The Effect of Immersion Time on Biodegradation Rate Of Mg-Zn-Ca Alloy

by

Mohd Faez Bin Ab Aziz

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CERTIFICATION OF APPROVAL

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Approved by,

_____

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TRONOH, PERAK

SEPTEMBER 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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MOHD FAEZ BIN AB AZIZ

ABSTRACT

In recent years, there has been growing interest in magnesium alloys as a new generation of biodegradable stents for medical treatment especially in cardiovascular disease. In order to prevent the vessel ruptured, stent needed to hold and open up the vessels. Magnesium and its alloy has sufficient mechanical strength to act as a stent. However, fast degradation of magnesium due to corrosion in the human bio-environment limits its effective use as stent. The stent is expected not to degrade within 6-12 months for the vessel to be healed. Current stents just can last for 3-6 months before it dissolved. Magnesium alloy plays an important role to prolong the degradation onset time. In the present research, zinc and calcium have been chosen as the alloying elements in biodegradable magnesium alloys for biomedical applications. This product is soluble material so it will dissolve in our body. Experimental study on corrosion rate of Magnesium alloy is carried out in simulated body fluid (SBF) to determine the weight loss. Currently, the standard time for immersion test is not established for weight loss determination during SBF experiment. This project will study the influence of immersion time on corrosion rate. The immersion time rates are 1 hour, 3 hour and 5 hours. The corrosion rate of Mg-0%Zn-Ca, Mg-1%Zn-Ca and Mg-2%zn-Ca was examined with these immersion time.

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ABBREVIATIONS AND NOMENCLATURES

CVD	Cardiovascular Disease
SBF	Stimulated Body Fluid
Mg	Magnesium
Zn	Zinc
Ca	Calcium
FESEM	Field Emission Scanning Electron Microscopy

CHAPTER 1

INTRODUCTION

1.1 Background of the study

Cardiovascular disease (CVD) is a second rank killer in the world that refer to any cardiovascular system involve the heart or blood vessels arteries, capillaries and veins (Maton, 1993). CVD is leading cause of deaths worldwide and usually effects older adults. It caused by fat deposition in the vessel wall that could narrowed and weakened it. This deposition could make blood clot, undistributed and deposited in the wall vessels. In order to prevent the vessel ruptured, stent which has a good mechanical strength is needed to hold and open up the vessels. The stent has to be ductile because it will expanded using a balloon catheter and planted by surgeon to open up weaken and narrowed vessel (Erbel, 2007). The period of implanted stent is required to last from 6-12 months for remodelling the vessel. After that, presence of permanent stent will dysfunction and need to be removed by another surgeon after remodelling which can effect another risk to the patient (Erne et al., 2006).

Basically, the manufacture of the stent is provision of polymeric or metallic or combination scaffolding. Polymeric stents have been used both for scaffolding and as a vehicle for drug delivery (D' Souza et al., 2008). Various polymer stents have been developing such as the igaki-tamai stent, the REVA stent and the Everolimus-eluting stent. However, metals have superior mechanical properties over polymer for replicating the stents (Hermawan et al, 2010).Therefore, biodegradable metal stents become an option for this reason because of this metal gain more interest than the polymer and assessed by the essentiality and effect on human metabolism. In this study, the metal that will be used for stent is magnesium and zinc as an alloying

element. Both of these elements have low toxicity and the mechanism of clearance of their degradation from human body is relatively understood (Hermawan et al., 2010).

Magnesium based alloys possess a natural ability to biodegrade due to corrosion when placed it is within aqueous substances, which is promising for cardiovascular and orthopaedic medical device applications. These materials can serve as a temporary scaffold when placed in vivo, which is desirable for treatments when temporary supportive structures are required to assist in the wound healing process. The nature of these materials to degrade is attributed to the high oxidative corrosion rates of magnesium (Hermawan et al., 2010).

The present work aims to study the corrosion resistance on magnesium alloy based on the degradation rate. The selection of metal as alloying metal will be affected and longer application could be achieved by improving the bio-corrosion resistance. Besides that, the modification of element should be compatible with body fluids. The Fig. 1 below shows the mechanisms of the stent in coronary artery.

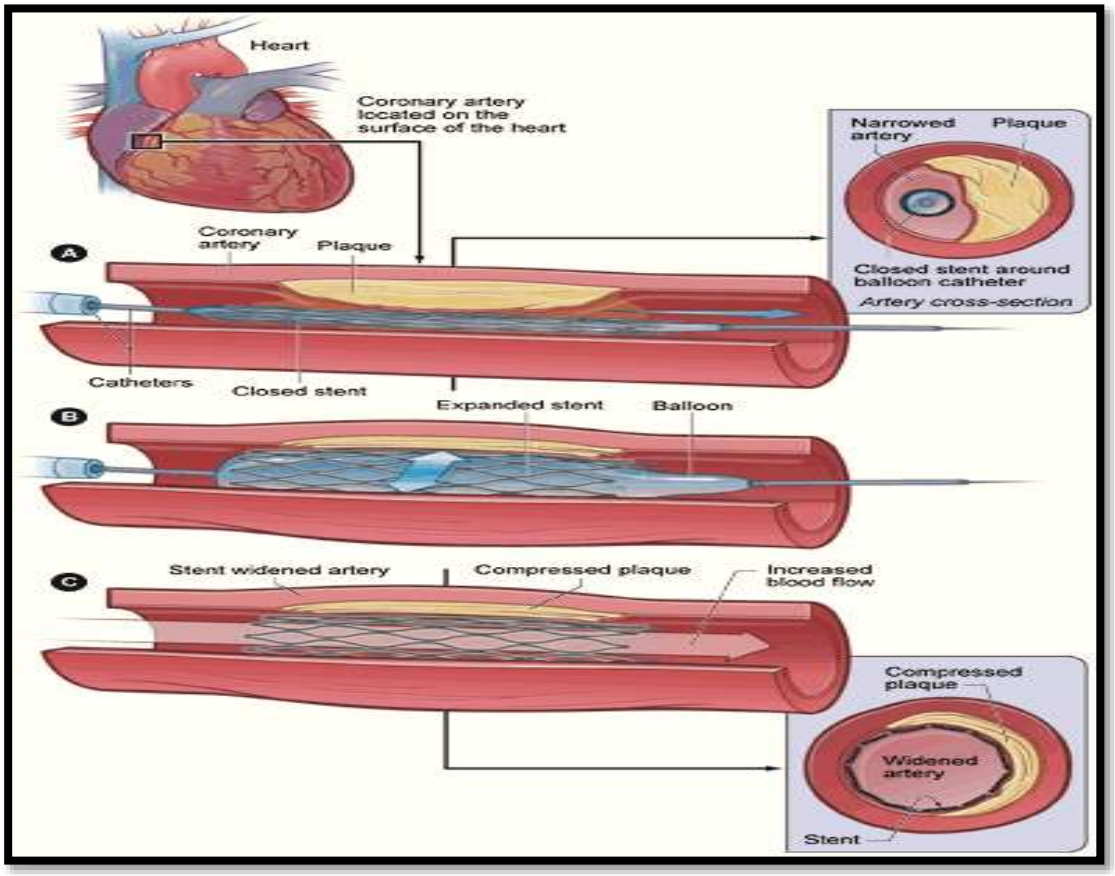


Figure 1: the mechanism of the stent in coronary artery

1.2 Problem statement

Nowadays, the study of degradable biomaterial has become most revolutionary research topics. The biodegradable stent are developing to replace the permanent stent to prevent another surgery after healing process which can lead to another risk and incur further cost to the patient. The requirements need for fully remodelling of arterial vessel process is between 6-12 months. But, the degradation rate for existing metal stent is 3-6 months. Therefore, the degradation rate needs to be increased to prevent complication such as restenosis of the vessel wall and it will lead to thrombosis. Fig. 2 below shown the relationship between mechanical integrity and degradation of biodegradation stent.

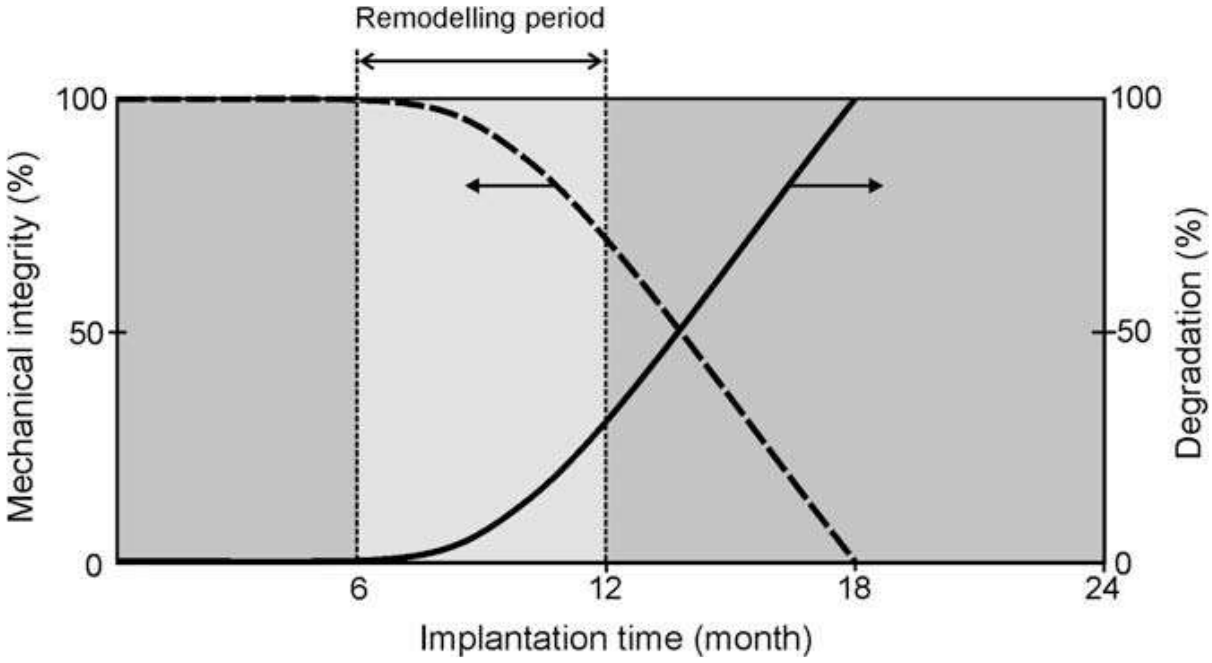


Figure 2: Illustration of an ideal compromise between mechanical integrity and degradation of a biodegradable stent.

