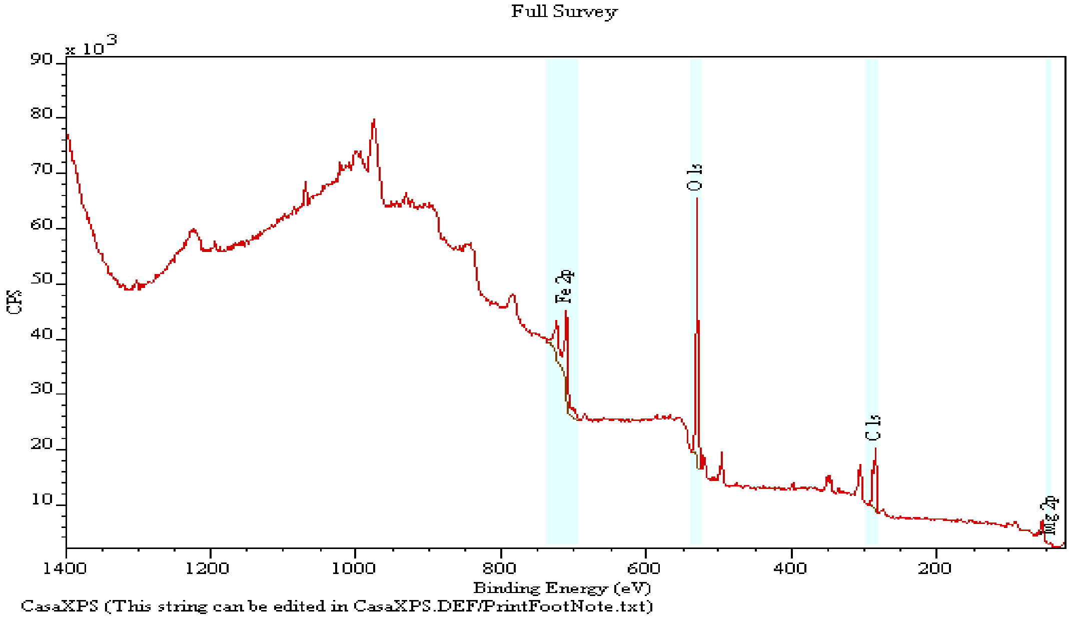
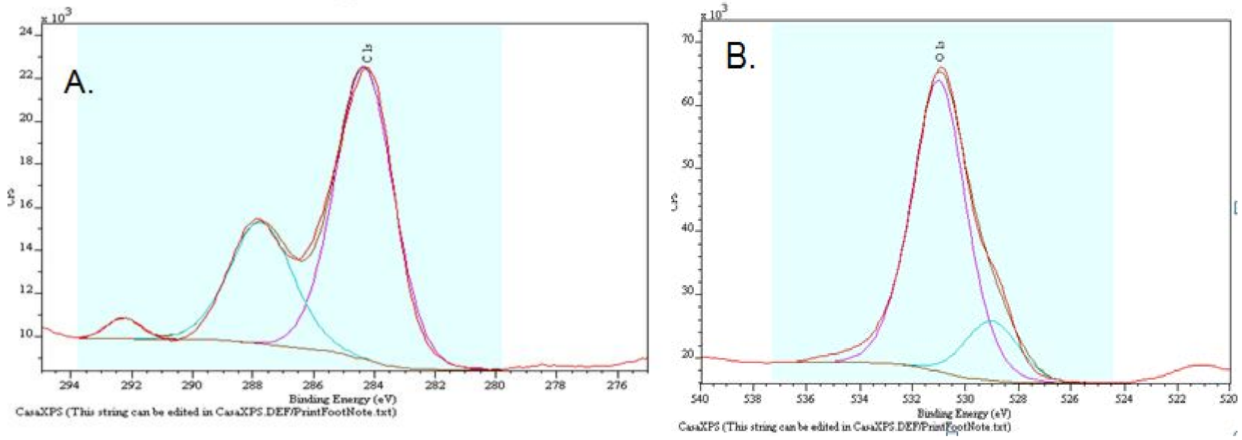


