The Effect of Zinc Composition on the Degradation Rate of Magnesium Alloy for Developing Biodegradable Stent

By

Muhammad Ashraf bin Zainal 13205

Dissertation submitted in partial fulfillment of the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

SEPTEMBER 2013

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

The Effect of Zinc Composition on the Degradation Rate of Magnesium Alloy for Developing Biodegradable Stent

By

Muhammad Ashraf bin Zainal 13205

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfillment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

_____

(Dr. Anis Suhaila binti Shuib)

UNIVERSITI TEKNOLOGI PETRONAS

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 as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

_____

MUHAMMAD ASHRAF BIN ZAINAL

ABSTRACT

In recent years, study on degradable biomaterials has become an essential part especially in terms of medication. A lot of studies were carried out since decades ago on the treatment of cardiovascular disease. The use of stent has been practices for the treatment of this disease. Metallic stent might be permanent or biodegradable metals. Biodegradable metals have break traditional thought that material for implant must be from inert metals. Inert metals have several disadvantages for long time application and it needs to be removed after vessel healing. Biodegradable stent is the solution for this problem. Stent implanted could maintain its mechanical integrity during wall vessels healing and dissolve after the healing process complete. Magnesium is suitable for biodegradable implant due to its mechanical strength and properties. It is compatible and needed by human body for biological reaction and as co-factor in enzymes. However in chloride abundant environment like in human body fluid, it degrades faster therefore modification by alloying is one of the recommended techniques to solve this problem. In this project, the effect of zinc composition in Mg-Zn-Ca alloy on the biodegradability is investigated. Zinc composition is varied between 0%, 1% and 2 %. Results show that the Mg-Zn-Ca alloy with one weight percent zinc has the lowest weight loss. This indicate that the alloy has the highest corrosion resistance and would prolong degradation rate of stent.

ACKNOWLEDGEMENT

First and foremost I would like to praise Allah the Almighty as I manage to finish my final dissertation for Final Year Project. The past 28 weeks were toughed and taught me many things related to engineering and their applications in our everyday life. A lot of hard work was put in this project in order to make sure this experimental study finish successfully. I had to face many problems throughout this project. One of it is, I failed to fabricate the alloys in the beginning. Then, more problems come regarding the lab booking process but luckily I managed to complete the experiment before the due date. I would like to take this opportunity to thank my supervisor Dr. Anis Suhaila binti Shuib. She has been supporting our research team in term of information, guidance and financial throughout this project. Her help and guide is highly appreciated and without her I will never be able to finish this project. My next appreciation goes to Mr. Kusniar, a PHD student who helped me in conducting the experiment. He taught me how to perform the experiment and provides me with valuable informations. In fact, he is the one who help me in booking the SEM slot as UTP give priority to postgraduate students in term of booking slot. Special thanks to my best friend Mr.Faez who is also in our research team. He accompanied me since the beginning of this project until the end. His cooperation and efforts are highly appreciated. We helped each other throughout this project and our cooperation and determination enable us to finish the experimental study successfully. I will like to express my gratitude to my FYP 1 and 2 course coordinator Dr. khasyayar and Dr. Asna for providing all the FYP students guidelines in completing the report. They are tolerate and patient in entertaining our behaviour which makes them the best coordinator ever.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS AND NOMENCLATURES

PLLA Poly-L-lactic acid

PGA Polyglycolic acid

PDLA Poly (D,L-lactide/glycolide) copolymer

PCL Polycaprolactone

SEM Scanning Electron Microscopy

EDX Energy Dispersive X-ray Spectroscopy

XRD X-ray Diffraction

SBF Simulated Body Fluid

CHAPTER 1

INTRODUCTION

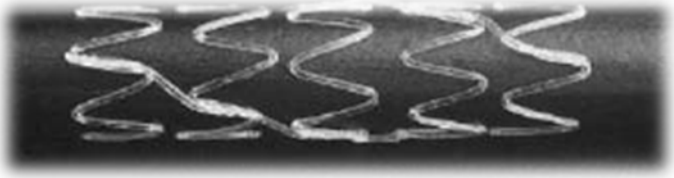
1.1 Cardiovascular Disease and Treatment

Cardiovascular disease (CVD) is refers to any cardiovascular system affected diseases. This disease causes more than 15 billions deaths in the world each year. They are major cause of death in adults. Many of the cardiovascular incidents are not necessarily fatal but they may impair the ability of human to lead a normal daily life (Priest, 2000). Cardiovascular disease includes heart or blood vessels (Maton, 1993) cause the vessels to become weaken due to fat deposition in vessels wall thus narrowing the vessels. In order to prevent vessel ruptured, stent is inserted to open up the weaken and narrowed vessels. Stent is perforated tubular-shaped material used for cardiovascular disease treatment for artery scaffolding (Peuster et al., 2006). A stent must have good mechanical strength to hold and prevent vessel close up and it has to be ductile because it will be expanded using balloon catheter (Erbel et al., 2007). The implanted stent required to last for 6-12 months for vessel healing (Erbel, 2007). After this period the stent will not give any benefits to the vessels. Besides that, it needs to be removed by another surgery after healing. There are also cases involving long term vessel wall dysfunction, blood clothing and inability to adapt the vessel growth which give another risk to the patient as well as increasing medication cost (Erne et al., 2006). Besides that, long term results of bare metals stents are affected by in-stent restenosis, which can occur in up to 30% cases, and stent thrombosis which can be life threatening (D'Souza et al., 2008). In order to solve this problem biodegradable stent is an option. Biodegradable stent has the same function with the current stent but the difference is it will dissolve in body fluid without any surgery (J.B. Park and R.S. Lakes, 2007). Biodegradable stent provide temporary vessel opening until the vessel complete the remodeling and healing process.

