Fabrication and Properties of Magnesium-Calcium Alloy via Powder Metallurgy Technique

by

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LIST OF ABBREVIATIONS

Mg	Magnesium
Ca	Calcium
SBF	Stimulated Body Fluid
PM	Powder Metallurgy
ASTM	American Standard Measurement
CR	Corrosion Rate
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscopy
EDS	Electron Dispersive Spectrometry
VH	Vickers Hardness

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LIST OF SYMBOLS

γ	Specific Surface Energy
ΔS	Increase of the Specific Surface
α-Mg	Alpha Magnesium Phase
E_{corr}	Corrosion Potential (V)
i_{corr}	Corrosion Current Density (g/cm^3)
T_1	Sintering Temperature at 500 °C
T_2	Sintering Temperature at 550 °C
T_3	Sintering Temperature at 600 °C

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Fabrikasi dan Penyifatan Kebolehan Terbiodegradasikan Aloi Magnesium Kalsium melalui Teknik Metalurgi Serbuk

ABSTRAK

Komposisi aloi Mg-Ca telah disediakan melalui kaedah metalurgi serbuk (PM) dengan penambahan bilangan kandungan kalsium dan suhu pensinteran yang berbeza. Ini adalah untuk menilai kesan yang disebabkan oleh jumlah kandungan kalsium dan pengaruh pensinteran suhu pada matriks aloi tersebut. Kalsium bertindak sebagai elemen aloi dalam Mg-Ca ditambah dengan kalsium pada kadar 0.5, 1, 1.5 dan 2 secara berat peratusan (wt.%) kemudiannya disinter pada suhu yang berbeza 500, 550 dan 600 ° C (T_1, T_2 dan T_3) dalam persekitaran argon. Kesan pensinteran juga disiasat dengan memberi tumpuan kepada mikrostruktur dan sifat-sifat sampel tersinter. Analisis XRD menunjukkan bahawa penambahan kalsium membawa kepada pembentukan fasa Mg_2Ca di sempadan α-Mg. Hal ini menyebabkan penambahan dalam nilai kekerasan sampel. Lebih banyak kandungan kalsium membawa kepada struktur bijian kecil dan meningkatkan tekanan antara zarah. Dengan itu menyebabkan kerapuhan dalam sampel komposit. Ketumpatan setiap komposit sampel juga meningkat bermula dari 1.78 g/cm^3 sehingga 1.83 g/cm^3. Walau bagaimanapun profil keliangan menunjukkan ciri-ciri songsang kepada penambahan kalsium. Analisis morfologi dijalankan menggunakan mikroskop optik menunjukkan peningkatan liang dengan peningkatan suhu pensinteran bersama-sama dengan kandungan kalsium dalam aloi Mg-Ca. Disebabkan oleh pembentukan fasa antara logam Mg_2Ca ini juga, tren kadar kakisan menunjukkan profil meningkat apabila terdapat peningkatan kandungan kalsium. Graf Tafel ekstrapolasi menunjukkan kadar kakisan komposit Mg-Ca meningkat apabila kandungan kalsium bertambah. Walau bagaimanapun, terdapat perbezaan kecil pada kadar kenaikan iaitu 8.52x10^{-1} mpy kakisan paling tinggi pada sampel Mg-2Ca yang disinter pada 600 °C dan kadar paling perlahan adalah 1.59x10^{-4} mpy pada sampel asal Mg yang disinter pada 500 °C.

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Fabrication and Properties of Biodegradable Magnesium-Calcium Alloy via Powder Metallurgy Technique