Fig.4.13 Full XPS survey showing binding energies of different element



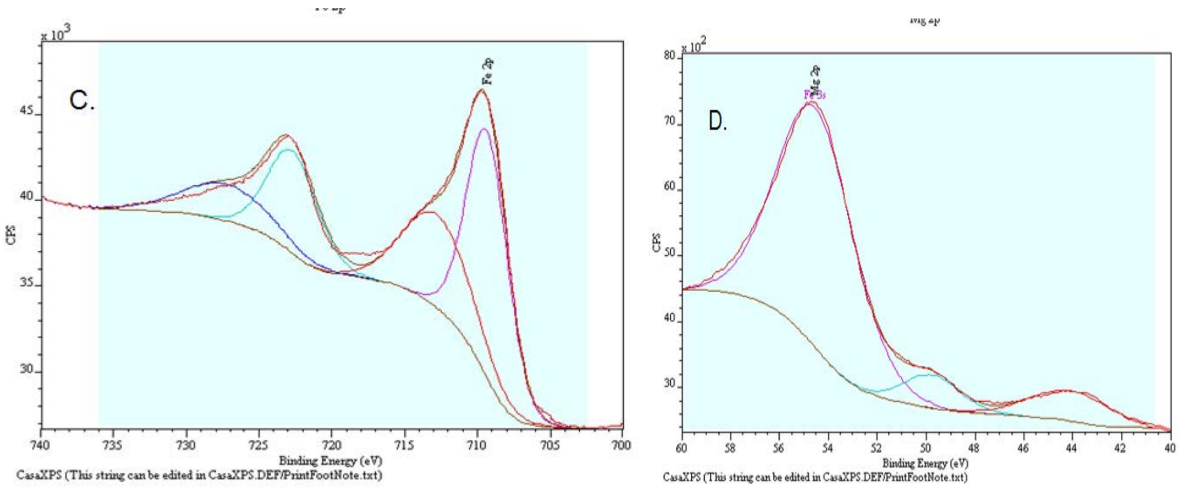


Fig.4.14 XPS zoomed binding energy peaks for A) Carbon 1s B) Oxygen 1s C) Iron 2p D) Magnesium 2p

Table 4.7 XPS analysis results for iron coated AZ31 magnesium samples with an intermediate layer

	Relative Sensitivity Factors(RSF)		Position	Full Width at Half Maximum(FWHM)	Area
C 1s	1	Peak 1	284.333	2.25	33108
		Peak 2	287.728	2.45	15073
		Peak 3	292.272	1.22	1318.9
O 1s	2.93	Peak 1	529.001	2.37	122151.2
		Peak 2	530.989	2.37	23839.9
Fe 2p	16.4	Peak 1	709.337	3.34	51815.6
		Peak 2	712.754	4	32512.4
		Peak 3	722.703	5.52	25907.8
		Peak 4	727.291	7	16256.2

4.8 Roughness Evaluation

The surface of iron coated AZ31 magnesium alloy with an intermediate layer was evaluated using a VK-X100/X200 which is a surface roughness analyzer. This surface roughness values give an idea about texture of the iron coated sample. The image of the sample was taken at 10X magnification. Fig 4.17, 4.18 and 4.19 shows the 3D images of the surface coatings in different angles. The rectangular window in Fig.4.16 shows the area taken for roughness evaluation. The average surface roughness was 10.4776µm which can be inferred from Fig 4.15. Fig 4.18 gives the 3D image of the surface and shows the varying thickness on the surface due to surface dents.