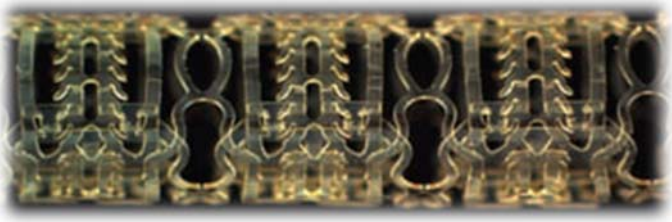
1.2 Material for Biodegradable stents

There are 2 classes of materials that have been proposed for biodegradable stents which are polymers and metals (Hermawan H. et al., 2010). Polymers stents have been used for scaffolding and as a vehicle delivery. There are more flexible than metals. There are various polymeric materials which have been widely studied such as poly-L-lactic acid (PLLA), polyglycolic acid (PGA), poly (D,L-lactide/glycolide) copolymer (PDLA) and polycaprolactone (PCL). The polymer stents including The Igaki-Tamai stent, The REVA stent and The Everolimus-eluting stent. Due to metals which have superior mechanical properties compared to polymer in term of replicating the properties SS316L, the reference material for coronary stents (Hermawan H. et al., 2010), therefore biodegradable stents made from metals give more interest compared to polymers. Magnesium is common metal used to make biodegradable stents. Types of biodegradable stents is represented in Figure 1.

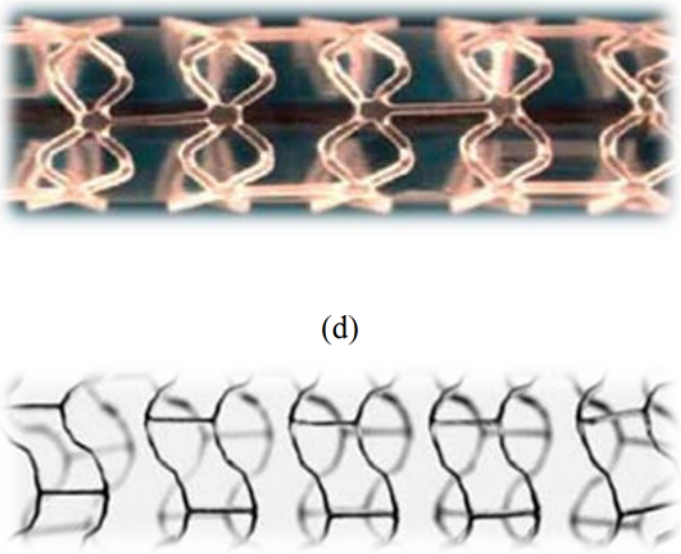
(a)



(b)



(c)



(d)

Figure 1 Types of stents (a) Igaki-Tamai Self-expanding PLLA Polymer Stent (b) REVA Tyrosine–Polycarbonate Slide and Lock Polymer Stents (c) Everolimus-eluting PLLA/PDLLA Polymer Stent (d) Absorbable Magnesium Metallic Stent (D'Souza et al., 2008).

1.3 Problem statement

In recent year, study of degradable biomaterials has become one of the most revolutionary research topics at the forefront of biomaterials. Magnesium alloys was found out to be compatible to be used in human body as biodegradable stent for biomedical application but the problem arise as Mg alloy element that can degrade in body is limited therefore novel alloy element need to be explored more for future biodegradable steel. Mg-Zn-Ca alloy has the potential as biodegradable stent. The present of zinc in magnesium alloy are proven to increase the mechanical strength of the alloy. Human body consists of abundant of chloride. The present of zinc and calcium causing the microstructure become more compact thus preventing chloride from enter and react directly with magnesium. However, the effect zinc composition on degradation rate of magnesium alloys need to be further investigated.

1.4 Objective

The objectives of this project are:

1. To develop biodegradable Mg Alloy (Mg-Zn-Ca).
2. To study the effect of zinc composition on biodegradation rate of magnesium alloys.
3. To make comparison on weight loss for different zinc composition in magnesium alloys.
4. To study and analyses the surface morphologies of the alloys developed.

1.5 Scope

In this project, I will mainly focus on experimental study of developing magnesium alloy using zinc and calcium as alloying elements. This experiment involves the study on the effect of zinc composition in magnesium alloys on degradation rate for developing biodegradable stents. The weight loss in magnesium alloys are measured after being immersed in simulated body fluid for 5 hours. The surface morphologies for all the alloys are analyses.

CHAPTER 2

LITERATURE REVIEW

2.1 Magnesium in Cardiovascular Applications

Based on Kammer C, 2000, biodegradable magnesium implants started shortly after the discovery of elemental magnesium by Sir Humphrey Davy in 1808.The versatile clinical applications and reports from a physician from Graz, Australia Erwin Payr has inspired clinicians to advance the field of biodegradable magnesium implants to various surgical areas (Witte F., 2010).

Biodegradable stents were first developed in 1990s.They are not yet entered clinical practiced but early studied shown their feasibility and potential to be used for the treatment of vessels in cardiovascular disease. Magnesium (Mg) in cardiovascular applications started in 1878 where Huse use a Mg wire ligature successfully to stop bleeding vessel in radial artery and operation for varicocele. He also suggested using Mg wires for ovariotomy and haemorrhoids (Witte F., 2010).

In 1924, Seelig found that the available Mg wire at the market were too brittle. He was then encourage by the Bureau of mines of the Department of the interior to used pure Mg that has been produced by distillation in vacuum to obtain more ductile Mg wires. It was also suggested that noble materials be alloyed with Mg to increase the ductility (Witte F., 2010). Seelig was working in cooperation with the American Magnesium Cooperation. The company supplied 99.99% pure Mg which was then extruded and drawn into wire ranging from 0.005 inch upward. He started the experiment once he received the pure Mg but these first wires had a low tensile strength and were not sufficiently pliable. In 1935, Gotthard Gossrau patented an Mg rope which consists with mesh of thin wires(less than 0.1mm) around and inner stronger guiding wire. This invention has overcome the usually

observed low tensile strength and knot stiffness of Mg wires. E.W. Andrew tried to improve the ductility, flexibility and toughness on magnesium alloys by preventing oxidation mixing. He produced Mg alloys consisting of equal parts of Mg and Al, Mg and Cd, and Mg and Zn as well as one mixture of 25% Mg, 35% Zn and 40% Al. However, he discovered all of them are too hard, brittle and do not have sufficient tensile strength for cardiovascular application (Witte F., 2010).

Magnesium is started to be used as connectors for vessel anastomosis in 1900 (Witte F., 2010). Payr used pigs and the femoral artery of dogs for his experiments on vessel connectors made of magnesium .He was able to used tubal Mg connectors for the anastomosis of arterial and venous blood vessels. Later, he placed the inner part into peripheral end of the vessel to take into account the venous blood flow direction. Connection of the vessels ends become solid after 8 days and thickness of the vessels returned normal after more than 8 days. Payr stated that only intravascularly placed Mg tubes exhibited thrombotic blood clotting at the ends of the tubes which however never closed the remaining lumen (Witte F., 2010). Besides that, no thrombosis was observed with extravascularly placed Mg tubes. In 1910, Lespinasse introduced a technique for extravasal sutures of vessels using metallic ring plates with punch holes to fix the vessel ends and connect the rings with a pressure of less than 5 lbs. The magnesium rings maintained their original shape for about 30 days before they began to breakdown. Besides that, he also introduced Mg plate with holes suitable for the repair of lateral slit in a vessel (Witte F., 2010). Magnesium connectors designed by Payr for vessel anastomosis is represented in Figure 2.