For this purpose, a novel of Mg alloy which consists of Magnesium, Zinc and Calcium are being developed for this purpose. Hence, the corrosion behaviour needs to be studied in order to measure the rate of degradation. Besides that, the effect of immersion time on biodegradable rate of magnesium alloy also needed to measure the weight loss of the magnesium alloy time by time.

1.3 Objective

The objectives of the research works are:

i. To develop the magnesium alloy
ii. To study the effect of immersion time on biodegradable rate of Mg-0%Zn-Ca, Mg-1%Zn-Ca and Mg-2%Zn-Ca
iii. To determine the surface morphology of the sample
iv. To measure the weight loss of Magnesium alloy before and after treated in simulated body fluid (SBF)
v. To determine the corrosion rate of Magnesium alloy

1.4 Scope of study

The present studying involve experimental study on fabrication of magnesium alloy with zinc and calcium as alloying elements. Besides that, several experiments were conducted to determine the effect of immersion time on biodegradation rate that involves measurements of weight loss before and after treatment in simulated body fluid (SBF) solution. The corrosion rate was calculated to identify the best composition to make an alloy.

CHAPTER 2

LITERATURE REVIEW

2.1 Degradation of Magnesium in aqueous environment

Biodegradable metals have been developed in biomaterial science which increasing the corrosion resistant of the metal in order to increase the degradation rate. The mechanical strength and properties of magnesium are suitable for biodegradable implant. Magnesium also compatible with the body because it is essentially needed in several biological reaction and as co-factor in enzymes. However, magnesium will degrade faster in human body fluid when face with chloride-abundant environment. In an electrochemical reaction, magnesium degrades in aqueous environment which produces magnesium hydroxide and hydrogen gas because the human body fluid contains 90 % water, so magnesium would be oxidized easily. Magnesium hydroxide will form layer in the surface to protect from corrosion (Witte, 2006). Thus, magnesium corrosion is relatively insensitive to various oxygen concentrations in aqueous solutions which occur around implants in different anatomical locations (Witte et al., 2008). The overall corrosion reaction of magnesium in aqueous environments is given below:

Partial reaction of magnesium oxide formation:

$Mg_{(s)} \leftrightarrow Mg^{2+}_{(aq)} + 2e^-$ (anodic reaction) (1)

$2H_2O_{(l)} + 2e^- \leftrightarrow H_{2(g)} + 2OH^-_{(aq)}$ (cathodic reaction) (2)

Magnesium oxide formation:

$Mg^{2+} + 2OH^- \leftrightarrow Mg(OH)_{2(s)}$ (3)

Overall reaction:

$Mg_{(s)} + 2H_2O_{(l)} \leftrightarrow Mg(OH)_{2(s)} + H_{2(g)}$ (4)

Reaction between chloride ion and magnesium hydroxide:

$$Mg(OH)_{2(s)} + Cl^-_{(aq)} \leftrightarrow MgCl_{2(aq)} + 2OH_{-(aq)} \quad (5)$$

However, when the chloride concentration in the corrosive environment rises above 30mmol/l (Shaw, 2003), magnesium oxide starts to convert into highly soluble magnesium chloride. Therefore, severe pitting corrosion will be formed on magnesium alloy due to this reaction. The corrosion morphology of magnesium and its alloys depends on the alloy chemistry and the environmental conditions. Besides that, in human body fluid contain about 150mmol/l chloride ion (P.Xu, 2007), therefore, the possibility of magnesium to corrode is high. However, biomaterials processing could be used to alter bulk properties, surface properties and other properties in order to change its biocompatibility.

2.2 Effect of Zinc concentration on corrosion behaviour

Magnesium alloys consist of two categorized as cast Mg alloy and wrought Mg alloys. The cast Mg alloy with the typical example of AZ91,AM60 and AM50 have been investigated wisely. In recent years, the growing of wrought Mg alloy is needed in the automotive and aerospace industries (Song et al., 2012).In general, the strength and ductility of the wrought Mg alloys is higher than cast Mg alloy. Development of wrought Mg alloy consists of Mg-Zn, Mg-Al and Mg-Mn has been investigated. Mg-Zn alloys has attracted great interest among others. In this study, Mg-xZn alloys with various concentrations were investigated to identify the microstructure and corrosion resistance of this metal. Y. Song et al have conducted experiment to investigate the corrosion resistance of different alloys at various concentration of 2% wt, 3 % wt, 4 % wt and 5% wt. The corrosion resistance of the four alloys was evaluated by polarization curves and immersion test. In the polarization curves of the four alloys in 3.5 NaCl solution, it is found that the four curves showed similar characteristic and cathodic sides that are controlled by hydrogen evolution reaction and the anodic sides are visible with passivation tendency at the anodic sides implies the presence of oxide films on the surface of the Mg-xZn alloys (Song et al., 2012). The result of the experiment showed that the densities at the same potential of breakdown potential reduce in the order of Mg-5Zn>Mg-4Zn>Mg-3Zn>Mg-2Zn, implying decrease of hydrogen evaluation rate in the same order. Thus, the polarization curves results indicated that the corrosion resistance of the four alloys reduced in order of Mg-2Zn>Mg-3Zn>Mg-

4Zn>Mg-5Zn and the Mg-2Zn alloy showed the best corrosion resistance while Mg-5Zn alloy was the worst one as shown in Fig 3.

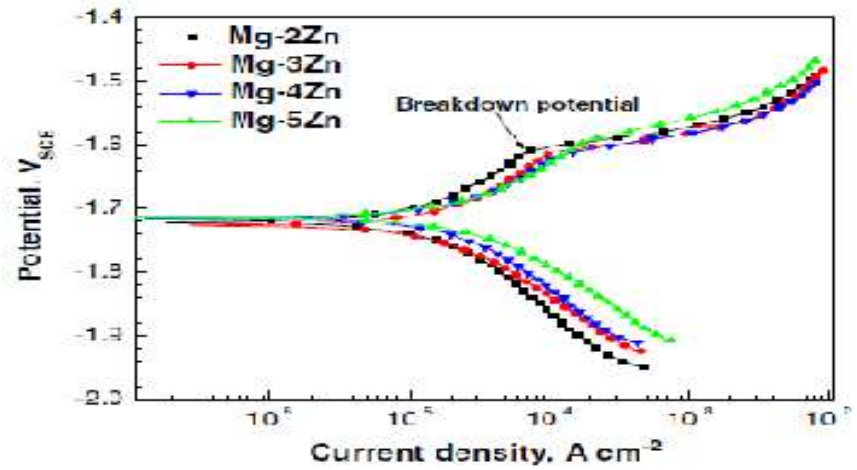


Figure 3: polarization curves of the Mg-xZn alloys in 3.5 wt% cl

The corrosion morphologies are determined using immersion test in 3.5 NaCl solution for 6h as shown in Fig 4. Based on the experiment carry out, only a small area of the Mg-2Zn alloy is covered with black corrosion products (Song et al., 2012). In Mg-3Zn alloy, approximate half areas of the Mg substrate are visible with black corrosion products. For the case of Mg-4Zn, a small area of the light regions is present and finally Mg-5Zn, a black and thick corrosion product film completely covers the Mg substrate. As a conclusion from this experiment, it is evident that the coverage percent of the corrosion product gradually increase in the order of Mg-2Zn<Mg-3Zn<Mg-4Zn<Mg-5Zn. In the other word, the polarisation curves and immersion test show that corrosion resistance reduce as Zn concentration increase. However, Bakhsheshi- Rad et al 2012 found that the corrosion resistance of the cast Mg alloys was first improved with increasing Zn concentration then reduced with further increasing Zn concentration.

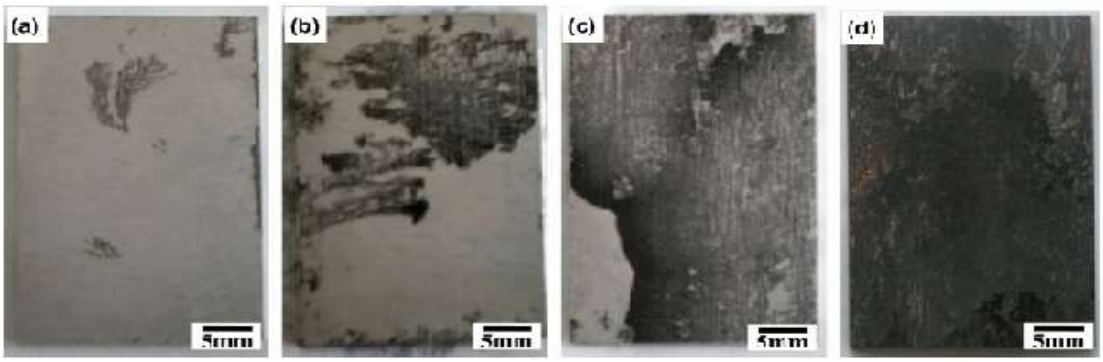


Figure 4. Corrosion morphology of (a) Mg-2Zn; (b) Mg-3Zn; (c) Mg-4Zn; (d) Mg-5Zn after immersion in 3.5wt% NaCl solution for 6h.

