DEVELOPMENT OF BIODEGRADABLE Mg-Zn/HA COMPOSITE VIA MECHANICAL ALLOYING

by

EMEE MARINA BINTI SALLEH

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Emee Marina Binti Salleh,
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LIST OF ABBREVIATIONS

Ar	Argon
BPR	Ball to powder weight ratio
BSE	Back scattered electron
DSC	Differential Scanning Calorimetry
EDX	Energy Dispersive X-ray
FESEM	Field Emission Scanning Electron Microscopy
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
MA	Mechanical Alloying
MMC	Metal Matrix Composite
PM	Powder Metallurgy
Rpm	rotation per minute
XRD	X-ray Diffraction

LIST OF SYMBOLS

Å	Angstrom
2θ	Diffraction angle
e^-	Electron
a, c	Lattice parameter
Hv	Vickers hardness
V	Voltage
E_{corr}	Corrosion potential
R_p	Polarization resistance
T_m	Melting temperature

PEMBANGUNAN KOMPOSIT BIODEGRADASI Mg-Zn/HA MELALUI PENGALOIAN MEKANIKAL

ABSTRAK

Kajian ini bertujuan untuk membangunkan bahan logam biodegradasi menggunakan pengaloian mekanikal (MA). Magnesium (Mg) adalah calon yang paling menjadi tumpuan bagi aplikasi bioperubatan berdasarkan kelebihan sifat-sifatnya berbanding bahan bio yang lain. Tetapi kadar degradasi yang cepat dalam persekitaran fisiologi menghadkan prestasinya. Oleh itu, Mg telah dialoikan dengan zink (Zn) bagi meningkatkan kerintangan kakisan dan mengekalkan integritimekanikal. Dalam mencapai sasaran ini, bahan bio berasaskan Mg telah difabrikasi melalui MA diikuti dengan pemadatan di bawah 400 MPa dan pensinteran pada 350°C. Empat parameter MA iaitu masa pengisaran, kelajuan pengisaran, nisbah berat bola kepada serbuk (BPR) dan kandungan Zn telah disiasat. Ketumpatan 1.80 hingga 1.99 g/cm^3 yang setara dengan tulang manusia dan kekerasan mikro yang lebih baik daripada Mg tulen (39.30 HV) iaitu antara 53.76 hingga 94.37 HV telah diperolehi. Berdasarkan rekabentuk faktorial pecahan (FFD), keadaan MA optimum dalam menghasilkan aloi Mg-Zn dicapai dengan menambah 6.5 wt% Zn yang dikisar selama 5 jam pada 200 rpm dengan 7: 1 BPR. Kekuatan mampatan yang lebih tinggi (249.28 MPa) dan kadar kakisan yang lebih rendah (1.13 x10^{-2} mm/y) daripada Mg tulen (178.04 MPa dan 13.77 x10^{-2} mm/y) telah diperolehi. Penambahbaikan sifat-sifat tersebut telah dicapai dengan menambah 10 wt% HA ke dalam aloi Mg-6.5wt%Zn. Kekuatan mampatan (292.33 MPa) dan kadar degradasi (0.72 x10^{-2} mm/y) yang bagus diperolehi. Komposit Mg-Zn/HA memberikan bioaktiviti paling tinggi dengan nisbah Ca:P sebanyak 1:1.46 diikuti oleh aloi Mg-Zn 1:1.29 memenuhi keperluan pemineralan awal tulang iaitu 1:1 kepada 1:1.67.

