Surface Degradation Studies of Nanostructured Magnesium Tested in Simulated Body Fluid

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Certificate

This is to certify that work in this thesis has been carried out by **Miss Iqra Malik** andcompletedunder my supervision in Microscopy and corrosion laboratory School of Chemical and Materials Engineering, National University of Sciences and Technology, H-12, Islamabad, Pakistan.

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It is dedicated to my parents and siblings who have helped me

Abstract

Magnesium has attracted a lot of attention as a new biodegradable material. The chemical and physical processes, in simulated body fluid (SBF), of magnesium metal were carried out in current research work. Cast magnesium samples with different surface characteristics were prepared which were then placed in SBF for 2, 4 and 8 days. This led to the emergence of hydroxyl apatite coating on surfaces of magnesium. The solution was changed at regular intervals to maintain a pH of 7.6. Other Mg samples were anodized at 40V and 60V to create a uniform layer of oxide on them and then their activity in SBF was contrasted with as cast samples of Mg. It was observed that rate of corrosion varies as the immersion time increases. Magnesium undergoes corrosion and cracks were formed on the surface of the samples. This was attributed to the aggressive corrosive nature of SBF.

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CHAPTER 1: INTRODUCTION

Titanium and stainless steel have been used from quite a time in the formation of biomaterials. They both remain inert in the bodily environment and do not degrade over time; however, they do show electrochemical degradation due to corrosive environment of the body. In recent years, magnesium has taken much attention in this field due to its biodegradable nature. Magnesium would be distinctive to biomaterials field, it would provide the mechanical advantages of a metal in addition to the advantage of biodegradability that was previously provided by some polymers.

In view of excellent biodegradability and biocompatibility, magnesium and its alloys are quite potential candidate materials to manufacture the components for biomedical applications. There are some key advantages that magnesium and its alloys possess over current materials. It includes the low density of magnesium (1.75-2.1 g/cm^3)[1], it's the lightest of all structural metals. Magnesium has high damping capacity, in biomedical applications this can be very useful in high load bearing applications, where vibration absorbing properties of magnesium can be advantageous. It is very easy to machine magnesium and so complex shapes can be easily made. Biomedical applications require fabrication of intricate parts that can be manufactured easily using this property of magnesium.

Although the biodegradability of magnesium is the significant feature for which magnesium is getting high popularity in biomedical applications, this feature can cause a few complications. The rate of degradation of magnesium is very intense and this can lead to high evolution of hydrogen gas. The hydrogen gas can cause formation of gas pockets at the site of healing. These gas pockets can in turn delay the healing at the surgical sites. If gas pockets form near the implant then separation of tissues can occur, worst case scenario can be the blocking of blood stream by these gas bubbles eventually leading to death. Thus, keeping all these problems in mind that may occur due to the intense rate of corrosion of magnesium, it is very important to control the rate of corrosion of magnesium, when used as a body implant.

It is a multidisciplinary challenge to come up with a suitable biodegradable implant. One solution of controlling the rate of degradation of magnesium is to add other elements in it and use it in alloy form. However, if alloying additions is to be done to decrease the rate of

degradation of magnesium then they should be added in an amount that they remain nontoxic in the body.

Magnesium makes up to 13% of the earth's body and is one of the most common element in the Earth, next only to only these three elements , iron, oxygen and silicon. Magnesium is an attractive metal due to its light weight and formability. It is important for nucleic acid's basic structure that is present in the cells of all living beings. Due to this reason, it is required by the human body for its normal function. Magnesium has been previously used in different industries including aerospace, automotive and electronics. Due to its role in human cells, it has been used in pharmaceutical industries too.

Table 1 shows a brief overview of the benefits of Mg as a biomaterial over other metals and alloys that are being already used as a biomaterial.

Table 1.1: Advantages of Mg as a biomaterial

Low Density	It is lightest in all structural materials. (1.738g/cm^3).
Dimensional Stability and Machinability	Mg is easy to machine and can be easily fabricated into intricate shapes, according to the requirement.
Elastic Modulus	The elastic modulus of magnesium is approx. 45GPA which is near to that of bone which has approx. 20GPA while titanium has 110-120 GPA.
Biocompatibility	Ti and SS remain inert in human body while Mg is biodegradable.
Safe degradation	SS and Ti implants undergo some electrochemical degradation in human body but their release in human body causes discomfort to tissues, while magnesium shows safe degradation and is non toxic to human cells.

While Table 2 shows a little summary of disadvantages of other materials when they are used as a biomaterial.

Table 1.2: Disadvantages of other materials

Ceramics: Zirconia, alumina etc.	They are brittle and non-resilient when used as a biomaterial
Polymers: Polyesters, polyethylene etc	They are not strong.
Composites: Amalgam etc	They are difficult to machine.

1.1 Corrosion Resistance of Magnesium

Corrosion can be described as the degradation of the materials by chemical reactions with the environment. Magnesium, due to its high reactivity behavior amongst metal, has a high corrosion rate. However, in the application of biomaterials, it is taken as a positive attribute as this salient feature makes it as a potential element to be used in making of biodegradable implants.

Corrosion mechanism:

In the corrosion of magnesium, metallic Mg is converted into stable ion, Mg^{+2} at the anodic site whereas at the cathodic site, hydrogen is liberated. The reactions occur as given belowg[2]:

$$Mg \longrightarrow Mg^{++} + 2e \qquad \text{(anodic reaction)}$$
$$2H_2O + 2e \longrightarrow H_2 + 2OH^- \qquad \text{(cathodic reaction)}$$
$$Mg + H_2O \longrightarrow Mg(OH)_2 + H_2 \qquad \text{(product formation)}$$
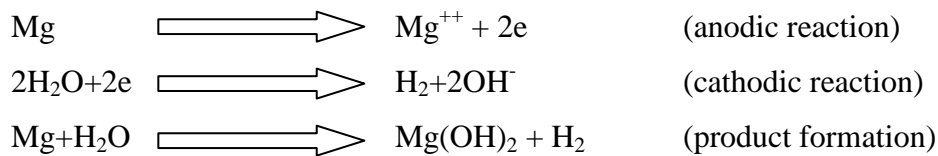
$Mg(OH)_2$ is deposited on the surface of the metal but it's not a very effective coating to provide corrosion resistance and doesnot provide protection in chlorinated environment like SBF.

It seizes up to form magnesium salt:

$$Mg(OH)_2 + 2Cl^- \longrightarrow MgCl_2 + 2OH^-$$
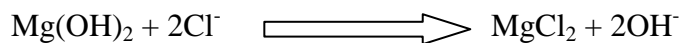
The breaking down of Magnesium hydroxide causes pitting and high and intense degradation initiates at these points which then behave as small anodic sites.

The intense corrosion of magnesium samples creates a problem when high hydrogen evolution, this problem is summarized in the flowchart below:

High hydrogen evolution

Formation of gas pockets

Delay in surgical sites
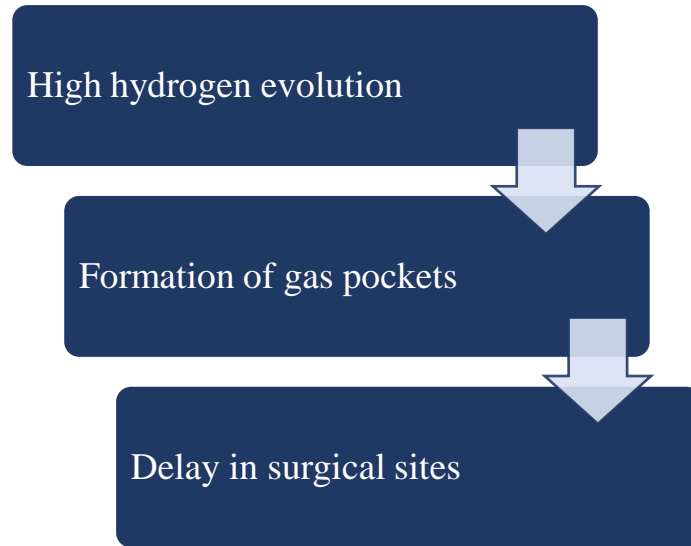
1.2 Types of Corrosion

Given below are some of the kinds of corrosion:

1.2.1 Pitting corrosion

Magnesium experiences pitting at free corrosion potential as it's actually a naturally passive metal. Pitting of magnesium metal and alloys of magnesium takes place in alkaline and neutral salt solutions. In low acidic solutions, pitting also occurs. However, in case of hydrofluoric acid, it does not attack magnesium to much extent as it forms an insoluble coating on magnesium of magnesium fluoride.

1.2.2 Crevice Corrosion

Magnesium and its alloys does not undergo crevice corrosion because corrosion of magnesium is not dependent on differences in oxygen concentration.

1.2.3 Stress Corrosion Cracking

This type of corrosion cracking seen is trans granular. However, intergranular SCC occurs in magnesium when it is paired with aluminum and zinc. With pH above 10.2, stress

corrosion cracking does not occur in magnesium alloys. But in neutral solutions even in distilled water, magnesium and its alloys are sensitive towards cracking.

1.2.4 Galvanic Corrosion

When paired with another metal or due to the presence of second phases, alloys of magnesium are very sensitive to galvanic corrosion. The degradation rate in this case is independent of purity of magnesium when it is coupled with another metal and depends on potential difference between cathode and anode and on medium's conductivity and distance between anodic and cathodic electrodes.