2.3 Corrosion behaviour of biodegradable Mg-Ca implant alloys

Besides the study about behaviour of corrosion resistance of zinc as alloying elements to the magnesium, the effect of calcium on microstructure, texture and mechanical properties of Mg-Zn-Ca also were studied. For the application in bone replacement, calcium is a known alloying element for magnesium alloys. This is because calcium is main composition in human bone and the release of Mg and Ca ions can improve the bone healing process (Rad et al., 2012).Besides that, density of calcium 1.55 g/cm^3 is quite similar to density of the magnesium (1.74 g/cm^3) which will maintain its specific properties. However, its application is limited due to the relatively poor corrosion resistance, the release of hydrogen gas and a relatively high degradation rate when exposed to human body (Witte et al., 2008). Zheng at el have studied tensile properties, corrosion properties and cytotoxicity of Mg-Ca composites produced by powder metallurgy. The result of the study indicated for corrosion resistance of Mg-1Ca composite compared to those with higher in Ca content.

To determine the corrosion behaviour of the calcium, the study on the effect of various Ca content on the degradation and corrosion mechanisms was carried out in Kokubo solution. The compositions of the as cast Mg-xCa alloys are prepared as listed in Table 1. Based on the results shown in the Fig 5, it showed that the amount of Mg_2Ca intermetallic phase (light area) increased with addition of Ca content. In the Fig 5d, it showed the large amount of Mg2Ca with lamellar structure in the grain boundaries. As increasing the Ca content, the width of the grain boundary thicker than Mg-Ca alloy with lower content of calcium as show in Fig 5e.

Table 1: the composition of the Mg-xCa (Zhang et al., 2010)

Wt(%)	Mg-0.5Ca		Mg-1.25Ca		Mg-2.5Ca		Mg-5Ca		Mg-10Ca	
	Mg	Ca	Mg	Ca	Mg	Ca	Mg	Ca	Mg	Ca
Nominal composition	99.5	0.5	98.75	1.25	97.5	2.5	95	5	90	10
Analysed composition	99.43	0.57	98.73	1.27	97.46	2.54	94.87	5.13	89.76	10.24

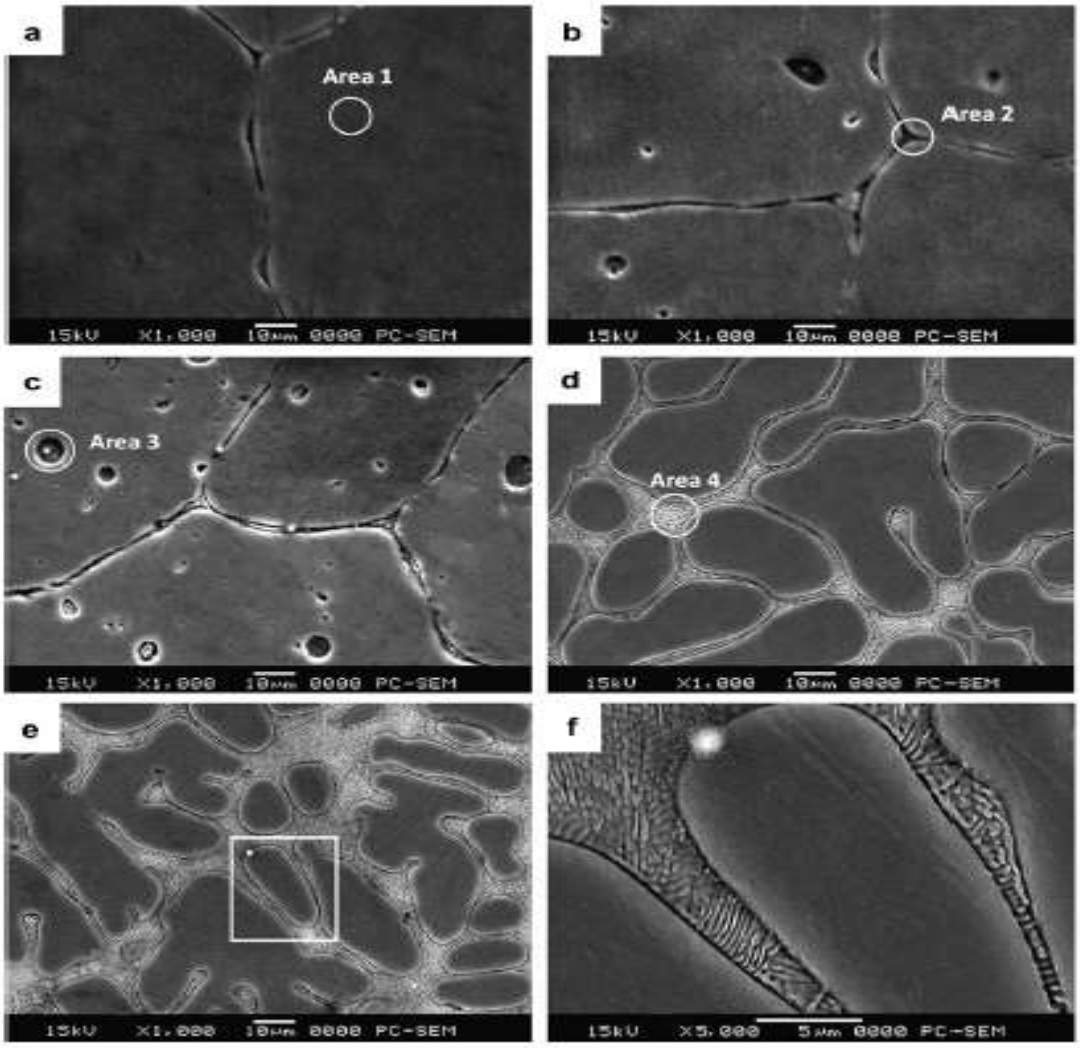


Figure 5. SEM micrographs of various Mg-Ca alloys with different calcium content: (a) 0.5, (b) 1.25, (c) 2.5, (d) 5, (e) 10 wt% (f) high magnification of framed region. (Rad et al., 2012)

H.R.B. Rad et al also have conducted the immersion test to study the effect of various concentration of calcium in magnesium alloy. The experiment was conducted for 84h in the SBF shown in the Fig 6. As we can see, the crack formation by the corrosion is deeper and thicker with an increase in Ca concentration due to higher corrosion rate. The degradation of Mg alloys in the SBF occurred according to the following equation: (Rad et al., 2012)

$$Mg + 2H_2O = Mg(OH)_2 + H_2 \uparrow$$

Subsequently due to the formation of $Mg(OH)_2–nH_2O$ protective layer, the corrosion rate of the specimens decreased noticeably. Because of the formation of this protective

layer the CO_2^{-3} , PO_3^{-4} and Cl^- ions were attracted to the surface of the specimen causing more accumulation of OH^- ion that is vital for apatite nucleation (Zhang et al., 2010). As we can see in the Fig 6(e) that a large amount of deep corrosion pits are presence on the surface of Mg–5Ca and some of these pits were covered with white substance consisting of Ca and P. Difference happen in the higher concentration of calcium Mg–10Ca was completely degraded at an earlier immersion time of 12 h as shown in Fig 6(f) depicts the deep pitting corrosion on the surface of Mg–10Ca which confirms the high dissolution rate of this specimen. During the immersion test, the surface of the specimens will dissolve first before the release of Ca ions. The generation of apatite layers was due to the collection of these ions on the surfaces of Mg-Ca alloy.