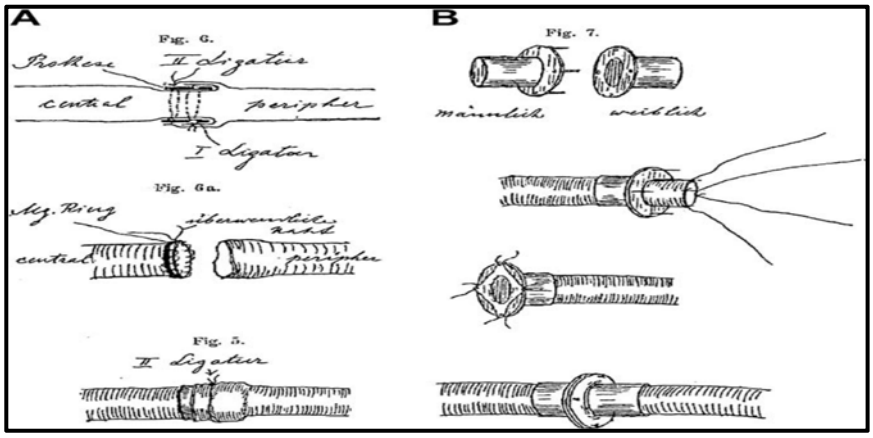


Figure 2 Tubal magnesium connectors designed by Payr for vessel anastomosis. Method (A) use extravasal magnesium rings. Method (B)uses two part extravasal connector with a male and female part. In both methods the Mg connector is extravasal and the anastomosis is achieved by duplication of intima. Thus no foreign material is located intravasal after the anastomosis (Witte F., 2010).

Magnesium continues to be used in cardiovascular application as wires for aneurysm treatment (Witte F., 2010). In 1951, Stone and Lord looked for a thrombogenic material to favour intrasaccular clotting in aortic aneurysms. Pure Mg wires and Mg-Al wires are used in dog's aortas as double coiled wires. It was found that Mg wires were twice as thrombogenic as stainless steel and Mg-Al wires are three times higher than stainless steel (Witte F., 2010).

2.2 Zinc and Calcium as alloying elements in magnesium alloys

In this project, the focus point will be in developing Magnesium alloys with Zn and Ca as alloying elements. The magnesium itself has melting point of 650^{o}C. Magnesium alloys can be divided into three major groups which are pure magnesium (Mg) with traces of other elements, aluminium (Al) containing alloys and alloys free of aluminium (Al). Magnesium alloys have some specific properties which are light weight, not too expensive, high specific strength and favorable environmental properties. Mg-Zn magnesium alloy was researched as degradable biomedical material. Mg-Zn alloy which fabricated with high purity raw materials and clean melting process had very low level of

impurities (S.Zhang et al., 2010). The grain size was finer and a uniform single phase was obtained after solid solution treatment and hot working (S.Zhang et al., 2010). It is found that the mechanical properties of the alloys are suitable for implant application (S.Zhang et al., 2010). The tensile strength and elongation achieved were approximately 279.5 Mpa and 18.8% respectively (S.Zhang et al., 2010). Zinc is one of the most abundant nutritionally essential elements in human body (Zhang B. et al., 2012) and has basic safety for biomedical applications. Zinc can improve mechanical properties of magnesium as well as effectively strengthen magnesium through solid solution hardening.

Apart from that, calcium is also a known alloying element for magnesium alloys. Calcium has melting point of 842^0C. It has a low density of 1.55 g/cm^3 which is also similar to magnesium with density of 1.74g/cm^3 which will maintain its specific properties (Rad H.R.B. et al., 2012). The reasonable cost of calcium also making it as an option to use for medical applications (Rad H.R.B. et al., 2012).

2.3 Effect of Calcium in magnesium alloys

In one study, a series of Mg-Zn-Ca alloys with micro alloying additions of calcium element in range of 0-0.5wt% were successfully fabricated by extrusion of the cast billet. The compositions and grain size for the alloys examined in this study are represented in Table 1.

Table 1 Compositions and grain size for the alloys (Zhang B. et al., 2012)

Alloy	Zn (wt%)	Ca (wt%)	Grain Size (μm)	Ductility (%)
Mg-1.0Zn	1.0	0	20-50	16.2±1.5
Mg-1.0Zn-0.2Ca	1.0	0.2	5-20	35.5±3.0
Mg-1.0Zn-0.5Ca	1.0	0.5	6-10	44±5

Based on the study, it is found that the refining effects are dependent on the concentration of Ca. The refinement of the grain size in the extruded alloys is most likely a sequence if the influence of Ca element on dynamical recrystallization (Zhang B. et al., 2012). According to previous study on Ca containing alloys, it was suggested that they were many Mg_2Ca precipitates particles in the Ca-containing alloys (Zhang B. et al., 2012). This due to the maximum calcium solubility in magnesium was only 0.82% at 516.5^{o} C and not more than 0.2% at room temperature (Zhang B. et al., 2012). The Calcium contains in the study are 0.2wt% and 0.5 wt% and showed that Ca-containing alloys are not single phase but contain inclusion of precipitates (Zhang B. et al., 2012).

