MECHANICAL AND BIODEGRADABLE PROPERTIES OF HYDROXYAPATITE COATED MAGNESIUM DEPOSITED BY COLD SPRAY

by

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TABLE OF CONTENTS

CHAPTER THREE: MATERIALS AND RESEARCH METHODOLOGY

LIST OF TABLES

LIST OF FIGURES

LIST OF ABREVIATIONS

SS	Stainless steel
Ti	Titanium
Mg	Magnesium
HAP	Hydroxyapatite
Cu	Copper
Al	Aluminium
Zn	Zinc
Mn	Manganese
Fe	Iron
Ni	Nickel
Ca	Calcium
Pb	Lead
XRD	X-ray diffraction
AFM	Atomic force microscope
SEM	Scanning electron microscope
EDX	Energy-dispersive X-ray analyser
SBF	Simulated body fluid
XRF	X-ray fluorescence
HCP	Hexagonal close-packed
CS	Cold spray
LPCS	Low pressure cold spray
Vp	Particle velocity
Vc	Critical velocity
CFD	Computational fluid dynamic
DOE	Design of experiment
HVOF	High velocity oxy fuel
D	Desirability

SIFAT MEKANIK DAN BIODEGRADASI MAGNESIUM BERSALUT HIDROKSIAPATIT DIENAP MELALUI SEMBURAN SEJUK

ABSTRAK

Proses semburan sejuk yang mudah dan telah diubahsuai digunakan untuk menyalut serbuk hidrosiapatit ke atas substrat magnesium tulen yang dipanaskan kepada 350°C atau 550°C dan dihaluskan permukaan samada 240 atau 2000 gred kekasaran dengan jarak ‘standoff’ 20 mm atau 40 mm. Prosedur ini diulang lima dan sepuluh kali. Satu reka bentuk faktorial pecahan (2^{4-1}) telah digunakan untuk menjelaskan faktor-faktor proses yang memberi kesan kepada ketebalan, kekuatan dan modulus elastik sampel. Analisis kaedah tindihan digunakan untuk menentukan nilai domain yang optimum. Kemudian, kaedah kecuraman digunakan untuk mengesah dan memindahkan nilai domain yang optimum. Sifat mekanik yang maksimum telah diperolehi pada jarak 30mm, gred kekasaran permukaan Ra=0.14 dan 460°C suhu pemanasan substrat yang menghasilkan salutan optimum dengan ketebalan 49.77µm, 462.61 MPa kekuatan dan 45.69 GPa modulus elastik. Lapisan hidroksiapatit tidak menunjukkan perubahan fasa pada suhu 550°C. Daya mikroskop atom menunjukkan topografi lapisan seragam dan mikroskop imbasan elektron menunjukkan ikatan yang baik antara lapisan bersalut dan substrat. Kajian biodegradasi menunjukkan bahawa lapisan apatit tulang yang terbentuk di atas permukaan lapisan selepas 24 jam boleh menggalakkan ikatan tulang dengan tisu hidup dan meningkatkan jangka hayat lapisan. Kajian kehilangan berat menunjukkan bioaktiviti bagi sampel bersalut lebih baik berbanding dengan sampel tidak bersalut. Ujian lekatan mendedahkan bahawa pengurangan kekuatan ikatan datang dari pembubaran lapisan kimia yang berterusan. Selepas 24 jam rendaman, kekuatan ikatan adalah 40 MPa. Ujian percepatan kakisan

menunjukkan bahawa lapisan hidroksiapatit melindungi dan mencegah magnesium daripada kakisan dalam persekitaran mengakis.

MECHANICAL AND BIODEGARADABLE PROPERTIES OF HYDROXYAPATITE COATED MAGNESIUM DEPOSITED BY COLD SPRAY

ABSTRACT

A simple and modified cold spray process was developed in which hydroxyapatite powder was coated onto pure magnesium substrates preheated to 350°C or 550°C and ground to either 240 grit or 2000 grit surface roughness, with standoff distances of 20 mm or 40 mm. The procedure was repeated five and ten times. A fractional factorial design (2^{4-1}) was applied to elucidate the process factors that significantly affected the thickness, nanohardness and elastic modulus of the coating sample. The overlaid method analysis was employed to determine trade off optimal values from multiple responses. Then, steepest method was used to reconfirm and relocate the optimal domain. The maximum mechanical properties of the coating were determined at 30mm standoff distance, surface roughness Ra=0.14µ and 460°C substrate heating temperature which accommodate the optimum coating of 49.77µm thickness, 462.61 MPa nanohardness and 45.69 GPa elastic modulus. The hydroxyapatite coatings did not show any phase changes at 550°C. Atomic force microscopy revealed a uniform coating topography and scanning electron microscopy revealed good bonding between the coated layers and the substrates. The biodegradable study suggested that bone-like apatite layer formed on the surface of the coatings at 2 hours may promote bone bonding with living tissues and increase the