1.2.5 Intergranular Corrosion

The grain boundaries phases of magnesium act as cathode to the grain interior and as a result concentration of corrosion occurs in the area joining the grain boundaries

1.3 Factors effecting corrosion of magnesium

Following are some of the factors that affect corrosion of magnesium:

1.3.1 Type of solution used

The corrosion attack of different solutions on magnesium is not only dependent on the type of solution but also on concentration, movement and temperature of that solution. Cold water has low conductivity due to which attack of cold water that is pure on magnesium is very slow. It forms a layer of hydroxide on magnesium that can dissolve. In case of vapors, both MgO and $Mg(OH)_2$ are developed on the face of magnesium. For solutions of chloride like salt solutions, the corrosion attack on magnesium is aggravated by the presence of carbon dioxide in the solution. The role of dissolved oxygen in these solutions is not much significant. If alkali solutions are used with PH greater than 10.4 then magnesium shows a resistance towards corrosion as this PH corresponds to the PH of saturated $Mg(OH)_2$ and the tendency of film formation increases.

1.3.2 Temperature (Corrosion mechanism)

With rise in temperature, the corrosion rate increases. However, this is more apparent in magnesium alloys than in pure magnesium. In alloys, the increase in temperature, increases the activity of impurities thus a considerable increase in corrosion rate is seen.

1.3.3 Static V Dynamic conditions [3]:

In dynamic conditions, the rate of corrosion was higher in comparison to static conditions. Solution agitation or flow of solution prevents proper deposition of protective film on the surface of magnesium and it also prevents local increase in PH, thus attributing to higher corrosion rate than observed in static conditions.

CHAPTER 2: LITERATURE REVIEW

Zhao studied "Influence of β phase on corrosion rate of AZ91 annealed sample". He used AZ91 magnesium alloy to study the effect of structure that is micro, specifically the act of beta phase's morphology, on corrosion. The beta phase influences the corrosion rate in two ways:

- Increasing corrosion by acting as the galvanic cathode
- Decreasing corrosion by acting as a barrier.

The influence of beta phase in this case is governed by the alpha-beta area ratio and by its distribution in the structure. If decrease in corrosion rate is required then the beta phase should be finally divided and continuous.

Nassif studied "Corrosion Protection and Surface Treatment of Magnesium Alloys used for orthopedic applications." He and his coworkers did a review on the benefits of magnesium alloys in orthopedic implementations. They studied in detail the alloying elements and their effect in human body. Al-Mg alloys are not suitable to be used as biomaterials as aluminum ions presence in human body can lead to Alzheimer disease. The long terms effects of rare earth metals in human body are still unknown and need some extensive study although lithium has been used in medicines from quite a long time. Manganese is a favorable allying element as it decreases the adverse results of impurities like Fe but problem with manganese arises when it is used in excessive amounts as it can lead to neurological disorders. Zinc and Calcium are quite favorable as elements for use in alloys as these both metals are not harmful. Ca reduces oxidation during heat treatment and improves rollability while Zn combined with Mg produces the least hydrogen.

Ghayad studied "Corrosion Control of Mg-Zn Implant Alloys in Simulated Body Fluid" In this study Mg-Zn alloys (1-4% Zn) were used. The wearing of the materials was measured by measuring release of hydrogen released from alloys due to corrosion reactions. Corrosion of this alloy was effected by the concentration of Zn, with increase in concentration of Zn after 3 wt.% corrosion rate of the samples increased. This may be due to the following factors:

- Decrease in Magnesium's grain size
- Absence of continuous protective film
- Precipitation of second cathodic phases

Wang studied "Corrosion process of pure magnesium in simulated body fluid". He and his colleagues immersed pure magnesium samples for 3,7,14 and 21 days in SBF. They didn't change the SBF solution of immersion and studied the change in pH over time. The pH of the solution was seen to increase with the increase in immersion time. H^+ ions were consumed while OH^- ions remained in the solution. This lead to the development of $Mg(OH)_2$. This then prevented the nucleation and growth of hydroxyapatite on the sample to promote its nucleation, $Mg(OH)_2$ formation should be depressed. However, Cl^- ions available in the solution of SBF can inhibit the developement of $Mg(OH)_2$ by forming $MgCl_2$.

Kirkland and Travis studied "Magnesium biomaterials: past, present and future". They highlighted the major flaws that researchers usually make in studying magnesium as a biomaterial. Most of the researchers study its behavior at different temperatures range, though the human body temperature is 37oC and changing the temperature influences the corrosion rate a lot. The pH of the solution should be kept between 7.4-7.6 and measures should be taken to maintain the pH as human body has a constant pH. It is not only important for controlling the corrosion rate but it also influences the formation of layers on the surface of the sample under study.

Xin studied "Degradation behavior of pure magnesium in simulated body fluids with different concentrations of HCO_3".Different concentrations of HCO_3, 4, 15 and 27mmol/L were observed. The sample of pure magnesium didn't showed pitting in all these three SBFs. The corrosion rate was slowed down by higher concentrations of HCO_3. The concentration of 27mmol/L induced passivation and corrosion potential was enhanced. This was due to the promotion of carbonates precipitation on the magnesium sample which enhanced the corrosion protection. Fig shows the wearing rate of pure samples of magnesium in solutions of three different concentrations. The pure magnesium sample that was dipped in SBF solution with 27mmol/L showed the greater corrosion resistance than the samples that were dipped in the other two solutions of SBF.

Esmaily and his coworkers studied "Fundamentals and advances in magnesium alloy corrosion". The work discusses the detailed corrosion of magnesium in atmosphere and in SBF solution. The human body environment consists of 0.14M NaCl solution with some inorganic

species like Ca^{+2}, P04 (-3) and HCO (-3). The phosphates and carbonates encourage the formation of corrosion product layers that are protective or partially protective, however chloride ions increase the corrosion rate Mg corrosion leads to increase in alkanity of the solution as a result of the presence of hydroxide ions formed due to reactions of corrosion. This increase pH leads to killing of bacteria inside the body which is not favorable in long terms. The role of proteins is also studied in detail. They favor dissolution of magnesium sample, however in some cases they also adsorb on magnesium surface to develop an intact layer. This depends upon alloy of magnesium being used and also on the type of the protein under study. This work also explains the dissimilarities in the vivo and in vitro degradation of Mg alloy. The main difference arises due to the change in nature of attack below the coatings. In case of in vivo, strong localized attack was seen whereas in case of in vitro the attack was uniform. The in vivo attack can be explained due to lower diffusivity and this occurred due to implant/tissue interface. Their study explains some of the reactions that may occur when a magnesium alloy is placed of in the biological environment. The basic reactions that are same for the alloys of magnesium are following:

- Corrosion of magnesium
- Release of hydroxide ions that harm cells
- Ca-P precipitation
- Killing of bacteria
- Carbonates are incorporated into the film
- Chloride ions attack
- Proteins adhere to film
- Complex cations of Mg are released in the electrolyte

Harpreet studied "Magnesium as a Biodegradable and Bio-absorbable Material for Medical Implants". This study discusses benefits of magnesium as a biomaterial over other materials being already used like stainless steel and titanium. These materials were biocompatible but not biodegradable. Pure Mg, ZX152 alloy and AZ91 alloy degradation behaviors were discussed in SBF solutions. The ZX152 alloy that is an alloy of Mg-15 wt.% Zn-2 wt.% Ca showed better corrosion resistance than the other two. This was due to the presence of Ca and development of eutectic phase.

CHAPTER 3: EXPERIMENTAL WORK

This chapter describes all the experimental details including solution preparation, sample preparation and about all the equipment and experimental setups used in the whole process.

3.1 Formation of Electrolyte

The electrolyte used for the corrosion testing was simulated body fluid. The tests were carried out in 200ml of solution of simulated body fluid. The formation of simulated body fluid was done using a hot plate that maintained a temperature of $37^{o}C$, magnetic stirrer helped to keep a constant temperature throughout the solution and to help in mixing of the reagents. The reagents were added according to the composition mentioned in the following table 3.1 :

Table 3.1: Composition of reagents

Order No.	Reagent	Amount
1.	Sodium chloride	7.996g
2.	Sodium carbonate	0.35g
3.	Potassium chloride	0.224g
4.	Potassium phosphate	0.228g
5.	Magnesium chloride	0.305g
6.	1M Hydrochloric acid	40 ml
7.	Calcium chloride	0.278g
8.	Sodium sulphate	0.071g
9.	Tris hydroxyl methyl amino methane	6.057g

3.2 Sample preparation:

The procedure for the sample preparation was followed as stated below to produce sample size of 1.2 cm^2 to be used for corrosion experiments.

1. A copper wire was soldered to the face opposite the surface exposed.
2. The samples were then cold mounted into a thermoset.

3. Grind the exposed surface up to 1000 grit size to remove scale, dust and other contamination.

4. Place the wire into a glass tube for the potentio-dynamic setup.

3.3 Types of magnesium samples used for Corrosion testing:

Four different types of magnesium samples were prepared prior to corrosion testing in simulated body fluid. There samples were as following:

- As casted

- Anodized at 40V

- Anodized at 60V

The samples that were used as casted were not given any surface treatment and they were used as it is. However, metallography and etching was done on the anodized samples. The samples were grinded at 250-1200 grit size paper of SiC and were washed with ethyl glycol during the grinding processes. After that they were polished with aluimina powder and etching was done for 10 secs. Following etchant was used after performing the metallography:

Table 3.2: Etchant

HNO3	1ml
Distilled water	19ml
Acetic acid	20ml
Ethylene glycol	60ml

The magnesium samples were then anodized in NaOH solution for 22 minutes at 37°C, temperature was maintained using hot plate. Current during anodization was used of 1A and magnesium was used as cathode while lead as anode. Two different types of voltages were used i.e. 40V and 60V, to make a comparison between the layers formed at two different voltages and how they would later affect the corrosion rate.