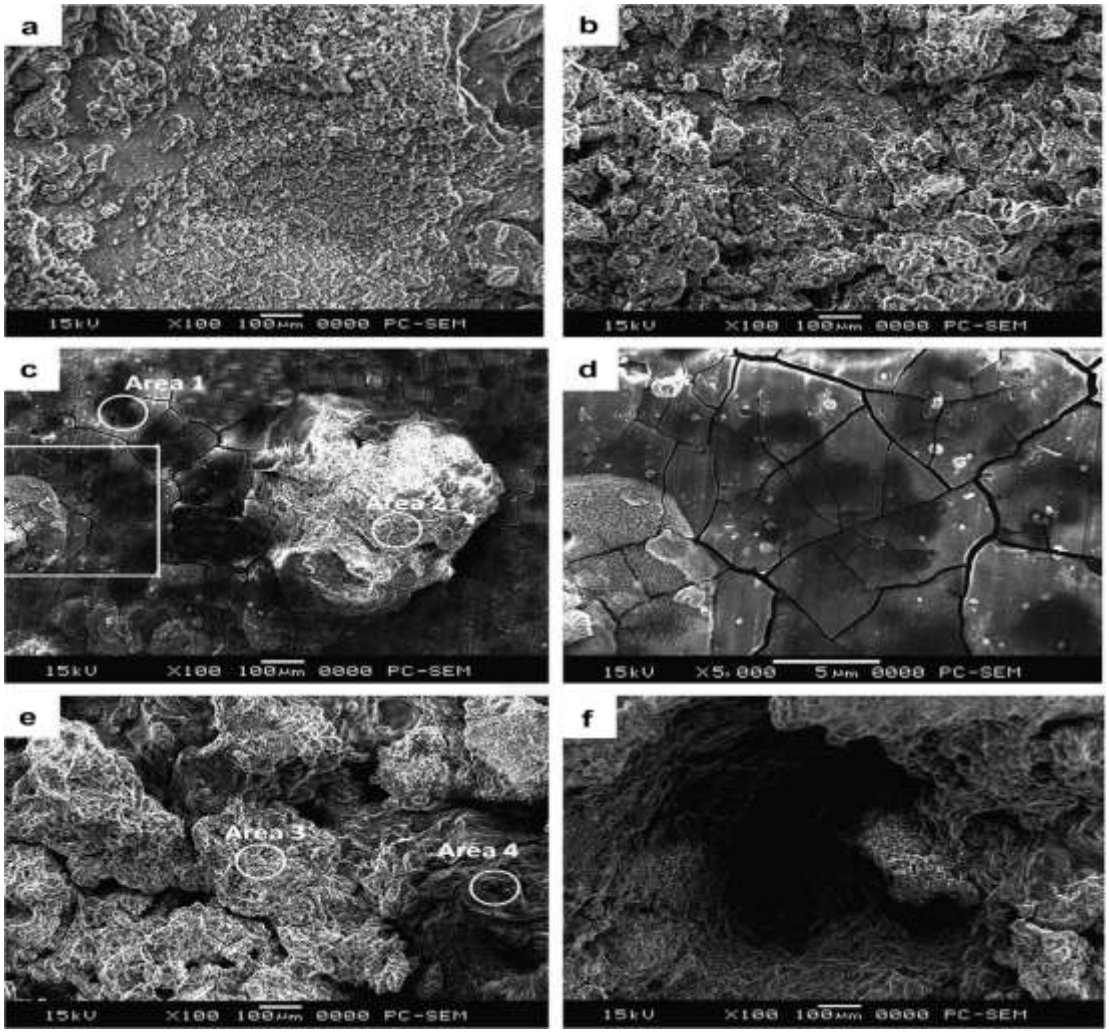


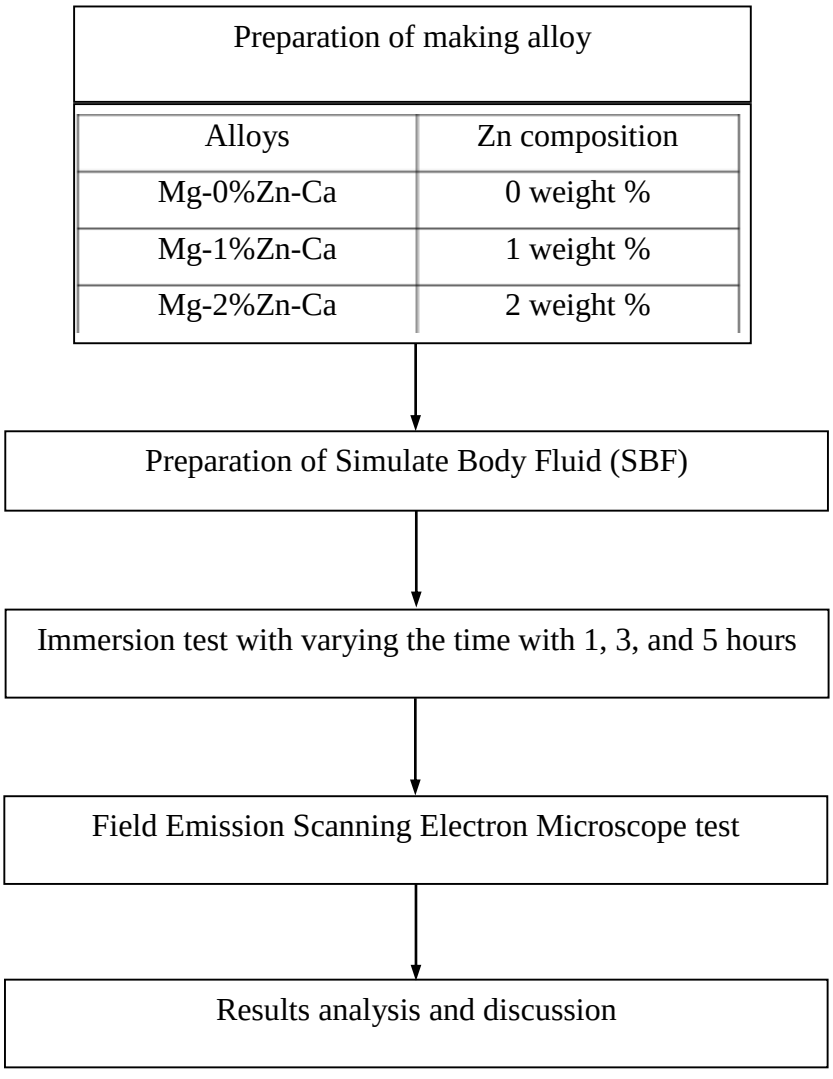
Figure 6. SEM micrographs of Mg–Ca alloys with different calcium content: (a) 0.5, (b) 1.25, (c and d) 2.5, (e) 5 wt.% with immersion duration of 84 h in SBF, (f) 10 wt.% with immersion duration of 6 h in SBF. (Rad et al., 2012)

CHAPTER 3

METHODOLOGY

3.1 Flow Chart

The experiments was carried out in a three samples of different composition of magnesium alloy. After the preparation of making alloy, the immersion test with varying the time with 1, 3, and 5 hours was conducted in simulated body fluid. Then, the results will undergo field emission electron microscope test for the surface morphology and last discussion on the results and analysis. The summarization of the experiment was shown in the flow chart below.



3.2 Fabrication of Magnesium alloy

In this alloy, there are three main element that are need to be formed which are from magnesium, zinc and calcium. Initially, the shape of magnesium is in a form of strip where it need to be cut into a small pieces to get the exact value during measuring their weight. There are 3 samples of different composition of magnesium alloy that need to fabricated which are Mg-Zn-Ca, Mg-0%Zn-Ca and Mg-2%Zn-Ca. First, every element must be weighted based on the weight percentage of the 5000mg of the total alloy. Then, the samples are placed in the different crucible with label with its composition. After that, the samples are heated by using tube furnace and argon gas is used to prevent from oxidised. The step for fabrication is shown in Fig 7 below. The temperature profile is set on 870^0C. Mg-1%Zn-Ca weight percentage is shown below and it is repeated using the same step of the calculation for others sample based on the different composition show in Table 2. The sample preparation of making alloy and also graph for the heating and cooling condition that is used on tube furnace are also shown below.

Table 2 : Total weight percent of the element in the alloy samples

Alloys	*Magnesium (Mg)*	*Zinc (Zn)*	*Calcium (Ca)*
Mg-0wt%Zn-Ca	4950mg	0mg	50mg
Mg-Zn-1wt%Ca	4900mg	50mg	50mg
Mg-2wt%Zn-Ca	4850mg	100mg	50mg

Sample calculation for Mg-1%Zn-Ca

Mass Zn = $\frac{1}{100} x\ 5000\ mg$

= 50 mg

Mass Ca = $\frac{1}{100}$x 5000 mg

= 50 mg

Mass Mg = 5000 mg – 50 mg – 50mg

= 4900 mg

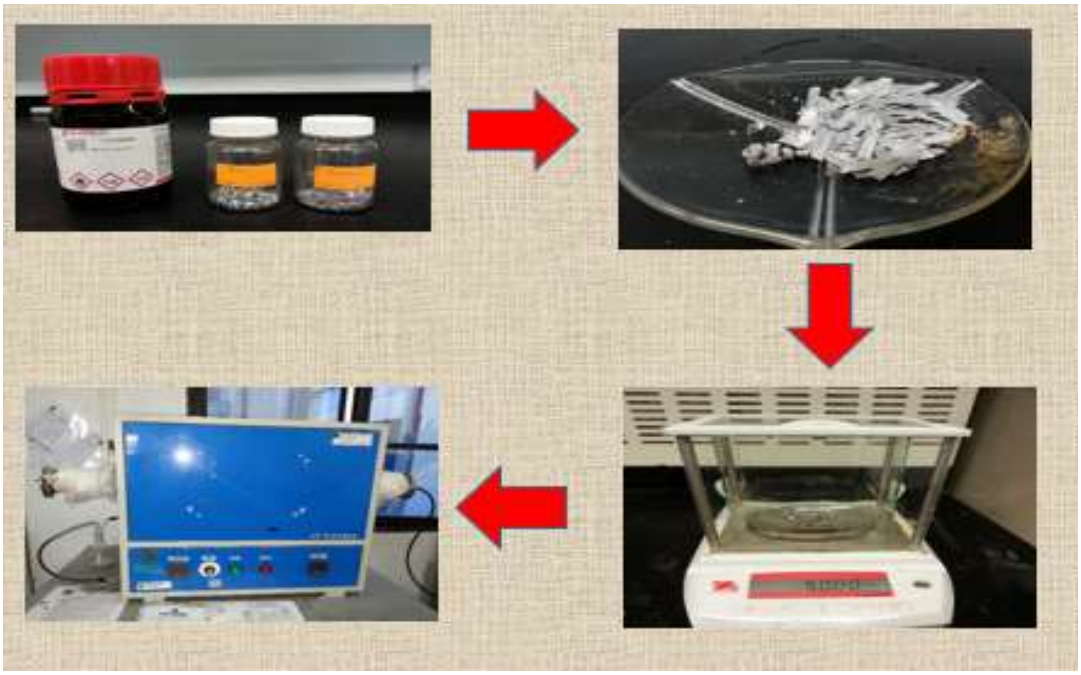


Figure 7: Magnesium alloy fabrication process

The temperature set on the tube furnace for the heating condition is shown in the Fig 8 below. In order to make sure the melting process are successfully, the temperature that are used all above the melting point of magnesium, zinc and calcium.

