EFFECT OF HEAT TREATMENT ON THE MICROSTRUCTURES AND CORROSION BEHAVIOUR OF QUATERNARY Mg-2.2Zn-3.7RE-0.5Ca ALLOYS FOR BIOMEDICAL APPLICATIONS

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Specially dedicated to *Mak* and *Ayah*

And family members

For their support and inspiration

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ABSTRACT

Some of magnesium alloys have poor corrosion resistance in ambient air or aqueous environment due to their electrochemically active state. Different surface coating techniques, alloying and heat treatment are the ways to enhance the corrosion performance of magnesium alloys. The goal of this research is to study the characteristic and corrosion behaviour of quaternary Mg-Zn-RE-Ca alloys due to thermal treatment. The effects of two types of heat treatments, T4 (solution treatment) and T6 (aging treatment) on corrosion behaviour of quaternary Mg-2.2Zn-3.7RE-0.5Ca alloys were studied. Microstructural evaluations were characterized using optical microscope and scanning electron microscope (SEM). The compositions of the material were determined by X-ray diffractometer (XRD) and energy dispersive X-ray spectrometer (EDS). The corrosion features were examined *in-vitro* by potentiodynamic polarization, pH variation and immersion test in Hank's solution at room temperature (27 °) with pH 7.4. It was found that α-Mg matrix, eutectic phase $Mg_{12}RE$ and $Mg_{29}Zn_{25}RE$ with intermetallic IM1 precipitates formed in the quaternary Mg-Zn-RE-Ca system. T4 treatment produced supersaturated α-Mg while the secondary phases were mostly dissolved in the matrix. The lamellar structure which composed of IM1 precipitated after T6-treated were detected along the grain boundaries. The hardness of quaternary magnesium based alloy decreased significantly after T4 treatment and increased after T6 treatment. The pH value for T6 treatment shows the lowest after 96 hours immersion in Hank's solution. Electrochemical measurement shows that T4 and T6 treatments increased the corrosion resistance of the quaternary magnesium alloy. It was found that the corrosion products consists mainly pure magnesium, magnesium hydroxide ($Mg(OH)_2$), and hydroxyapatite (HA).

ABSTRAK

Sebahagian daripada aloi magnesium mempunyai ketahanan kakisan yang teruk apabila berada dalam persekitaran yang berudara atau persekitaran yang berair kerana mempunyai tahap elektrokimia yang aktif. Teknik salutan permukaan yang berbeza, pengaloian dan rawatan haba adalah kaedah untuk meningkatkan prestasi kakisan terhadap aloi magnesium. Matlamat kajian ini adalah untuk mengkaji ciri-ciri aloi magnesium dengan menambahbaikan tingkah laku kakisan dengan rawatan haba terhadap kuaterner aloi magnesium. Kesan dari dua jenis perlakuan haba T4 (perawatan larutan) and T6 (rawatan penuaan) kepada kelakuan-kelakuan kakisan aloi Mg-2.2Zn-3.7RE-0.5Ca kuaterner telah dikaji. Pengcirian mikrostruktur dilakukan dengan mengunakan mikroskop optik dan pengimbasan elektron mikroskop (SEM). Komposisi unsur-unsur telah ditentukan melalui meter belauan sinar-X (XRD) dan spektrometer serakan tenaga sinar-X (EDS). Ciri-ciri kakisan telah diperiksa melalui *in vitro* melalui pengutuban potentiodinamik, variasi pH dan ujian rendaman dalam larutan Hank pada suhu bilik (27°) dan pH 7.4. Kajian ini mendapati α-Mg matrik, fasa eutektik $Mg_{12}RE$ and $Mg_{29}Zn_{25}RE$ antara logam IM1 terbentuk dalam sistem kuaterner Mg-Zn-RE-0.5Ca. Rawatan T4 menghasilkan larutan tertepu α-Mg, manakala fasa sekunder kebanyakannya telah terlarut di dalam matrik. Struktur lamela yang terdiri daripada mendakan IM1 selepas rawatan T6 dikesan sepanjang sempadan bijiran. Sifat kekerasan aloi kuaterner berasaskan magnesium menurun dengan ketara selepas rawatan T4 dan meningkat selepas rawatan T6. Nilai pH bagi rawatan T6 menunjukkan terendah selepas 96 jam rendaman di dalam larutan Hank. Pengukuran elektrokimia menunjukkan bahawa rawatan T4 dan T6 meningkatkan ketahanan kakisan aloi kuaterner magnesium. Hasil kajian mendapati produk kakisan kebanyakan terdiri daripada magnesium tulen, magnesium hidroksida ($Mg(OH)_2$), dan hidroksiapatit (HA).

