ENHANCEMENT OF CORROSION RESISTANCE OF MAGNESIUM BY ALLOYING, FLUORIDE TREATMENT AND NANO-HYDROXYAPATITE COATING FOR BIOMEDICAL APPLICATIONS

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A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy (Mechanical Engineering)

Faculty of Mechanical Engineering,
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JUNE 2013

ABSTRACT

Compared to the traditional metallic implant materials such as stainless steels, titanium alloys and cobalt chromium alloys, magnesium (Mg) has received great attention as biodegradable medical implants as it does not require second surgical procedure for removal. Mg and its alloys also possess suitable mechanical properties for orthopaedic and cardiovascular applications. However, clinical applications of Mg have been limited due to its relatively poor corrosion resistance, rapid degradation rate and hydrogen gas evolution in human body fluid. This research is aimed at decreasing the Mg degradation and corrosion rate by alloying with calcium (Ca) and zinc (Zn), surface treatment by hydrofluoric acid and coating with nano-sized hydroxyapatite (HA) and brushite (DCPD) using electrodeposition method. The first stage of the research is to enhance the corrosion resistance of pure Mg by the addition of Ca (0.5 to 10 wt.%). In the second stage, Zn at different percentages (0.5 to 9 wt.%) was added to the binary Mg-Ca alloy to further enhance the corrosion properties. Both strategies were found to enhance the corrosion resistance of the alloy, however, the effect was not significant. To further enhance the corrosion resistance fluoride treatment by using different concentrations of hydrofluoric acid (35 and 40%) for the duration of 6 to 24 hrs were employed on binary Mg-Ca and ternary Mg-Ca-Zn alloys. Finally, nano-HA and Brushite were coated on the fluoride-treated specimens via electrochemical deposition (ED) method at different voltages (0.15 to 0.8 mA/cm^2) and deposition times (10 to 60 min). Microstructural evolutions were characterized by XRD, AFM, FTIR, SEM, and TEM. Corrosion resistance was examined by potentiodynamic polarization and immersion test in Kokubo solution at room temperature. The results revealed that the grain size and dendrite cell size decreased with the addition of Ca and Zn contents into the binary and ternary alloys respectively. The addition of 0.5 wt.% Ca content was found to produce the lowest dissolution rate and the highest corrosion resistance. However, further addition of Ca led to an increased dissolution rate and pH value. The corrosion resistance of Mg-0.5Ca alloy was enhanced with the addition of up to 1 wt.% Zn, but further addition produced the reverse effect. Mg-0.5Ca-1Zn alloy, which has α-Mg+$Ca_2Mg_6Zn_3$+Mg_2Ca phases showed lower corrosion rate than those alloys with Zn/Ca atomic ratio higher than 1.23. After fluoride treatment the degradation rates of the alloys were significantly reduced compared to the untreated alloys. Electrochemical tests showed a significant decline in corrosion current density from 365.2 to 5.23 $\mu A/cm^2$ on Mg-0.5Ca-1Zn alloys coated with composite nano-HA/MgF_2. The application of composite coating of nano-HA/MgF_2 on Mg-Ca-Zn alloys could be used to reduce the corrosion rates of Mg alloys for biodegradable medical applications.