Immersion Test:

All these samples were dipped in simulated body fluid for 2, 4 and 8 days. They were put in an incubator with 250 rpm and a temperature of 37°C. The purpose of dipping in simulated body fluid was to form a layer of HA on them so that a comparison of their corrosion rate can be

made. The solution was changed at a regular interval of 24 hrs., the solution was changed at regular intervals due to the following reasons:

- To maintain pH of the solution
- To provide fresh ions for the deposition of layer on the samples.

3.4   Setup of Electrochemical Cell:

Following the test of immersion the samples were taken out from incubator at respective time periods and were tested for corrosion rate using three-electrode cell. It consists of three electrodes dipped in the electrolyte and is the part of GAMRY hardware. The parts of the Electrochemical cells have been briefly explained below.

Reference Electrode: It provides the reference potential for the working electrode. In this experiment, saturated calomel was used.

 Working Electrode: It is the sample which may act both as cathode and anode depending on the type of scan. In this experiment, magnesium was taken as working electrode which behaved as anode.

Auxiliary Electrode: A platinum wire is used as auxiliary electrode. It acts as counter electrode to the working electrode. [21]

3.5   Techniques for Corrosion Analysis:

There are many ways to study the corrosion behavior of a material. We used GAMRY FRAMEWORK for this purpose. In this system, scripts are written in Explain to define the electrochemical experiments. GAMRY framework is used to launch all experiments. The framework is actually an Explain interpreter. When a procedure is initiating on the system of Gamry, it is a compilation of intense complied software for decent timing control of this procedure and software (Explain) for relaxation in experimental produce. An easy to handle dialog box is used to enter the experimental parameters; it is a setup for each experiment. During data acquisition, you get informed throughout the experiment by real time data display. The framework gives a consistent instrumental display and a user interface, regardless of the electrochemical experiment.

3.6 Tafel analysis by Gamry:

Degradation rate of a metal in a solution is calculated accurately by Tafel technique. During slow sweep of the potential, cell current is measured. I_{corr} is measured when a fit of the data is made to a standard model, this is used in calculating corrosion rate. The output of the procedure is a graphical plot of log current vs potential. Given types of studies can be obtained by analyzing the curve:

- Corrosion potential
- Corrosion current and corrosion rate
- Kinetic information for cathodic and anodic reactions.

3.7 Experimental setup along with parameters:

The square test specimens of pure magnesium were prepared. After this grinding of the samples up to a 1200 grit surface finish was done and distilled water was used for cleaning. The corrosion characteristics were studied using potentiodynamic polarization technique. The corrosion resistance of magnesium was tested at temperature maintained at $37^{o}C$ that is the body temperature of human beings. A specimen holder was used to hold the specimen during the testing such that exposed area of surface of the samples was in the solution for testing. The testing was done using DC105 module of the GAMRY Equipment at 1 mV/sec scan rate and 1s sample period. The potentials used are from -0.25 to 0.25V. Corrosion Analysis software Echem Analyst was applied to find out the corrosion rate. A three electrode cell of standard measurements comprising of working electrode as magnesium, reference electrode (SCE) as saturated calomel, and counter electrode as graphite was used to carry out the tests.

3.7.1 Scanning Electron Microscope:

After corrosion testing, images of some of the magnesium samples were taken by scanning electron microscope. The samples are mounted on a specimen holder, rigidly and then electron beam is used to scan the image the samples should be able to withstand the high energy of beam and vacuum conditions. This microscope uses electrons to interact with the surface of sample under study and then these electrons produce signals to create an image of the sample. The image is used for understanding the topography of the sample. SEM is usually used to study

the surfaces of solid objects. Following are some of the requirements of a sample to be examined under SEM:

- Samples should be able to withstand high energy of electron beam.
- Samples should be able to fit in the specimen stage.
- Sample should be electrically conductive.
- Non-conductive samples should be given an ultrathin conductive coating

3.7.2 XRD:

This technique is used to understand the following features of a sample under study:

- Chemical composition
- Physical properties
- Molecular structure

It uses X-rays that are targeted on the sample under study, these X-rays get deflected according to Braggs law and their diffraction is used to understand the sample and its chemical composition.

CHAPTER 4: RESULTS AND DISCUSSION

This chapter includes the images of scanning electron microscope and results obtained from potentiodynamic testing of as casted and anodized samples of magnesium using Gamry Framework and Gamry Echem Analyst.

4.1 Corrosion Rates and Potentiodynamic Plots of As Casted Samples

Exposed surface area=1.2 cm^2 (marine)

Density=4.43g/cm^3

Equivalent weight=11.86

Table 4.1: Corrosion rates and current densities of as casted samples of Magnesium

Immersion Time (days)	Temperature (^{o}C)	E$_{corr}$ (mV)	I$_{corr}$ (μA/cm^2)	Corrosion Rate (mpy)
2	37±1	-733 V	1.43	0.6585
4	37±1	-437 V	6.75	3.116
8	37±1	-543V	112	59.58

4.1.1 Equivalent Weight

Equivalent weight EW is the mass in grams that will be oxidized by the passage of one Faraday (96 489 C (amp-sec)) of electric charge.
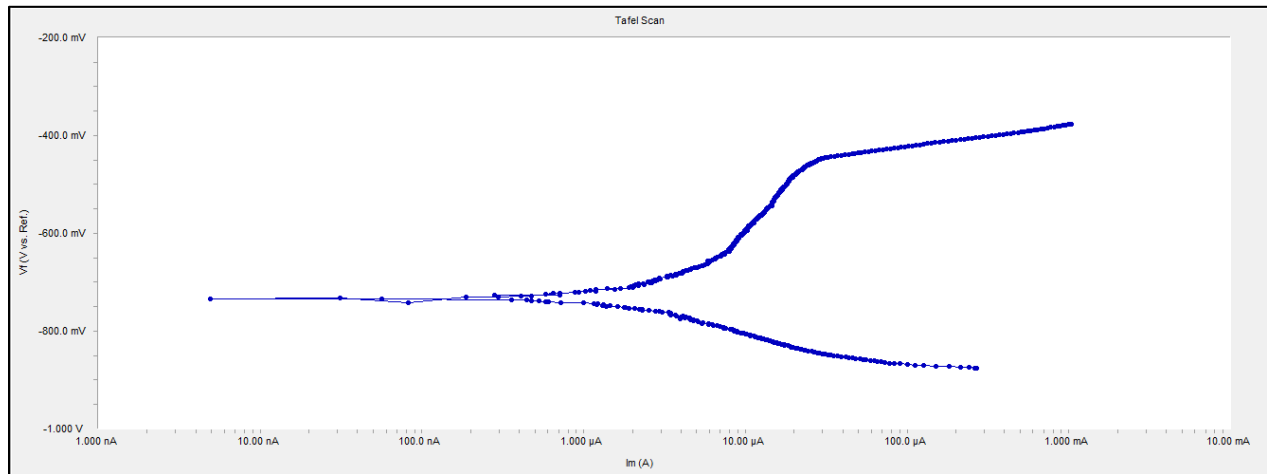
4.1.2 Potentiodynamic Curves

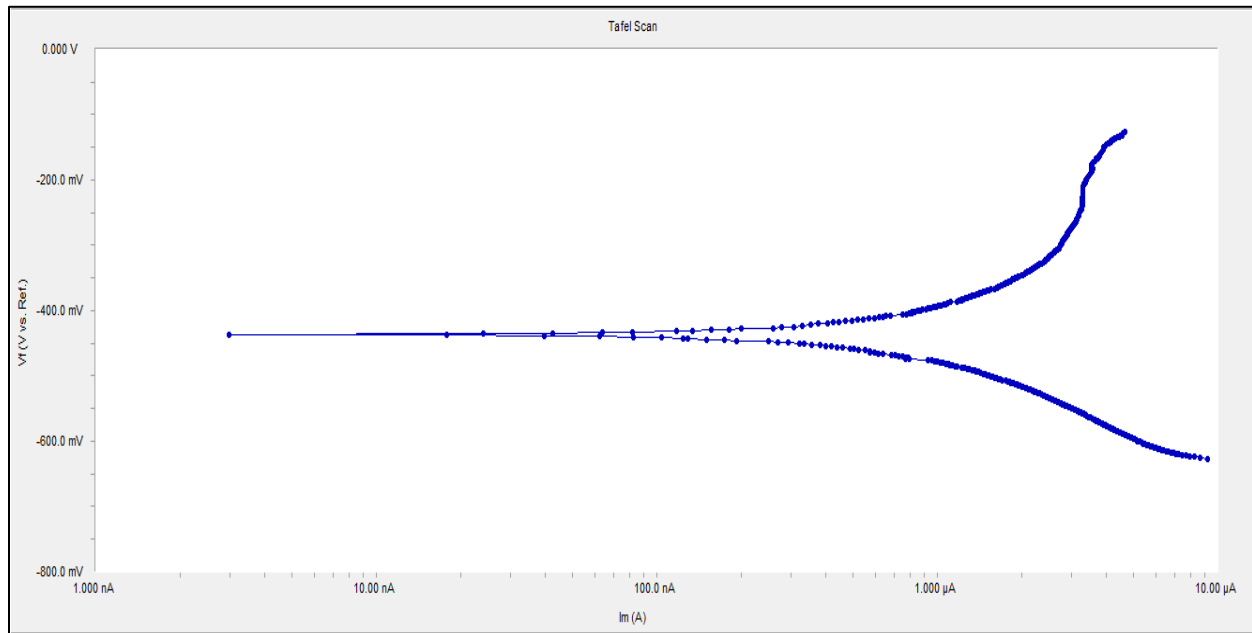**Figure 4.1:** A potentiodynamic curve of as casted magnesium dipped in sbf for 2 days.

