STUDY ON MECHANICAL PROPERTIES AND CORROSION BEHAVIOR OF POROUS MAGNESIUM ALLOY FOR BIOMEDICAL APPLICATION

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Study on Mechanical Properties and Corrosion Behavior of Porous Magnesium Alloy for Biomedical Application.

by

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LIST OF ABBREVIATIONS

Al	Aluminium
Al_2O_3	Alumina
ANOVA	Analysis of Variance
Cu	Cuprum
Cl^-	Chloride Ion
Cr	Chromium
CaO	Calcium Oxide
$(CONH_2)_2)$	Carbamide
DOE	Design of Experiment
EDX	Energy Disperse X-ray
Fe	Iron
Mg	Magnesium
Mo	Molybdenum
MgO	Magnesium Oxide
$MgCl_2$	Magnesium Chloride
$Mg\ (OH)_2$	Magnesium Hydroxide
N	Nitrogen
Ni	Nickel
Nb	Niobium
NaCl	Sodium Chloride
NH_4HCO_3	Ammonium Hydrogen carbonate
OA	Orthogonal Array
PLLA	Poly-l-lactic-acid

PLGA	Poly-l-glycolic-acid
PMMA	Polymethylmetacrylate
P_2O_5	Phosphorus Pentoxide
SEM	Scanning Electron Microscope
SBF	Simulated Body Fluid
SiO_2	Silicon Dioxide
S/N	Signal to Noise ratio
Ti	Titanium
Tcp	Tricalcium Phosphate
UHMWPE	Ultra High Molecular Weight Polyethylene
V	Vanadium
XRD	X-Ray Diffraction
Zn	Zinc
ZrO_2	Zirconia

LIST OF SYMBOLS

ρ	Density
ρ_s	Density of Porous Material
n	Number of Measurement for each trial
x	Individual measured output
W_a	Dry weight
W_b	Submerged weight
W_c	Saturated weight

Kajian ke atas Sifat Mekanikal dan Kelakuan Kakisan Aloi Magnesium Berliang untuk Aplikasi Bioperubatan

ABSTRAK

Trend dalam aplikasi bioperubatan semakin meningkat terhadap bahan implan biodegradasi dan prestasi implan adalah sangat berkaitan dengan sifat-sifat sesuatu bahan. Bahan bio logam mempunyai ciri-ciri yang sangat baik terhadap kekuatan mekanikal yang tinggi dan lebih diutamakan untuk membantu pembaikan atau penggantian tisu tulang yang telah dihidapi penyakit atau rosak. Walau bagaimanapun, bahan bio logam yang sedia ada seperti (keluli tahan karat (316L), aloi kobalt kromium (Co-Cr-Mo dan Co-Ni-Cr-Mo) dan aloi titanium (Ti6Al4V)) adalah terhad dari segi sifat biodegradasi dan kehadiran implan untuk jangka panjang akan menyebabkan kesan berbahaya kepada tubuh manusia disebabkan oleh ketidaksepadanan modulus diantara bahan implan dan sekitar tisu tulang. Oleh itu, aloi magnesium (Mg) adalah menarik untuk dijadikan sebagai bahan implan kerana mempunyai sifat yang baik seperti, biodegredasi dan biokompatibiliti, kekuatan mekanikal setanding dengan tulang semulajadi dan ringan. Pada masa kini, bahan implan berliang juga mempunyai potensi yang menarik untuk aplikasi bioperubatan. Aplikasi keliangan terhadap bahan implan akan mengurangkan ketidaksepadanan diantara bahan logam dan sekitar tisu tulang, dimana struktur berliang ini dapat memberikan penetapan biologi yang stabil dan meningkatkan pertumbuhan tisu tulang melalui struktur berliang tersebut. Kajian ini telah dijalankan untuk menghasilkan aloi Mg berliang daripada serbuk unsur (aloi Mg dan ammonium bikarbonat (NH_4HCO_3) melalui kaedah metalurgi serbuk berdasarkan teknik pengisi ruang. Teknik ini menggunakan dua fasa proses pensinteran iaitu untuk memanaskan sampel pada suhu rendah untuk membakar bahan pengisi ruang untuk membuat liang pada sampel dan akhirnya di bakar pada suhu tinggi untuk pensinteran sampel. Tujuan kajian ini adalah untuk mengkaji kesan parameter pemprosesan terhadap keliangan, ketumpatan, mikrostruktur dan sifat mekanik bahan aloi Mg berliang yang telah difabrikasi. Ujian in-vitro juga telah dijalankan dengan menggunakan larutan cecair badan simulasi (SBF) untuk menentukan sifat kakisan dan sifat biodegradasi daripada aloi Mg berliang. Rekabentuk eksperimen (DOE) dengan menggunakan kaedah Taguchi telah digunakan untuk menentukan kesan parameter pemprosesan (pensinteran suhu, kadar pemanasan dan masa pensinteran) terhadap prestasi mekanikal aloi Mg berliang dan menentukan set parameter yang dikehendaki untuk menjalankan eksperimen. Hasil daripada kajian ini mendapati bahawa suhu pensinteran menyumbang kepada peratusan yang paling tinggi diikuti dengan kadar pemanasan dan masa pensinteran. Suhu pensinteran yang lebih tinggi akan meningkatkan sifat mekanikal aloi Mg berliang yang setanding dengan tulang 'cancellous'. Pemerhatian ini disokong oleh ujian mampatan, ujian kekerasan, mikrostruktur dan analisis pembelauan sinar-X (XRD). Hasil ujian-ujian ini terhadap aloi Mg berliang telah menunjukkan nilai julat tipikal untuk bahan yang digunakan dalam aplikasi bioperubatan, iaitu untuk kekuatan mampatan adalah (1-15MPa), saiz liang adalah (200-500μm) dan peratusan keliangan adalah (42% -64%). Manakala, ujian in vitro telah menunjukkan keupayaan aloi Mg berliang untuk degradasi secara