In one study on microstructure analysis and corrosion behavior of biodegradable Mg-Ca implant alloys, the interaction between microstructure, phase transformation and corrosion resistance are investigated. This experiment involves pure magnesium ingot (99.98% Mg) and Mg-40Ca master alloy as starting materials. The materials were melted under argon gas in a mild steel crucible at a temperature of 740^{o}C for 45 minutes holding time. 30 minutes for melting procedures and another 15 minutes for complete melt homogenization (Rad H.R.B. et al., 2012). Immersion test was carried out in which 20 specimens with a size of 15mm x 5mm x 5mm were and subsequently grounded with 400-2000 grit SiC papers (Rad H.R.B. et al., 2012). The specimens were then washed entirely with distilled water, rinsed, ultrasonically decreased with ethanol, and then dried at room temperature. The specimens were then immersed into a beaker containing 200 ml of Kokubo simulated body fluid with a following chemical composition: (Na 142.0 mmol/L, K 5.0 mmol/L, Ca 2.5 mmol/L, Mg 1.5 mmol/L, HCO3 4.2 mmol/L, Cl 147.8 mmol/L,HPO4 1.0 mmol/L, SO4 0.5 mmol/L) (Rad H.R.B. et al., 2012). Following preparation procedure according to ASTM-G31-72 the beakers were sealed with a pH value adjusted to 7.66 and incubated at a constant temperature of 37 ˚C for 84 h. The specimens were then taken out of the solution, rinsed with distilled water and dried at room temperature. The pH values of the solution were monitored during the immersion

test (Rad H.R.B. et al., 2012). The chemical compositions of the as-cast Mg-xCa alloys and the SEM micrographs analysis are represented in Table 2 and Figure 3.

Table 2 Chemical compositions of the as-cast Mg-xCa alloys (Rad H.R.B. et al., 2012).

Alloy	**Mg-0.5Ca**		**Mg-1.25Ca**		**Mg-2.5Ca**		**Mg-5Ca**		**Mg-10Ca**	
Composition	Mg	Ca	Mg	Ca	Mg	Ca	Mg	Ca	Mg	Ca
Nominal composition wt%	99.5	0.5	98.75	1.25	97.5	2.5	95	5	90	10
Analyzed Composition wt%	99.43	0.57	98.73	1.27	97.46	2.54	94.87	5.13	89.76	10.24

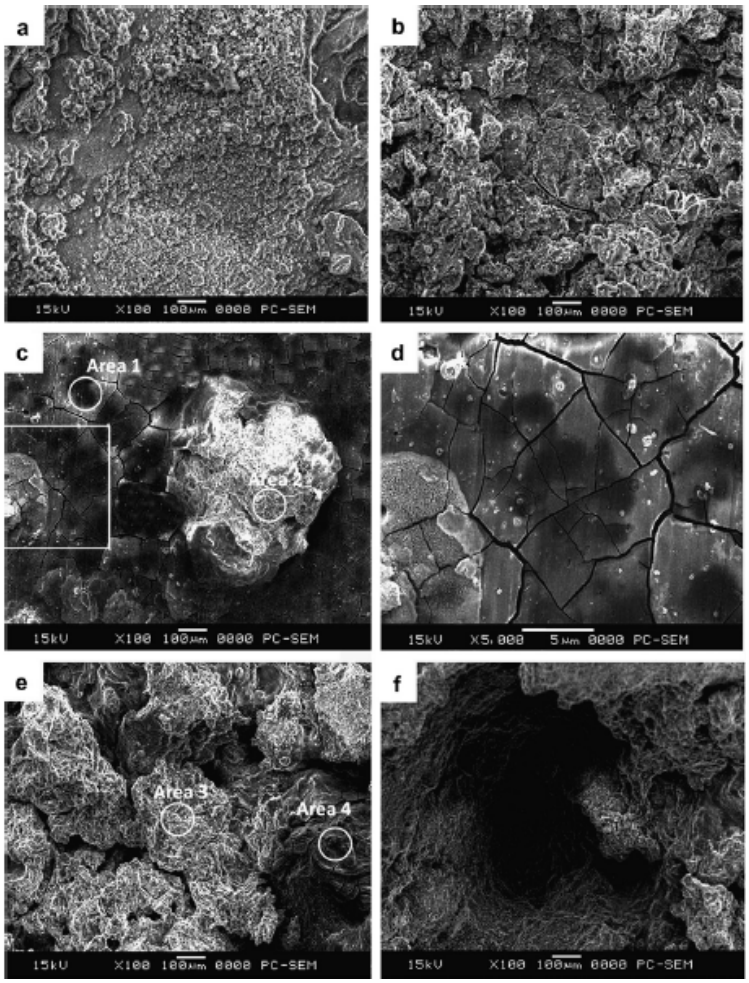


Figure 3 SEM micrographs of Mg-Ca alloys with different calcium content: (a) 0.5, (b) 1.25, (c) 2.5, (d) 5 with immersion duration of 84 hour in SBF, (e) 10wt% with immersion duration of 6 hours in SBF (Rad H.R.B. et al., 2012).

Based on Figure 3a and b, the surface of Mg–0.5Ca and Mg–1.25Ca are covered by white insoluble corrosion film Mg (OH)2 (Rad H.R.B. et al., 2012). Cracks can be seen as a result of dehydration of the surface layer in the air. These cracks were thicker and deeper for Mg–2.5Ca (Fig. 3c) due to a higher corrosion rate than Mg–1.25Ca (Fig. 3b) (Rad H.R.B. et al., 2012). The degradation of Mg alloys in the SBF occurred according to the following equation:

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

The formation of $Mg(OH)_2–nH_2O$ protective layer subsequently decrease the corrosion rate of the specimens. Through the formation of this protective layer the CO_3^{2-} , PO_4^{3-} and

Cl^- ions were attracted to the surface of the specimen causing more accumulation of OH^- ion that is vital for apatite nucleation (Rad H.R.B. et al., 2012). In Fig. 3e, a large amount of deep corrosion pits are presence on the surface of Mg–5Ca. Some of these pits were covered with white substance consisting of Ca and P. On the contrary, Mg–10Ca was completely degraded at an earlier immersion time of 12 h. Fig. 3f depicts the deep pitting corrosion on the surface of Mg–10Ca which confirms the high dissolution rate of this specimen (Rad H.R.B. et al., 2012).

2.4 The effect of Zinc concentration on Mg-xZn alloys

In one experiment to investigate the Zinc effect on corossion of Mg-xZn alloys, various Zinc concentrations are used. The experimental material used were the extrusion Mg-2Zn, Mg-3Zn, Mg-4Zn and Mg-5Zn alloys plates with nominal composition of 2 wt% Zn, 3 wt% Zn,, 4 wt% Zn and 5 wt% Zn respectively as well as other trace elements of Ca, Si, Mg balance. The morphologies of the samples were observed using a Philips XL30 scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectroscopy (EDX). The microstructure of the Mg-xZn alloys was measured usinga Philips PW1700 X-ray diffraction (XRD) with Cu target (λ=0.154nm). The XRD patterns was analyzed with MDI jade 5.0 software. Microstructure of the alloys are represented in Figure 4.