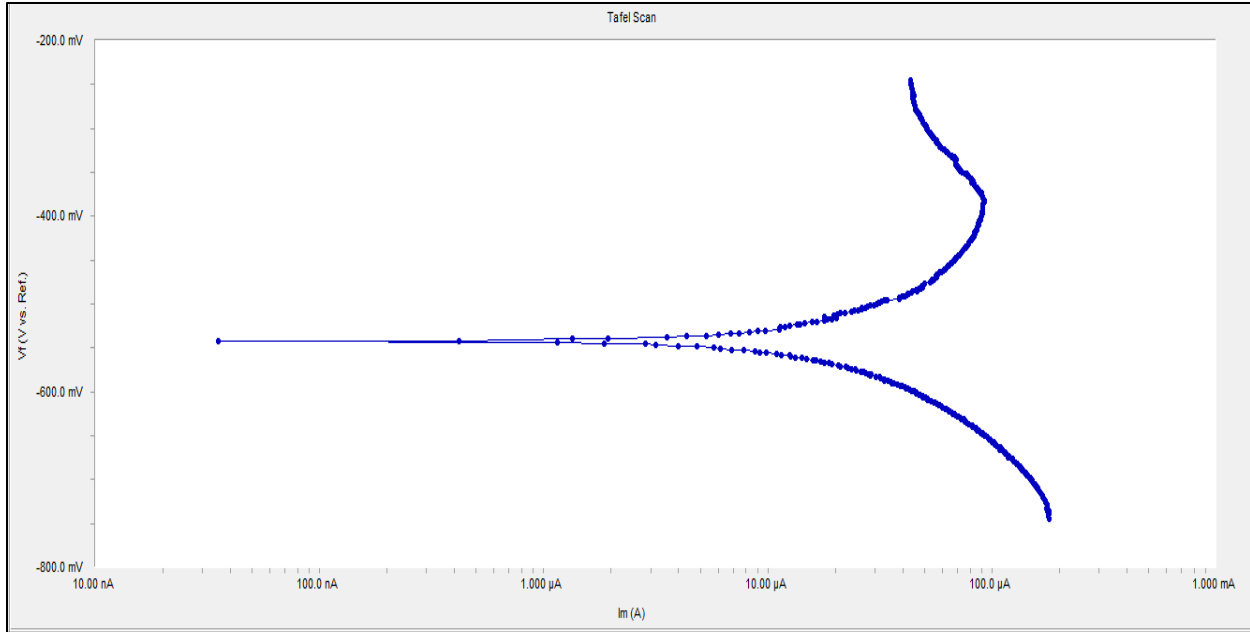**Figure 4.2:** A potentiodynamic curve of as casted magnesium dipped in sbf for 4 days.

Figure 4.3: A potentiodynamic curve of as casted magnesium dipped in SBF for 8 days.

Data of (Table 4.1) revealed that the rate of degradation of magnesium varies as the days of immersion in SBF.

- It is seen that the rate of magnesium's corrosion was seen to rise with increase in immersion time in SBF. The as casted magnesium sample is covered with a magnesium oxide layer, this layer is formed when magnesium reacts with dry air[3]:

  $$Mg \text{ (s)} + \frac{1}{2} O_2 \quad \Longrightarrow \quad MgO \text{ (s)}$$
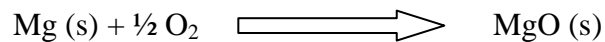
  However, this layer breaks down instanteously when the magnesium sample is immersed in simulated body fluid and magnesium forms magnesium hydroxide. The reaction that occurs is as follows:

  $$MgO \text{ (s)} + H_2O \quad \Longrightarrow \quad Mg(OH)_2 \text{ (s)}$$
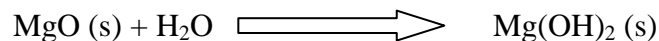
  Magnesium hydroxide is also soluble in water and as water is the main constituent of simulated body fluid, thus this film is non-protective in neutral water solutions. Magnesium ions prevent the nucleation and growth of hydroxyapatite and for this reason no formation of hydroxyapatite occurs after two days in immersion. A uniform degradation of surface occurs as pure magnesium is single phase. After 4 days, the corrosion rate is seen to increase as magnesium is a active metal and it degrades fast.

- When the magnesium sample dipped in SBF for 8 days is checked for corrosion rate, it shows an increase in corrosion rate as compared to 4 days magnesium sample. With

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increase in immersion time, $Mg(OH)_2$ prevents deposition of hydroxyapatite. There is also presence of Cl ions in the medium, which are widely known for their role in acceleration of corrosion. Cl ions compete with OH ions and form $MgCl_2$ and they in turn accelerate corrosion.

4.2   Corrosion Rates and Poteniodynamic Plots of Samples Anodized at 40V

Exposed surface area=1.2 cm^2

Density=4.43g/cm^3

Equivalent weight=11.86

Table 4.2: Corrosion rates and current densities of samples anodized at 40V

Immersion Time (days)	Temperature (ºC)	E_{corr} (mV)	I_{corr} ($\mu A/cm^2$)	Corrosion Rate (mpy)
2	37±1	-743	73.10	41.13
4	37±1	-1.45V	22.3	11.39
8	37±1	-688	65.4	37.74