DEVELOPMENT OF BIODEGRADABLE Mg-Zn/HA COMPOSITE VIA MECHANICAL ALLOYING

ABSTRACT

This work aims to develop biodegradable metallic material using mechanical alloying (MA). Magnesium (Mg) is the most highlighted candidate for biomedical applications because of its advantageous properties as compared with other biomaterials. But a rapid degradation rate in physiological environment limits its performance. Hence, Mg was alloyed with zinc (Zn) in order to improve its corrosion resistance and sustain its mechanical integrity. In achieving the target, Mg based biomaterials were fabricated using MA followed by compaction under 400 MPa and sintering at 350 °C. Four MA parameters namely milling time, milling speed, ball-to-powder-weight ratio (BPR) and Zn content were investigated. The density of 1.80 to 1.99 g/cm^3 which is comparable to human bone and improved microhardness of 53.76 to 94.37 HV as compared to pure Mg (39.30 HV) were attained. By fractional factorial design (FFD), an optimized MA condition in producing Mg-Zn alloy was achieved by adding 6.5 wt% Zn and milled for 5 hours at 200 rpm with 7:1 BPR. A higher compressive strength (249.28 MPa) and lower corrosion rate (1.13x10^{-2} mm/y) than pure Mg (178.04 MPa and 13.77 x10^{-2} mm/y) were acquired. A further improvement of those properties was attained by incorporating 10 wt% HA into optimized Mg-6.5wt%Zn alloy. An enhanced compressive strength (292.33 MPa) and degradation rate (0.72 x10^{-2} mm/y) was attained. Mg-Zn/HA composite provided the highest bioactivity due to highest Ca:P ratio of 1:1.46 followed by Mg-Zn alloy of 1:1.29 which is in agreement with the required Ca:P ratio of 1:1 to 1:1.67 for initial bone mineralization.

CHAPTER 1

INTRODUCTION

1.1 Introduction

The use of metallic materials for medical implants can be traced back to the 19th century, leading up to the era when the metal industry began to expand during the Industrial Revolution (Kraus *et al*., 2012). The development of metallic implants was primarily driven by the demands for approaches to bone repair, typically internal fracture fixation of long bones. However, almost no attempts of implanting metallic devices, such as spinal wires and bone pins made from iron, gold or silver, were successful until Lister's aseptic surgical technique was implemented in the 1860s (Xin *et al*., 2011). Since then, metallic materials have predominated in orthopaedic surgery, playing a major role in most orthopaedic devices, including temporary devices (e.g. bone plates, pins and screws) and permanent implants (e.g. total joint replacements) (Zeng *et al*., 2008).

The conventional metallic implant materials namely titanium (Ti) alloys, stainless steels and (Co-Cr) alloys possess excellent mechanical capabilities and highly resistance to corrosion (Hermawan *et al*., 2010; Castellani *et al*., 2011; Anghelina *et al*., 2013). However, when these conventional alloys are used as temporary implant devices, a second surgical procedure is required for the implant removal after the traumatized tissues have healed which markedly increases the health care cost. Besides, there is an increased risk of local inflammation due to potential release of cytotoxic ions as well as the physical irritation due to the rigidity of these conventional implants (Li *et al*., 2012).

Currently, the development of new biodegradable metallic biomaterials combining excellent strength retention properties and improved biocompatibility for several applications such as stents for blood vessels and screws and plates for fixing hard tissues are highly desirable (Hort *et al*., 2010). The main driving force to develop biodegradable implants is an elimination of secondary surgical procedure as they have ability to biodegrade in the bioenvironment during the implantation duration. Hence, the paradigm of metallic implants must be highly inert and corrosion resistance has now been challenged by advent of the new class of degradable biomaterials (Lei *et al*., 2012).

Magnesium (Mg) and its alloys have attracted increasing attention as innovative biodegradable materials for temporary orthopaedic implants due to their excellent biological performance and biodegradability in bioenvironment. In terms of mechanical properties, Mg is well compatible with natural bone. Its density (1.74 g/cm^3) and Young's modulus (40 - 48 GPa) are closer to those of bone (1.8 - 2.1 g/cm^3 and 40 - 57 GPa) than in the case of other currently used biomaterials for fixation of fractured bone, like Ti alloys, stainless steels or Co-Cr alloys at approximately 100, 180 and 210 GPa respectively (Li *et al*., 2004; Sudhakar, 2005; Gupta and Sharon, 2011). In term of biocompatibility, Mg ions are present in a large amount in the human body and they are involved in many metabolic reactions and biological mechanisms. The human body usually contains Mg at approximately 35 g per 70 kg body weight and the daily demand for Mg is about 375 mg (Gill *et al*., 2011).