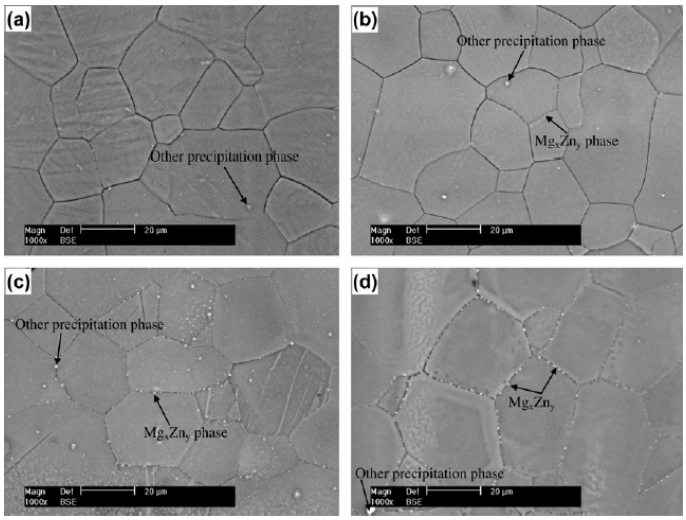


Figure 4 Backscattered electron (BSE) microstructure of (a) Mg-2Zn; (b) Mg-3Zn; (c) Mg-4Zn and (d) Mg-5Zn alloys (Song Y., 2012).

Based on Figure 4, the average grain sizes of the four alloys are similar which are 30.2, 29.0, 33.2 and 33.6μm respectively. The grain size within each alloy is inhomogeneous. The smallest grain size is less than 10μm and the biggest one is more than 60μm (Song Y., 2012).There is a great difference in the distribution of the white precipitation phases in four alloys according to the observation of surface morphologies. The very fine white particles which just locate on the grain boundaries are mainly composed of Mg and Zn. These fine white particles are named as Mg_xZn_y second phases. These Mg_xZn_y second phases present a discrete distribution along the grain boundaries and their volume fractions gradually rise with increasing Zn concentration from Mg–2Zn to Mg–5Zn alloys (Song Y., 2012).The fine Mg_x- Zn_y precipitation phases can be clearly observed on the Mg–5Zn alloy. Besides these fine Mg_xZn_y second phases, other white precipitation particles with a larger scale than the MgxZny second phases are visible in the four alloys. Most of these white particles locate in the interior of the crystal grains, and only several of them are visible on the grain boundaries. The volume fractions of these white precipitation particles are very low, and there is no change observed with increasing Zn concentrations in the four alloys (Song Y., 2012).

These 4 alloys were immersed in 3.5% NaCl solution for 6 hours. After immersion test were carried out, the results showed that only small area is covered with black

corrosion products in Mg-2Zn alloys compared to the other 3 alloys. The coverage percent of the corrosion products gradually increase in the order of Mg-2Zn < Mg-3Zn < Mg-4Zn < Mg-5Zn [14]. Mg-2Zn alloys exhibits the best corrosion resistance while Mg-5Zn suffers the severest attack (Song Y., 2012).The experiment shows that corrosion resistance of Mg-*x*Zn alloys reduce with increasing Zinc concentration (Song Y., 2012).

CHAPTER 3

METHODOLOGY

3.1 Process of making alloy

3.1.1 Weighing raw materials (magnesium, calcium, and zinc)

In this project, element such as magnesium, zinc and calcium is used in the preparation of making novel Mg-Zn-Ca alloys. The first step is weighing the raw materials. The total weight for each sample will be constant which is 5g or 5000mg. In this experiment, Zinc concentrations are varied from 0 wt%, 1wt% and 2wt%. The weight of sample is measured by using weighing balance in milligrams scale for better accuracy. The prepared samples are put in a small container and labeled. The details about the samples are shown in Table 3.

Table 3 Composition of element in Mg-*x*Zn-Ca

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

3.1.2 Heating, melting and cooling process

The mixture of magnesium, zinc and calcium are then put into 4.8cm x 3.8cm x 1.8cm crucible and transfer to tube furnace for heating and melting process under argon gas. The heating and melting process is shown in Figure 5.