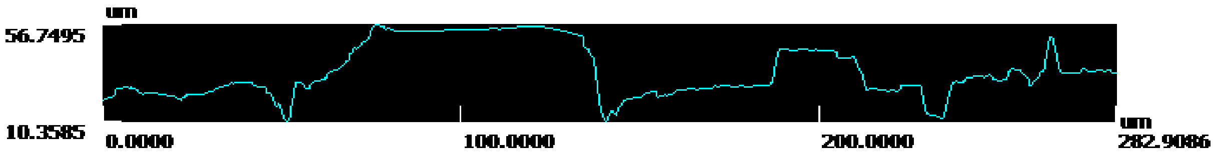


Fig.4.15 Variation of coating roughness due to dents on the surface

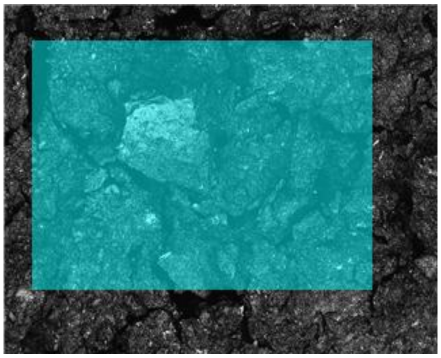


Fig.4.16 Roughness evaluation window of the dented substrate

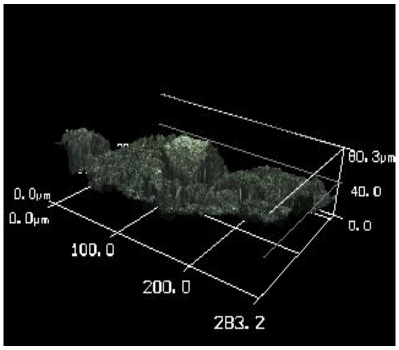
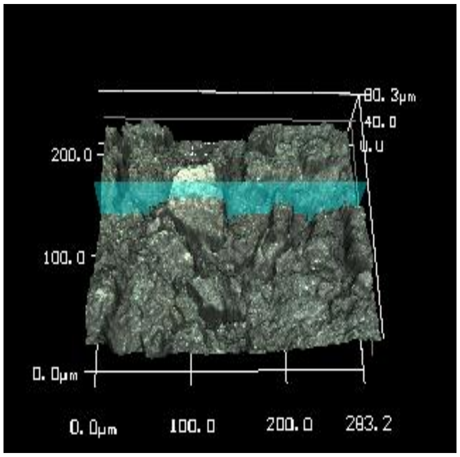


Fig.4.17 3D image of the surface coating



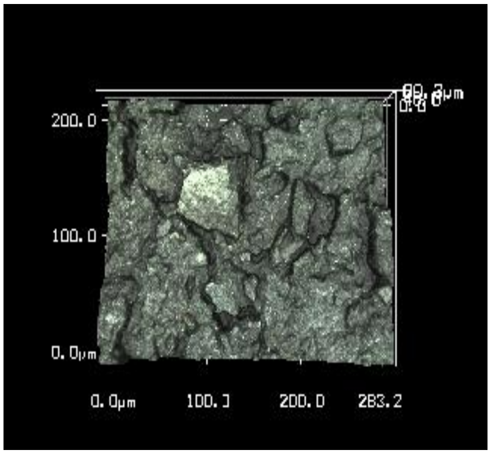


Fig.4.18 3D image of the surface

Fig.4.19 3D top view of the substrate

4.9 Thickness Evaluation

The side view of the broken sample was taken using an SEM and it is shown in Fig 4.20. The sample was broken up after dipping it in liquid nitrogen so as to get a clean break and not shear it. The entire sample thickness as measured by the SEM was 280.8µm. The image was taken at a magnification of 100µm. The thickness of the uncoated sample was 250µm and the thickness measured after coating it was 280.8µm. Doing some simple math the final thickness of the iron layer was found to be 30.8µm.

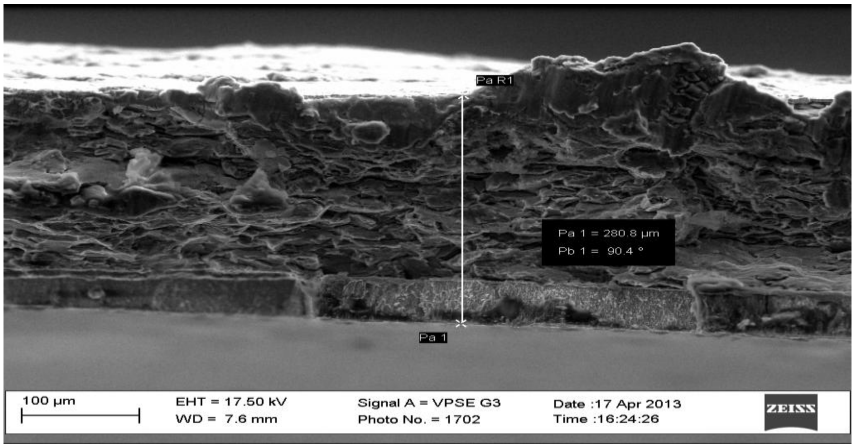


Fig.4.20 Cross sectional view of iron coated AZ31 magnesium sample for thickness evaluation

