INFLUENCE OF HEAT TREATMENT AND SEVERE PLASTIC DEFORMATION (SPD) ON Zn-3Mg ALLOY PROPERTIES FOR BIO-IMPLANT APPLICATION

MURTALA SULE DAMBATTA

UNIVERSITI TEKNOLOGI MALAYSIA

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MURTALA SULE DAMBATTA

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Dedicated to

My mother, **Hajiya Binta Zakariyya Chira**, whose sacrifice;
My late father, **Alhaji Sule Ibrahim Dambatta**, whose dream;
My **Brothers and sisters**, whose support and encouragement;
And
My wife, **Rukayya Haruna Ishaq**, whose patience;
Lead to achieve my doctoral degree

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ABSTRACT

Unlike permanent implant materials, biodegradable metallic implants can avoid a revision surgery for implant removal. Recently, Zn and its alloys have received a lot of attention as an alternative to Mg-based alloys, especially for temporary implant applications such as fractured bone fixation devices. Advantage of zinc, apart from its significance for many biological functions, it also supports wound healing and exhibits superior degradation performance in physiological environment than Mg-based alloys. Earlier investigations have shown that, Zn-based alloys have limitations on its strength and ductility. In addition, the biocompatibility status of this alloy is also unknown. This work attempts to improve these properties, particularly on Zn-3Mg alloy via heat treatment followed by severe plastic deformation technique, i.e equal channels angular pressing (ECAP). Eutectic Zn-3Mg alloy samples were prepared using the casting process. During casting, solidification behaviours were analysed to determine the feasible range of heat treatment temperature. Heat treatment was conducted using a vacuum tube furnace at 370°C for 5, 10, 15 and 25 hours dwelling time followed by quenching in three different media: water bath, inside the furnace and open air to room temperature. Corrosion behaviours of the untreated and treated alloy were evaluated using electrochemical polarisation and immersion methods. The experiments were conducted in Kokubo simulated body fluid (SBF). Apart from mechanical properties (hardness, tensile and compressive strengths), the samples were subjected to cytotoxicity test. As-cast microstructure consisted of star-like dendrites of Zn-rich and rectangular structures of Zn_2Mg_{11} phases dispersed in segregated pattern. These phases were partially dissolved after heat treatment and became more homogenised. It was noticed that the ductility of the alloy improved by 64 % while the strength reduced by 45 %. A remarkable decrease in grains size up to 96.34 % was observed after the cast alloy was subjected to heat treatment followed by 2-ECAP passes. In addition, other properties such as ultimate tensile strength, yield strength and elongation were substantially increased by 2.63 fold, 3.15 fold and 4.98 fold respectively. Improvements on strength and ductility were attributed to the combined influence of microstructural changes, elimination of dendrite structure, as well as the existence of high-volume density of dislocations that occurred on the refined microstructure during 2-ECAP pressing. Assessment of corrosion showed that the corrosion rate decreased from 0.269 to 0.188 mm/year after the cast alloy was severely deformed. This was attributed to improved microstructure homogeneity and reduction in casting defects. The study also reveals that extract of Zn-3Mg alloy exhibits good biocompatibility towards normal human osteoblast cells (NHOst) in low concentration (<0.5 mg/ml). The proposed hybrid processing method seems able to enhance the properties of developed Zn-3Mg alloy after 2-ECAP passes. These encouraging findings would improve the prospects of Zn-3Mg alloy as a new alternative metallic biodegradable implants material.