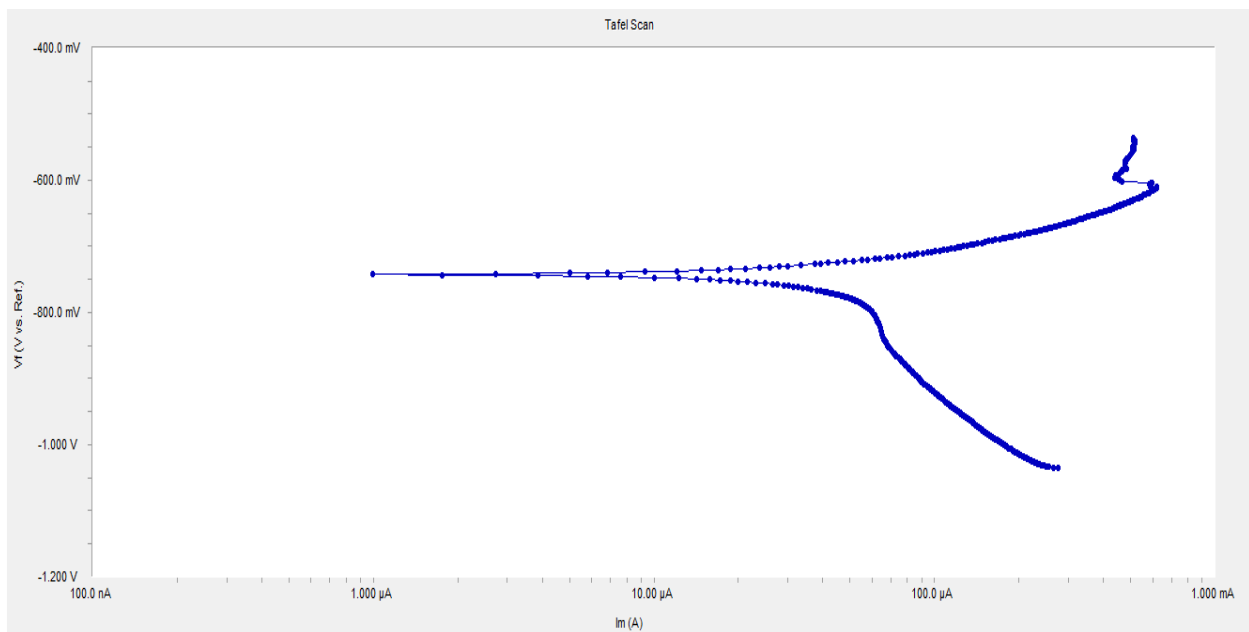### 4.2.1   Potentiodynamic Curves

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Figure 4.4: A potentiodynamic curve of magnesium anodized at 40V and dipped in simulated body fluid for 2 days
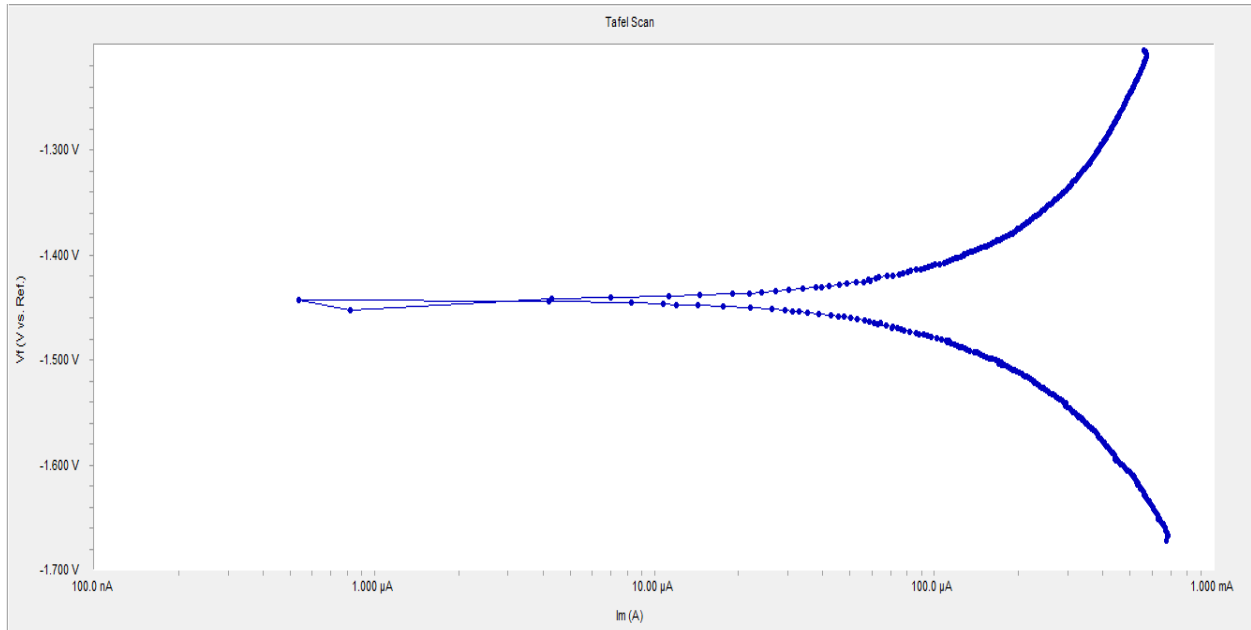

Figure 4.5: A potentiodynamic curve of magnesium anodized at 40V and dipped in simulated body fluid for 4 days
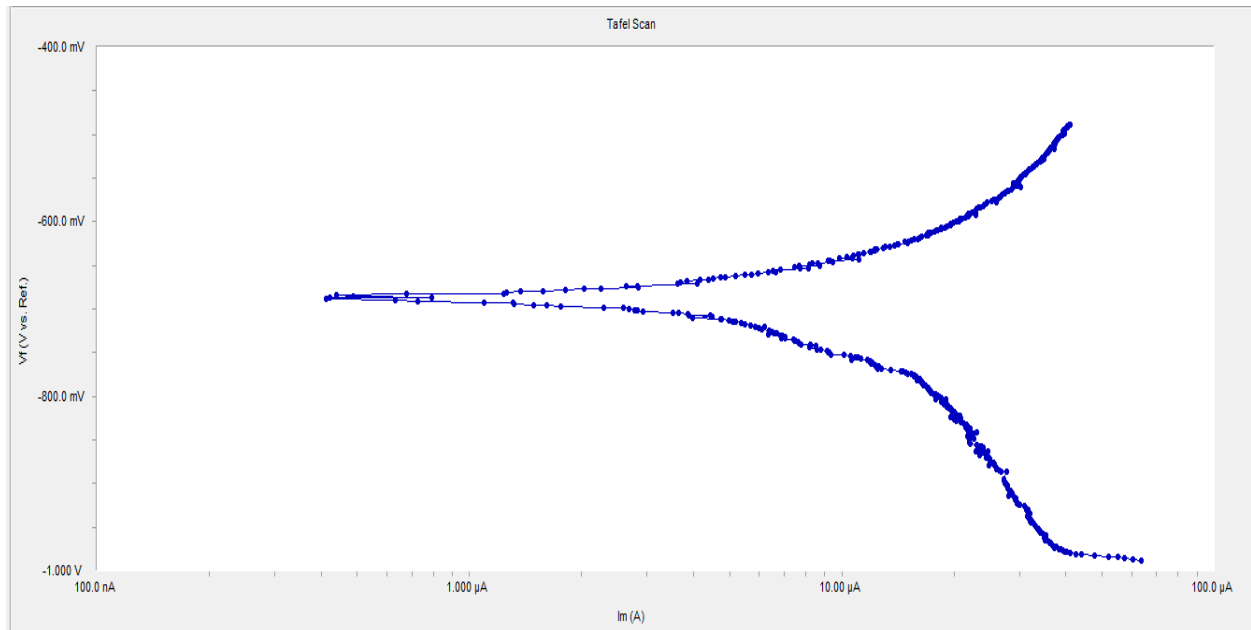

Figure 4.6: A potentiodynamic curve of magnesium anodized at 40V and dipped in simulated body fluid for 8 days

The trend of corrosion rate shown by magnesium sample anodized at 40V is same as trend shown by as cast sample. Anodization was done using 1M NaOH solution with 1A current and 40V. The purpose of anodization was to form a uniform coating of hydroxide/oxide on magnesium and to analyze how this would influence the rate of magnesium's corrosion. The coating formed by anodization can enhance the corrosion resistance of magnesium by covering the defective sites on the pure magnesium as these sites are regions of active site and corrosion starts from here. A passivating film is formed on magnesium that would reduce the area exposed for corrosion. These preventive measures are dependent on the porosity of the film formed and the thickness of this film. A decrease in film porosity will lead to an increase in corrosion resistance [4].

- The highest corrosion rate was shown by magnesium sample that was immersed in SBF for 2 days. The sample didn't have a uniform coating and cracks appeared on the coating. These cracks are thick enough to allow the penetration of corrosive medium inside them and eventually high corrosion rate is observed. Secondly the conversion of oxide of magnesium into hydroxide of magnesium leads to blocking of pores due to volume expansion. Further expansion with time results in breaking down of pores and cracking of film, providing a pathway for penetration of Cl- ions and corrosion of substrate.

- After 4 days in SBF, the magnesium sample that was anodized at 40, showed low corrosion rate. The sites that were not covered by $Mg(OH)_2$ coating were covered by hydroxyapatite, this lead to decrease in porosity and the active sites were reduced. The presence of hydroxyapatite decreased the corrosion rate. The sample along with hydroxyapatite was also covered with corrosion products. These corrosion products reduced the active sites available for degradation.

- However, after 8 days in SBF, the magnesium sample, anodized at 40V, again showed increase in corrosion. The continuous exposure to SBF solution lead to cracking of the hydroxyapatite layer and magnesium hydroxide ions prevented further deposition. Also, the chloride ions in the medium played their role and increased the localized corrosion. The places covered with hydroxyapatite also occurred as cathode to active sites available, thus increasing the rate of corrosion.

4.3 Corrosion Rates and Poteniodynamic Plots of Samples Anodized at 60V

Exposed surface area=1.2 cm^2

Density=4.43g/cm^3

Equivalent weight=11.86

Table 4.3: Corrosion rates and current densities of samples anodized at 60V

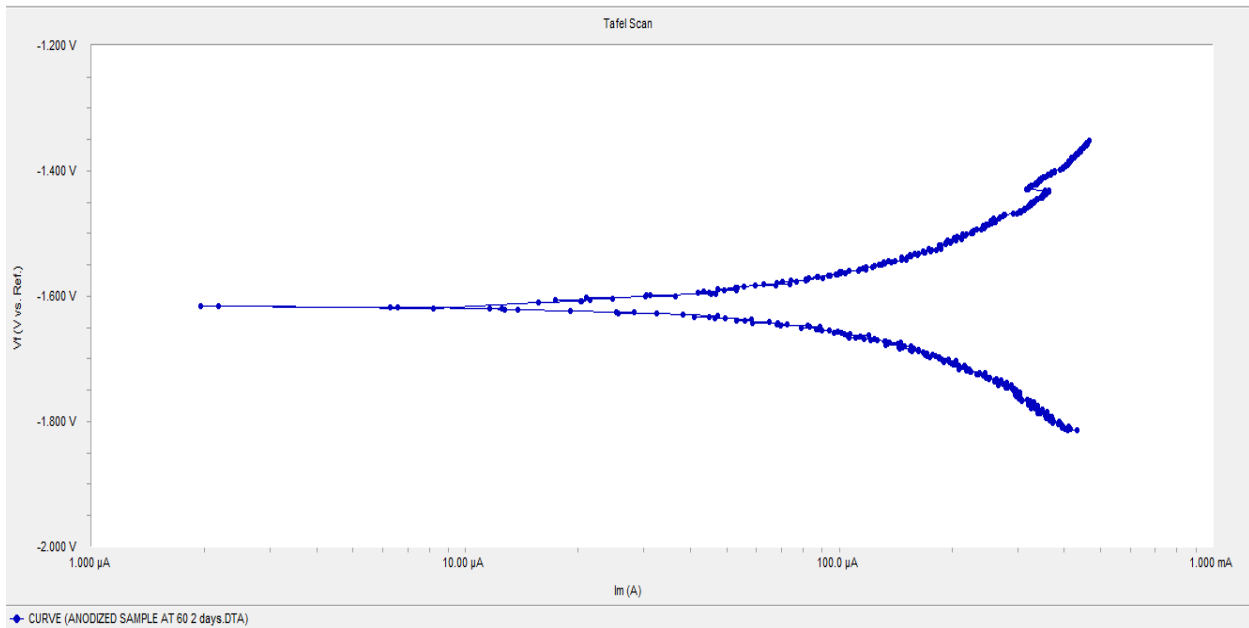| Immersion Time (days)	Temperature (^{o}C)	E_{corr} (V)	I_{corr} (μA/cm^2)	Corrosion Rate (mpy)
2	37±1	-1.62	1.09mA	504.6
4	37±1	-1.66	39.3	22.94
8	37±1	-1.29	336	183.2