ABSTRAK

Berbanding dengan implan tradisional yang dibuat dari bahan logam seperti keluli tahan karat, aloi titanium dan aloi kromium kobalt, magnesium (Mg) telah mendapat perhatian besar sebagai bahan biodegradasi implan perubatan kerana tidak memerlukan prosedur pembedahan kedua untuk penyingkiran implan. Mg dan aloinya memiliki sifat mekanikal yang juga sesuai untuk aplikasi ortopedik dan kardiovaskular. Walau bagaimanapun, aplikasi klinikal Mg adalah terhad disebabkan oleh mutu rintangan kakisan yang rendah, kadar degradasi yang tinggi dan evolusi gas hidrogen yang pantas dalam cecair badan manusia. Kajian ini bertujuan untuk mengurangkan kadar degradasi dan kakisan Mg secara pengaloian menggunakan unsur kalsium (Ca) dan zink (Zn), rawatan permukaan oleh asid hidrofluorik, dan salutan hydroxyapatite (HA) bersaiz nano dan brushite (DCPD) dengan kaedah elektroenapan. Peringkat pertama kajian adalah untuk meningkatkan rintangan kakisan Mg tulen dengan penambahan unsur Ca (0.5-10 wt.%). Pada peringkat kedua, unsur Zn pada peratusan yang berbeza (0.5-9 wt.%) ditambah kepada aloi binari Mg-Ca untuk menambah baik sifat kakisan. Kedua-dua strategi ini didapati berjaya menambah baik rintangan kakisan aloi, tetapi kesannya tidak ketara. Untuk mempertingkatkan lagi sifat rintangan kakisan, rawatan fluorida menggunakan kepekatan asid hidrofluorik yang berbeza (35 dan 40%) untuk tempoh 6 hingga 24 jam telah digunakan ke atas aloi binari Mg-Ca dan aloi pertigaan Mg-Ca-Zn. Akhirnya, HA dan Brushite telah disalut pada spesimen yang telah menjalani rawatan fluorida dengan kaedah pemendapan elektrokimia (ED) pada voltan (0.15-0.8 mA/cm^2) dan masa pemendapan (10-60 min) yang berbeza. Evolusi mikrostruktur telah dilakukan menggunakan XRD, AFM, FTIR, SEM, dan TEM. Kerintangan kakisan telah diteliti menggunakan polarisasi potentiodynamic dan ujian rendaman dalam larutan Kokubo pada suhu bilik. Keputusan menunjukkan bahawa saiz bijian dan saiz sel dendrit menurun dengan penambahan kandungan Ca dan Zn ke atas aloi binari dan aloi pertigaan masing-masing. Penambahan 0.5 wt.% Ca dikenalpasti menghasilkan kadar keterlarutan terendah dan rintangan kakisan tertinggi. Walau bagaimanapun, penambahan Ca yang seterusnya membawa kepada peningkatan kadar keterlarutan dan nilai pH. Rintangan kakisan aloi Mg-0.5Ca telah dipertingkatkan dengan penambahan sehingga 1 wt.% Zn, tetapi penambahan seterusnya menghasilkan kesan yang sebaliknya. Aloi Mg-0.5Ca-1Zn yang mempunyai fasa α-Mg+$Ca_2Mg_6Zn_3$+Mg_2Ca menunjukkan kadar kakisan lebih rendah berbanding dengan aloi lain yang mempunyai nisbah atom Zn/Ca lebih daripada 1.23. Selepas rawatan fluorida kadar degradasi aloi dikurangkan dengan ketara berbanding dengan aloi yang tidak dirawat. Ujian elektrokimia menunjukkan penurunan yang ketara dalam ketumpatan arus kakisan; 365.2-5.23 $\mu A/cm^2$ bagi aloi Mg-0.5Ca-1Zn yang disalut dengan komposit nano-HA/MgF_2. Salutan komposit nano-HA/MgF_2 aloi pada Mg-Ca-Zn boleh digunakan untuk mengurangkan kadar kakisan aloi Mg untuk aplikasi perubatan biodegradasi.

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LIST OF ABBREVIATIONS

CA-CCTA	-	Computer Aided Cooling Curve Thermal Analysis
CCA	-	Cooling Curve Analysis
DCP	-	Dendrite Coherency Point
EDX	-	Energy Dispersive X-ray
FESEM	-	Field Emission Scanning Electron Microscopy
OM	-	Optical Microscopy
FTIR	-	Fourier-Transformed Infrared Spectroscopy
SEM	-	Scanning Electron Microscopy
TA	-	Thermal Analysis
TEM	-	Transmission Electron Microscopy
AFM	-	Atomic-Force Microscopy
UTS	-	Ultimate Tensile Strength
UCS	-	Ultimate Compressive Stress
XRD	-	X-ray Diffraction
SBF	-	Simulated body fluid
HA	-	Hydroxyapatite
DCPD	-	Dicalcium Phosphate Dihydrate (Brushite)
ED	-	Electrodeposition
SiC	-	Silicon Carbide
VHN	-	Vickers Microhardness
SCE	-	Saturated Calomel Electrode
HF	-	Hydrofluoric Acid
PBR	-	Pilling-Bedworth Ratio
Ca-P	-	Calcium Phosphates
MgF_2	-	Magnesium Fluoride
$Mg(OH)_2$	-	Magnesium Hydroxide (Brucite)

