Characterization and In-Vitro Activity of Powder Metallurgy Magnesium-Zinc / Bioglass Composite for Biomedical Applications

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LIST OF ABREVIATIONS

$((HOCH_2)_3CNH_2)$(Tris)	Tris- Hydroxymethyl Aminomethane
$(Ca)_{10}(PO_4)_6(OH)_2$	Apatite
45S5 Bio-glass	A type of bio-glass
A.D	Anno Domini/ Before Christ (B.C)
Al	Aluminum
Al_2O_3	Aluminum Oxide/ Alumina
AM60	Magnesium- Aluminum (6%) - Manganese (0.35%) Alloy
AMS	Absorbable Metal Stent
aq	Aqueous
AZ63	Magnesium- Aluminum (6%) - Zinc (3%) Alloy
BG	Bio-glass
Ca^{2+}	Calcium Ions
$Ca_3Mg_3(PO_4)_4$	Calcium Magnesium Phosphate
$Ca_5(PO_4)_3X$	Stoichiometry of Calcium Phosphate materials
$CaCl_2$	Calcium Chloride
$CaCo_3$	Calcium Carbonate
CaO	Calcium Oxide
Cl^-	Chloride Ions
CO_3^{2-}	Carbonate Ions

Co-Cr	Cobalt Chromium
Co-Cr-Mo	Cobalt Chromium Molybdenum
DI	Deionized Water
e^-	Electron
EDS	Energy Dispersive Spectroscopy
ERMI ®	Endosseous Ridge Maintenance Implant
F^-	Fluoride Ions
F-75	Cobalt- Chromium (30%) - Molybdenum (7%) Alloy
FAp	Fluoroapatite
H_2	Hydrogen Gas
H_2O	Water
HAp	Hydroxyapatite
HCA	Hydroxycarbonate Apatite
HCl	Hydrochloric Acid
I_B	Bioactivity Index
$K_2HPO_4.3H_2O$	di- Potassium Hydrogen Phosphate Anhydrous
KCl	Potassium Chloride
l	Liquid
LTI	Low Temperature Isotropic Carbon
MEP ®	Middle Ear Prostheses
Mg	Magnesium
$Mg(OH)_2$	Magnesium Hydroxide
Mg^{2+}	Magnesium Ions
$MgCl_2$	Magnesium Chloride

$MgCl_2.6H_2O$	Magnesium Chloride 6-hydrate
MgF_2	Magnesium Fluoride
MgZn	Magnesium Zinc Alloy
Na^+	Sodium Ions
Na_2O	Sodium Oxide
Na_2SO_4	Sodium Sulfate Anhydrous
NaCl	Sodium Chloride
$NaHCO_3$	Sodium Hydrogen Bicarbonate
OH^-	Hydroxide Ions
OM	Optical Microscope
P_2O_5	Phosphorus Pentoxide
PBS	Phosphate Buffered Saline Solution
pH	pH Values
PO_4^{3-}	Phosphate Ions
PSR	Particle Size Ratio
RE	Rare Earth Elements
rpm	Rotation per Minute
s	Solid
SBF	Simulated Body Fluid
SEM	Scanning Electron Microscopy
SiO_2	Silicon Dioxide
SiO_4^{4-}	Silicate
$t_{0.5bb}$	Time taken for bioactive material to bind at the bone surface so that it covers more than of 50% of the bone surface

TCP	Tricalcium Phosphate
Ti	Titanium
XRD	X-Ray Diffraction
Zn	Zinc
ZrO_2	Zirconium Oxide/ Zirconia

LIST OF SYMBOLS

%	Percentage
°/min	Degree per Minute
°C	Degree Celsius
°C/min	Degree Celsius per Minute
Å	Angstrom
f_i	Mass Mole Fraction of Composite Constituent
g	Grams
g/cm^3	Grams per Cubic Centimeter
g/l	Grams per Liter
gm^{-2}/24hr	Grams per Meter Square per 24 hours
GPa	Giga Pascal
M	Molar
$mg/cm^2.hr$	Milligram per Centimeter Square Hours
MHz	Mega Hertz
mL	Milliliter
mm	Millimeter
MPa	Mega Pascal
$MPam^{1/2}$	Mega Pascal per Meter Square
N/A	Not Available
wt. %	Weight Percentage

Θ	Theta
λ	Lambda
μm	Micrometer
ρ_{Bulk}	Bulk Density
ρ_i	Theoretical Density of Composite Constituent
$\rho_{Relative}$	Relative Density
ρ_{Theory}	Theoretical Density
ρ_{True}	True Density

Pencirian dan Aktiviti In-Vitro Komposit Magnesium-Zink/Bioglas Secara Metalurgi Serbuk Untuk Aplikasi Bioperubatan

