

**PROPERTIES OF BIOCOMPATIBLE
Mg-Zn/HYDROXYAPATITE COMPOSITES
FABRICATED BY DIFFERENT POWDER
MIXING TECHNIQUES**

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TECHNIQUES**

by

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TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENT	ii
TABLE OF CONTENTS	iv
LIST OF TABLES	viii
LIST OF FIGURES	xi
LIST OF ABBREVIATIONS	xv
LIST OF SYMBOLS	xvi
ABSTRAK	xvii
ABSTRACT	xix
CHAPTER ONE: INTRODUCTION	
1.1 Introduction	1
1.2 Problem Statement	7
1.3 Research Objectives	10
1.4 Scope of Work	11
1.5 Thesis Outline	12
CHAPTER TWO: LITERATURE REVIEW	
2.1 Chapter Outline	13
2.2 General Requirement of Biomaterials	13
2.3 Permanent Metallic Biomaterials for Bone Fixation	15
2.3.1 Titanium Based Bone Implant	16
2.3.2 Cobalt-Chromium (Co-Cr) Based Bone Implant	22

2.3.3	Stainless Steel Based Bone Implant	25
2.3.4	Summary on Conventional Permanent Bone Fixation Devices	26
2.4	Biodegradable Metal-based Bone Implant	28
2.4.1	Magnesium-based Bone Implant	29
2.4.2	Zinc-based Bone Implant	30
2.4.3	Iron-based Bone Implant	33
2.4.4	Summary on Biodegradable Metal-based Bone Implant	36
2.5	Magnesium as Biodegradable Bone Fixation Device	37
2.5.1	Properties of Magnesium	37
2.5.2	Tolerable Alloying Elements Added to Magnesium Alloy	39
2.5.3	Zinc as Alloying Element	44
2.5.4	Solid Solution Strengthening Mechanism	47
2.6	Magnesium-based Composite Incorporated with Bioactive Materials	50
2.7	Fabrication of Mg-based Composite via Powder Metallurgy	55
2.7.1	Mechanism of Mechanical Alloying (MA) and Mechanical Milling (MM)	56
2.7.2	Compaction of Powder	58
2.7.3	Sintering	60
2.8	Corrosion Behaviour of Magnesium	61
2.9	Summary	63
 CHAPTER THREE: RESEARCH METHODOLOGY		
3.1	Introduction	65
3.2	Starting Materials	68
3.2.1	Magnesium, Zinc and Hydroxyapatite	68

3.2.2	n-heptane	68
3.3	Fabrication of Mg-Zn Based Composite	69
3.3.1	Powder Mixing Process through Two Distinct Techniques	69
3.3.2	Compaction	70
3.3.3	Sintering	70
3.4	Characterization and Testing	71
3.4.1	X-Ray Diffraction	71
3.4.2	Microstructural Analysis	72
3.4.3	Density Measurement	73
3.4.4	Microhardness Measurement	74
3.4.5	Compression Test	74
3.4.6	Immersion Test	74
3.4.6.1	Sample Preparation for Microstructural Assessment	76
3.4.7	Electrochemical Polarization by Tafel Plot Extrapolation	77

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1	Introduction	80
4.2	Characterization of Raw Materials	80
4.3	Effect of Powder Mixing Techniques on the Properties of Mg-Zn/HA Composite	83
4.3.1	Phase Formation, Crystallite Size and Internal Strain of the Composite	84
4.3.2	Morphological Study of the Composite	91
4.3.3	Density and Microhardness Measurement	94
4.3.4	Compression Properties Measurement	95

4.3.5	Electrochemical Polarization by Tafel Plot Extrapolation	98
4.3.6	Weight Loss Measurement by Immersion Test	102
4.3.7	Optimization of Powder Mixing Techniques of Mg-Zn/HA Composites	107
4.4	Effect of Milling Time on Mg-Zn/HA (pm) Composite	108
4.4.1	Phase and Structure Analysis	108
4.4.2	Microstructure Analysis	112
4.4.3	Density and Microhardness Measurement	115
4.4.4	Compression Measurement on Mg-Zn/HA Fabricated by Planetary Mill	117
4.4.5	Electrochemical Polarization of Mg-Zn/HA Fabricated Through Planetary Mill	119
4.4.6	Weight Loss Measurement of Mg-Zn/HA Fabricated Through Planetary Mill	121
4.4.7	Optimization of Milling Time of Mg-Zn/HA Composite Fabricated Through Planetary Mill	129
CHAPTER FIVE: CONCLUSION AND RECOMMENDATION		
5.1	Conclusion	132
5.2	Recommendations for Future Work	134
REFERENCES		135
LIST OF PUBLICATIONS		149