An attractive characteristic of Mg due to its corrodibility makes it as a potential biodegradable metallic implant. However, the fast degradation rate of Mg in human bioenvironment containing chloride anions (Cl^-) about 100 mmol/l

concentration limited its clinical application (Wang *et al*., 2012). A rapid degradation rate during implantation results in a deterioration of its mechanical performance which then causes a worst injury to a traumatized hard tissue. Elemental alloying is one of the most effective way to improve corrosion resistance as well as mechanical properties of Mg. Mg alloys containing aluminium (Al) and rare earth (RE) elements showed relatively high strength and good corrosion resistance against sodium chloride (NaCl) solution such as AZ61 (Mg-6wt%Al-1wt%Zn) and WE43 (Mg-(3.7-4.4wt%) Y-(2.4-4.4 wt%) E-0.42wt%Zr) alloys (Gupta and Sharon, 2011). However it has been reported that the Al release from Mg alloy into human body could induce Alzheimer's disease, allergic reaction and neurological disorder (Silva *et al*., 2004; Zhang *et al*., 2010b).

The exploration of high strength biodegradable Mg alloys without Al for medical implants has gained great attention in the past years and it is still ongoing. In certainty, there are only a small number of elements that can be tolerated in human body and can also retard the biodegradation of Mg alloys including calcium (Ca), manganese (Mn), zinc (Zn) and perhaps very small amount of low toxicity rare earth including niobium (Nb) and tantalum (Ta). Zn has been found to be next to Al in strengthening effectiveness as an alloying element in Mg. Adding Zn to Mg may improve both tensile strength and the corrosion resistance (Yin *et al*., 2008). Biologically, Zn is a necessary microelement and component of many amino acids and nucleic acids syntheses of human body. Moreover, Zn is an inexpensive alloying element with a potential of accelerating the metabolism of cells and bone healing (Jang *et al*., 2013). Therefore, it is a contributing approach to develop Mg-Zn alloy with good corrosion resistance for a temporary bioimplant in biomedical applications.

Typically, metallic materials including Mg based alloy have been produced using conventional liquid state processing such as casting (Zeng *et al*., 2011; Lei *et al*., 2011; Kubok *et al*., 2013). However due to some defects that are usually found in cast Mg alloy causing poor final properties, further treatments may be required to improve the situation. Recently, powder metallurgy (PM) process coupled with mechanical alloying (MA) to synthesize Mg based alloys is of growing interest (Gonzalez *et al*., 2012; Patel and Morsi, 2012). This technique is a solid state powder metallurgical process in which elemental powders are being alloyed by repeated deformation mechanism under frequent mechanical impacts (Suryanarayana, 2001). MA is one of the simplest and most economical routes for the fabrication of nanocrystalline materials. In addition, MA offers the possibility to scale up the quantity of processed material to tonnage amount and be employed for the processing of nearly all types of materials (Yadav *et al*., 2012). This makes MA the ideal processing route for small as well as for large scale production of nanocrystalline materials.

Another important point for a biomaterial is the ability of the implant to establish bonding with the surrounding bone tissue which is the bioactivity of the implant (Khanra *et al*., 2010). Therefore, it seems necessary to increase the bioactivity of Mg based alloys by introducing bioactive materials into the matrix (Khalil, 2012). Bioactive ceramic such as hydroxyapatite (HA; $C_{10}(PO_4)_6(OH)_2$) has been widely used as an implant material for hard tissues owing to its excellent biocompatibility to human tissues because it has similar structure with the mineral part of bone. HA has calcium (Ca) and phosphorus (P) elements in its hexagonal structure (Veljovic *et al*., 2009). These elements present the inorganic of the bone. Therefore, strong bonds are spontaneously generated to living bone via an apatite