4.10 Corrosion Evaluation

Accelerated corrosion tests were conducted on the iron coated AZ31 sample and compared with the uncoated AZ31 magnesium sample. Open circuit potential test and potentiodynamic polarization test were conducted on the coated and uncoated samples.

4.10.1 Open Circuit Potential

The open circuit potential (OCP) is also called as the corrosion potential or equilibrium potential is the potential at which there is no current. OCP of different layers and uncoated samples were evaluated in the Gamry potentiostat/galvenostat in PBS solution over a period of 10 seconds. The results were overlaid using excel. The values for the data entered are shown in methodology. Higher OCP refers to higher corrosion resistance. Fig 4.21 shows the OCP comparison. Iron coated AZ31 without an intermediate copper showed very low OCP of -1.5V which was same as zinc immersion coated AZ31 substrate. OCP of copper coated AZ31 was -1.42V and OCP of iron coated AZ31 magnesium with an intermediate copper layer was -0.90V. There was an increasing trend in OCP values as the number of layers increased. The OCP curve justifies the presence of an intermediate copper layer for electroplating of iron on AZ31 magnesium alloy.

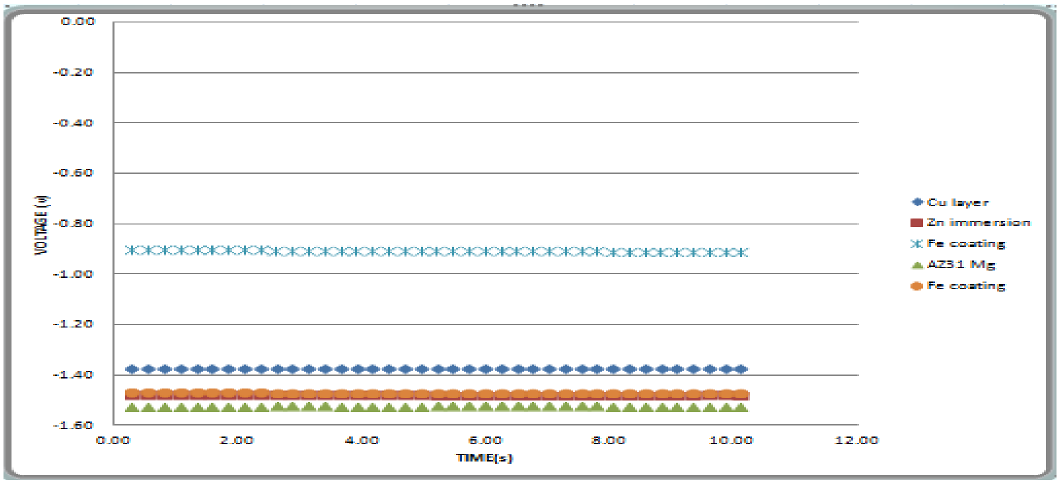


Fig.4.21 Open Circuit potential comparison

4.10.2 Potentiodynamic Polarization

The tafel technique can be used to get an accurate value of corrosion rate of a metal in a solution. The corrosion current is measured during a sweep of potential. The voltage was swept from -2.50V to 2.50 V relative to Eoc. The data is fitted against a standard model (butler-volmer model) which gives an estimate of Icorr which helps to calculate a corrosion rate(Burstein, 2005). The graphical output of the experiment is a plot of log current versus potential. From the tafel curve it is possible to obtain corrosion current, corrosion rate, kinetic information for the anodic and cathodic reactions. The tafel test was run using a GAMRY reference 600™ potentiostat/galvenostat with the iron coated AZ31 magnesium sample in PBS solution. The results were overlaid with the results of uncoated AZ31 magnesium samples and coated magnesium without an intermediate layer. Table 4.7 shows the comparison between corrosion rates of iron coated and uncoated AZ31 magnesium substrates.