LIST OF TABLES

		Page
Table 2.1	Some properties of selected biomaterials (Witte et al., 2008; Eddy et al., 2012; Tan et al., 2013)	15
Table 2.2	α and β stabilizers of titanium alloys (Chen & Thouas, 2015)	17
Table 2.3	Comparison of tensile properties between cortical bone with various types of Ti and Ti-based alloys (Dewidar et al., 2006; Chen & Thouas, 2015; Bai et al., 2016)	19
Table 2.4	Main alloying elements that made up Co-based alloys and their roles (Ibrahim et al., 2017; Chen & Thouas, 2015)	22
Table 2.5	Co-Cr alloys used in surgical implants (Chen & Thouas, 2015)	23
Table 2.6	Approximate mechanical performance of stainless steels and its alloys (Ratner et al., 2013)	26
Table 2.7	Advantages and disadvantages of permanent orthopaedic metallic implant materials (Dewidar et al., 2006; Chen & Thouas, 2015)	27
Table 2.8	Properties of Mg-based biodegradable implants in comparison to the currently applied and developed implants (Tan et al., 2013)	38
Table 2.9	Solubility limits of the main alloying elements in magnesium (Gu et al., 2009; Chen et al., 2014)	42
Table 2.10	The pathology and toxicology details on Mg and its alloying elements (Witte et al., 2008; Chen & Thouas, 2015)	43
Table 2.11	Physical properties of pure Zn (Campbell, 2008; Callister & Rethwisch, 2011)	44
Table 2.12	Mechanical and corrosion properties of various Mg-Zn-based alloy system reported in literature	45

Table 2.13	Typical mechanical properties of dense hydroxyapatite ceramics (Ratner et al., 2013)	52
Table 2.14	The effects of HA addition into Mg and Mg-Zn alloy matrix	53
Table 2.15	Comparison of compaction parameters	59
Table 3.1	Coding of samples being fabricated by different powder mixing techniques	65
Table 3.2	General properties of Mg, Zn and HA (Callister & Rethwisch, 2011; Eddy et al., 2012; Mezbahul-Islam et al., 2014)	68
Table 3.3	Details of n-heptane	69
Table 3.4	Composition of the materials used to synthesize the Mg-Zn/HA composite	70
Table 3.5	Ion concentrations of human blood plasma and HBSS (Jalota & Bhaduri, 2006; Kokubo & Takadama, 2006)	78
Table 4.1	Average particle size of the raw powders	81
Table 4.2	Lattice parameter of Mg (pm) and Mg-Zn (pm)	84
Table 4.3	Lattice parameter of Mg-Zn alloy and Mg-Zn/HA composites fabricated via different powder mixing techniques	87
Table 4.4	Crystallite size and internal strain of Mg-Zn alloy and Mg-Zn/HA composites	90
Table 4.5	Sintered density and microhardness of Mg-Zn alloy and Mg-Zn/HA composites	95
Table 4.6	Ultimate compressive strength of Mg-Zn alloy and Mg-Zn/HA composites	97
Table 4.7	Corrosion behaviour of Mg-Zn alloy and Mg-Zn/HA composites based on electrochemical polarization	100

Table 4.8	EDX analysis of Mg-Zn alloy and Mg-Zn/HA composites fabricated through various powder mixing techniques after being immersed in HBSS for 24 hours	107
Table 4.9	Optimization of mechanical compatibility and degradation behaviour of Mg-Zn alloy and Mg-Zn/HA composite fabricated through various powder mixing techniques	108
Table 4.10	Lattice parameters of Mg for Mg-Zn/HA composite under various milling time	112
Table 4.11	Data extracted from electrochemical polarization test of Mg-Zn/HA composite fabricated by planetary mill (pm) as a function of milling time	120
Table 4.12	Data extracted from immersion test of Mg-Zn/HA composites fabricated by planetary mill (pm) as a function of milling time	124
Table 4.13	EDX profile of Mg-Zn/HA composites fabricated through planetary mill (pm) through various milling time after being immersed in HBSS for 24 hours	130
Table 4.14	Optimization of mechanical compatibility and degradation behaviour of Mg-Zn/HA composite fabricated through planetary mill (pm)	131