4.3.1 Potentiodynamic Curves

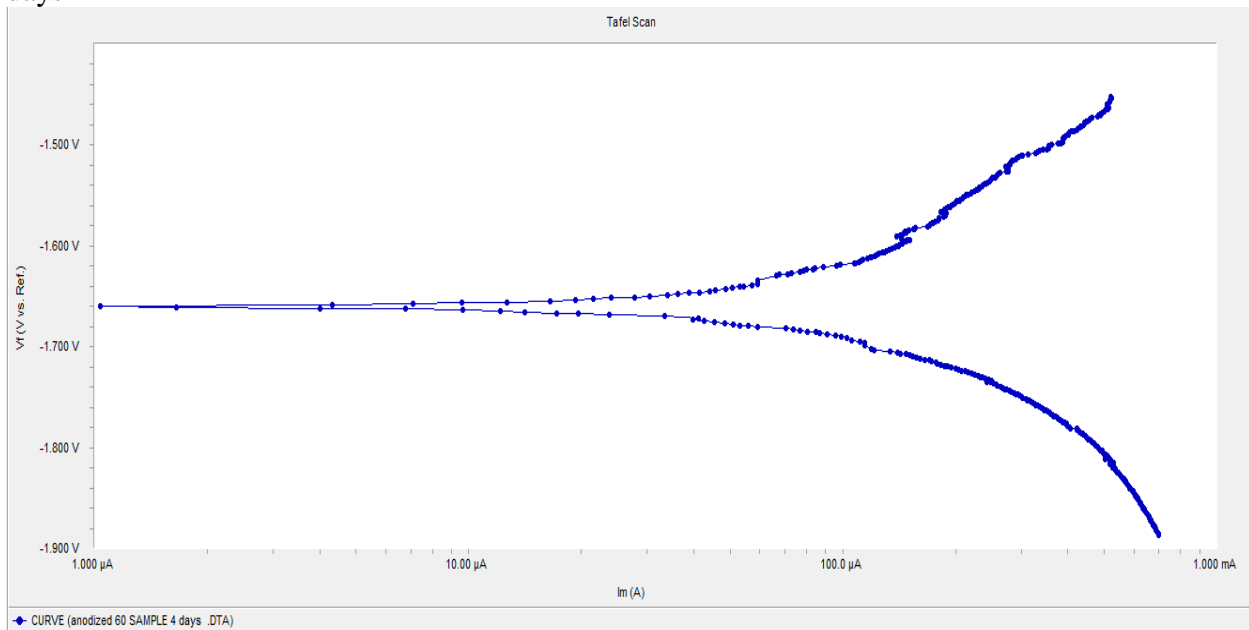**Figure 4.7:** A Potentiodynamic curve of magnesium anodized at 60V and dipped in SBF for 2 days

Figure 4.8: A potentiodynamic curve of magnesium anodized at 60V and dipped in SBF for 4 days
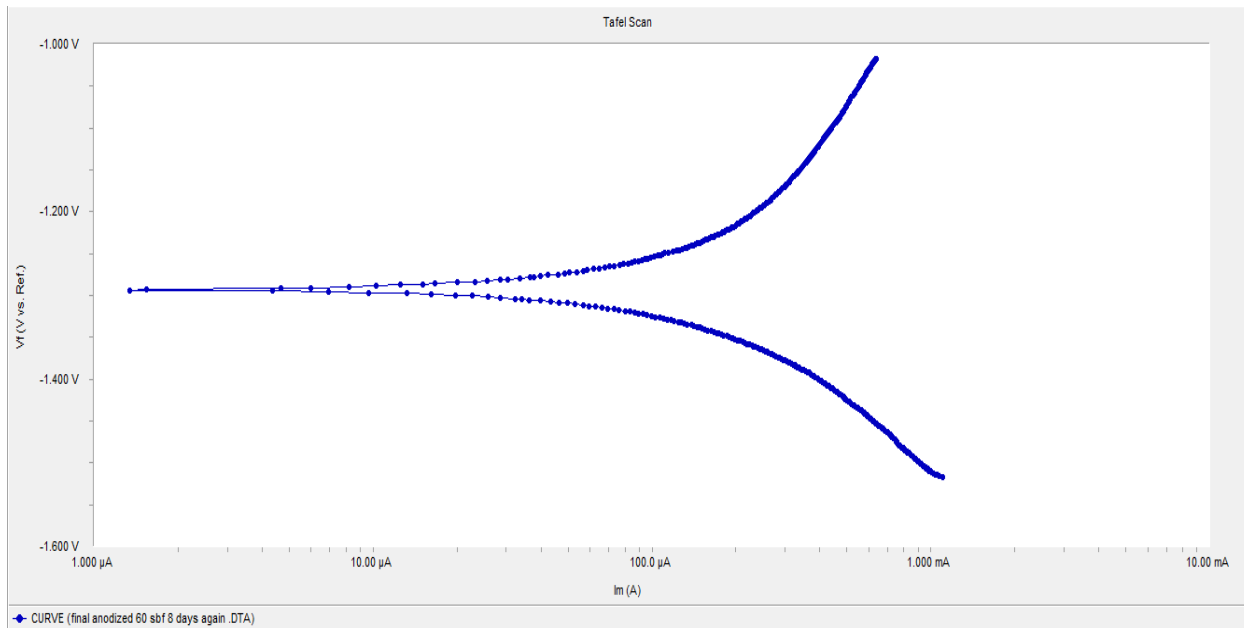
Figure 4.9: A potentiodynamic curve of magnesium anodized at 60V and dipped in SBF for 8 days

Pure magnesium sample that was anodized at 60V followed the same trend as the other two samples. The high voltage used in the anodization created a thick film on magnesium sample but the film developed cracks on its surface and had high porosity. High porosity prevents proper cohesion of the passivating coating and leads to an increase in corrosion rate[5]. Porosity is actually the solidified or un-melted particles that get trapped in the coating. The high voltage used for this sample led to the formation of a coating that was thick, it covered the active sites but had a lot of porosity in it. The corrosion behavior shown by these samples after an immersion of 2, 4 and 8 days in SBF is as follows:

- After 2 days in SBF, the magnesium sample anodized at 60V showed the highest rate of corrosion. The increased in porosity increases the exposed area present on the sample and leads to poor cohesion of the coating on it. It was the main reason for high corrosion of magnesium after dipping in SBF for 2 days.

- The sample showed a decrease in corrosion after 4 days in SBF. It was largely as a result of deposition of hydroxyapatite on the magnesium sample's surface. The hydroxyapatite covered the active sites and this led decreased the corrosion rate. The deposition of hydroxyapatite is a spontaneous process and it increases with an increase in immersion

time. The decrease can also be attributed to the fact that the sample surface is covered by the corrosion products that have formed over the period of time.

- However, after dipping of 8 days in SBF, the magnesium sample anodized at 60V again showed an increase in rate of corrosion. The increase occurred due to break down of Ca-P layer on the sample. This break down occurs due to the Mg ions's presence in the solution. Mg ions have reported to slow down and retard the nucleation and growth of hydroxyapatite. Thus, the breaking of Ca-P layer led to area exposed of active sites and increase in rate of corrosion. This along with the availability chloride ions in the solution are the factors of increase in degradation.

4.4   Results of SEM

Following are some of the SEM images that were taken after corrosion testing of magnesium samples:

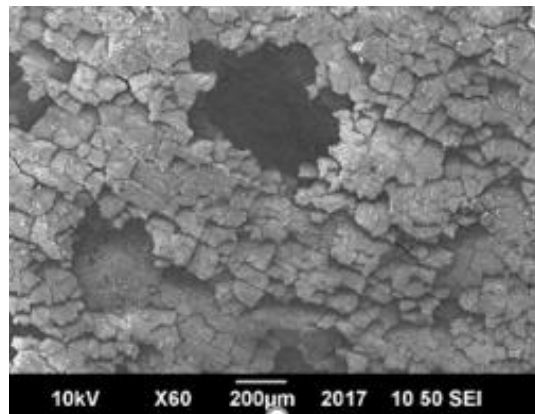### 4.4.1   After 2 days of immersion in SBF

Figure 4.10: SEM image of as casted magnesium sample after 2 days in SBF

The as cast magnesium sample shows the presence of hydroxide of magnesium after dipping of 2 days in SBF. The layer is inhomogeneous and a non-uniform coating is formed.