DMEM	-	Dulbecco's Modified Eagle Medium
MEM	-	Minimum Essential Medium
PBS	-	phosphate buffered saline
ACP	-	Amorphous Calcium Phosphate
OCP	-	Octacalcium Phosphate
TCP	-	Tricalcium phosphate
CDHA	-	Calcium-Deficient Hydroxyapatite
PLLA	-	Poly L-Lactic Acid
PGA	-	Polyglycolic Acid
PEO	-	Polyethylene Oxide
mpy	-	Mils Per Year
PO_4^{3-}	-	Phosphate
OH^-	-	Hydroxide
$CO3^{2-}$	-	Carbonate

LIST OF SYMBOLS

Z_{re}	-	Impedance
C_P	-	Specific heat
f_{DCP}	-	Solid fraction at dendrite coherency point
f_S	-	Solid fraction
f_L	-	Liquid fraction
T	-	Temperature
T_s	-	Start of solidification temperature
T_e	-	End of solidification temperature
T_{EU}	-	Eutectic temperature
t_s	-	Start of solidification time
t_e	-	End of solidification time
ΔT	-	Solidification range
Δt	-	Total solidification time
T_N	-	Nucleation temperature
t_N	-	Nucleation time
T_{DCP}	-	Coherency temperatures
α-Mg	-	Primary magnesium dendrite
ρ	-	Density
°C	-	Centigrade degree
β	-	Diffraction peak width at mid-height,
t	-	Average crystallite size (nm)
θ	-	Bragg diffraction angle
λ	-	X-ray wave length
R_a	-	Average roughness
R_{MS}	-	Mean spacing roughness
i_{corr}	-	Corrosion current density
E_{corr}	-	Corrosion potential

βc	-	Cathodic Tafel slops
βa	-	Anodic Tafel slopes
R_P	-	Polarization resistance
P_i	-	Corrosion rate
E_{pit}	-	Pitting potential
Q	-	Growth restricted factor
m	-	Gradient of the liquidus line of a binary alloy
c_o	-	Bulk concentration of the solute
k	-	Equilibrium partition coefficient of the solute
Q_s	-	Rate of heat released
T_f	-	Final temperature
Cp	-	Specific heat of the alloy
T_W	-	Temperature at wall thermocouple
T_C	-	Temperature at centeral thermocouple

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CHAPTER 1

INTRODUCTION

1.1 Background

Metallic materials have fundamental roles for repair or replacement of bone tissue particularly for load-bearing applications due to their good fracture toughness and high mechanical strength [1]. However, the release of toxic metallic ions during corrosion has limited their applications as implant materials [2]. This released ion can result in inflammatory, which in turn decrease biocompatibility [3]. Compared to the traditional metallic implant materials such as titanium alloys, stainless steel and cobalt-chromium alloys, biodegradable implant materials do not require second surgical procedure to remove them once the bone healed and they are replaced by natural tissue. In addition, second surgical procedures always have risk and cost involved [4]. Furthermore, the presence of permanent implants in the human body may cause allergy and sensitization.

Recently, polymeric-based biodegradable materials, mostly polylactic have shown a feasible approach to the development of completely degradable devices for biomedical applications. However, polymers can create significant adverse reactions and have inadequate mechanical strength, thus their applications are limited to low load-bearing applications [5]. In addition, polymeric implants are more expensive compared to the typical metallic implants [4,5]. As an alternative to biodegradable polymer implants is the biodegradable metallic implants which received great attention owing to the high load-bearing capacity [4]. Magnesium and its alloys have shown great potential in cardiovascular applications where temporary stents are

required. They have also been used as bone substitute materials owing to their biocompatibility and biodegradability and have similar mechanical properties with natural bone. Mg is one of the fundamental elements in the human body and the fourth most dominant component in the human serum [6]. According to Song [5] a normal adult consumes about 300–400 mg of Mg every day and an excess of Mg^{2+} is not harmful since it excretes through urine. Mg as biodegradable material is lightweight (1.74 g/cm^3), which is 1.6 and 4.5 times lighter than that of aluminum and steel respectively.