ABSTRAK

Tidak seperti bahan implan kekal, implan logam terbiorosot boleh mengelakkan pembedahan semula untuk menanggal implan. Baru-baru ini, Zn dan aloinya telah mendapat perhatian sebagai alternatif kepada aloi berasaskan-Mg, terutama sekali untuk aplikasi implan sementara seperti peranti bagi menetapkan tulang yang patah. Kelebihan zink, selain ia penting untuk kebanyakan fungsi biologi, ia juga menyokong penyembuhan luka dan memberikan prestasi yang baik dalam penurunan persekitaran fisiologi berbanding aloi berasaskan-Mg. Kajian sebelum ini menunjukkan bahawa aloi berasaskan-Zn mempunyai kekuatan dan kemuluran yang terhad. Di samping itu, status keserasian-bio aloi ini juga tidak diketahui. Kajian ini berusaha untuk memperbaiki sifat-sifat ini, terutamanya pada aloi Zn-3Mg melalui rawatan haba yang diikuti dengan teknik ubah bentuk plastik yang teruk, iaitu saluran sama sudut mampatan (ECAP). Sampel aloi eutektik Zn-3Mg telah disediakan dengan menggunakan proses tuangan. Semasa proses tuangan dilakukan, tingkah laku pemejalan telah dianalisis untuk menentukan julat suhu rawatan haba. Rawatan haba telah dijalankan menggunakan tiub relau vakum pada 370 ^{o}C dengan masa pemanasan selama 5, 10, 15 dan 25 jam diikuti dengan sepuh lindap kejut dalam tiga media yang berbeza: dalam takungan air, dalam relau dan dalam udara terbuka kepada suhu bilik. Tingkah laku kakisan aloi yang tidak dirawat dan dirawat telah dinilai menggunakan kaedah polarisasi elektrokimia dan ujian rendaman. Kajian ini telah dijalankan di dalam cecair badan tersimulasi Kokubo (SBF). Selain dari sifat-sifat mekanikal (kekerasan, tegangan dan kekuatan mampatan), sampel tersebut juga tertakluk kepada ujian sitotoksiti. Mikrostruktur sampel tuangan terdiri daripada struktur seakan-akan bintang dendrit Zn-asal dan struktur segi empat tepat fasa Zn_2Mg_{11} yang tersebar dalam corak yang berasingan. Fasa-fasa ini sebahagiannya larut selepas rawatan haba dan menjadi lebih homogen. Didapati bahawa kemuluran aloi meningkat sebanyak 64% manakala kekuatannya berkurangan sebanyak 45%. Penurunan saiz bijian yang luar biasa sehingga 96.34% telah diperhatikan selepas aloi tuangan dikenakan rawatan haba yang diikuti dengan 2 kali laluan ECAP. Di samping itu, ciri-ciri lain seperti kekuatan tegangan, kekuatan alah dan pemanjangan masing-masing telah meningkat dengan ketara sebanyak 2.63, 3.15 dan 4.98 kali ganda. Peningkatan kekuatan dan kemuluran adalah disebabkan oleh gabungan pengaruh perubahan mikrostruktur, penghapusan struktur dendritik dan juga disebabkan oleh kewujudan kehelan pada kepadatan yang tinggi yang terjadi kepada mikrostruktur halus semasa mampatan 2-ECAP. Penilaian kakisan menunjukkan bahawa kadar kakisan berkurangan dari 0.269 kepada 0.188 mm/tahun selepas aloi tuangan terhakis teruk. Ini disebabkan oleh kehomogenan mikrostruktur yang lebih baik dan pengurangan kecacatan tuangan. Kajian ini juga mendedahkan bahawa sari aloi Zn-3Mg mempamerkan keserasian-bio yang baik terhadap sel-sel kanser tulang manusia normal (NHOst) dalam kepekatan yang rendah (<0.5 mg/ ml). Kaedah pemprosesan kacukan yang dicadangkan ini menampakkan peningkatan sifat-sifat baru aloi Zn-3Mg selepas 2 kali laluan ECAP. Penemuan yang menggalakkan ini meningkatkan prospek aloi Zn-3Mg sebagai satu logam alternatif bahan implan boleh-biorosot yang baru.

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LIST OF ABBREVIATIONS

DNA	-	Deoxyribunuclei Acid
ROS	-	Reactive Oxygen Species
SPD	-	Severe Plastic Deformation
NHOst	-	Normal Human Osteoblast cell
OM	-	Optical Microscope
FESEM	-	Field Emission Scanning Electron Microscope
EDX	-	Energy Dispersive Electron Microscope
XRD	-	X-Ray Diffraction
MTS	-	Methylthiozol Tetrazolium Salt
ALP	-	Alkaline Phosphatase
SBF	-	Simulated Body Fluid
PTFE	-	Polymer-ply-tetra-fluorethylene
PMMA	-	Polymethyl-metheacralyte
HA	-	Hydroxyapatite
ECAP	-	Equal channels angular pressing
HCP	-	Hexagonal Closed-Packed
B.C	-	Before Christ
R.E	-	Rare Earth
HPT	-	High Pressure Torsional
SSMR	-	Super-Short Multi pass Rolling
RCS	-	Repetitive Corrugated and Straightening
CEC	-	Cyclic Extrusion Compression
DCCAP	-	Double Channel Angular Pressing
MDF	-	Multi-Directional Forging
F.C.C	-	Face Centered Cubic
B.C.C.	-	Body Centered Cubic
A.A.S	-	Atomic Absorption Spectrum