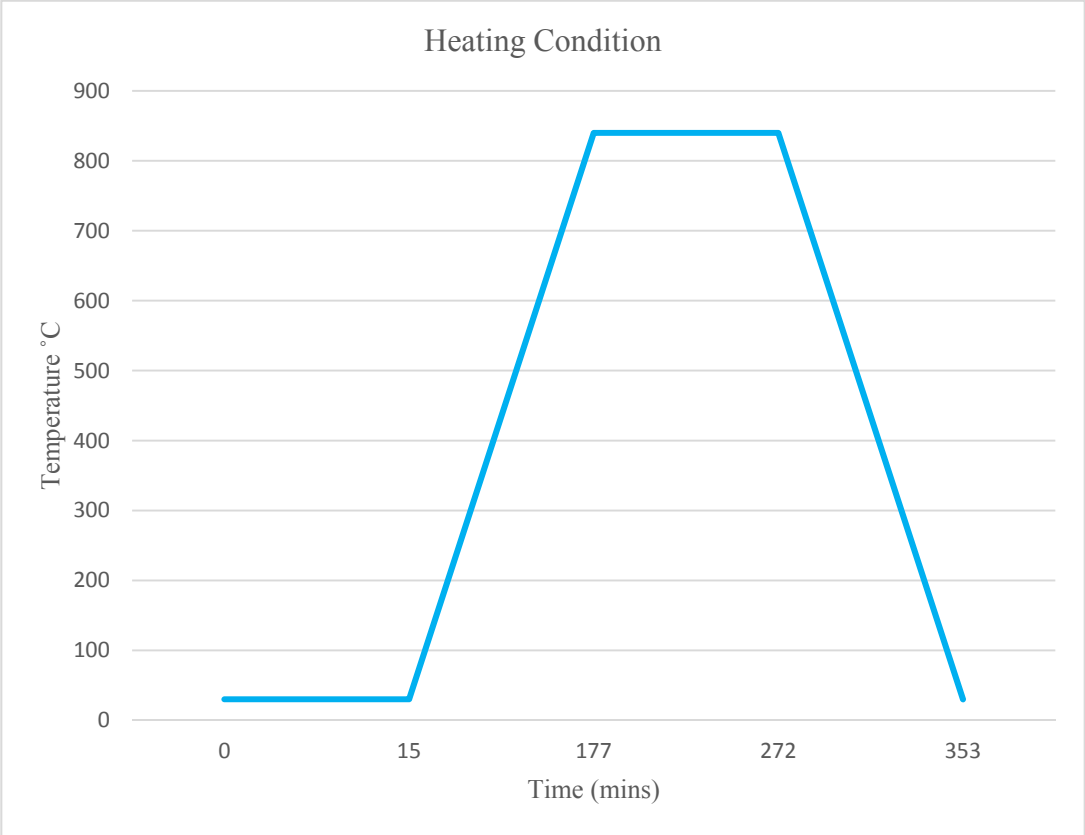


Figure 5 Temperature profile of alloys heating condition

Figure 5 is the heating condition of the alloys. Argon gas is let to flow for 15 minutes at 30˚C into the tube furnace to clear the oxygen inside the tube which can cause the samples to oxidize. The samples are put in crucibles and heated to 840˚C at heating rate of 5˚C per minute. The holdup temperature 840˚C is maintained for 1 hours and 30

minutes to make sure complete melting process. Then, the samples are let to be cooled to 30˚C at cooling rate of 10˚C per minute.

3.1.3 Laboratory Tube furnace

The Laboratory tube furnace has the maximum temperature of 1500˚C with a heating area of 1100 cm^2. The maximum no graph segment that can be produced is 8. Figure 6, 7 and 8 are the main parts in tube furnace.

Figure 6 LT furnace

Figure 7 inside tube

Figure 8 Argon gas tank

3.2 Immersion in Simulated body fluid solution (SBF)

The immersion tests are carried out using simulated body fluid. Alloys that have been fabricated are cut into piece and weighed first to obtain the initial weight of the alloys before immersion test is carried out. Alloy is immersed in a beaker containing simulated body fluid solution (SBF) together with the magnetic stirrer. The stirring process is conduct for 5hours to measure the different in weight of the alloy before and after immersed in SBF. The magnetic stirrer is set to be constant at 30rpm. After 5 hours, the samples are remove from the solution. The sample is put in oven at 100˚C for 5 minutes and into desiccator for drying purpose to prevent the solution affect in the weighing process. The weight of the sample is measured again to determine the total weight loss of the alloys. The weight loss for each alloys shows degradation occur.

3.3 Surface morphologies analyses by Field Emission Scanning Electron Microscopy (FESEM)

FESEM is used to see the microstructure. In this experiment, FESEM is used for structure uniformity determination, small contamination feature geometry and for elemental composition measurement. The surface morphologies of the alloys will be observed in this experiment. The surface morphologies analyses are done before the alloy undergo immersion test and after the immersion test to see the differences in the morphologies of the alloy. The FESEM machine use in this project is represented in Figure 9.

Figure 9 Zeiss Supra 55 VP (Carl Zeiss SMT, n.d.).

Zeiss Supra 55VP is a FESEM machine that is used in this experiment. It is used for imaging, qualitative analysis and elemental mapping (Carl Zeiss SMT, n.d.).Supra 55VP specifications are represented in Table 4.

Table 4 Supra 55 VP specifications (Carl Zeiss SMT, n.d.).

Essential Specifications	Supra 55VP
Resolution	1.0 nm @ 15 kV 1.7 nm @ 1 kV 4.0 nm @ 0.1 kV
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
Optional detectors	cap mounted AsB detector
Chamber	330 mm (Ø) x 270 mm (h) 2 EDS ports 35° TOA CCD-camera with IR illumination, x-free ports
Optional Chamber	Additional 3rd EDS port 35° TOA or WDS chamber for fully focussing spectrometer
Specimen stage	5-Axes Motorised Eucentric Specimen Stage X = 130 mm, Y = 130mm Z = 50mm T = -3 - +70° R = 360° (continuous)
Image processing	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	SmartSEM with Windows XP, operated by mouse, keyboard and joystick with optional control panel

CHAPTER 4

RESULT AND DISCUSSION

4.1 Alloying

After heating, melting and cooling process which carried out for 6 hours, alloys in Figure 10, 11 and 12 are obtained. Alloys of Mg-0%Zn-Ca, Mg-1%Zn-Ca and Mg-2%Zn-Ca have shiny and hard surfaces.

Figure 10 Mg-0%Zn-Ca

Figure 11 Mg-1%Zn-Ca

Figure 12 Mg-2%Zn-Ca

4.2 Weight loss in alloys

The weight loss in alloys after immersed in SBF for 5 hours are represented in Table 5.

Table 5 weight loss in alloys

Material	Weight before immersed in SBF (mg)	Weight after immersed in SBF for 5 hours (mg)	Total weight loss (mg)($Weight_{before}$ -$Weight_{After}$)
Mg-0wt%Zn-Ca	30 mg	8mg	22mg
Mg-1wt%Zn-Ca	30mg	26mg	4mg
Mg-2.0wt%Zn-Ca	30mg	15mg	15mg

The weight of the alloys decrease from its initial weight which is 30 mg. Alloy with 0wt% Zinc experienced a weight loss of 22 mg while alloy with 1wt% and 2wt% Zinc have a weight loss of 4 mg and 15 mg respectively.

4.2.1 Weight loss versus Alloy compositions

The graph of weight loss with respect to alloys composition is represented in Figure 13