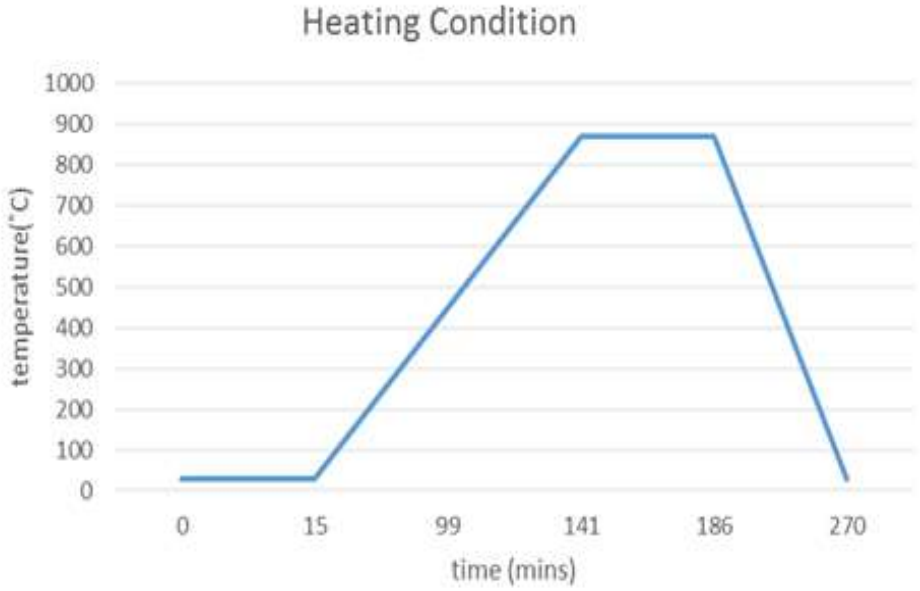


Figure 8: Heating and cooling temperature profile

The heating sequence for the tube furnace as the graph shown in figure 8. For the first part, argon is flow for 15 minutes to ensure the stabilities of the gas before heat up the sample. Argon also is used to clean up any other gases especially oxygen so that oxidation will not take place. Then the sample is heated until it reach 450 ^{o}C with heating rate about 5^{o}C/min. After that, the heating process continues until it reached to 870 ^{o}C with heating rate 10^{o}C/min to ensure all the element of the alloying are completely melt. At 870^{o}C the temperature is maintained constant for 45minute to get the optimum results and lastly when all of the heating process have been done the sample is cooled to 30^{o}C.

3.3 Preparation of stimulated body fluid

In order to measure the degradation rate of Mg-Zn-Ca, the immersion test were performed in a simulated body fluid (SBF) shown in Fig 9. The preparation containing 6.800 g 1^{-1} NaCl, 0.200 gl^{-1} $CaCl_2$, 0.400 g l^{-1} KCl, 0.100 g l^{-1} $MgSO_4$, 2.200 g $l^{-1}$$NaHCO_3$, 0.126 g l^{-1} Na_2HPO_4 and 0.026 g l^{-1} NaH_2PO_4. The pH value of SBF was adjusted with HCl and NaOH solution to 7.44 and the temperature was maintained at 37 ± 0.5 ^{0}C with a water bath.

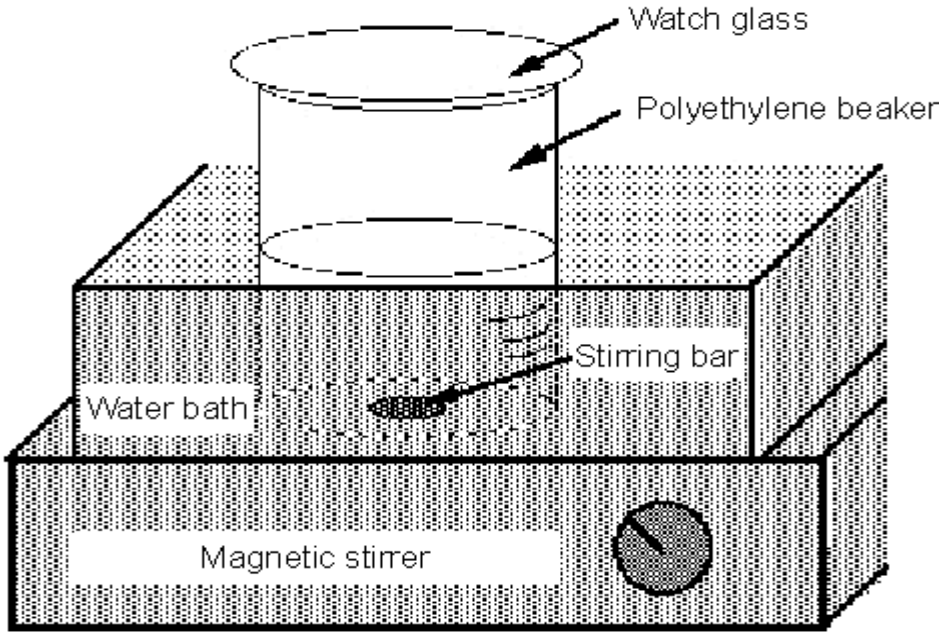


Figure 9: Experiment set-up during preparation simulated body fluid

3.4 Weight loss and corrosion rate of Mg-Zn-Ca in SBF measurement

After the SBF solution is prepared, the immersion tests are carried out. Three samples of Mg-0%Zn-Ca, Mg-1%Zn-Ca and Mg-2%Zn-Ca are weighted. The samples then are put in the solution with hold by the holder in magnetic stir. The process of stirring is conducted for 1 hours to measure the different of the metal when corroded in the solution. The magnetic stirrer is set to be constant at 30rpm. Then after the first 3 hours, the sample is putted in the oven at 100 ^{o}C and desiccator for drying purpose to prevent the solution affect in the weighting process. The immersion test are continued until another 3 hours and last for 5 hours. After that, remove the sample from the solution by filtration and repeat the drying process. Lastly, the samples were measured again to determine the total weight loss of the alloys. The experiment were repeated with different composition of magnesium alloy with the same procedure. The corrosion rate also is calculated based on the given equation: (Zhang et al., 2010)

$$\text{Corrosion rate} = (K \times W) \div (A \times T \times D)$$

Where the coefficient $K = 8.76 \times 10^4$, W is the weight loss (mg), A is the surface are of the sample exposed to solution (cm^2), T is the exposure time (h) and D is the density of the material ($mg\ cm^{-3}$). The pH value of the solution was also recorded during the immersion test.

3.5 Field Emission Scanning Electron Microscopy (FESEM) test

After the immersion test, the surface morphology was observed by FESEM. It was used to determine the phase of corrosion products on the Mg-Zn-Ca surface. From the Fig 10, it shows the mechanism of the FESEM. Under vacuum, electrons generated by a Field Emission Source are accelerated in a field gradient. The beam passes through electromagnetic lenses, focussing onto the specimen. As result of this bombardment different types of electrons are emitted from the specimen. A detector catches the secondary electrons and an image of the sample surface is constructed by comparing the intensity of these secondary electrons to the scanning primary electron beam. Finally the image is displaced on a monitor. The type of FESEM that are currently used in Universiti Teknologi PETRONAS is supra 55 VP. The detailed technical data for this type as shown in the Table 3.