Table 4.7 Comparison of corrosion rates of Iron coated AZ31 with a copper layer, Iron coated AZ31 without a copper layer and pure AZ31

	Iron Coated AZ31 with a copper layer	Iron coated AZ31 without a copper layer	Pure AZ31
Beta A	$482.1\ e^{-3}$ V/decade	1.043 V/decade	1.281 V/decade
Beta C	$241.6e^{-3}$ V/decade	1.641 V/decade	1.793 V/decade
Icorr	147.0µA	3.800 mA	4.300Ma
Ecorr	-1.140 V	-1.440 V	-1.570V
Corrosion Rate	54.08mpy(1.373632mm/yr)	$1.089e^{3}$mpy(27.6606 mm/yr)	$1.591e^{3}$mpy(40.4114 mm/yr)

After the plots were overlaid it was found that the corrosion rate of iron coated AZ31 magnesium with an intermediate copper layer offered better corrosion resistance than the uncoated AZ31 magnesium and iron coated AZ31 magnesium without an intermediate layer. More the graph is to the right the corrosion current increases which means an increase in the rate of corrosion. Iron coated AZ31 magnesium with an intermediate was found higher and to the left of the other graphs which says that the corrosion current decreases and the corrosion voltage increases. Higher open circuit means higher corrosion resistance. The fig. 4.22 shows the tafel plots of iron coated AZ31 magnesium with an intermediate, iron coated AZ31 magnesium without an intermediate layer and uncoated AZ31 magnesium alloy.