longevity of coatings. The mass loss experiment concluded that coated sample shows a better bioactivity compared to uncoated sample. The adhesion test revealed that reduction of bond strength comes mostly from the continuation of chemical dissolution of coatings. After 24 hours of immersion, the bond strength was 40 MPa which satisfied the requirement for bioimplant application. The accelerated corrosion test concluded that the hydroxyapatite coating remarkably protect and prevent magnesium from corrosion in the corrosive environment.

CHAPTER ONE

INTRODUCTION

1.1 Research background

The desire to bring man-made materials into the treatment of human body has raised an influx of research into the field of biomaterials. A challenge in the region of biomaterials is to enhance the interface between biomaterial implants and the living tissue surrounding them. The thought of using materials to replace or supplement human biological functionsis not a recent phenomenon. Sutures were first used in around 4000 BC and the implantation of gold plates for skull repair is recorded back to 1000 BC (Patrick et al., 2014).

Nowadays, patients leading to broken bone incidence are increasing which leads to the necessity of bone implant surgery (Picciolo et al., 2013). Therefore, there have been several studies on the possibilities of using different implant system in the human body considering cost, life and bio/mechanic compatibility. Unfortunately, the choice is limited with stainless steel (SS), cobalt chromium and titanium (Ti) being the most preferred materials (Manivasagam et al., 2010). Although currently in use for the vast majority of applications there are still number of problems associated with these implants. One of the major ones is that if these implants exist in the human body for a long time, they will release toxic elements to impair human body's health. For example, metal ions (e.g. aluminium and vanadium ions) are discharged from the Ti–6Al–4V implant to the bloodstream and these may cause local irritation of the tissues encompassing the implant (Manivasagam et al., 2010). The application of bio-degradable implants can solve this issue. The biodegradable implants can progressively be dissolved, absorbed, consumed or excreted after the bone tissue heals. In correlation, magnesium (Mg) and its alloys are potential biodegradable materials because of their attractive biological performances (Song, 2007; Kirkland et al., 2012; Seal et. al., 2009).

The idea of utilizing Mg as implant are strengthen by the superior biodegradability of metal Mg in body fluids by corrosion. It has been known that there are no serious concerns on the harm that can be caused by Mg ions to the human body (Silleken et al., 2011). It has been suggested that Mg can accelerate the development of new bone tissue and mechanical properties of Mg are the closest to those of bones (Poinern et al., 2012). Thus, Mg and its alloys are better than some other metallic or polymeric implants at bone repairing or orthopaedics. However, the use of currently available Mg alloys is generally not advisable as most alloying elements may be toxic for the human body. Furthermore, preparation of these alloys adds to the cost of the implant without giving any decisive advantage. Thus, use of pure Mg in bio implants is being seriously considered (Poinern et al., 2012).

However, Mg is susceptible to attack in chloride containing solutions, e.g. the human body fluid or blood plasma (Song et al., 2005). If the implants being made of

Mg are utilized to repair the diseased bone tissue, Mg tendsto lose the mechanical property before the healing of bone tissue due to the rapid corrosion. Recently, a few research have been done to slow down the biodegradation rate of Mg alloys, including fluoride conversion coating (Chiu et al., 2007), alkali heat treatment (Li et al., 2007) and plasma immersion ion implantation (Liu et al., 2007).

Other than reducing the biodegradation rate of Mg, the biocompatibility should also be considered.Some researchers in the field of orthopaedic biomaterials direct their emphasis on the manufacture and improve of bioactive properties of calcium-phosphates and in particular much interest has been directed towards the use of hydroxyapatite (HAP). Hydroxyapatite coating whose primary component is composed of the same ions responsible for the construction of the mineral part of bone and teethcan fulfil the dual properties. It is bioactive with bone-bonding ability, making it suitable for clinical use as bone spacers and fillers. The nonappearance of cytotoxic effect makes HAP biocompatible with both hard and soft tissue (Choudhuri et al., 2009).