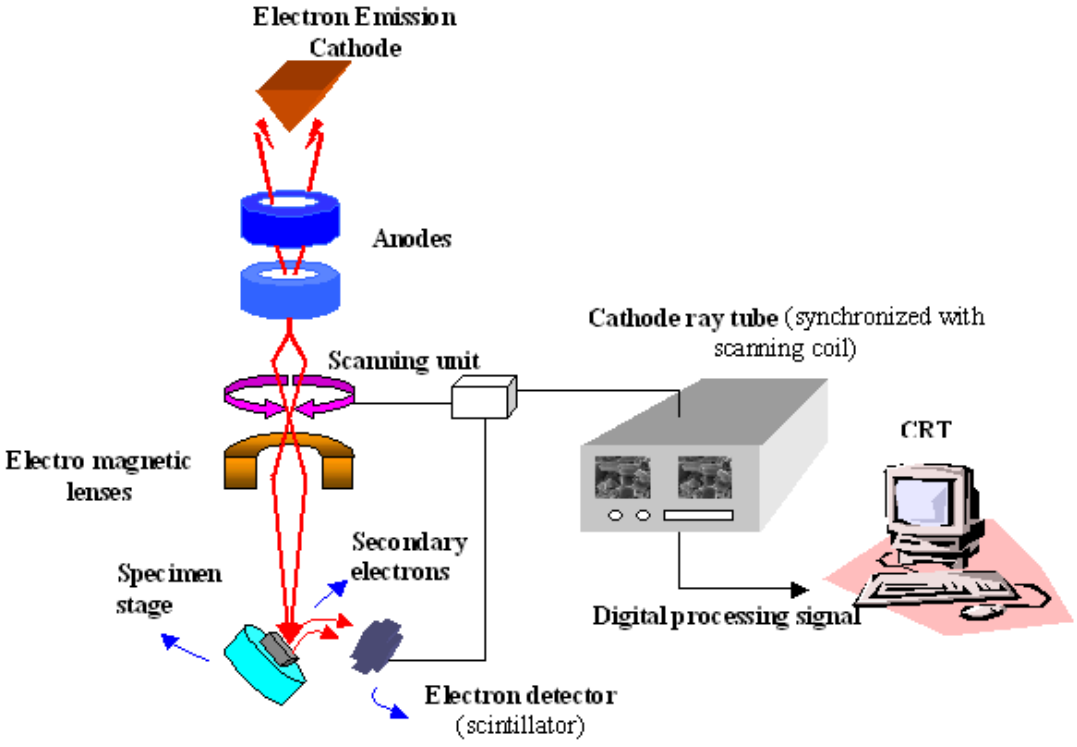


Figure 10: FESEM principle

Table 3: Technical data for FESEM

Essential specification	Supra 55 VP (FESEM)
Resolution	1.0 nm @ 15 kV 1.7 nm @ 1 kV 3.5 nm @ 0.2 kV 2.0 nm @ 30 kV (VP mode)
VP vacuum	2 - 133 Pa, adjustable in steps of 1 Pa
Magnification	12 - 900,000 x
Emitter	Thermal field emission type
Acceleration voltage	0.1 - 30 Kv
Probe current	4 pA - 10 nA (20 nA optional)
Standard detectors	High efficiency In-lens detector, Everhart-Thornley Secondary Electron Detector, VPSE Detector
Chamber	330 mm (Ø) x 270 mm (h) 1 EDS port 35° TOA CCD-camera with IR illumination
Specimen stage	5-Axes Motorised Eucentric Specimen Stage X = 130mm Y = 130mm Z = 50mm T = -3 to 70° R = 360° (continuous)
Image processing	Resolution: Up to 3072 x 2304 pixel, Noise reduction: Seven integration and averaging modes
Image display	Single 19" TFT monitor with SEM image displayed at 1024 x 768 pixel
Image hardcopy	Choice of Windows® driven laser, inkjet or video print media
System control	SmartSEMTM* with Windows®XP, operated by mouse, keyboard and joystick with optional control panel

3.6 Tools, Equipment and materials

These are the chemicals that will be used in this project:

i. Magnesium
ii. Zinc
iii. Calcium
iv. Sodium chloride
v. Potassium chloride
vi. Calcium chloride
vii. Magnesium sulphate
viii. Sodium bicarbonate
ix. Disodium phosphate
x. Hydrochloric acid
xi. Sodium hydroxide

These are the equipment or tools that will be used in this project:

i) FESEM
ii) Beaker
iii) Magnetic stirrer
iv) Measuring Cylinder
v) Crucible
vi) Watch glass

3.7 Several safety precaution

There are several precaution during this experiment in order to maintain the purity of the metal alloys.

1) The development of these element must be melt carefully to maintain the purity of the element. Magnesium is a sensitive element and the selection type of heating is important to prevent the magnesium from oxidize easily.

2) The quantity of the material must be measured accurately to ensure the degradation rate and weight loss during the treated in the SBF solution are correct.

3) Sample of material must be get in the shape of that can be calculated. So, during the melting process, it is important to rebuild the combination of these elements in form of calculated shape.

4) The surface morphology of the corrosion caused by the tendency of these element to release the ion and become oxidize. So, the surface of metals to react with other that can cause corrosion is high.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Fabrication of the Magnesium Alloy

The process of making alloys have been conducted by using tube furnace at SIRIM Kedah. Three samples with different composition of magnesium alloy were obtained as shown in Fig 11. The samples were then taken out from the crucible by using spatula for the next experimental test.

Figure 11: Fabrication of Magnesium alloy

4.2 FESEM Analysis on Surface Morphology

The corrosion morphologies were determined using immersion test in 3.5 NaCl solution in 5h as shown in Fig 12. Based on the experiment carry out, in the Figure 12(a) Mg-0%Zn-Ca a black and thick corrosion product film completely covers the Mg substrate. After treated in SBF, the sample become worst with the crack formation, dark surface and form hole on top of the surface. For the case of Mg-1%Zn-Ca, only a small area of black corrosion present. When it immersed in the SBF, the surface morphology of this magnesium alloy form a small crack in the right bottom of the sample. This is because the sample was degraded into the solution but only a small amount of the alloy. In Fig 12 (c), approximate half areas of the Mg substrate are visible with black corrosion products. After immersed into the solution, the Mg-2%Zn-Ca shows the crack formation by the corrosion is deeper and thicker but only a certain part of the sample.

As the conclusion of this experiment, it is evident that the present of these 3 elements slow down the rate of degradation so that it can achieve the requirement needed for the remodelling of the vessel. From the surface morphology, it is clearly seen that the best composition between these elements is Mg-1%Zn-Ca follow by Mg-2%Zn-Ca and lastly Mg-0%Zn-Ca. During the immersion test, the surface of the specimens will dissolve first before the release of Ca ions. The generation of apatite layers was due to the collection of these ions on the surfaces of Mg-Zn-Ca alloy. The longer the immersion time, the higher the degradation rate to be occurs.

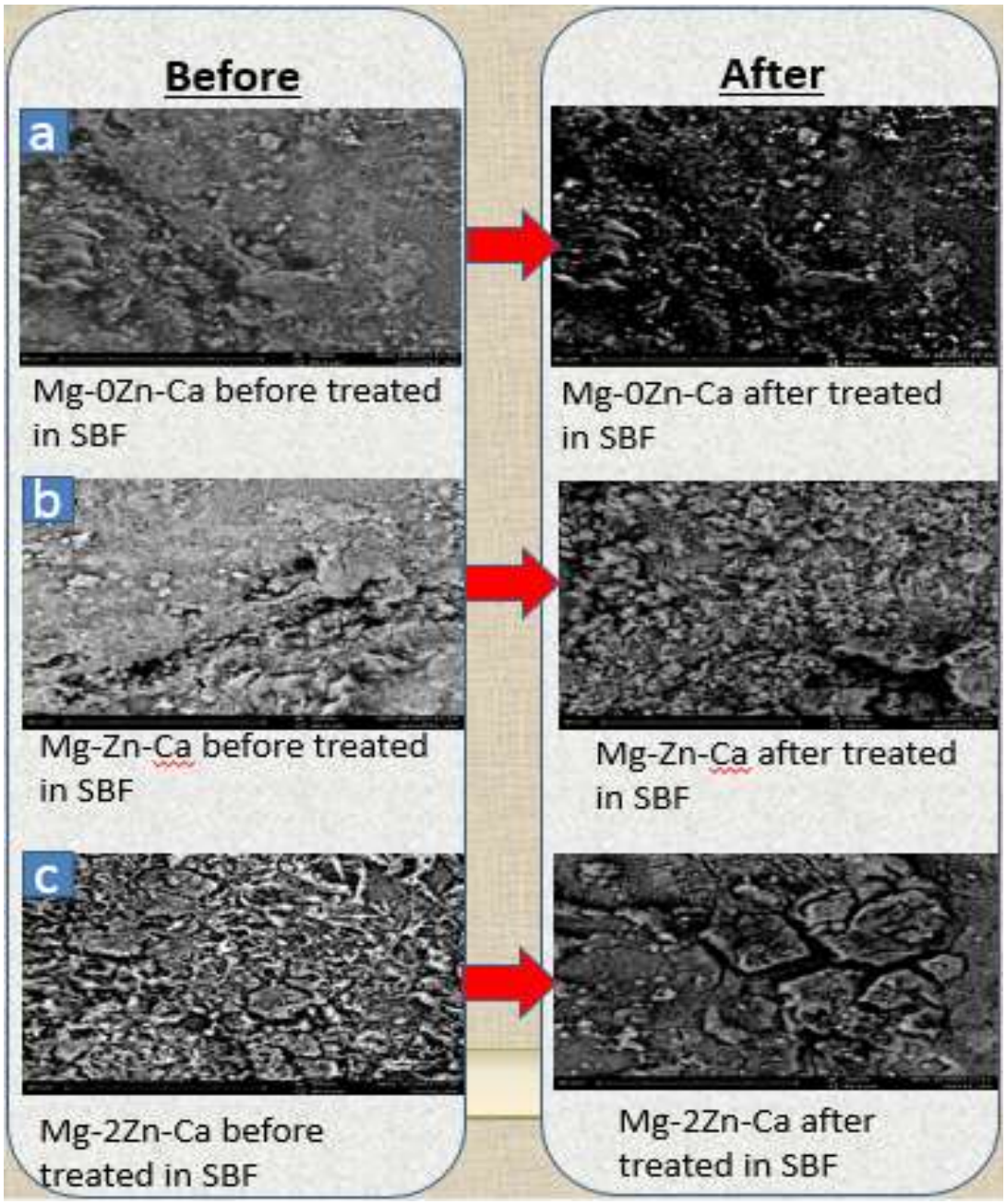


Figure 12: SEM images of magnesium alloy before and after treated in SBF solution

4.3 Result of weight loss of magnesium alloy in SBF solution

Immersion test was carried out to measure the weight loss of the alloy. This test have been done in SBF solution that already been prepared in bottle of 2L containing solution for the 1, 3 and 5 hours. Based on the test, three samples of weight loss gained and record in the Table 4 below. Besides that, the corrosion rate of the sample is calculated as show in the equation below for these alloy. (Zhang et al., 2010)

Corrosion rate = (K x W) ÷ (A x T x D)

Where, the coefficient K = 8.76×10^4, W is the weight loss (mg), A is the sample are exposed to solution (cm^2), T is the exposure time (h) and D is the density of the material ($mg\ cm^{-3}$).