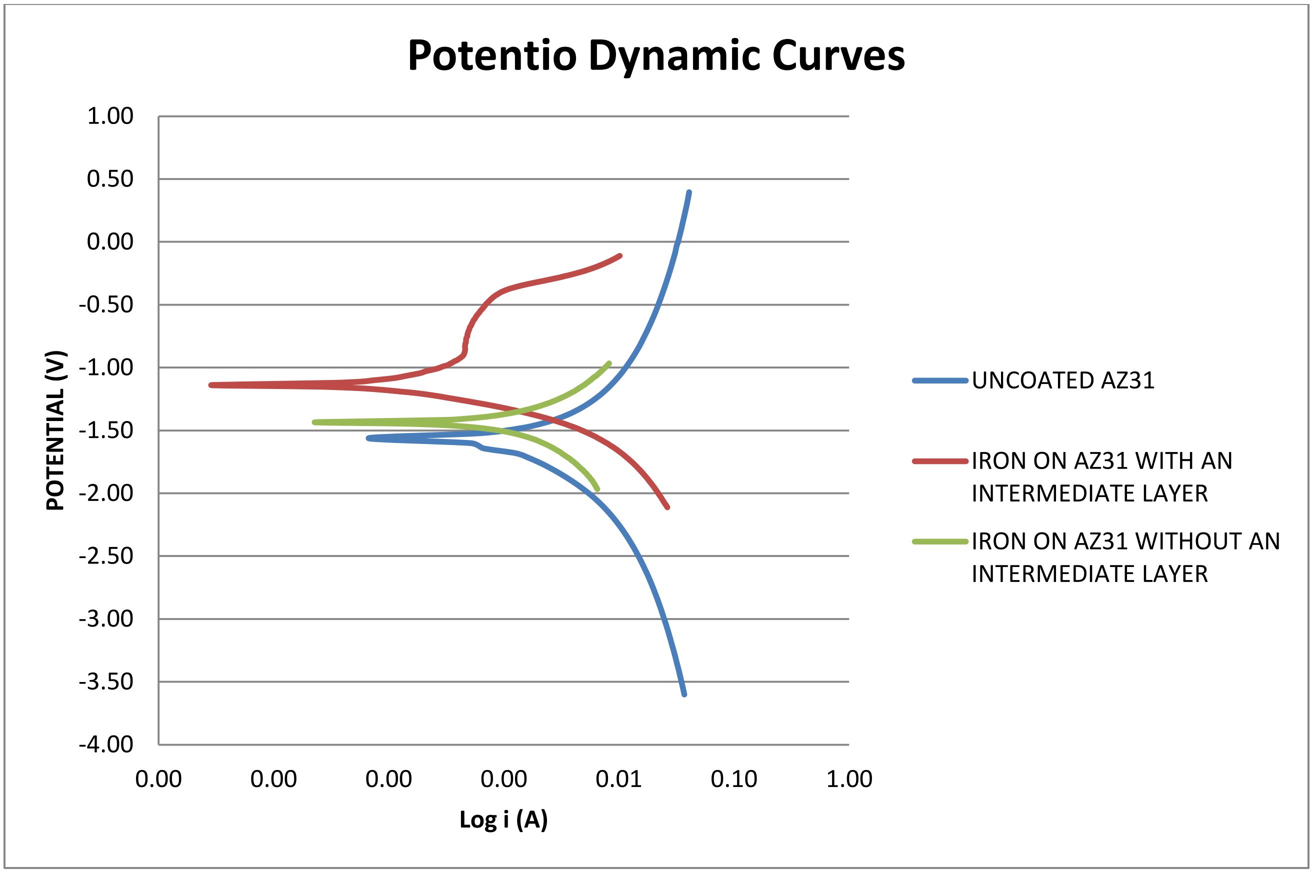


Fig.4.22 Potentiodynamic polarization curves

CHAPTER 5

5. CONCLUSION AND FUTURE WORK

5.1 Conclusion

In this thesis electroplating of iron on AZ31 magnesium alloy has been studied. A protocol for electroplating iron on magnesium at an acidic pH was developed. Presence of iron was proved by EDX analysis. Iron can be plated only at low pH since magnesium corrodes at a low pH, the surface of magnesium had to be made non reactive. An intermediate copper layer was electroplated on the surface of magnesium. This intermediate layer prevented attack by the acidic electrolyte. A zinc immersion layer was formed before the copper layer to the prevent magnesium interaction with copper electrolyte and also to ensure better adhesion of copper on the magnesium surface. Presence of iron was confirmed by EDX, XRD and XPS. Percentage of iron detected by EDX was 40% by atomic weight. XRD analysis confirmed the presence of iron in magnetite form. Peak position at 709.337 obtained as per XPS analysis is similar to XPS analysis already performed on iron surfaces which confirms the presence of iron by XPS.

Thickness of the coating was found to be 21.8µm and surface roughness was found to be 10.4476µm. Corrosion rate from tafel plots shows the corrosion rate of iron coated magnesium is 1.373632mm/yr and bare magnesium substrate is 40.4114 mm/yr which is lower than bare magnesium substrate. All the corrosion tests were conducted in PBS.

5.2 Future Research

This thesis mainly focuses on electroplating iron on AZ31 magnesium alloy so that it can be used as biodegradable arterial stents and offer better corrosion resistance than the bare Magnesium substrate. The following things can be improved in this research

2 sub layers before the primary iron layer makes the process very complicated, so finding possible ways to coat iron without several intermediate at the same time without any compromise in corrosion resistance can help reduce the complexity of the process(Zhao, Huang, & Cui, 2008).

Using ferric chloride salt instead of ferrous ammonium sulfate might help in running the process at better current density and increase the throwing power of the cathode. Since magnesium undergoes attack in chloride medium ferric chloride was neglected but if the intermediate layer is 8µm thick ferric chloride can be used of plating. Using this bath might help get better corrosion resistance compared to ferrous ammonium sulfate.

Performing corrosion tests in dynamic conditions will give an insight of how the material corrodes in flowing liquid. Performing in-vitro tests will give an idea about biocompatibility.

The current technology of stents is drug eluting stents which release drugs constantly over a period of time. The iron coated stents can be made to function as drug eluting stents by a Self Assembled Monolayer(SAM) coating. The drug molecules can be attached on to the tail of the SAM's.

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