EDM	-	Electric Discharge Machining
CNC	-	Computer Numerical Control
ASTM	-	American Society for Testing and Materials
PDP	-	Potentiodynamic Polarization
EIS	-	Electrochemical Impedance Spectroscopy
SCE	-	Saturated Calomel Electrode
OPC	-	Open Circuit Potential
OBM	-	Osteoblast Basal Medium
S.D	-	Standard Deviation
ECP	-	Eutectic Coherency Point
CR	-	Corrosion Resistance
GDS	-	Glow Discharge Spectrometer
ROI	-	Region Of Interest
HAGB	-	High Angle Grain Boundary
ISO	-	International Standard Organization
IC50	-	50% Inhibition Concentration

LIST OF SYMBOLS

ϕ	-	Channels internal intersection angle
Ψ	-	Channels outer intersection angle
Icorr	-	Corrosion current density
Ecorr	-	Corrosion potential
µ	-	Micron
Rt	-	Charge transfer Resistance
W	-	Warburg impedance
Cdl	-	Double layer capacitance
Rs	-	Resistance of electrolyte surface films
Tm	-	Melting Temperature

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CHAPTER 1

INTRODUCTION

1.1 Background of the Research

The phenomenon of population aging and less engagement of the human body in physical activities by individual persons due to technologically advanced innovative life systems gives major causes of reduction in bone mineral weight, bone quality and strength in human being muscles [1]. These mentioned factors coupled with accidental bone damaged or fractures signify increases in the incidence of bones failures or damages during the life cycle of human population. Proper healing of fracture bone needs an appropriate alignment and fixation of fractured fragments during it healing period.

For the past two decades, the field of biomaterial implants has received tremendous research activities aimed towards enhancing or improving quality and longevity of the human life. Biomaterial implants mean a device that is designed, fabricated and applied to alter, replace, augment or repair a missing or damaged biological components [2]. Implant for load bearing and fracture fixation applications such as artificial hip and knee prostheses, fixation screws and pins need to have the same properties as close to the bones to be replaced or repaired. Metallic implant such as stainless steels, titanium, cobalt-chromium materials and their alloys play a dominant role compared with ceramics and polymeric materials. These metallic materials remain as permanent fixtures, which means they must be removed by a second surgical procedure after the tissue has healed [3]. In addition, durable metallic implant signifies a foreign body and the risks of local inflammation [4]. Higher young’s modulus of a metallic fixation device causes a phenomenon known as “stress shielding effect. This obstructs the transfer of mechanical load to the bone tissue which is needed to maintain it rigidity during implants healing period [5, 6]. Another significant problem associated with the use of durable metallic implant fixation devices is their higher mechanical properties than the bones to be replaced. This makes the newly repaired or formed bone tissue not to be subjected to mechanical loading, which is a major requirement for bone growth and remodelling [7].

In an ideal scenario, implant materials should not be used as permanent but as intervention and should be remove from the body as soon as it finished its require functions. This is to prevent potential risks of local inflammation, late-stage infection, bone resorption or immune reactions [8, 9]. Furthermore, the required stabilization of bone fracture with the use of fixation devices on the surrounding bones using screws, pins, plates or nails, means another surgical operation to remove the fixation devices. This may cause serious morbidity to the newly repaired bone, cost of another surgical operation and discomfort for the patient, especially for old people where successful post-surgery is not always possible.

To overcome the above-mentioned limitations of durable metallic implant for fracture bone fixation devices, biodegradable implant materials as an alternative was investigated [10]. Widely researched biodegradable metallic materials for potential implant applications include magnesium, iron and their alloys [11, 12]. Among the investigated potential biodegradable metals, magnesium and its alloys have received the highest attention compared to other metals [10, 13, 14]. One good characteristics of magnesium is it high strength/weight ratio and appropriate mechanical properties closer to the human bone.

Previously studied biodegradable magnesium alloys as potential implant materials are mostly conducted using alloys designed for industrial applications. These alloys contain some potential harmful rare earth elements (RE) such as Praseodymium (Pr), Cerium (Ce), Neodymium (Nd) and some transition metals (TM) such as Yttrium (Y) [3, 15]. It has already been proved that aluminium (Al) has neurotoxicant effects on a human body [16]. It is also a risk factor for Alzheimer diseases and can cause muscle fibre damage [17, 18]. Furthermore, intense hepatotoxicity was detected after the administration of some rare earth elements [19]. Few of the novel magnesium alloys developed specifically for biodegradable implant applications are Mg-1Zn, Mg-5.12Zn-0.32Ca, Mg-6Zn-0.6Zr, Mg-3Ca, Mg-6Zn, Mg-5.19Zn-0.72Mn-0.99Ca, Mg-3Zn-xY(x = 0.36-1.54wt %), Mg-Zn1-Gd2.5, Mg-6Zn-1Si, Mg72-Zn26.5-Y1.5 [20-29]. Unfortunately, the major limitations of magnesium and its alloys for biodegradable implant applications are its rapid degradation rate in physiological (pH 7.4 to 7.6) environment [30, 31] and the excessive hydrogen gas released during the degradation process may also hinder the healing process [32]. Observed from the earlier mentioned alloying systems of Mg-base alloys, zinc is among the most preferred alloying element to magnesium.