LIST OF FIGURES

		Page
Figure 2.1	The illustration describing the stress shielding phenomenon (Arifin et al., 2014)	16
Figure 2.2	Schematic diagram of artificial hip joint. Femoral head and hip stem were made of titanium and its alloys (Liu et al., 2005)	21
Figure 2.3	Bone screw and bone plate of titanium and its alloys (Liu et al., 2005)	21
Figure 2.4	Femoral bearing head and cups fabricated by F799 CoCrMo alloy (Chen & Thouas, 2015)	25
Figure 2.5	Photograph of different orthopaedic implant geometries made of magnesium alloys (Waizy et al., 2013)	30
Figure 2.6	Status of present research on Fe-based biodegradable metals (Zheng et al., 2014)	35
Figure 2.7	HCP crystal structure of pure Mg (Friedrich & Mordike, 2006)	37
Figure 2.8	Types of implant-tissue response (Ratner et al., 2013)	40
Figure 2.9	Important considerations of alloying element selection of Mg-based alloys development (Chen et al., 2014)	40
Figure 2.10	Mg-Zn binary phase diagram (Friedrich & Mordike, 2006)	47
Figure 2.11	Lattice distortions caused by additions of solute (Campbell, 2008)	49
Figure 2.12	An overview of a macroscopic aspect of a right femur (thigh bone) (A) strong cortical bone on the outside and inner spongy bone (B) a magnified image of the cortical bone and inner spongy bone (Galen et al., 2008)	51
Figure 2.13	General composition of bone (Ratner et al., 2013)	52

Figure 2.14	Schematic diagram indicating the ball motion inside the ball mill	57
Figure 3.1	Flow chart of overall experimental work	67
Figure 3.2	Temperature profile of sintering process	71
Figure 3.3	Completely submerged pellet in HBSS	76
Figure 3.4	Illustrative diagram of samples preparation for corrosion test	79
Figure 3.5	Schematic diagram of electrochemical polarization test	79
Figure 3.6	Actual experimental setup of electrochemical polarization test	79
Figure 4.1	Characteristics peak and morphology (inset image) of as-received Mg elemental powders	82
Figure 4.2	Characteristic peak and morphology (inset image) of as-received Zn elemental powders	82
Figure 4.3	Characteristic peak and morphology (inset image) of as-received hydroxyapatite (HA)	83
Figure 4.4	XRD diffractograms comparing sintered pellets of (i) Mg (pm) and (ii) Mg-Zn (pm) being milled for 4 hours	85
Figure 4.5	XRD patterns of (i) as-milled Mg-Zn (pm) and (ii) sintered Mg-Zn (pm)	86
Figure 4.6	XRD diffractograms of sintered (i) Mg-Zn alloy (pm) and Mg-Zn/HA composites fabricated through (ii) SSP pm (iii) SSP bm and (iv) DSP	87
Figure 4.7	Diffraction patterns comparing (i) as-milled and (ii) sintered Mg-Zn/HA composite fabricated through ball milling (SSP bm) mixing technique	88

Figure 4.8	Crystallite size and internal strain of Mg-Zn alloy and Mg-Zn/HA composites fabricated through various powder mixing techniques	90
Figure 4.9	The optical micrographs of (a) Mg-Zn alloy (pm) (b) Mg-Zn/HA (SSP pm) (c) Mg-Zn/HA (SSP bm) and (d) Mg-Zn/HA (DSP)	94
Figure 4.10	Sintered density and microhardness of Mg-Zn alloy (pm) and Mg-Zn/HA composites fabricated through various powder mixing techniques	95
Figure 4.11	Compressive strength of Mg-Zn alloy and Mg-Zn/HA composites	97
Figure 4.12	Corrosion rate of Mg-Zn alloy and Mg-Zn/HA composites based on electrochemical polarization	99
Figure 4.13	Electrochemical polarization curves of Mg-Zn alloy and Mg-Zn/HA composites	102
Figure 4.14	Degradation rate of Mg-Zn alloy and Mg-Zn/HA composites by immersion test in HBSS	103
Figure 4.15	Micrograph of Mg-Zn alloy (pm) after being immersed in HBSS for 24 hours	105
Figure 4.16	Micrograph of Mg-Zn/HA composite (SSP pm) after being immersed in HBSS for 24 hours	105
Figure 4.17	Micrograph of Mg-Zn/HA composite (SSP bm) after being immersed in HBSS for 24 hours	106
Figure 4.18	Micrograph of Mg-Zn/HA composite (DSP) after being immersed in HBSS for 24 hours	106
Figure 4.19	XRD patterns of sintered Mg-Zn/HA milled by planetary mill (pm) for (i) 2 hours (ii) 4 hours (iii) 6 hours and (iv) 8 hours milling time	110
Figure 4.20	Crystallite size and internal strain of Mg-Zn/HA (pm) under various milling time	111