beransur-ansur di bawah kawalan pH. Oleh itu, penemuan ini menunjukkan bahawa, aloi Mg berliang adalah sesuai dan berpotensi untuk digunakan dalam aplikasi bioperubatan.

Study on Mechanical Properties and Corrosion Behavior of Porous Magnesium Alloy For Biomedical Application

ABSTRACT

The trend in the applications of biomedical has been increasing for biodegradable implants material and the performance of an implant is highly related to the properties of the material. Relying on an excellent properties in high mechanical strength, metallic biomaterials is preffered to assist with repair or replacement of bone tissue that has become diseased or damaged. However, previously metallic biomaterials (stainless steel (316L), cobalt chromium alloy (Co-Cr-Mo and Co-Ni-Cr-Mo) and titanium alloy (Ti6Al4V)) are limited in terms of degradability and the presence of long term implants will leads harmful effect to human body due to mismatch between modulus of implant materials and surrounding bone tissue. Thus, magnesium (Mg) alloy is attractive to serve as implant materials due to its favorable properties such as, biodegradability and biocompatibility, its mechanical strength comparable to natural bone and light weight. Recently, porous material have attracted significant attentions in biomedical applications. The application of porosity into the implant will reduce the mismatch between metallic materials and surrounding bone tissue, as the porous structure able to provide stable biological fixation and enhance bone ingrowth through porous network. The present study was carried out to develop porous Mg alloy from elemental powder (Mg alloy and ammonium bicarbonate (NH_4HCO_3) through powder metallurgy method based on the space holder technique. This technique utilized two phase of sintering process which is to heat treated the sample at low temperature to burn out the space holder to create pores and eventually sintered at high temperature. The aims of this research are to investigate the effect of processing parameters on the porosity, density, microstructure and mechanical properties of fabricated porous Mg alloy body. An in vitro test was conducted using simulated body fluid (SBF) solution to determine the corrosion and biodegradable behavior of fabricated porous Mg alloy. A design of experiment (DOE) using Taguchi method was initially used to determine the effect of processing parameters (sintering temperature, heating rate and sintering time) on the mechanical performance of porous Mg alloy and the desired setting parameters to set up the experiment. It was found that sintering temperature contribute to the highest percentage followed by heating rate and sintering time. Higher sintering temperature, on the other hand, leads to a better mechanical performance of porous Mg alloy which is comparable to the cancellous bone. This observation is supported by compression, hardness, microstructure and x-ray diffraction (XRD) analysis. It should be noted that the range of compressive strength (1-15MPa), pore size (200-500µm) and porosity percentage (42%-64%) exhibited in this study for the fabrication of porous Mg alloy showed the typical range of values noted for materials used in biomedical applications. In vitro test demonstrated the ability of porous Mg alloy to degrade gradually under pH control. These findings suggest that, porous Mg alloy is suitable for biomedical applications.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The developments of artificial implants have been continuously studied for a wide functional performance in biomedical applications. Indeed, the types and properties of biomaterials are still being examined to the requirements of artificial implant products. This is mainly due to the current huge demand in biomedical applications due to the major bone losses, affected by cancer trauma and other diseases (Mediaswanti et al., 2013; Nasab et al., 2010). It is estimated that, by end of the year 2030, total hip and knee replacement will grow by 137% and 601% respectively. The prevalence of this problems will leads to revision surgery which require high costs, patient morbidity and furthermore the success rate is rather small. Accordingly, the development of new biocompatible, biodegradable implant materials with zero level of revision surgery is highly anticipated.

There is a recent and fast growing interest in the use of biodegradable metals for biomedical application due to their reliability in mechanical performance. Mg alloy with outstanding properties than other current implant materials such as degradable polymers and ceramics, non-degradable stainless steel (316L), cobalt chromium alloy (Co-Cr-Mo and Co-Ni-Cr-Mo) and titanium alloy (Ti6Al4V). Although polymers and ceramics shows the appealing properties of biodegradable and osteoconductive, yet this materials are inappropriate to be applied in load bearing applications due to brittleness, low fracture toughness and are not as resilient (Eddy et al., 2012; Nouri, 2010). On the contrary, the aforementioned metallic biomaterials are notably known to be stronger, ductility and have better corrosion resistance. A matter of concern by using these alloys are the possible released of toxicity ions and debris production from this alloys able to initiate adverse reaction to the soft tissue (Alvarez & Nakajima, 2009). More importantly, current metallic biomaterials are limited in terms of degradability and the presence of long term implants will leads harmful effect to human body due to stress shielding between implant materials and surrounding bone (Wang et al., 2013). Therefore, owing to its favorable properties, Mg alloy with biocompatible, biodegradable, mechanical strength comparable to natural bone and light weight have shown the most potential biodegradable implants over current implant materials.