Limitations of Mg-based alloys widens the search to other fast degradable metals in physiological environment, which includes Zn and Zn based alloys [33, 34]. While investigating the possible improvement to magnesium based alloys, a novel Zn and Zn based alloys were reported as alternative potential degradable implant fracture fixations devices [34-37]. This is because in terms of corrosion resistance, zinc is nobler metal due to it higher Pilling-Bed Worth than magnesium [38]. In addition, from biocompatibility point of view, zinc is very significant for various biological functions in the human body due to its function as an essential micronutrient and it also aid cellular metabolism and gene expression [38]. Zinc was also reported to aid immune functions, DNA synthesizer and helps in wound healing with additional support for normal bone growth [22-25, 39]. These points indicate that zinc could pass the basic safety level for physiological environment utilization. Early interest shown to zinc metal arose because of the success reported on Mg-Zn-Ca bulk metallic glasses (with about 50 wt.% of Zn contain) by Zberg *et al*. [40]. Another important factor for Zn based alloy is its cheaper cost of production due to its low melting temperature, cheaper material cost and ease to fabricate. The above information leads to development of Zn based alloys as an alternative metallic biodegradable implant material. However, newly developed Zn-based alloys properties still failed to meet some of the requirements for biodegradable implant applications such as fracture fixation screws and plates. Previous studies have recommended the need to improve the mechanical properties of developed Zn and Zn based alloys tailored towards bone implant applications [34, 35]. Some of the probable methods to enhance its properties for better clinical performance are through alloying process, heat treatment and thermo-mechanical processing.

1.2 Problem Statements

Zn-based alloys are expected to be an alternative to other physiologically degradable metallic materials. This is highlighted in the recently reported studies [34, 41] of zinc based alloys as an alternative to magnesium based alloys for biodegradable implant applications. However, previous investigated zinc based alloys have some limitations on their properties, which affect their potential as implant materials. Some research activities have been conducted to investigate the mechanical and degradation properties of zinc based alloys for probable utilization as metallic biodegradable implant materials [34-37]. However, these studies have reported the need to improve the properties of zinc based alloys. Currently observed limitations of these alloys are low ductility (1.8 % less than human cortical bone) and low strength (133 MPa less than human cortical bone). Limited toxicity study of developed Zn-Mg alloys was also noticed [34, 36, 42]. The biocompatibility investigation is of significant issue due to doubtful toxicity of zinc intake at high concentration [43]. Furthermore, its degradation performances need to be enhanced for maintaining its mechanical integrity during degradation process. Various techniques such as alloying systems and heat treatment have been investigated to improve the mechanical and degradation properties of zinc based alloys [34, 36, 37]. Recently, magnesium was alloyed to a zinc matrix (Zn-Mg alloys) to improve its mechanical and degradation properties for implant applications, but little success was observed. Literatures have been reported on a thermo-mechanical technique of metal processing called severe plastics deformation (SPD), which influences grain size refinement to give an improvement on both mechanical and sometimes corrosion properties on processed materials [44-48]. Equal channels angular pressing (ECAP) is one of the effective SPD techniques used to improve the mechanical properties of metallic materials. However, it is hardly found in the literature the use of this technique to enhance the properties of Zn-Mg alloys, especially for biomedical implants applications. Therefore, this study systematically evaluates the influence of severe plastic deformation (SPD) on mechanical and degradation properties of newly developed Zn-3Mg alloy for potential bio-implant application.

1.3 Objectives of the Research

The primary objective of this research is to investigate the influence of thermomechanical processing technique called severe plastic deformation (SPD) on mechanical and degradation properties of newly developed eutectic Zn-3Mg alloy for biodegradable implants utilizations. The specific objectives of the research include the following:

1. To cast and characterize the microstructure, mechanical and degradation behaviours of developed Zn-3Mg alloy before and after being homogenised through a heat treatment process.
2. To evaluate the effect of hybrid heat treatment and SPD process on the microstructure homogeneity, mechanical and degradation properties of Zn-3Mg alloy via hybrid heat treatment and SPD processes.
3. To evaluate the biocompatibility of developed Zn-3Mg alloy towards normal human osteoblast cells (NHOst) for biomedical implant applications.