Figure 4.21	The micrographs of Mg-Zn/HA composite fabricated by planetary mill for (a) 2 hours (b) 4 hours (c) 6 hours and (d) 8 hours	113
Figure 4.22	The plot of sintered density and microhardness of Mg-Zn/HA fabricated by planetary mill (pm) as a function of milling time	117
Figure 4.23	The ultimate compressive strength of Mg-Zn/HA composite fabricated by planetary mill (pm) through various milling time	118
Figure 4.24	Corrosion rate assessment by electrochemical polarization of Mg-Zn/HA fabricated by planetary mill (pm) through various milling time	120
Figure 4.25	Electrochemical polarization curves of Mg-Zn/HA composite fabricated by planetary mill (pm) as a function of milling time	122
Figure 4.26	Degradation rate of Mg-Zn/HA composite fabricated by planetary mill (pm) after being immersed in HBSS for 24 hours	124
Figure 4.27	Micrographs of Mg-Zn/HA milled for 2 hours (a) general view (b) formation of apatite on the surface after being immersed in HBSS for 24 hours	126
Figure 4.28	Micrographs of Mg-Zn/HA milled for 4 hours (a) general view (b) formation of apatite on the surface after being immersed in HBSS for 24 hours	127
Figure 4.29	Micrographs of Mg-Zn/HA milled for 6 hours (a) general view (b) formation of apatite on the surface after being immersed in HBSS for 24 hours	128
Figure 4.30	Micrographs of Mg-Zn/HA milled for 8 hours (a) general view (b) formation of apatite on the surface after being immersed in HBSS for 24 hours	129

LIST OF ABBREVIATIONS

Ar	Argon
bm	Ball mill
BPR	Ball-to-powder ratio
DSP	Double step processing
EDX	Energy dispersive x-ray
FESEM	Field emission scanning electron microscope
HCP	Hexagonal closed-pack
HBSS	Hanks' balanced salt solution
MA	Mechanical alloying
MM	Mechanical milling
PM	Powder metallurgy
pm	Planetary mill
Pt	Platinum
OM	Optical microscope
SCE	Saturated calomel electrode
SSP	Single step processing
SSP pm	Single step processing (planetary mill)
SSP bm	Single step processing (ball mill)
XRD	X-ray diffraction

LIST OF SYMBOLS

\AA	Angstrom
2θ	Diffraction angle
E_{corr}	Corrosion potential
e^-	Electron
a, c	Lattice parameter
HA	Hydroxyapatite
HV	Vickers hardness
i_{corr}	Corrosion current density
Mg	Magnesium
nm	Nanometers
Zn	Zinc