ABSTRACT

Composition of Mg-Ca alloys were prepared by powder metallurgy (PM) method with addition of different calcium content and sintering temperature. This is to evaluate the effect caused by the amount of calcium content and the influence of sintering temperature in the metal matrix alloy. Calcium act as the alloying element in Mg-Ca is added in by 0.5, 1, 1.5 and 2 weight percentage (wt.%) and sintered at 500, 550 and 600 °C (T_1, T_2 and T_3 respectively) in argon atmosphere. The effect of sintering is also investigated by focusing on the microstructure and properties of sintered sample. XRD analysis shows that the addition of calcium leads to the formation of intermetallic Mg_2Ca phase at the border of α-Mg grain boundaries. Particularly, causing an increment in hardness values of the samples. More calcium content leads to smaller grain structure and increase stress between particles. Hence causes embrittlement in the sample alloy. The density of each sample alloy increased from 1.78 g/cm^3 to 1.83 g/cm^3 while porosity profiles show inverse characteristics upon addition of calcium. Morphological analysis carried out by optical microscope shows increase pores refinement with the increase of sintering temperature together with calcium content in Mg-Ca alloys. Due to the formation of Mg_2Ca in the alloy, the trend of corrosion rates show increase profile as calcium content increased. The samples also show an increment as sintering temperature increased. Tafel extrapolation graph shows that the corrosion rate of Mg-Ca alloy increases as calcium content increases. However, there is an only small increment rate difference that is $8.52\text{x}10^{-1}$ mpy value of most rapid corrosion on Mg-2Ca sintered at 600 °C sample and the slowest rate is $1.59\text{x}10^{-4}$ mpy on pure Mg sample sintered at 500 °C.

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Magnesium is the third most abundant structural metal in the earth's crust after aluminium and iron. The relative density of magnesium is 1.74 g/cm^3 which are approximately two thirds of that of aluminium, one quarter of zinc, and one fifth of steel. The general properties of this element are known to be light weight, low density and good to excellent corrosion resistance. For engineering applications, magnesium is usually alloyed with one or more elements to enhance its characteristic. However, compared to other structural metals, magnesium alloys have a relatively low absolute strength, especially at elevated temperatures. Presently, the most widely used magnesium alloys are based on the Mg-Al system (Gu & Zheng, 2010). Their applications are usually limited to temperatures of up to 120 °C (Ye & Liu, 2004). Their high strength-to-weight ratio makes magnesium alloys extremely promising for applications requiring light weight, such as aerospace and automotive industry. Today, these characteristics of very high specific strength and lightweight of magnesium are also applicable for biomedical purposes (Wan et al., 2008). However, there is no systematic study to date that presents the development of Mg–Ca alloys for biomedical use. To our knowledge, the previous studies on biomedical magnesium alloys mainly focused on the Mg-Al and Mg-RE alloy systems (Li et al., 2008). The need for high-performance and lightweight materials for some demanding applications

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has led to extensive research and development efforts in the development of magnesium matrix alloys and cost-effective fabrication technologies.

In the present work, selection of calcium as alloying element to develop binary magnesium-calcium alloys is due to the following considerations. It is well known that calcium is a major component in human bone and calcium is also essential in chemical signalling with cells. Calcium has a low density (1.55 g/cm^3), which endues the Mg-Ca alloy system with the advantage of similar density to bone. Magnesium is necessary for the calcium incorporation into the bone which might be expected to be beneficial to the bone healing with the co-releasing of Mg and Ca ions (Li et al., 2008).

The mechanical properties of a product vary with its fabrication technique. Using powder metallurgy (PM) technique, the physical and mechanical property of magnesium calcium alloy is studied to compare its compatibility for biomedical purpose and bodily function application. This fabrication technique is chosen because using the PM approach, dimensional tolerances are commonly improved by one to two orders of magnitude and alloy chemistry limitations are essentially eliminated. This is expanded through alloy development research wherein a PM processing route designed to simulate industrial practices is used in the most recent work based on the effects of metals additions on selected mechanical properties of magnesium alloys.

The study by Wan et al., (2008) on biomedical magnesium alloys focused mainly on bone substitution. The biomedical researchers have devoted themselves to the corrosion and biocompatibility evaluations of commercial magnesium alloys. PM magnesium

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calcium alloy is to be used for bone grafting that replaces missing bone in order to repair bone fractures. Even though pure magnesium itself has the properties of lightweight, low density and high specific strength, it has low absolute strength at elevated temperature and very rapid corrosion rate. Reinforcing magnesium with calcium causes reduction in grain size hence leads to increase of corrosion resistance value of the product. Nevertheless, the amount calcium content can affect the mechanical properties of Mg-Ca alloy. Excessive quantity of calcium content causes more Mg_2Ca intermetallic phase to appear in grain boundaries leads to reduction in grain size. Hence, producing low ductility characteristic of the alloy. Very stiff alloy is not suitable for artificial bone application.