Table 4: results of corrosion resistance of magnesium alloy

Material	pH value of the solution	Initial weight of the sample (mg)	Weight loss at 1 hour (mg)	Weight loss at 3 hours (mg)	Weight loss at 5 hours (mg)	Total weight loss (initial – final)	Corrosion rate ($mm\ year^{-1}$)
Mg-0%Zn-Ca	7.44	30	20	15	8	22	1.87×10^7
Mg-1%Zn-Ca	7.44	30	30	29	26	4	3.41×10^6
Mg-2%Zn-Ca	7.44	30	25	18	15	15	1.27×10^7

Sample of calculation,

For Mg-0%Zn-CA

$$Corrosion\ Rate = \frac{(K \times W)}{A \times T \times D}$$

Where, K = 8.76 x 10^4

W = 22 mg

A = 1cm^2

T = 5 h

D = 1800 mg/ cm^3

Therefore, by substituting the value into the formula,

$$Corrosion\ Rate = \frac{(8.76 \text{ x } 10^4 \times 22\ mg)}{1\ cm^2 \times 5\ h \times 1800 \frac{mg}{cm^3}}$$

= 214.13 cm/h

= 1.87 x 10^7 mm / year

For Mg-1%Zn-Ca,

All of the value are the same except the weight loss. The weight loss of Mg-0Zn-Ca is, W = 4 mg

$$Corrosion\ Rate = \frac{(8.76 \text{ x } 10^4 \times 4\ mg)}{1\ cm^2 \times 5\ h \times 1800 \frac{mg}{cm^3}}$$

= 38.93 cm/h

= 3.41 x 10^6 mm / year

For Mg-2%Zn-Ca

Weight loss, W = 15 mg

$$Corrosion\ Rate = \frac{(8.76 \text{ x } 10^4 \times 15\ mg)}{1\ cm^2 \times 5\ h \times 1800 \frac{mg}{cm^3}}$$

= 146 cm/h

= 1.27 x 10^7 mm / year

4.4 Results analysis and Discussion

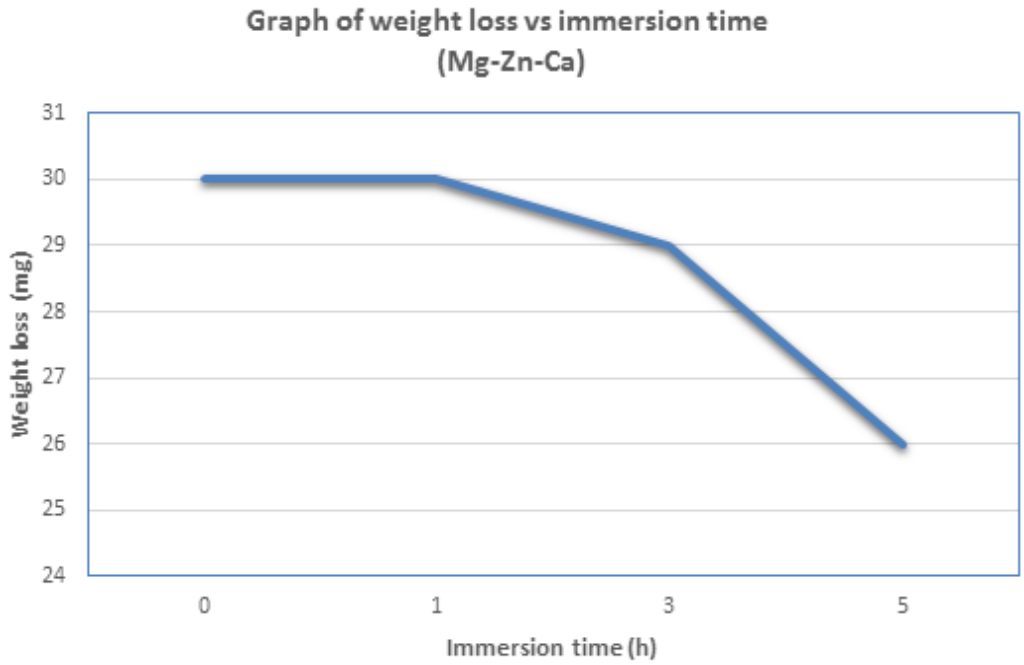


Figure 13: Graph of weight loss vs immersion time (Mg-Zn-Ca)

From the graph shown in Fig 13, the weight loss of the magnesium alloy is increasing as the immersion time increases. This is because the sample will slowly degrade into the solution due to the present of these elements that protect the magnesium from degrading faster. At the early stage, the degradation does not occurs as the immersion time was very short for the sample to degrade. It means that, the corrosion resistance of the sample is strong to protect the sample from degrading. Once it was immersed into the SBF solution for 3 hours, the Mg-Zn-Ca start to degrade while losing its weight to 29 mg. During the 5 hours of immersion time, the sample continues to degrade until the remains of the weight is 26mg. From the initial weight of 30 mg, the total weight loss of this sample is about 4 mg for 5 hours of immersion time. It clearly indicated that, the present of this element as alloying element slow down the rate of degradation as the immersion time increase.

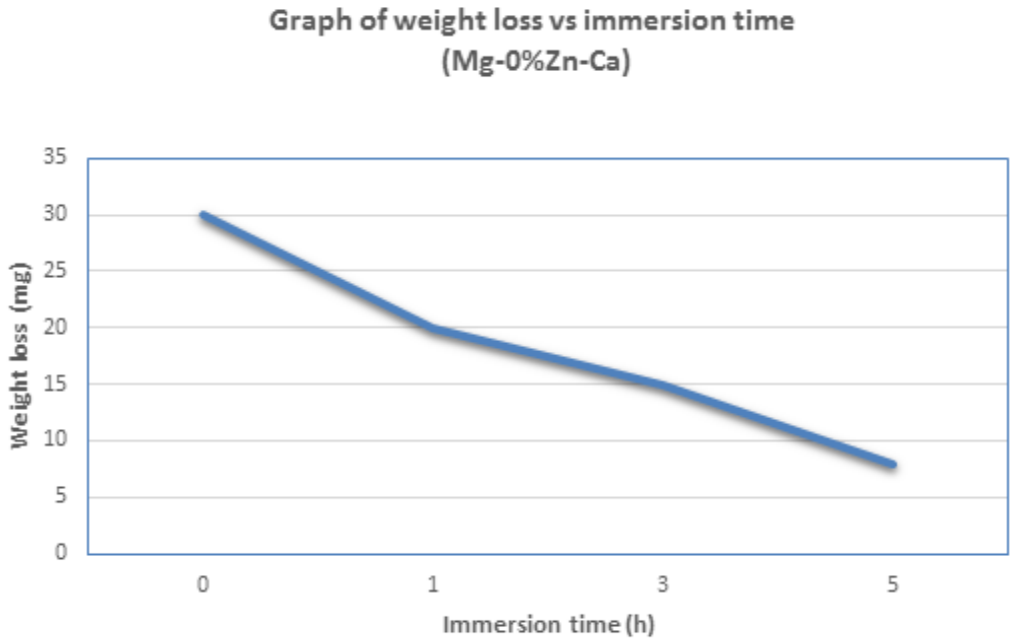


Figure 14: Graph of weight loss vs immersion time (Mg-0Zn-Ca)

The Fig 14 above shows the weight loss of Mg-0% Zn- Ca vs immersion time. The weight loss was obtained by change the composition of Mg-0Zn-Ca to determine the optimum corrosion resistance of the alloy. The initial weight is constant for all samples which is 30 mg. Then, at 1 hour the weight loss clearly decreased to 20 mg. The degradation occur fast at this point because the zinc was not include as the alloying element. Therefore, the hydroxide from the solution react fastly with magnesium to form magnesium hydroxide which is soluble substance. Then, as the immersion time proceeded to 3 hours, the weight loss of the sample become higher which is 15 mg. Eventually, for 5 hours the remaining of the sample is 8 mg. The weight loss reduced faster in this composition. So the combination of this element is not enough to avoid from corrosion. In another words, the corrosion resistance of Mg-0Zn-Ca is very low in order to hold in a long time of immersion in stimulated body fluid.

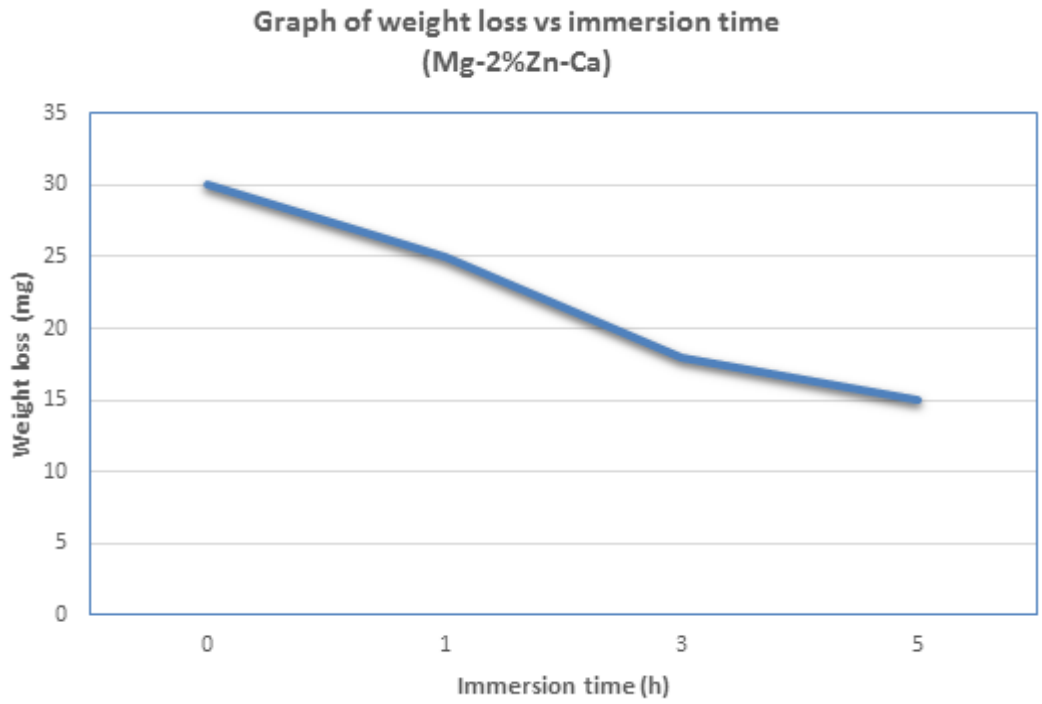


Figure 15: Graph of weight loss vs immersion time (Mg-2Zn-Ca)