**SIFAT-SIFAT KESERASIAN BIO KOMPOSIT Mg-Zn/HIDROKSIAPATIT
DIFABRIKASI MELALUI TEKNIK CAMPURAN SERBUK YANG
BERBEZA**

ABSTRAK

Kajian ini bertujuan untuk mengkaji sifat mekanikal dan biodegradasi komposit magnesium-zink/hidroksiapatit (Mg-Zn/HA) yang difabrikasi melalui teknik-teknik campuran serbuk yang berbeza. Teknik campuran serbuk komposit tersebut dibahagikan kepada dua, iaitu pemprosesan langkah tunggal yang melibatkan teknik pengalioian mekanikal dan pengisaran mekanikal, sementara pemprosesan langkah berganda melibatkan gabungan pengalioian mekanikal dan pengisaran mekanikal. Sifat-sifat mekanikal dan biodegradasi komposit tersebut didapati mencapai tahap terbaik apabila serbuknya dihasilkan melalui teknik pengalioian mekanikal dengan masa pengisaran selama 4 jam dan kelajuan kisanan pada 220 putaran per minit. Komposit yang dihasilkan melalui kaedah pengalioian mekanikal kemudiannya dikisar dengan tempoh yang berbeza untuk mengkaji kesan masa kisanan kepada sifat komposit tersebut. Komposit Mg-Zn/HA yang difabrikasi melalui kaedah pengalioian mekanikal dan dikisar selama 6 jam mempunyai kombinasi terbaik dari segi penambahbaikan pada sifat kakisan dan sifat mekanikal, iaitu kadar kakisan terendah (0.1487 mm/tahun melalui pengutuban elektrokimia dan $0.34 \times 10^{-3} \text{ mm/tahun}$ melalui ujian rendaman) dan kekerasan mikro (64 HV) juga kekuatan mampatan (193 MPa) yang sesuai. Komposit biodegradasi yang difabrikasi melalui teknik pengalioian mekanikal selama 6 didapati sangat sesuai untuk aplikasi implan, berdasarkan kekuatan mekanikal dan ciri-ciri biodegradasi yang baik. Dari segi keserasian bio, secara keseluruhannya komposit Mg-Zn/HA mempamerkan sifat bioaktiviti melalui

ujian rendaman yang dijalankan, namun masa rendaman selama 24 jam didapati tidak mencukupi untuk menghasilkan komposit yang mempunyai bioaktiviti yang dapat memenuhi keperluan pemineralan awal tulang iaitu nisbah Ca:P daripada 1:1 kepada 1:1.67. Namun begitu, komposit Mg-Zn/HA yang dihasilkan melalui kaedah pemprosesan langkah tunggal pengisaran mekanikal (nisbah Ca: P sebanyak 1.76) didapati mempunyai bioaktiviti yang paling tinggi mengatasi komposit-komposit yang dihasilkan melalui kaedah pemprosesan langkah tunggal pengalioian mekanikal dan pemprosesan langkah berganda.

**PROPERTIES OF BIOCOMPATIBLE Mg-Zn/HYDROXYAPATITE
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ABSTRACT

This work aims to investigate the mechanical performance and biodegradation behaviour of magnesium-zinc/hydroxyapatite (Mg-Zn/HA) composite that was fabricated via different powder mixing techniques. The powder mixing techniques of the composite was mainly divided into two, the first one is single step processing which involved the mechanical alloying and mechanical milling techniques, while the second is double step processing which involved the combination of mechanical alloying and mechanical milling. The optimum mechanical properties and biodegradation behaviour of the composite was achieved when the powders were prepared using mechanical alloying technique with the milling time of 4 hours and milling speed of 220 rpm. The composite prepared through the mechanical alloying technique was then subjected to various milling time to investigate the effect of milling time towards the properties of the composite. Mg-Zn/HA composite which was fabricated through the mechanical alloying technique and milled for 6 hours attained the best combination of improved corrosion behaviour as well as mechanical properties which is due to lowest corrosion rate (0.1487 mm/year by electrochemical polarization and 0.34×10^{-3} mm/year by immersion test) and acceptable microhardness (64 HV) and compressive strength (193 MPa). Fabrication of the biodegradable composite through the mechanical alloying technique within the 6 hours milling time was found to be suitable for the implant application, due to good mechanical strength and biodegradation behaviour. In term of biocompatibility, generally Mg-Zn/HA

composite possessed good bioactivity characteristics through the immersion test, however immersion time of 24 hours was found to be insufficient to produce composites that can satisfy the initial bone mineralization which the Ca:P ratio in the range of 1:1 to 1:1.67. However, Mg-Zn/HA composite that was fabricated through single step processing of mechanical milling (Ca:P ratio of 1.76) was found to have the highest bioactivity over the other two composites that was fabricated through single step processing of mechanical alloying and double step processing.

CHAPTER ONE

INTRODUCTION

1.1 Introduction

Biomaterials are defined as artificial or natural materials used to replace the lost or injured biological structure, with aims to restore its form and function. It is used in different parts of the human body as stents in blood vessel, artificial valves in heart, replacement implants in knees, hips, elbows, shoulders, ears and orodental structures (Geetha et al., 2009). Along with the advancement in the medical technology, several types of materials such as metals, ceramics, polymers and composites have been extensively utilized for implants into human body (Adeosun et al., 2014).