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LIST OF ABBREVIATION

Al	–	Aluminium
ASTM	–	American Society for Testing and Material
BSE	–	Backscattered Electron
Ca	–	Calcium
Cd	–	Cadmium
Ce	–	Cerium
Co	–	Cobalt
Cr	–	Chromium
EDS	–	Energy Dispersed Spectroscopy
Fe	–	Iron
HA	–	Hydroxyapatite
H_2	–	Hydrogen Gas
Lu	–	Lutetium
Mg	–	Magnesium
Mn	–	Manganese
$Mg(OH)_2$	–	Magnesium Hydroxide
Nd	–	Neodymium
OM	–	Optical Microscope
Pr	–	Praseodymium
SBF	–	Simulated Body Fluid
SCE	–	Saturated Calomel Electrode
SEM	–	Scanning Electron Microscope
SiC	–	Silica Carbide
Sn	–	Tin
RE	–	Rare Earth
XRD	–	X-ray diffraction
Zn	–	Zinc

LIST OF SYMBOLS

%	–	percentage
℃	–	centigrade degree
cm^2/mL	–	centimetre squared per millilitre
E	–	Young's Modulus
E_{corr}	–	Corrosion potential
g	–	Gram
g/cm^3	–	gram per centimetre cubed
GPa	–	gigapascal
kV	–	kilovolt
mg	–	milligram
mA	–	milliamps
mg/ (cm^2.d)	–	milligram per centimetre squared per day
mm^2	–	millimetre squared
MPa ($m^{1/2}$)	–	megapascal-root meters
mmol/L	–	milimol per litre
mV	–	millivolt
P_i	–	Corrosion rate
T6	–	Aging treatment
T4	–	Solid solution treatment
V	–	Volt
θ	–	Bragg diffraction angle
λ	–	X-ray wavelength
°	–	degree
ρ	–	Density

CHAPTER 1

INTRODUCTION

1.1 Introduction

In biomedical applications, metallic materials now continue to play a vital role as biomaterials that are functioning to repair or replacement of diseased or damage bone tissue (Shaw, 2003). Due to load-bearing application, which required both of high mechanical strength and fracture toughness, metals are most appropriate compared to ceramics or polymeric materials (Table 1.1). Currently, most permanent metallic implants, e.g., as bone plates, bone screw, and bone pins are commonly made of stainless steel, titanium, and cobalt-chromium based alloys. However, metallic metals become limited in biomaterial applications due to less biocompatibility since some toxic metal is released through corrosion or wear processes that lead to inflammatory cascade which cause tissue loss and harmful to the human body. Besides, the elastic modulus of current metallic biomaterials are not well matched with natural bones, causing in stress shielding effect that can lead to drawback stimulation of new bones growth and remodelling which decreases implant stability. Most of metallic implants remain as a permanent fixture, have been used to treat serious fractures and then the implant should be removed out after the tissue has healed sufficiently at second surgical procedure. Repeat surgery can affect the costs to the health care system and causing further morbidity to the patient. These problems in commercial metallic implant had concluded as "stress shielding" effect and "surgical intervention" effect (Atrens, Liu, and Zainal Abidin, 2011; González, Pellicer, Suriñach, Baró, and Sort, 2013; Shaw, 2003; Zhou *et al.*, 2010). Therefore, a new domain research in magnesium alloy implants focuses on biodegradable implants, which dissolve in the biological environment dependent on time of functional use (Staiger, Pietak, Huadmai, and Dias, 2006)

Table 1. 1: Summary of the physical and mechanical properties of natural bone and some implant materials (Atrens, Liu, and Zainal Abidin, 2011; González, Pellicer, Suriñach, Baró, and Sort, 2013; Shaw, 2003; Zhou et al., 2010)

Materials	Density (g/cm^3)	Fracture Toughness (MPa ($m^{1/2}$))	Elastic Modulus (GPa)	Compression Yield Strength (MPa)
Natural bone	1.8-2.1	3-6	3-20	130-180
Ti alloy	4.4-4.5	55-115	110-117	758-1117
Co-Cr alloy	8.3-9.2	-	230	450-1000
Stainless Steel	7.9-8.1	50-100	189-205	170-310
Magnesium	1.74-2.0	15-40	41-45	65-100
Hydroxyapatite	3.1	0.7	73-117	600

Selection of biodegradable metallic implants depends on two criteria; firstly, the ability of bioactive materials to interact with biological environment in order to enhance the biological response as well as the tissue or surface bonding, and secondly, the ability to undergo a progressive degradation of biodegradable materials while the new tissue regenerates and heals (Kannan and Singh Raman, 2009).

In terms of biocompatibility and structural metals for an implant, magnesium, and magnesium-based alloys are more suitable candidates due to minimal toxicity potential of cells. The main reason is magnesium is one of the fundamental elements in the human body and the fourth most dominant component in the human serum. Most medical researchers agreed that a normal adult consumes between 300-400 mg of Mg every day and excess Mg^{2+} which is not harmful in the body and then excreted through urine. The concentration of magnesium in normal blood serum level shows in between 0.73-1.06 mmol/L.