Magnesium fracture toughness is higher compared to bio-ceramics such as hydroxyapatite, and has close elastic modulus and compressive yield strength to natural bone [3, 5]. However, applications of Mg alloys are limited due to the relatively poor corrosion resistance, the release of hydrogen gas and a relatively high degradation rate when exposed to human body fluid [7, 8]. These characteristics lead to a decline in the mechanical properties of pure Mg before new tissues are properly and adequately healed. Mg alloy as implant can maintain the mechanical stability for around 6 to 8 weeks, while implant need to maintain its mechanical integrity in the body for about 12 weeks [9]. Thus, various approaches have been employed to enhance corrosion resistance of pure Mg such as alloying, surface treatment and coating.

Most of the research reported on biodegradable magnesium alloys for biomedical application contains aluminium (Al) and/or rare earth (RE) elements. However, Al could cause nerve toxicity and RE could lead to hepatotoxicity [10, 11]. Other alloying elements such as zirconium (Zr) may lead to lung, liver, nasopharyngeal and breast cancers [5]. The addition of neodymium (Nd) and yttria (Y) into Mg alloys resulted in a disturbance at the implantation site [10, 11]. Clearly, to guarantee the biosafety of biodegradable materials, the constitutional elements of magnesium-based alloys should be toxic free [7,10]. To address this point, Ca and Zn were found to be toxic free.

Calcium is one of the main elements in the human bone and release of Mg and Ca ions may improve the bone healing process [12]. Calcium, with a density of 1.55g/cm^3, is also lightweight material similar to magnesium (1.74 g/cm^3) and will maintain its specific properties. The relatively reasonable cost of Ca should also attract its use as alloying element in medical applications [13]. Previous research also has shown that the corrosion resistance of Mg-Ca alloys increased significantly with the addition of 1 wt.% Ca [14]. Besides, the addition of Zn into magnesium alloys is very effective in increasing their mechanical strength [15, 16]. Zinc is also generally known to increase age hardening response, produce intermetallic compounds, refine grain size and improve castability and mechanical properties such as tensile and hardness of Mg-Ca [17-19]. The effect of Zn on corrosion resistance of Mg-Ca was not known for biomedical applications. Thus, there is a need to investigate the effect of Zn addition on Mg-Ca corrosion rate.

Since ensuring the implant remains its function until after the bone heals, corrosion resistance of Mg-Ca and Mg-Ca-Zn alloys should be enhanced further by double protective film composed of inner-layer. Several reports have shown that decreasing the corrosion rate of Mg in simulated body fluids is possible by surface treatment methods [20-23]. Surface treatment by hydrofluoric acid (HF) was found to be effective in increasing corrosion resistance at 48% concentration [4]. However, protection provided by the MgF_2 layer at that concentration was high at the initial phase, but stabilized with time and became less effective. Other HF concentrations and immersion time was not known to affect corrosion rate of Mg-Ca and Mg-Ca-Zn alloys. Micro sized hydroxyapatite (HA) as the top layer coat by electrodeposition was used without inter-layer on Mg-Ca substrates with the intention to prolong protection. It was found effective in increasing the corrosion resistance, however the hydrogen gas evolution was beyond the tolerance limit of human body [24, 25].

Therefore, this research is aimed at addressing a comprehensive use of alloying, fluoride treatment and nano-calcium phosphate coating in the form of nano-HA/MgF_2 and DCPD/MgF_2 composite coating to increase the corrosion resistance and minimize hydrogen production of Mg alloys for use in biomedical implant.