Biomaterial implants can either be used to replace a diseased part or to promote healing process. Implants are usually divided into two types, degradable or permanent implant, based on how long the implants are required to remain present in human body (Manivasagam et al., 2016). Permanent metallic implants available in the medical market such as titanium alloys, stainless steel 316L and cobalt-chromium alloys always require the implants to stay permanently in the body. In situations where the permanent implant is just required until the healing process is complete, the implant is no longer useful, thus conducting the secondary surgery is crucial to remove the implant (Park & Bronzino, 2003). The development of biodegradable implants clearly can obviate the need of secondary surgery, thus reduces the cost of health care and patient morbidity.

There is a wide variety of biomaterials introduced, mainly ceramics-based, polymers-based and metallic-based. Each of these three classes of materials possess their own unique characteristics to fit into the application of biomaterials. Ceramics-

based biomaterials, such as widely used calcium phosphate-based bioceramics, is acknowledged for its superior bioactivity (an ability of the implant material that allow the adherence and proliferation of bone cells on its surface and pores) and osseointegration (ability of the implant to be structurally and functionally bonded to the living bone (Bose et al., 2012; Parithimarkalaignan & Padmanabhan, 2013). Despite of the qualities of bioceramics, it exhibited poor mechanical properties and brittleness, which is strictly limits their application in load-bearing implants (Ibrahim et al., 2017).

As for polymer-based biomaterials, the major concern is the possibility of local inflammation due to the polymer itself or through its degradation products. The biodegradation and resorption process of the polymer begins once implanted in human body, and the process also caused the acidic by-products to be released, thus results in inflammatory reactions (Sheikh et al., 2015). Inherent poor mechanical properties of polymer and maintaining its mechanical strength until the bone is completely healed also becoming one of the major challenges faced in the researches of polymeric-based biodegradable implants, in addition to design an implant that slowly degrade in body environment (Cheung et al., 2007; Adeosun et al., 2014). These problems caused the application of polymer-based biomaterials to be limited to be used for load-bearing applications. Contrast to metal-based biomaterials, this class possess the sufficient mechanical compatibility, with excellent biocompatibility such as titanium and its alloys, cobalt-based alloys, stainless steels and new generation of biodegradable magnesium. From a perspective of biological, numerous researches reported that more new bone is formed when using bioceramics and magnesium alloys as bone fixation devices compared to polymers. This can be associated to the osteoconductive and osseoinductive of the ceramics and biocompatibility behaviour of magnesium alloys

(Sheikh et al., 2015).

The use of permanent or non-biodegradable metal-based implants such as titanium and its alloys, stainless steels and cobalt-based alloys are very dominant in the medical market due to their excellent mechanical performance and bioinertness. The use of metal-based medical implants can be traced back in 1920's, which stainless steel alloy was used as implant materials owing to its superior corrosion resistance. Since the discovery, researchers starting to focus on developing high corrosion resistant materials for medical application. This was the era of glorious findings of 316L stainless steels, cobalt-based alloys and titanium alloys, which all of the materials were proved to have excellent mechanical properties and also good biocompatibility in human body (Ibrahim et al., 2017). Even though these types of metals are predominant in the orthopaedic market, every materials possess their own advantages and disadvantages. The most highlighted issues associated with the use of these permanent implant are stress shielding problem and the needs of performing secondary surgery to remove the implant after healing process is completed (Chen & Thouas, 2015). These issues quickly becoming the driving forces to the development of new generation of biodegradable metals.

The challenge of developing the biodegradable metals explored three types of most promising metals, such as iron based alloy (Li et al., 2014), zinc based alloy (Mostaed et al., 2016) and magnesium based alloy (Witte et al., 2008; Feyerabend, 2014). The use of biodegradable metal as biomaterials has been discovered since 200 A.D. in Europe, which Fe dental implant was found to be properly integrated into bone (Zheng et al., 2014). Since Fe was reported to experience slower degradation rate based on animal experiments, surgeons have diverts the use of Fe to Mg and its alloy for countless clinical applications, for almost 100 years (Zhen et al., 2013; Li et al., 2014).