Regardless of the great progress in biomedical applications, fixation of the implants to the bone host remains a problem. The issue of mismatch between bone and different implant materials might cause stress shielding surrounding the bone tissue which leads to bone resorption in dense metallic implants (Geetha et al., 2009). Therefore, by introducing porosity in implantable materials, able to impart mechanical properties closer to those natural bone (Nagels & Stokdijk, 2003), particularly in the low Young's modulus which resemble the natural bone and may reduce or eliminate the stress shielding problem. The structure of porous metals is expected to be osteoconductive, which provide stable biological fixation and enhance bone ingrowth through porous network while remaining light weight (Wu et al., 2012). More importantly, the porosity permits body fluids transportation to induce bone healing and new bone tissue will able to incorporated to the implant. An ideal porous implant is expected to have sufficient strength in order to sustain stress and physiological loading during the implantation period, biocompatibility and osteoconductivity to allow integration between implant and bone without causing any harmful effect to the body, biodegradable and bioresorbable preferably at a controlled rate, eventually being replaced by new bone tissue (Bose et al., 2012).

To date, the manufacturing of porous cellular metals has primarily focused on the fabrication of random architectures (e.g. cellular foams) from different materials, such as Ti, Ti alloys, tantalum and aluminium (Al). For example, a three dimensional (3D) fibre deposition and powder sintering method was used to produce porous Ti-6Al-4V structures with interconnected pores and porosity of up to 90% (Li et al., 2006), whereas, in a different study, a multi-stage rapid prototyping technique produced porous Ti scaffolds aimed for orthopaedic applications (Ryan et al., 2006). However, while these random porous architectures may meet mechanical requirements, they are generally not suitable for the purposes of optimising scaffold properties such as porosity, stiffness and permeability, and do not allow precise control over pore architecture. These random porous structures typically have homogenous mechanical and biological properties at the macro level, but not at the micro level. This results in undesirable behaviour in the material, such as reduced effective stress and strut bending and twisting (Zhu et al., 2002).

Numerous techniques are feasible to manufacture porous Mg alloy, however the selection techniques is dependent on the quality and cost. Powder metallurgy route which use space holder filler to generate porous structure is the most preferable techniques. The properties of the fabricated porous structure can be altered by controlling the size, shape and quantity of the space holder material, which essentially can provide desired characteristics to tailor the biomedical application (Čapek & Vojtěch, 2013b; Hao et al., 2009).

Despite the great properties of Mg as biodegradable materials, concerns over the rapid dissolution rate in electrolytic and aqueous environment has been observed which result in potentially leading hyper magnesia (Staiger et al., 2006). Therefore, a number of methods have been investigated in order to improve the corrosion rate of Mg, primarily by alloying Mg with other elements hence allow the biomedical implant to maintain its mechanical integrity until the surrounding tissues completely heals.

1.2 Problem statement

i. Different techniques are available to manufacture porous cellular materials, such as fibre deposition, rapid prototyping and 3D printing. However, due to the difficulties in processing of Mg alloy, very few studies have focused on developing reliable, safe and relatively low cost methods for manufacturing porous Mg alloy by powder metallurgy.

ii. Rapid degradation rate of Mg in physiological environment.

1.3 Objectives

The objectives of this study are highlighted below:

i. To investigate the effect of processing parameter on the porosity, density, microstructure and mechanical properties of fabricated porous Mg alloy bodies.

ii. To study the corrosion and biodegradable behavior of fabricated porous Mg alloy using SBF solution.

1.4 Scope of the Research Study

This research will focus on the fabricated of porous Mg alloy, which can be serve as an implant materials through powder metallurgy routes utilizing space holder technique, with Mg alloy powder as a matrix and NH_4HCO_3 as a space holder filler. Design of experiment using Taguchi method is utilized to obtain desired parameter for experimental setup. Properties such as porosity, compressive strength, hardness and physical of the fabricated porous Mg alloy which compatible for biomedical applications will be evaluated. Immersion test using simulated body fluid (SBF) solution will be performed to evaluate the corrosion behavior of porous Mg alloy.

1.5 Structure of Dissertation

The content of this dissertation is separated into five chapters as follows:

Chapter 1 of this dissertation presents the background to the research study and problem statement. Subsequently, the objectives, the scopes and significant of study are defined in this chapter.

Chapter 2 presents the literature search on theoretical background related to the studies. This chapter describes the types of biomaterial for biomedical applications, with solid and porous structure of existing implants being reviewed in details.

Chapter 3 elaborates the experimental procedure, specifically the material selection and fabrication technique of porous samples. Sample characterizations including mechanical test, microstructure evaluation, corrosion behavior test and phase analysis are presented.