Conversely, the major drawbacks of magnesium alloys are low corrosion resistance, which can induce low mechanical strength in the physiological environment. The factor that contributed of reduce corrosion resistance is the evolution of hydrogen and increasing in pH. When corrosion rate is increasing, its lead to the formation of hydrogen and local alkalization, which may affect the pH dependent physiological reaction balance (G. Song and Song, 2007; Yang, Li, Zhang, Lorimer, and Robson, 2008). Besides some bone implant based magnesium alloys have improved osteogenesis response and increase the formation rate of new bones, such as AZ31, AZ91, WE43, LAE442, Mg-Ca and Mg-Mn. Nevertheless, some Mg alloys containing aluminium and heavy metal elements such as rare earth reported produce latent toxic in the human body during degradation. The aluminium (Al) element in AZ91 alloy can cause nerve toxicity and restraining growth of the human body while WE43 that contain neodymium (Nd) and yttrium (Y) distributed at the implantation site after the degradation process in magnesium implant (G. Song and Song, 2007; Yang, Li, Zhang, Lorimer, and Robson, 2008).

By appropriate selection of alloying elements can be effectively improved mechanical properties and corrosion resistance of pure magnesium. For degradable magnesium alloys, the range of alloying elements is rather limited. Zinc and calcium and perhaps a very small amount of low toxicity RE can be tolerated in the human body (F. Witte *et al.,* 2005). Zhang *et al.*, (2011) showed that the addition Zn and Ca into Mg matrix could improve the corrosion potential and reduced the degradation rate since Zn and Ca are abundant nutritional elements which have no toxicity form in the human body. Addition of rare earth (RE) element in Mg matrix can strengthen the material by solid solution strengthening which contributed complex intermetallic phases with limited solubility during solidification. This intermetallic phase can act as obstacles to the dislocation movement at elevated temperatures, which cause precipitation strengthening. The addition of rare earth (RE) is an effective way to improve corrosion resistance instead of creep resistances of in Mg alloys (F. Witte *et al.,* 2005).

The combinations of many alloying elements in magnesium alloy encourage the poor corrosion resistance. The major drawbacks that contribute poor corrosion resistance of magnesium and its alloy lies in two aspects: firstly, the oxide films forming on surface are not perfect and protective; and secondly, the formation of micro-galvanic or bimetallic corrosion occurs by impurities or secondary phases. The fully heat-treated T6 condition can influence the corrosion behaviour of these alloys which includes solid solution treatment, in order maximally dissolve microscopic segregation of cathodic phases (secondary phases) and followed artificial aging for improving the precipitation hardening (Tian and Liu, 2015; Veljovi, Babi, and Rakin, n.d.).

1.2 Problem Statement

Magnesium and its alloys that are chemically active can degrade naturally in the physiological environment by corrosion and have high potential candidates in biodegradable hard-tissue implants. Alloying elements play important roles in magnesium alloys and the mechanical properties are usually the primary consideration when introducing alloying elements to the materials. Heat treatment is one way to improve the corrosion rate besides improves their mechanical properties. The degradation of Mg alloy depends on the solution-aged treated in time and temperature. The solution treated acts as dissolve secondary phase in the matrix while aged-treated used to form more precipitate in the secondary phase.

1.3 Objectives of Research

The specific objectives of the project are:

i. To investigate the effect of alloying element on microstructure of magnesium based alloys.

ii. To determine the effect of heat treatment on the microstructures and corrosion behavior of Mg-based quaternary alloys.

1.4 Scope of Research

The intention of this research is to improve the bio-performance of quaternary Mg-2.2Zn-3.7RE-0.5Ca alloy in the fully heat-treated condition, which includes solid solution treatment and artificially aging treatment. The distribution of precipitate during solid solution and aging treatment are determined from microstructure, phase analysis, and corrosion behaviour in quaternary magnesium-based alloy.

For this experiment, the thermal heat treatment method was chosen to improve corrosion resistance and mechanical properties of quaternary Mg-2.2Zn-3.7RE-0.5Ca alloys. This experiment provides the variation of temperatures in the solid solution treatment (T4) and a variety of times and temperatures in aging treatment (T6) and determines the microstructure and corrosion behaviour of quaternary Mg-2.2Zn-3.7RE-0.5Ca alloy.

To prove the effect heat treatment on the quaternary Mg-Zn-RE-Ca, microstructure and morphology of the specimens before and after corrosion tests are determined by using optical microscope and scanning electron microscope (SEM). The chemical composition and phase analysis of specimens are derived by energy dispersive X-Ray and X-Ray diffraction (XRD). The corrosion properties are examined in-vitro by potentiodynamic polarization, immersion test and pH variation in Hank's solution at room temperature (27 ℃). The Vickers test also used to evaluate the hardness of quaternary Mg-Zn-RE-Ca alloy.

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