4.4.2 After 4 days of immersion in SBF

Below are the SEM images of as cast magnesium sample and magnesium sample anodized at 40V after 4 days of immersion in SBF.
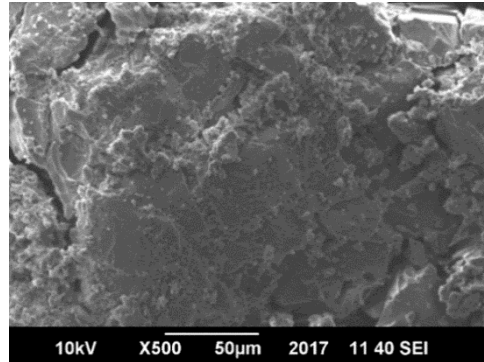

Figure 4.11: SEM image of rough sample immersed in SBF for 4 days

The SEM image shows the presence of hydroxide coating on magnesium. The coating looks intact and some of Ca-P is also developed on the sample's surface. There is no pitting on this sample of magnesium, although small cracks are present on the surface.

The sample of magnesium anodized at 60V is immersed in SBF for a duration of 4 days. The magnesium sample shows the presence of chlorine ions. the needle like structures are of chloride ions. Chloride ions presence lead to increase in pitting on the sample and high corrosion rate is attributed to them.
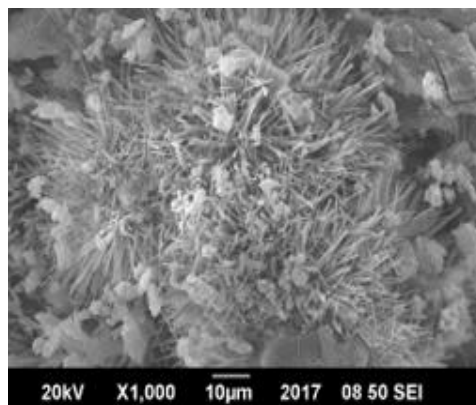

Figure 4.12: The needle-like structures of chloride ions on magnesium sample anodized at 60V

4.4.3 After 8 days immersion in SBF

Fig. shows the SEM image of magnesium sample anodized at 40V after 8 days dipping in SBF. The figure shows the presence of cracks which was due to the hydrogen evolution but no pitting is seen. The layer formed on it is passivating enough to prevent pitting even in availability of chloride ions.
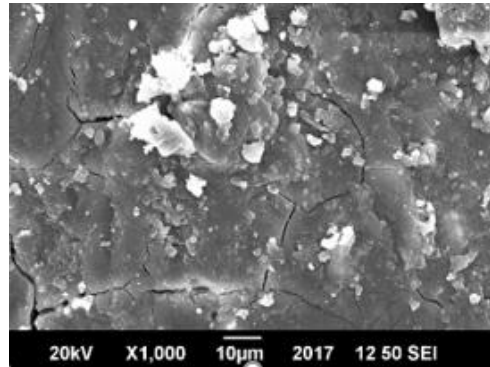

Figure 4.13: The SEM image of magnesium sample anodized at 40V and immersed in SBF for 8 days

4.5 XRD Results

The XRD technique was used to study the chemical composition of sample of magnesium anodized at 60V. All samples showed same type of chemical composition however there is a difference in their crystalline and non-crystalline nature. Following are the XRD graphs:
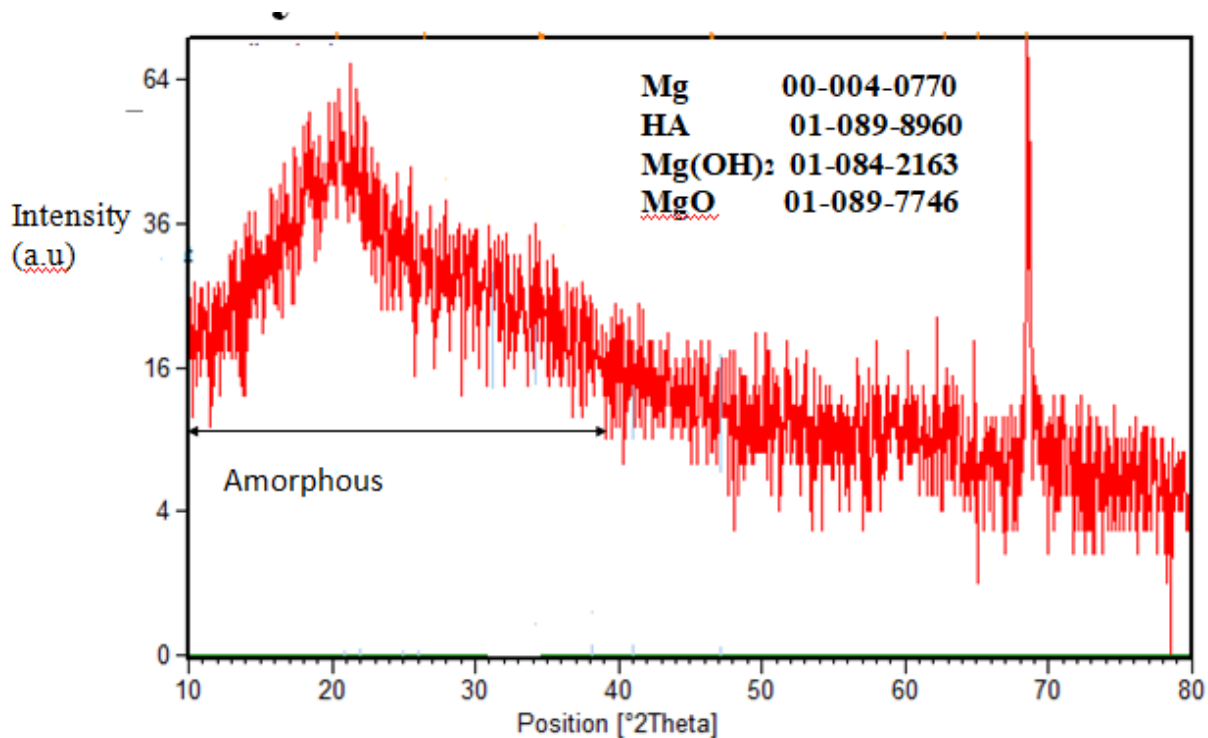

Figure 4.14: XRD graph of magnesium sample anodized at 60V and immersed in SBF for 2 days.

The graph shows the availability of MgO and Ca-P. This is in accordance with the fact that Ca-P is formed on magnesium as a layer after 2 days of dipping in SBF. The magnesium sample was anodized at 60V and dipped in SBF for 2 days in an incubator at 37 ± 1^{0}C.

The XRD result of this sample showed a bump from 10 to 35 2theta. The bump represents the amorphous structure of the sample with no or little crystallinity. While rest of the graph shows noise, which shows the presence of impurities.

Little information was obtained about the composition of the layer grown on magnesium from this graph due to non crystalline structure.
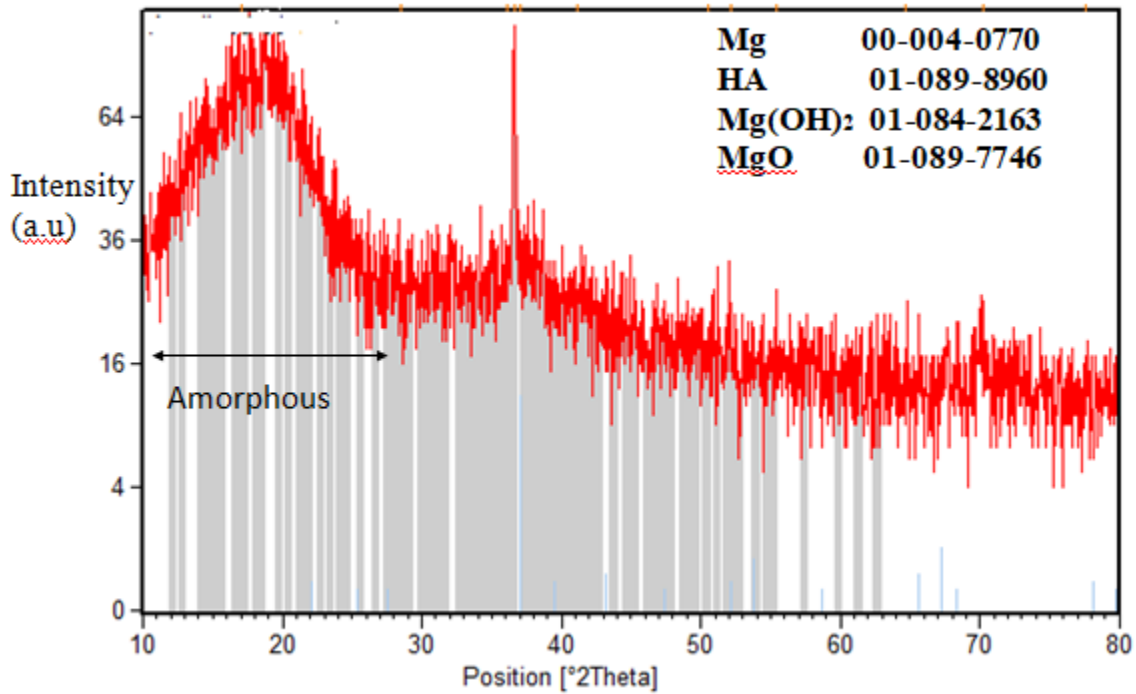
Figure 4.15: XRD graph of magnesium sample anodized at 60V and immersed in SBF for 4 days

The magnesium sample was anodized at 60V and immersed in SBF for 4 days in an incubator at 37 ± 1^0C.

The XRD result of this sample showed a bump from 10 to 24 2theta.