Based on the Fig 15 above, the weight loss for the Mg-2Zn-Ca is less compared with the Mg-0Zn-Ca but higher than Mg-Zn-Ca. In this analysis, the sample was also immersed in time of 1, 3 and 5 hours. From the early stage, some of the degradation occurs on Mg-2Zn-Ca. It can be clearly seen at 1 hours of immersion time, the remaining weight loss of the sample is about 25 mg. After 3 hours, the sample losses weight by 12 mg from initial weight which is 30 mg. The immersion time is continued until 5 hours to determine the weight loss. In 5 hours of immersion time, the weight loss drop until the last remaining is 15 mg. About half from the original weight is lost when immersed in the solution. It shows that, the degradation rate of the sample also happened but not as fast as Mg-0Zn-Ca.

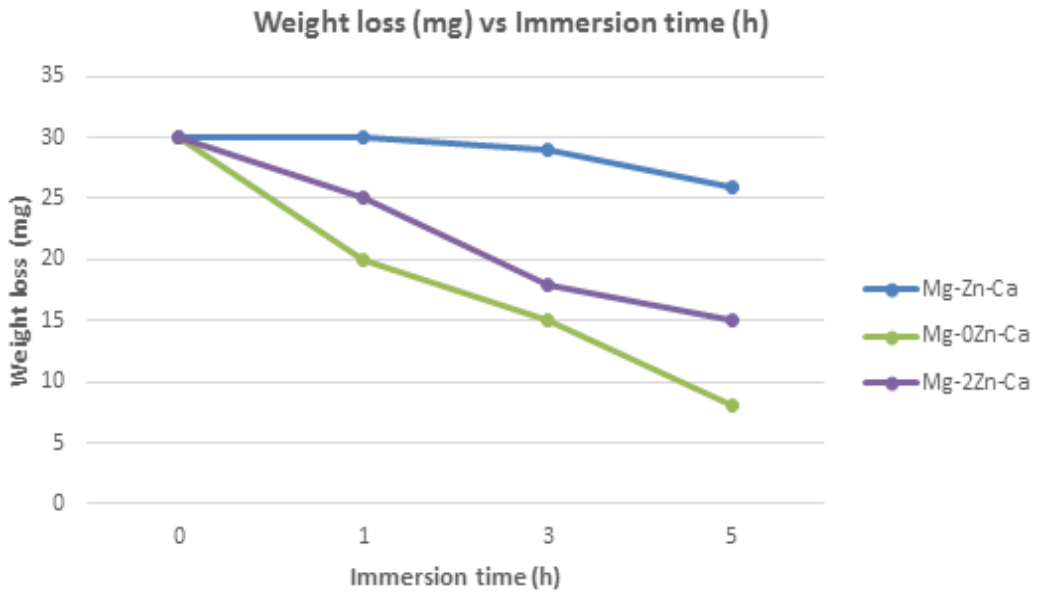


Figure 16: Graph weight loss of Magnesium alloy vs immersion time

The Fig 16 shows the different of three composition of magnesium alloy. From the graph, the blue graph of Mg-Zn-Ca is the best corrosion resistance as it lost its weight in lesser time compared to the rest samples. As the immersion time increasing, the weight loss is only a bit that means the sample have a good mechanical strength. The second best is the combination of Mg-2Zn-Ca and last for Mg-0Zn-Ca. In this experiment, it is important that the present of zinc to slow the degradation rate but excessive uses of zinc will also affect the degradation rate of the magnesium alloy. The effect of immersion time shows the longer the time, the faster magnesium alloy will degrade. As a conclusion from this experiment, it is evident that the coverage percent of the corrosion product gradually increase in the order of Mg-Zn-Ca > Mg-2Zn-Ca > Mg-0Zn-Ca.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

One of the methods to measure the biodegradability of Mg-Zn-Ca alloys is by determining the corrosion rate. In order to prolong the biodegradable rate, lower concentration rate is desired. Alloy having lower corrosion rate has high corrosion resistance. In the present work, the effect of immersion time on biodegradable rate of these alloys was performed to determine the corrosion resistance of the material. From the experiment that have been carried out, the longer the immersion time, the higher the degradation rate which corresponds to low corrosion resistance. In these three element which are Mg-0%wtZn-Ca, Mg-1%wtZn-Ca and Mg-2%wtZn-Ca, the best corrosion resistance alloy is Mg-Zn-Ca. The results shows that the total weight loss of this sample is 0.13% which is the lowest. It is evident that the 1 weight % of Zn is the optimum condition between these samples. In general for all samples, as the immersion time increases to 5 hours, the corrosion rate decrease. The zinc composition of 1 weight % gave the higher corrosion resistance. From the FESEM analysis, the surface morphology of the Mg-Zn-Ca shows that the degradation very hard to occurs. The surface just form a small area of black corrosion product after immersed into the simulated body fluid for 5 hours. From all of these sample, the corrosion resistance increase in order of Mg-0Zn-Ca > Mg-2Zn-Ca > Mg-Zn-Ca.

5.2 Recommendation

It is recommended to continue the present work especially on the study of corrosion resistance of magnesium alloy as it can be great reference in finding the best solution that can be prolong the period of degradation rate so that it can be safely apply to cardiovascular disease. The weight loss obtained is subjected to errors in determining the surface area. The calculations could be improved by considering robust method. It is also suggested that the immersion time of biodegradable rate need to be lengthen in order to determine the time of the weight loss become constant. The time for which the weight loss is constant shows the minimum time for immersion test to be conducted in order to investigate degradation rate. Besides, the experiment also can be conducted at different in varying the composition either in zinc or calcium to determine the effectiveness of the corrosion rate. For continuation of this project, the study can be more detail on with varying the composition of 0.5, 1, 1.5, 2 of calcium and 0.5, 1.5 of zinc. With a lot of the sample preparation, the different analysis can be seen clearly and can compare the result in order to get the optimum value toward to this project.

Suggestion concerning the lab facilities

Furthermore, the booking slot for the FYP student also need to organized properly. UTP should provide more equipment so that all student can do their experiment for analysis and submit their report on time. The equipment that does not working need to repair first in order to give priority to FYP student and also postgraduate student in completing their research or project.

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APPENDICES

Appendix 1 : Sample calculation for the composition of the magnesium alloy

1) Mg-0wt%Zn-Ca

Mass Zn = $\frac{0}{100}$ x 5000 mg

= 0 mg

Mass Ca = $\frac{1}{100}$ x 5000 mg

= 50 mg

Mass Mg = 5000 mg – 50 mg

= 4950 mg

2) Mg-2wt%Zn-Ca

Mass Zn = $\frac{2}{100}$ x 5000 mg

= 100 mg

Mass Ca = $\frac{1}{100}$ x 5000 mg

= 50 mg

Mass Mg = 5000 mg – 100 mg – 50 mg

= 4850 mg

Appendix 2 : Gantt's Chart and Key milestone FYP 1

Table 5: Gantt's Chart FYP 1

Activities	Weeks																										
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28
Final Year Project (FYP) background briefing														STUDY WEEK/ FINAL EXAMINATION													STUDY WEEK/ FINAL EXAMINATION
Information searching & Literature Review																												
FYP seminar "research Methodology"																												
Briefing on risk assessment / lab safety/ rules & regulations																												
Prepare Extended																												
Submission of Extended Proposal							★																					
Proposal Defense																												
Procurement of Chemicals, Equipment																												
Preparation of Mg-Zn-Ca																												
Modification the material using different concentration of Ca																												
Functionalization test of Mg-Zn-Ca • SBF • Immersion test • FESEM																												
Submission of Interim report													★															
Progress Report																						★						
Discussion on the results and their effect to the human body																												
Submission of Dissertation (Softbound) & Technical Paper																									★			
Oral Presentation																										★		
Submission of Project Dissertation (Hard Bound)																											★	

Appendix 3 : Gantt's Chart and Key milestone forFYP 2

Table 6: Gantt's Chart for FYP 2

Activities	Weeks													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Collection of the material														STUDY WEEK/ FINAL EXAMINATION
Preparation of the SBF solution														
Fabrication of Mg Alloy at SIRIM (Kedah)														
Booking lab for experimental test														
FESEM morphology														
Immersion Test														
Comparing result before and after														
Submission of progress report							☆							
Discussion on the results and morphology														
Preparation for the Pre-Sedex											☆			
Submission of the technical paper												☆		
Submission of dissertation (soft bound)												☆		
Oral Presentation													☆	
Submission of Project Dissertation (Hard Bound)													☆	