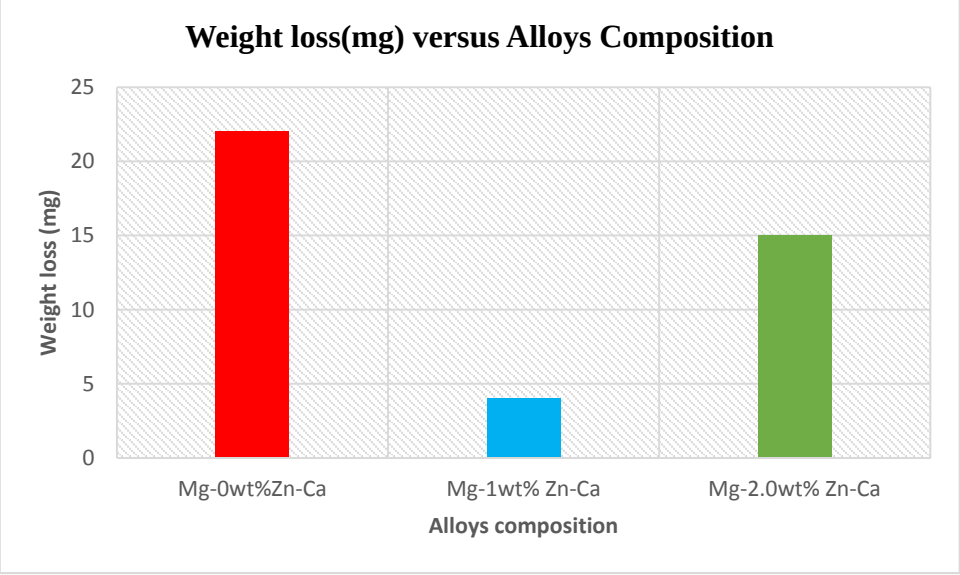


Figure 13 Weight loss in the alloys based on alloys composition

Based on the graph in Figure 13, alloy of Mg-0wt%Zn-Ca experienced huge weigh loss compared to alloy of Mg-1wt%Zn-Ca and Mg-2wt%Zn-Ca in which the final weight of the alloy is 8 mg. Half of the mass for alloy Mg-2wt%Zn-Ca degrade after 5 hours treated with SBF. Alloy of Mg-1wt%Zn-Ca only experienced minor corrosion as the initial weight only reduce by 4 mg. From the graph, Alloy Mg-1wt%Zn-Ca shows the lowest degradation rate compared to alloys Mg-0wt%Zn-Ca and Mg-2wt%Zn-Ca

4.3 Surface Morphologies Analyses

Surface morphologies analyses of the alloys developed are done before and after immersion test. The result of the analyses are shown below in Figure 14.

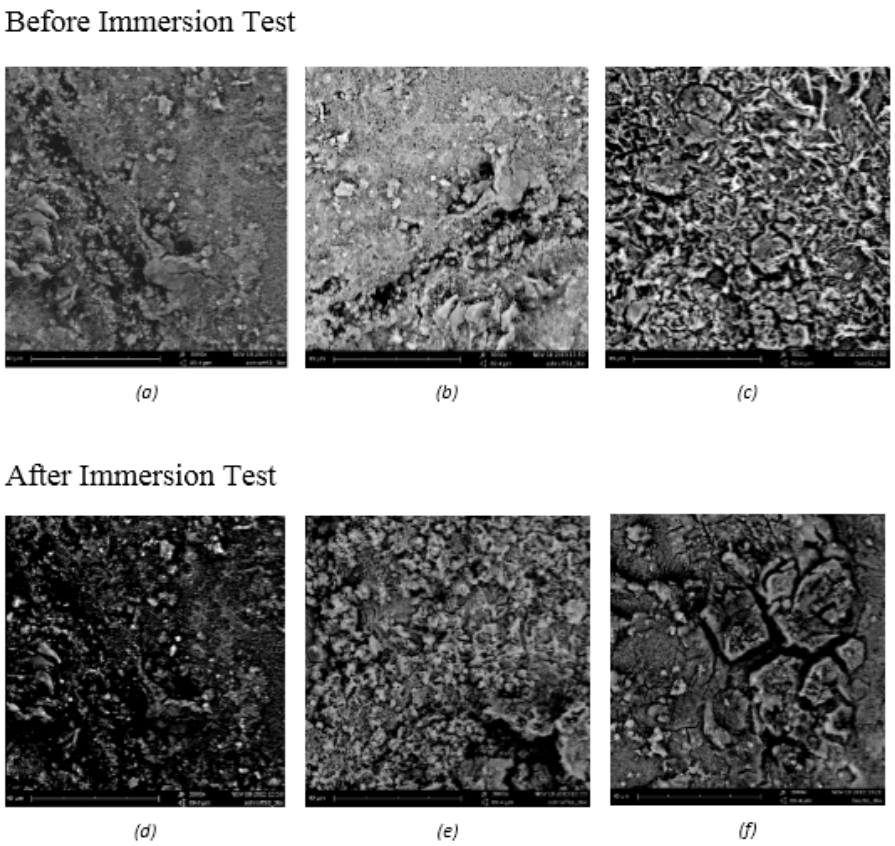


Figure 14 Morphologies of alloys before and after 5 hours immersed in SBF; (a) Mg-0wt%Zn-Ca before immersion test, (b) Mg-1wt%-Zn-Ca before immersion test, (c) Mg-2wt%Zn-Ca before immersion test, (d) Mg-0wt%Zn-Ca after immersion test, (e) Mg-1wt%-Zn-Ca after immersion test and (f)) Mg-2wt%Zn-Ca After immersion test

Figure 14 is the surface morphologies of alloys with different zinc composition before and after treated in SBF for 5 hours. After treated in SBF the result shows that the surface of all the three alloys become darker in colour compared to before immersion test which means that there are reduction in density of the alloys. Sample (d) experienced severe effect of corrosion due to absence of zinc which act as protective layer on the magnesium alloy. The surface appeared darker compared to sample (e) and (f). Black corrosion product has completely cover the magnesium substrate. Surface (e) experienced minor effect of corrosion since there is only small corrosion product on the surface of the alloy. The surface colour is clearer which means that the reduction in density experienced by sample (e) is not as much as sample (d) and (f). In the case of sample (f) approximately half of the surface is covered with black corrosion product. The surface colour appeared darker than sample (e) which means that reduction in density in sample (f) is higher than sample (e). From the surface morphologies analyses, reduction in density is greatest for Mg-0wt%Zn-Ca alloy followed by Mg-2wt%Zn-Ca and Mg-1wt%Zn-Ca. In order of increasing degradation rate, Mg-0wt%Zn-Ca has the highest degradation rate followed by Mg-2wt%Zn-Ca and Mg-1wt%Zn-Ca. Based on the results obtained, the optimum amount of zinc in magnesium alloy is one weight percent

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Experimental study on biodegradable stent and how alloying effect the degradation rate of alloy are carry out. In this experiment, the effect of zinc composition in magnesium alloy degradation rate for developing biodegradable stent is studied. The effect of zinc concentration are investigated in this experiment by increasing the weight percent of zinc in magnesium alloys. Besides that, problem regarding the alloying process such as the pure magnesium oxidize too fast and the difficulty to find optimum temperature for alloying process will be further investigate and solve. Previous research has proven that zinc and calcium effect the degradation rate of an alloy. The presence of zinc increases the alloy strength and its resistance towards corrosion. The presence of 1wt% of zinc in an alloy is found to be the most optimum amount. Any increase in composition of zinc more than 1wt% will result in reduction on corrosion resistance in an alloy. Based on the weight loss obtained, alloy with 1wt% zinc experienced the smallest weight loss and reduction in density compared to alloy with 0 and 2wt%. The surface morphologies that has been carried out using Scanning Electron microscopic (SEM) shows that alloy with 1wt% of zinc only experienced small effect of corrosion. The black corrosion product only appear in small area. The objectives of this project are achieved.