The presence of the bump may be indicates some hydroxyapatite and the structure is amorphous. While the rest of the graph is filled with noise which is due to impurities.Graph did not give much information due the amorphous structure and noise present.
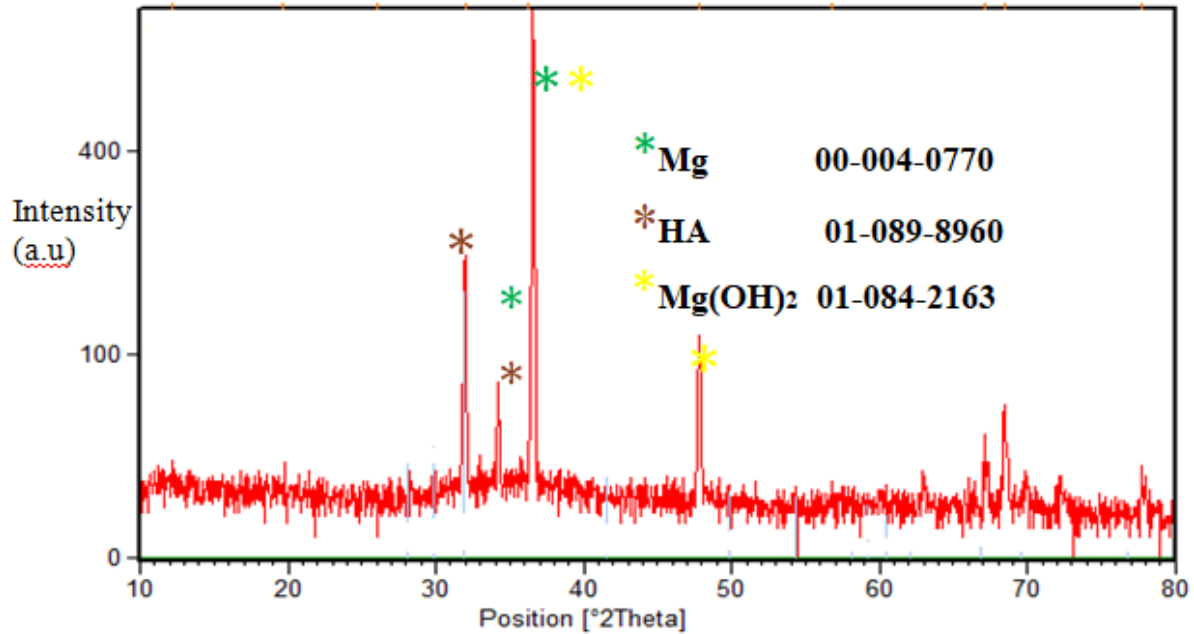
Figure 4.16: XRD graph of magnesium sample anodized at 60V and immersed in SBF for 4 days

The magnesium sample was anodized at 60V and immersed in SBF for 8 days in an incubator at 37 ± 1^0C. The XRD result of this sample showed peak of HA at 31.5 2theta.

A small peak that is seen at 32 of 2theta represents Mg. The next peak that is at 34 with miller indices 002 has overlapping of Mg and HA, both are observed at this place. A peak of high intensity is at 37.9 is again of magnesium.

CONCLUSION

Pure magnesium corrodes rapidly in SBF. With change in immersion time, the corrosion rate of magnesium samples changes. $Mg(OH)_2$ formed on the surface of magnesium is not an effective coating and the samples corrode at high rate. The highest corrosion rates are shown by magnesium anodized at 60V as the anodizing layer formed on it is more porous. The increase in porosity increases the rate of corrosion. OH^- ions present in the solution increases the pH of the solution which favors the deposition of Ca-P ions on the magnesium samples but Mg ions play a role in retarding the crystallization of hydroxyapatite and it fails to cover the active sites leading to increase in corrosion rate.

REFERENCES

[1] D. Annur, A. Erryani, F. P. Lestari, I. N. Putrayasa, P. A. Gede, and I. Kartika, "Microstructure and corrosion study of porous Mg – Zn – Ca alloy in simulated body fluid," *Mater. Res. Express, vol. 4, no. November 2016, p. aa65fd, 2017.*

[2] N. T. Kirkland, "Magnesium biomaterials: past, present and future," *Corros. Eng. Sci. Technol., vol. 47, no. 5, pp. 322–328, Aug. 2012.*

[3] H. S. Brar, M. O. Platt, M. Sarntinoranont, P. I. Martin, and M. V. Manuel, "Magnesium as a biodegradable and bioabsorbable material for medical implants," *JOM, vol. 61, no. 9, pp. 31–34, 2009.*

[4] W. Ding, "Opportunities and challenges for the biodegradable magnesium alloys as next-generation biomaterials," *Regen. Biomater., vol. 3, pp. 79–86, 2016.*

[5] G.-L. Song and Z. Shi, *Anodization and corrosion of magnesium (Mg) alloys, no. February. Woodhead Publishing Limited, 2013.*

[6] B. D. Craig and D. B. Andersen, *Handbook of Corrosion Data, 2nd ed. ASM International.*

[7] Y. Wang, M. Wei, J. Gao, J. Hu, and Y. Zhang, "Corrosion process of pure magnesium in simulated body fluid," *Mater. Lett., vol. 62, no. 14, pp. 2181–2184, 2008.*

[8] W. D. Müllera, M. L. Nascimentob, M. Zeddiese, M. Córsicoc, L. M. Gassa, and M. A. F. L. de Mele, "Magnesium and its Alloys as Degradable Biomaterials. Corrosion Studies Using Potentiodynamic and EIS Electrochemical Technique.," *Mater. Res., vol. 10, no. 1, pp. 5–10, 2007.*

[9] M. Esmaily et al., "Fundamentals and advances in magnesium alloy corrosion," Progress in Materials Science, vol. 89. pp. 92–193, 2017.

[10] Qian, J.-g., et al., Formation mechanism of pulse current anodized film on AZ91D Mg alloy. Transactions of Nonferrous Metals Society of China, vol.18(1): p. 19-23, 2008.

[11] Wang, Y., M. Wei, and J. Gao, "Improve corrosion resistance of magnesium in simulated body fluid by dicalcium phosphate dihydrate coating", Materials Science and Engineering: C, 2009. 29(4): pp. 1311-1316.

[12] Song, Y.W., D.Y. Shan, and E.H. Han, Electrodeposition of hydroxyapatite coating on AZ91D magnesium alloy for biomaterial application, Materials Letters, 2008. 62(17): pp. 3276-3279

[13] Luo, S.-l., et al., New anodizing process for magnesium alloys, Journal of Central South University of Technology, 2006. 13(2): p. 141-145.

[14] Polmear, I.J., Magnesium alloys and applications, Materials Science and Technology, 1994. 10(1): p. 1-16.

[15] T. Kokubo, H. Takadama, Biomaterials 27(2006) 2907

[16] M.V.Michelle, H.Norbert, "Magnesium: An Essential Nutrient for a Good Biomaterial", Biomedical Applications of Magnesium, vol.63,pp.7

[17] A.Andrej, G-L. Song, C.Fuyong, Z.Shi and B.K Patrick, "Advances in Mg corrosion and research suggestions", Journal of Magnesium and Alloys, vol.1,pp. 177-200, 2013.

[18] T. Lili, Y.Xiaoming,W.Peng and Y.Ke, "Biodegradable Materials for Bone Repairs A Review", Journal of Materials Science & Technology, vol.29, pp. 503-513, 2013

[19] F.Witte, H.Norbert, et al.," Degradable biomaterials based on magnesium corrosion", Current Opinion in Solid State and Materials Science, vol.12, pp.63-72,2008

[20] Mahesh, N., Investigating the in vitro corrosion behaviour of four as-cast magnesium-zinc alloys for orthopaedic applications in Simulated Body Fluid. 2015, University of British Columbia.

[21]Voort, G.F.V., Metallography, Principles and Practice. ASM International, 1984: p. 752.

[22].Taheri, M., Influence of the surface film stability on the corrosion resistance of Mg in aqueous solutions. 2013.

[23]Luo, S.-l., Dai, Lei, Zhou, Hai-hui, Chai, Li-yuan, Kuang, Ya-fei, New anodizing process for magnesium alloys. Journal of Central South University of Technology, 2006: p. 141-145.

[24]Khalil, K.A., E.-S.M. Sherif, and A.A. Almajid, Corrosion passivation in simulated body fluid of magnesium/hydroxyapatite nanocomposites sintered by high frequency induction heating. Int. J. Electrochem. Sci, 2011. 6(12): p. 6184-6199.

[25]T. Kokubo, H.K., S. Sakka, T. Kitsugi and T. Yamamuro, Protocol for Preparing Simulated Body Fluid (SBF). Department of Material Chemistry, Graduate School of Engineering, Kyoto University, 1990: p. 721-734.

[26] N.T. Kirkland, J. Lespagnol, N. Birbilis, M.P. Staiger, A survey of bio-corrosion rates of magnesium alloys, Corros. Sci. 52 (2010) 287–291

[27] C. Anja, H.I. Gerber, M. Schinhammer, J.F. Loffler, P.J. Uggowitzer, On the in vitro and in vivo degradation performance and biological response of new biodegradable Mg–Y–Zn alloys, Acta Biomater. 6 (2010) 1824–1833

[28] M.P. Staiger, A.M. Pietak, J. Huadmai, G. Dias, Magnesium and its alloys as orthopedic biomaterials: a review, Biomaterials 27 (2006) 1728–1734.