1.4 Scope of the Research

The research work was conducted within the following scope:

i. Zn-3Mg alloy was developed using casting process in-house and used as sample material.
ii. Thermal analysis was conducted to evaluate the phase reactions and solidification behaviour of the molten Zn-3Mg alloy based on temperature and time changes.
iii. Heat treatment was conducted on the as-cast sample prior to SPD process.

iv. A special die set was fabricated in-house for conducting SPD process. Samples were processed through the fabricated die with selected processing parameters that give smooth pressing without fracture being observed on the processed samples surface.
v. Appropriate pressing temperature between 100 ^{0}C to 250 ^{0}C was selected to conduct the SPD processing.
vi. Samples microstructure and surface characterizations were analysed under OM, FESEM, EDX and XRD.
vii. Biocompatibility assessment was conducted by MTS assay and Alkaline Phosphatase (ALP) extracellular enzyme assay using normal human osteoblast (NHOst) cells (CC-2538, Lonza, U.S.A)
viii. Mechanical properties of developed alloy were analysed using microhardness, tensile and compressive strength measurements according to ASM standard procedures.
ix. Degradation experiments were conducted using weight loss and electrochemical methods under Hank's simulated body fluid solution (SBF).

1.5 Significance of the Research

This study expects that combination of heat treatment, severe plastic deformation (SPD) processes will improve the mechanical, and degradation properties of newly developed Zn-3 Mg alloy. Significant improvement on these properties will increase the potential of Zn-3Mg alloy to meet the fundamental requirements of biodegradable implant materials, especially for fracture fixation devices. In addition, the success of the alloys biocompatibility behaviour would eliminate the doubtful toxicity of zinc intake at high concentration and hence further improving its prospects for use as alternative material for biodegradable implant utilizations. The possible positive outcomes of this research will help the researcher to further his/her work in *in vivo* studies. It is hoped that the outputs from this research will provide an alternative to the existing potential metallic biodegradable materials at a competitive manufacturing cost.

Furthermore, it is hoped that conducting detailed and comprehensive research on Zn-3Mg alloy will contribute to the scientific knowledge on metallic biodegradable implant. This would enrich the understanding of zinc based alloys for potential biomedical implant applications and contribute towards improving the life quality of the world populations at large.

1.6 Thesis Organisation

This thesis is classified into five different chapters. Chapter 1, which consists of sub-headings of background of the research, problem statement, objectives of the research, scopes of the research, and significant of the research highlights the introduction to this research work. Chapter 2 consists of comprehensive literature review based on the research topic. The literature reviewed covers the overview on biomaterials and major issues related to implanting materials. It also explained the advantages and disadvantages of biodegradable materials. The chapter further describes the historical overview of zinc metal and the contribution of Mg as allying element to Zn-based alloys. Previous reported heat treatment and severe plastic deformation techniques performed on other types of Zn-based alloys are highlighted under this chapter. Chapter 3 explains the experiments methodology, characterizations and analysis conducted to achieve the research objectives. The chapter discussed the research approach and overall research flow chart. The experimental tasks include mould design and fabrication, sample material development, thermal analysis for phase detection and melt solidification behaviour. It also described the developed alloys sample preparation and heat treatment performed. Equal channels angular pressing (ECAP) die design, fabrication and billets processing are explained in this chapter. The procedures followed to analyse the developed samples microstructures, mechanical, corrosion and biocompatibility properties are highlighted in this chapter. The experimental results are discussed in details under chapter 4. The discussions are classified into preliminary and final stage experimental results. The development of Zn-3Mg alloy, solidification behaviour, microstructural analysis and effect of heating durations are explained in the preliminary section. The influence of heat treatment cooling mediums on microstructure and microhardness of treated Zn-3Mg alloy is discussed in this section. In addition, discussion on significant of homogenisation treatment on developed alloys microstructure, mechanical and degradation property is done under this section. The final stage section consists of the result analysis from ECAP die material selection, processing of Zn-3Mg alloy via ECAP dies, ECAPed samples microstructure and grain size analysis. The chapter also explains the influence of combined heat treatment and ECAP processing on degradation behaviour of treated Zn-3Mg samples. Zn-3Mg alloys biocompatibility assessment is also discussed in the detail experimental section of chapter 4.

Finally, conclusions are made based on the results obtained from the experiments conducted and presented in chapter 5. Recommendations for further investigations based on the research vacuums acknowledge during this study are mentioned and highlighted in chapter 5.

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