To coat HAP powder onto highly degradable Mg substrate, any processing technique that melts the Mg substrate or accelerates the dissolution of Mg in fluid must be avoided. Thus, this work proposes the cold spray technique as a method suitable for coating HAP onto Mg substrate. This is also known as cold gas-dynamic spraying, kinetic spraying, high-velocity powder deposition and supersonic powder deposition (Lima et al., 2002). In principle, the feedstock powders are introduced into a high-velocity, gas dynamic stream and directed onto a substrate surface where they impact and form a coating(Li et al., 2003).

Cold spray technology overcomes the shortcomings of thermal spraying, which involves melting and solidification of the coating (Kang et al., 2013), as well as those of the dipping technique, notably the dissolution of Mg. Cold spray has been reported to produce coatings of proper density and adhesion with such substrates as copper (Cu) (Kang et al., 2013), aluminium (Al) (Lee et al., 2005),iron (Fe) (Steenkiste, 2006), Ti (Zheng et al., 2000),nickel (Ni)(King et al., 2007) and Mg alloys (Abdullah et al., 2013). However, to date, there has been no report dealing with the cold spraying of HAP powder to form a coating layer on a pure Mg substrate.

1.2 Problem statements

A deeper understanding of several cold spraying process factors (standoff distance, surface roughness, substrate heating temperature and number of sprays) including their interactions is needed to achieve a better comprehensive and control of the cold spray process (Moridi et al., 2014). Most of the typical published publications or reports on design of experiment are limited to the effects of the process parameters on a single response (Nathan et al., 2015). To determine the conditions that produce high-quality of HAP coating on Mg substrate, a trial and error method is not a good option which definitely involve high cost and time consuming since lots of experimental work need to be performed (Gosh and Flores, 2013). The solution to this problem is through the design of experiment because the results and conclusion that can be drawn from an experiment are depending to a large extent on the manner in which the data are gathered. Thus, the aim of this research is to evaluate the effect of cold spraying factors on the mechanical properties of HAP coating on Mg substrate including their interactions via design of experiment (DOE) method. The DOE developed using fractional factorial design (FFD) is able to establish the polynomial functions that describe the effects of processing conditions on the mechanical properties of HAP coating. Interestingly, only a fraction of actual experiment number is required to be run without forfeiting the accuracy of the final properties (Gomes et al., 2015).

Commonly, the existing techniques to coat HAP on Mg alloy is electrodeposition (Ivana et al., 2014). However, electrodeposition requires accurate control of variables. The failure to control the process variables could cause the base material intrusion into the deposit precipitating new phases. Furthermore, this technique always requires a conductive (metal) surface. Therefore, it cannot be used at all stages of a process (Walsh and Ponce 2014). On the other hand, the plasma spray technique has not been investigated possibly due to the low melting point of Mg. The plasma spray technique has not been investigated possibly due to the low melting point of Mg (Suo et al., 2012). Also, the plasma spray process requires high energy consumptions and complex unit. Therefore, the purpose of this study is to design a simple modified cold spray technique of HAP on pure Mg substrate at room temperature whereby the pressurized cold air is utilized. There is no heated gas required in this modified technique. Other than that, the Mg substrate was heated up below its melting point inside a muffle furnace.

It is important to understand the physics of the HAP-Mg bonding process established during HAP powder spraying process especially with respect to the interface so that high integrity interfaces could be obtained (Fauchais, 2014).

Thickness, nanohardness and elastic modulus of the HAP coating to pure Mg substrate are the crucial factors in ensuring sufficient coating biodegradation lifetime. Thus, the aim of this study is to investigate the thickness, nanohardness and elastic modulus of HAP coated on Mg substrate in modified cold sprayed condition using different characterization technique.

Moreover, the normal practice presented in literature just proposed optimal processing setting using response surface plot. However, the point still can be further refined as the optimum value would be outside the experimental design space. Since there are three responses studied in this research, the aim of this work is to proposed optimized cold spray parameters through the use of overlaid contour plots and the steepest ascent methods for multiple responses of thickness, nanohardness and elastic modulus. The overlaid contour plots is to find the feasible region and the steepest method will be applied to find the optimum value. Moreover, the steepest method itself is rarely reported.