1.2 Problem Statement

Magnesium alloys as biodegradable materials possess several advantages compared to the current metallic materials and biodegradable plastics and ceramics. Magnesium benefits include higher fracture toughness over ceramic biomaterials, higher strength than biodegradable plastics, and higher elastic modulus compared to other biomedical metals. However, the use of pure magnesium is hindered by its relatively poor corrosion resistance which causes the mechanical properties of the implant to significantly decrease resulting in the tissues being unable to heal. Furthermore, Mg corrosion process involves evolution of hydrogen gas which accumulates in vivo adjacent to the implant. The H_2 gas and subsequent formation of hydrogen bubbles can noticeably impair other clinical applications of Mg. Alkalization of the surroundings by the H_2 gas evolution during the corrosion process of Mg is another drawback. Thus, it is essential to increase the corrosion resistance of Mg and its alloys to meet the requirements of the synchronization between implant biodegradation and the new bone formation.

1.3 Purpose of the Study

The purpose of this study addresses the problem described above, namely to develop a new biodegradable magnesium alloy with adequate degradation rate for use as an implant material. To investigate the potential of fluoride treatment for the corrosion protection of magnesium alloys. The influence of parameters such as HF concentration, duration and coating performance will be investigated. To determine the developed process for synthesis a novel bi-layered coating composed of nano-HA and brushite as top layer and MgF_2 as interlayer that will demonstrate enhancement of corrosion resistance of magnesium alloy. The optimal coating conditions for deposition of nano-hydroxyapatite and brushite on fluoride treated magnesium alloy will be determined.

1.4 Objectives of the Research

The principal objective of the research is increasing corrosion resistance of magnesium alloys by alloying accompanied with surface treatment and nano-hydroxyaptite coating by electrodeposition (ED) method on Mg-Ca and Mg-Ca-Zn alloys. The specific objectives include:

1. To investigate the effects of calcium and zinc additions on the microstructure, degradation rate and corrosion properties as well as solidification behavior using thermal analysis of magnesium alloys.

2. To determine the effect of surface modification by hydrofluoric acid (HF) on microstructure, in-vitro degradation behavior and corrosion properties of Mg-Ca and Mg-Ca-Zn alloys.

3. To determine the effect of nano-HA/MgF_2 and DCPD/MgF_2 composite coating on microstructure and corrosion behavior of Mg-Ca-Zn alloys.

1.5 Significance of the Research

In recent years, the study of magnesium alloys as degradable biomaterials has become one of the most revolutionary research topics at the forefront of biomaterials research. However, its application has been limited due to the relatively poor corrosion resistance. Hence, it is expected that the outcome of the research will eliminate the need of secondary surgery for current implant materials eliminated. Using magnesium alloys as biodegradable implants resulted in reducing time, cost, risk and morbidity of the patients.

1.6 Scope of the Research

The research was conducted in the following limits:

1- Calcium and zinc additions to Mg were limited to between (0.5 and 10 wt.%) and (0.5 and 9 wt%) respectively.

2- The responses on the effect of calcium and zinc additions were limited to the microstructure, degradation rate, corrosion properties and solidification behavior of Mg-xCa and Mg-Ca-xZn alloys.

3- Hydrofluoric acid with concentrations between 35 and 40% as well as immersion duration of 6 to 24 hours was used for surface treatment of Mg-Ca and Mg-Ca-Zn alloys.

4- The current density used in electrodeposition of nano-HA and brushite coatings on magnesium alloys was regulated between 0.15 to 0.8 mA/cm^2 for durations of 10 to 60 min.

5- The specimens were subjected to microstructural characterization using optical microscopy, X-ray diffraction, atomic-force microscopy, Fourier-transformed infrared spectroscopy, scanning electron microscopy and energy dispersive X-ray spectroscopy and transmission electron microscopy.

6- The corrosion resistance was examined in vitro by potentiodynamic polarization test, immersion test and hydrogen evolution test in Kokubo solution at room temperature.

7- Solidification behavior of Mg-Ca and Mg-Ca-Zn alloys were examined via two thermocouple thermal analysis method.

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