Magnesium alloy dissolved if placed in aqueous solution contained chloride ion. Therefore, magnesium calcium alloy can be used for its biodegradable characteristic. Generally, degradable biomaterials should have sufficient strength, matching degradation rate with tissue healing rate and good biocompatibilities. In this research, the characteristic of this alloy is done by in-vitro method. Fabrication process starts with mixing of 99.9% pure magnesium powder and pure calcium powder. The method resumed with cold pressing process using manual hydraulic sample compressing machine. Subsequently, conventional sintering took place in tube furnace with supply with argon gas to create inert atmosphere. The physical, mechanical and electrochemical analyses are used for the materials characterisation of this research.

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1.2 Problem Statement

Fabrication of magnesium alloy has been done via various methods such as casting and forging. However, these techniques require a very high energy and sintering temperature. Generally, powder metallurgy (PM) technique needed less amount of energy compared to other fabrication method. Hence, PM technique is used in order to examine the compatibility in fabricating Mg-Ca alloy in low sintering temperature.

The alteration and selection of the alloy's properties is highly dependable on the application of the final product. The amount of calcium content in magnesium alloy and sintering temperature gives different effects on physical and mechanical properties of Mg-calcium alloy. In term of strength, pure magnesium is very low. However, when added with calcium the strength increases. Nevertheless, excess amount of calcium causes this mechanical property of alloy starts to decrease.

In this research, the relative optimum amount of calcium to be added is examined. The fitting of artificial substances to inside of our body depends on their ability to relate to regular bodily system and function. Compatibility of Mg-Ca alloy for biomedical application is measured by the corrosion rate calculation based on the current density and corrosion potential values from Tafel extrapolation via potentiostat electrochemical testing.

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1.3 Research Objectives

- To fabricate the Mg-Ca alloy via powder metallurgy method.
- To study the effects of amount of calcium content in Mg-Ca alloy to physical and mechanical properties.
- To examine the corrosion rate of Mg-Ca alloy to study its biodegradability.

1.4 Scope of Study

Research involves pure magnesium powder alloyed with calcium powder producing magnesium calcium (Mg-Ca) alloy via powder metallurgy (PM) technique. Manipulated variable is the calcium content in the Mg-Ca alloy varies for calcium at 0, 0.5, 1.5, 1 and 2 wt.%. In addition to that, sintering temperature also set to three different temperatures at 500, 550 and 600 °C (T_1, T_2 and T_3) respectively. This alloy undergoes physical testing which subsequently related to its microstructure orientation. The study is carried out by in-vitro to identify the mechanical properties of Mg-Ca alloy due to parameter of various calcium contents and sintering temperature. Electrochemical characterisation is done in SBF solution to relate the alloy compability to bodily function.

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CHAPTER 2

LITERATURE REVIEW

2.1 Metallurgy Fabrication Technique

2.1.1 Introduction

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Designing a microstructure for both strength and creep resistance is a practice of multiple compromises. It is mostly related to when considering the grain boundary effects. A decrease in grain size to improve strength brings with it an increase in the length of grain boundary in the structure, which may be deleterious to creep behaviour. It is extremely difficult to include all these features in any one microstructure. Powder metallurgical processing can avoid some of these problems, but can have limitations of its own primarily related to residual porosity and rely on the application of external pressure (Bettles, 2008).

Powder metallurgy (PM) approaches are advantageous in producing near net shapes of components and therefore, largely increase the utilization ratio of materials and reduce machining cost. Plus, homogeneous and fine microstructure can be obtained by means of this way too. PM forming technology turns out to be a significant method for reducing costs of alloys. It is possible that the most versatile processing technique when considering the ability to modify alloy chemistry and at the same time produce a near-net-shape product is powder metallurgy technique. Fundamentally, the process follows procedures developed historically by the ceramics sector and therefore the most important operating parameters include particle size distribution, blending techniques (including use of dispersants), pressing, and ultimately sintering (Kipouros et al., 2006).

Powder metallurgy technique can utilize rapid solidification to produce unique alloys and fine grain structures. This is due to the small size of particle with high surface area. Hence, increase the point contact between particles which initiates faster and uniform reaction. Mechanical properties of about 90% dense PM samples are similar to wrought product (Burke & Kipouros, 2007).