ABSTRAK

Dalam kajian ini, serbuk 45S5 bio-kaca telah ditambah ke dalam campuran serbuk Mg-Zn untuk menghasilkan biokomposit menggunakan kaedah metalurgi serbuk untuk aplikasi bioperubatan. Komposisi bio-kaca diubah daripada 0, 5, 10, 15, 20, 25, 30 wt. %. Objektif kajian ini adalah untuk mengkaji kesan penambahan bio-kaca ke dalam bio-bahan berasaskan Mg-Zn dari segi sifat fizikal, mekanikal, rintangan kakisan dan bioaktiviti. Mikroskop optik, Mikroskop Imbasan Elektron-Tenaga serakan Spektroskopi (SEM-EDS) dan pembelauan sinar-X (XRD) telah digunakan untuk mencirikan mikrostruktur dan fasa yang terdapat di dalam komposit. Keputusan mikrostruktur menunjukkan bahawa bio-kaca telah diedarkan dalam matriks Mg-Zn itu. Keputusan EDS menunjukkan bahawa Zn tidak meresap sepenuhnya ke dalam matriks Mg yang disebabkan oleh kesan parameter pemprosesan. Tidak ada bukti bio-kaca resapan ke dalam matriks. Corak pembelauan sinar-X sampel tersinter menunjukkan puncak Mg jangkaan dalam semua sampel. Sifat-sifat seperti ketumpatan dan kekuatan mampatan masing-masing telah ditentukan dengan menggunakan piknometer dan mesin Instron. Ketumpatan komposit telah dibandingkan dengan nilai teori dan trend terhasil menunjukkan bahawa ketumpatan meningkat seiring dengan peningkatan jumlah bio-kaca. Trend adalah sah untuk ketumpatan sebenar, teori, dan pukal. Kenaikan nilai ketumpatan boleh dikaitkan dengan pengisian bio-kaca pada ruang interpartikel. Walau bagaimanapun, jumlah keliangan juga meningkat kerana peningkatan jumlah bio-kaca. Ia boleh dikaitkan dengan pengasingan zarah bio-kaca. Oleh kerana jumlah bio-kaca meningkat, lebih bio-kaca terasing dan membawa kepada saiz masukan bio-kaca yang lebih besar di dalam komposit. Oleh kerana tiada tindak balas antara magnesium dan bio-kaca, semakin besar saiz masukan bio-kaca, lebih besar lompang yang terbentuk di antara muka magnesium dan bio-kaca, yang akhirnya akan memberikan meningkatkan kepada jumlah hasil keliangan. Kekuatan mampatan menunjukkan bahawa jumlah bio-kaca meningkat, kekuatan mampatan bagi komposit menurun. Ini juga boleh dikaitkan dengan lompang yang ditinggalkan di antara muka bio-kaca dan matriks yang bertindak sebagai pemula retak. Ujian in-vitro telah dijalankan, di mana sampel direndam dalam Bendalir simulasi Badan (SBF) untuk menentukan kadar hakisan dan bioaktiviti bagi komposit. Hasil kajian menunjukkan bahawa kadar kakisan sampel berkurangan dengan pertambahan kandungan bio-kaca. Pengumpulan produk kakisan, bersama-sama dengan pembentukan lapisan apatit membantut proses kakisan. Lapisan apatit yang digunakan untuk menunjukkan bioaktiviti itu juga dikesan di permukaan komposit. Lapisan apatit terbentuk mempunyai nilai yang lebih rendah daripada nisbah Ca / P berbanding hydroxyapatite kristal yang ideal, namun ia masih mematuhi keperluan bahan bio.

Characterization and In–Vitro Activity of Powder Metallurgy Magnesium-Zinc/Bioglass Composite for Biomedical Applications