5.2 Recommendations

There are some recommendations for improvement of this project. First, the composition of zinc is varied by the increment of 0.5wt% so that the results obtained will be more accurate. Since the effect of varying calcium composition in alloy on degradation rate has not yet been tested, the next FYP students could do the experimental study on varying calcium concentration. In term of the problem on booking the slot for laboratory session, UTP should provide more equipment so that there will be more booking slot for FYP students to carry out their experiments and enable them to finish their project successfully.

REFERENCES

Carl Zeiss SMT. (n.d.). Nanotechnology System Divison. Retrieved July 10, 2013 from www.smt.zeiss.com/nts

D'Souza S., Ferrante G., Tyczynski P., & Di Mario C. (2008).A New Era?. Biodegradable Stents.Department of Cardiology, Royal Brompton Hospital, London.

Erbel (2007). Temporary Scaffolding of Corronary Arteries with Bioabsorbable Magnesium Stents: A Prospective, Non-Randomized Multicentre Trial, Lancet, 369, 1869–1875.

Erne (2006). The Road to Bioabsorbable Stent: Reaching Clinical Reality? Cardiovasc. Interv. Radiol, 29, 11-16.

Hermawan H., Dube D., & Mantovani D.(2010).Developments in metallic biodegradable stents. Acta Biomaterialia 6, retrieved August 3, 2013 from http:// www.elsevier.com/locate/actabiomat.

J.B. Park, R.S. Lakes, Biomaterials on Introduction, 3rd ed. New York: Springer SpringerLink (Service en Ligue), 2007, p. 561.

Maton, 1993, Human Biology and Health, Englewood Cliffs, New Jersey: Prentice Hall.

Peuster. (2006), Are Resorbable Implants About to Become a Reality?, Cardiol. Young, 16, 107-116.

Priest S.H. (2000).Cardiovascular Diseases. Retrieved July 3, 2013 from http://biotech.nature.com.

R. Erbel. (2007). "Temporary Scaffolding of Corronary Arteries with Bioabsorbable Magnesium Stents: A Prospective, Non Randomized Multicentre Trial. Lancet, Vol 369, pp 1869 – 1875, 2007.

Rad H.R.B., Idris M.H., Abdul Kadir M.R., & Farahany S. (2012).Microstructure analysis and corrosion behavior of biodegradable Mg-Ca implant alloys. Material and Design, 33, 88 97, retrieved September 12, 2013 from http:// www.elsevier.com/locate/matdes.

S. Zhang., X. Zhang., C.Zhao., J. Li., Y. Song., C. Xie., … Y. Bian (2010). Research on an Mg-Zn alloy as a degradable biomaterial. Acta Biomaterialia 6, retrieved July 8, 2013 from http://www.elsevier.com/locate/actabiomat

Song Y. (2012). The effect of Zn concentration on the corrosion behavior of Mg-xZn alloys. Corrosion Science, 65, 322-330, retrieved July 8, 2013 from http://www.elsevier.com/locate/corsci.

Witte F. (2010).The history of biodegradable magnesium implants: A review. Acta Biomaterialia 6, retrieved August 2, 2013 from http:// www.elsevier.com/locate/actabiomat

Zhang B., Wang Y., Geng L., & Lu C. (2012).Effects of calcium on texture and mechanical properties of hot extruded Mg-Zn-Ca alloys. Materials Science and Engineering A, 539, 56-60, retrieved September 10, 2013 from http:// www.elsevier.com/locate/msea.

APPENDICES

APPENDIX 1-Calculation on the weight for each constituent element

First sample

$$\text{weight of zinc} = 0\text{wt\%}$$

$$\text{weight of calcium} = \frac{1}{100} \times 5000\text{mg}$$

$$= 50\text{mg}$$

$$\text{weight of magnesium} = 5000\text{mg} - (\text{weight of calcium} + \text{weight of zinc})$$

$$= 5000\text{mg} - (0\text{mg} + 50\text{ mg})$$

$$= 4950\text{ mg}$$

Second sample

$$\text{weight of Zinc} = \frac{1}{100} \times 5000\text{mg}$$

$$= 50\text{mg}$$

$$\text{weight of Calcium} = 50\text{mg since } 1\text{wt\%}$$

$$\text{weight of magnesium} = 5000\text{mg} - (\text{weight of calcium} + \text{weight of zinc})$$

$$= 5000\text{mg} - (50\text{mg} + 50\text{ mg})$$

$$= 4900\text{ mg}$$

Third sample

$$\text{weight of Zinc} = \frac{2}{100} \times 5000\text{mg} = 100\text{mg}$$

$$\text{weight of Zinc} = \frac{1}{100} \times 5000\text{mg} = 50\text{mg}$$

$$\text{weight of magnesium} = 5000\text{mg} - (\text{weight of calcium} + \text{weight of zinc})$$

$$\text{weight of magnesium} = 5000\text{mg} - (50\text{mg} + 100\text{mg})$$

$$= 4850 \text{ mg}$$

APPENDIX 2- FYP 1 Gantt Chart

Activities	Weeks													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Final year project(FYP) background briefing														STUDY WEEK/ FINAL EXAMINATION
Information searching & literature review														
FYP seminar "Research Methodology														
Briefing on risk assessment/safety rules and regulation														
Prepare extended proposal														
Submission of extended proposal							☆							
Proposal Defence														
Procurement of chemicals and equipment														
Submission of interim report													☆	

APPENDIX 3- FYP 2 Gantt chart

Activities	Weeks												
	1	2	3	4	5	6	7	8	9	10	11	12	13
Collection of the material													
Preparation of the raw materials ➢ Cut magnesium strips and zinc and weight materials													
Fabrication of Mg Alloy at SIRIM (Kulim hi-tech 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													
Pre-Sedex													
Submission of the technical paper													
Submission of dissertation (soft bound)													
Oral Presentation													
Submission of Project Dissertation (Hard Bound)													