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The advantages of this processing method include the capability of incorporating a relatively high volume fraction of reinforcement and fabrication of alloys with matrix alloy and reinforcement systems that are otherwise immiscible by liquid casting. The cost-effective processing of alloy materials is, therefore, an essential element for expanding their applications. The availability of a wide variety of reinforcing materials and the development of new processing techniques are attracting interest in alloy materials. This is especially true for the high performance magnesium materials, not only due to the characteristics of alloys, but also because the formation of an alloy may be the only effective approach to strengthening some magnesium alloys (Ye & Liu, 2004).

Basically, powders are described to be in a dispersed system which arrangements of matter is said to be consisting of at least one disperse phase and a continuous surrounding medium. The dispersed phase contains of a number of individual elements or particles. Hence, using the term powder particle to indicate undeveloped primary particles formed directly from production process. Collectively, the most important consideration in powder metallurgy is particle fineness. Besides the actual geometrical dimensions of the particle and its projection, every physical property which is related to the dimensions even by a slight value function can be used. Technically, the range < 40 µm is called sub-sieve range, as normal dry sieving is difficult to apply to such small particles. Hence, it has to be > 40 µm in order to be considered at the sieve range (Thummler & Oberacker, 1993).

Powder metallurgy is the manufacturing science of producing solid parts of desired geometry and material from powders. It may also be referred to as powder processing considering that non-metal powders can be involved. Powders are compacted into certain geometry then sintered to solidify the part. The first consideration in powder metallurgy is the powders used are for manufacturing process. Several different measures are used to quantify the properties of a certain powder. Powders can be pure elements or even alloys. A powder might also be a mixture of different kinds of powders. It could be a combination of elemental powders, alloy powders or both elemental and alloy powders together. In this study, pure magnesium and calcium powder with purity of 97.0 % and 98.0 % respectively are used as raw materials.

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Generally, powder selection and processing will depend on cost, desired purity and mechanical properties of finished product. Environmental control is critical in proper storage and the handling of powders. Powder contamination can results in powder degradation and should be avoided. High surface areas cause powders to react readily with outside materials. Hence, oxidation takes place caused by the oxygen present in the air. The surface is measured by considering the combined surface area of all the particles and relating that to the volume of powder usually expressed in the unit cm^2/g. Powders have an extremely high surface area to volume ratio. Surface area to volume increases as particle size decreases.

Particle shape also is one of the factors affecting surface area. The higher the surface area, the more activity takes place during sintering. However, there are both advantages and disadvantages to increased surface area of powders. Increased surface area will increase the area for oxides and other surface films to develop. Also agglomeration, or the sticking together of powder particles, tends to occur in smaller sized particles. Smaller particles are advantageous in a way that they provide more uniform material distribution in the manufacturing process and better mechanical properties in the product (Veerapandian, 2013).

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2.2 Powder Metallurgy Methodology

2.2.1 Ball Milling

Calcium is not readily available in powder form due to its property to be flammable when high surface area exposed to an environment with high temperature. Calcium is also easily reacts to its surrounding and oxidized. Hence, it is only can be obtain in a form of granules from Sigma-Aldrich with purity of 99.6 %. Granular calcium was then further sorted in order to fabricate powdered calcium via milling process. Use of milling in powder metallurgy is limited due to the disintegration of metallic materials which mostly exhibit considerable plasticity that is less effective. Even so, materials such as intermetallic compounds and ferroalloys can be comminuted by mechanical means. Plus, there are important mechanical disintegration process in powder metallurgy mainly those involving high energy milling procedures. In which severe embrittlement of the metal occurs. Due to the combined action of centrifugal force and the friction between balls and container wall, the balls move together with the container wall until the gravitational force is balanced by the centrifugal force and subsequently fall down in free space causing an impact with the powder particles (Purohit et al., 2012).

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Generally, there are mechanisms for size reductions in the solid state are based on fracture mechanics. Starting with the nucleation of cracks followed by crack propagation and fracture hence, new surfaces are formed. A further decrease of mean particle size can take place only when these processes occur continuously. Specifically, the kinetic energy