ABSTRACT

In this study, bio-glass 45S5 powder was added into the mixture of Mg-Zn powders to produce biocomposite using powder metallurgy method for biomedical applications. The bio-glass composition was varied from 0, 5, 10, 15, 20, 25, to 30 wt. %. The objective of this works is to study the effect of bio-glass addition into Mg-Zn based biomaterials in terms of physical, mechanical, corrosion resistance and bioactivity properties. Optical microscope, Scanning Electron Microscope-Energy Dispersive Spectroscopy (SEM-EDS) and X-Ray Diffraction (XRD) were used to characterize the microstructure and phases present in the composites. Microstructure result shows that bio-glass was distributed in the matrix Mg-Zn. EDS results show that Zn has not completely diffuse into the Mg matrix due to the effect of processing parameter. There is no evidence of bio-glass diffusion into the matrix. XRD diffraction patterns of as sintered samples show expected peak of Mg in all samples. Properties such as density and compressive strength were determined using the pycnometer and Instron machine respectively. Density of the composite was compared with the theoretical value and the result trends indicated that the density has increased as the amount of bio-glass increased. The trends are valid for the true, theoretical, and bulk densities. Increment of densities value could be subjected to the filling of interparticles spacing by bio-glass. However, the total porosity also increased as the bio-glass amount increased. It could be attributed to the segregation of bio-glass particles. As the amount of bio-glass increase, more bio-glass segregate and leads to bigger size of bio-glass inclusion size inside the composite. Since no reaction between magnesium and bio-glass, the bigger the size of bio-glass inclusions, the larger the voids form at the interface, which will eventually give raise to total porosity results. The compressive strength shows that as the amount of bio-glass increased, the compressive strength of the composites decreased. This also could be attributed to the voids left at the interface of bio-glass and matrix which acts as crack initiators. In vitro test was conducted, in which samples were immersed in Simulated Body Fluid (SBF) to determine the corrosion rate and bioactivity of the composites. The results showed that corrosion rate of the samples decreases with increasing content of bio-glass. The accumulation of corrosion products, alongside with the formation of apatite layer retarded the corrosion process. The apatite layer that used to indicate the bioactivity was also traced on the surface of composites. The apatite layer formed has a lower value of Ca/P ratio compared to the ideal crystalline hydroxyapatite, however it is still compliant with biomaterials requirement.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Biomaterials are defined as materials intended or any substance (other than drug), whether synthetic or natural, used to interface with biological systems and can be used as a system or part of a system that treat, augments, or replaces any tissue, organ, or the function of the body (William, 1999; Pirhonen, 2006).

Biomaterials are the results obtained as the population ages. It is intended to help human to have more quality life. The research and development progress of biomaterials have had a significant effect on the production of medical implant and devices over the last 40 years (Holzapfel et. al., 2013). However, the use of biomaterials has started from since ancient times. According to historical records, there is a finding that the dental implants were used by the Mayan people in 600 A.D. Besides, there are also finding that proving the metal dental implants were used back in 200 A.D by discoveries of corpses in Europe (Ratner et. al., 2004).

The rapid development of biomaterials field, however came after the World War II. During World War II, many soldiers injured and this has put the attention of researchers to

develop implants that can be implanted in the human body and must be able to adapt to its new environment which is biological environment (William, 1999). Materials that originally applied as machinery or vehicles were implemented as materials for medical devices. Since then, the research and studies, innovation and development, and industrial productivity of biomaterials have developed sustainably. Nowadays, biomaterials representing market size about over $9 billion per year in the United States (US) only (Temenoff & Mikos, 2008).

Biomaterials could be classified into three types of materials, which are metals, ceramics, and polymers. Metals and ceramics are inorganic materials which have different types of bonding. Metals have metallic bonding with the high mobility of electrons while ceramics possessed ionic bonding. Metals are generally strong and offers a high degree of design complexity and suitable for orthopedic applications. Ceramics, however are generally hard and brittle materials, but are more corrosive resistant than metals. Polymers are organic materials that made up from long chains of covalent bonding elements. Due to its properties such as elasticity and high water content, polymers are suitable to be implemented in cardiovascular and soft tissue applications. Composite is another class of materials which combines any of the three materials to fulfill the requirement of the biomaterials (Temenoff & Mikos, 2008).

In present times, researchers are attracted towards studies on magnesium alloys as a potential biodegradable bone implant materials. Magnesium and its alloys is a lightweight metals (1.74 – 2.0 g/cm^3 in density) and biocompatible because of its biodegradable properties (Gu & Zheng, 2010). Biodegradable materials are defined as resorbable,

degrades materials at the same rate at which the host tissue regenerates. The developed interest of magnesium is due to their properties such as biodegradability in bioenvironments, mechanical properties such as elastic modulus which may decrease the shielding effect problems. Shielding effect is defined as bone remodeling by starving the new tissue of the fluctuating loads that are necessary to stimulate strong and healthy tissue formation (Parsons et. al., 2010).

Magnesium alloys have shown its excellent degradation properties inside in- vitro experiment conducted in earlier research. This degradation properties rate is fast and caused by electrochemical reaction or corrosion. The products of this reaction are $Mg(OH)_2$ and H_2 (Liu et. al., 2007; Witte et. al, 2008; Kirkland et. al, 2012). So, there is a need to study the new process to slow down the corrosion rate and perhaps, new alloying elements to be added with magnesium. This is important since the corrosion or degradation rate may affect the structure integrity of the implants and the alloying elements added may have a negative effect in human body (Kirkland et. al., 2012).

Although magnesium is known to be one candidate of biodegradable and biocompatible materials, it also has its own weakness, which is, its bioactivity. The key element for a biomaterial to perform well its functions, especially for bone regeneration or orthopedics applications is the formation of apatite layers. Since the discoveries of bio-glass, the apatite layer formation has been used as an indicator of bioactivity of a biomaterial. Apatite is one of a subgroup originates from phosphate minerals. It is one component of bone minerals. Apatite exhibits a miscellaneous structure with assorted lattice and morphologies. This mineral stoichiometry may be written as $Ca_5(PO_4)_3X$, where