Despite the encouraging incentives from the design of experiment as an alternative to typical experiment design for enhancing the mechanical properties of HAP coating on Mg substrates there are still great challenges to overcome (Kraus et al., 2012). This is because the coated samples were meant for load bearing application where time bound healing should start before the whole implant dissolves. Thus, the aim of this study is to find the bioactivity and biodegradation rate when the coated sample was subjected to physiological medium like in the simulated body fluid (SBF). This work also focused on the accelerated corrosion test to investigate the protectiveness of HAP coating in the 3.5wt% NaCl solution towards immersion time intervals as Mg is generally known to degrade in aqueous environment.

1.3 Objective of the research

The main objectives of this research work are:

1. To investigate the thickness, nanohardness and elastic modulus of HAP coated pure Mg developed using modified cold spraying technique.
2. To propose optimized cold spray parameters through the use of overlaid contour plots and the steepest methods for multiple responses of thickness, nanohardness and elastic modulus of the coating.
3. To investigate compatibilities of HAP coated on pure Mg substrate in term of biodegradation in simulated body fluid and corrosion properties in 3.5wt% NaCl solution

1.4 Research Approach

This current work was conducted to fabricate an implant biodegradable material of HAP coated on pure Mg using modified cold spray technique. Four parameters of cold spray including standoff distance, substrate heating temperature, substrate roughness and number of sprays were statistically developed and evaluated using two-level of half fractional factorial design (FFD) and subsequently optimized using overlaid contour plot. Moreover, steepest method was used as to further optimize the responses which are coating thickness, nanohardness and elastic modulus of the coating. The phase presence was characterized using X-ray fluorescence (XRF), X-ray diffraction spectroscopy (XRD). The morphology of coating sample were characterized by Field Emission Scanning Electron Microscopy (FESEM) equipped with energy dispersive X-ray microanalysis (EDX). The mechanical properties were performed under nanoindentation testing to evaluate nanohardness and elastic modulus of the coating sample. The in vitro biodegradation behaviour of HAP coated Mg and pure Mg as a control sample was performed by immersing the samples in SBF solution for various immersion time. The biocompatibility test of coated sample was performed in 3.5wt% NaCl solution.

1.5 Scope of Thesis

This dissertation was organized in five chapters consecutively. In the first chapter, the introduction of the research work, problem statement, objective and research outline were pinpointed. In the second chapter, the evolution of metallic biomaterials, development of biodegradable metallic based materials, bioceramic, cold spray technique, basic principles of mathematical modelling and correlated test regarding to the biomaterials characteristics were reviewed. In the third chapter, procedures of experimental works and characterization technique performed in this research were explained. In the fourth chapter, the results and discussion on HAP coated onto Mg substrate as well as their performance on biodegradability in artificial surrounding were reported. In the fifth chapter, the conclusion of the findings and suggestions for the enhancement in future work were presented.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

This chapter aims to present a comprehensive literature review on work relating to the coating of HAP on Mg substrate. It starts with the review about biomaterials, the desired properties of implantable biomaterials, metallic biomaterials and bioceramics. Magnesium and its atomic properties and crystal structure, its physical properties and its potential as biomaterial for orthopaedic implant are reviewed next. Next a review about HAP and its properties such as physical, mechanical, chemical properties, the use of HAP as an implant coating and the HAP coating on Mg by cold spray technique are reviewed.

In this work, the cold spray technique which applies low temperature processing technique was used. Frequency, standoff distance, surface roughness, substrate heating temperature and number of sprays are used as the parameters of coating. Therefore, the work done by previous researches on that particular parameter process have been discussed. The fractional factorial design of 2^{4-1}, the use of contour plot to explore the potential relationship between variables, the multiple responses analysis using overlaid contour plot and desirability function and lastly steepest method for searching the optimal condition has been discussed in detail under design of experiment section. Biodegradable study in SBF solution and finally the accelerated corrosion test study in 3.5wt% NaCl have been discussed at the end of this chapter.

2.2 Biomaterials

Biomaterial can be defined as any synthetic material used to make devices to replace a part or a function of the body in a safe, reliable, economic and physiologically satisfactory way (John et al., 2007). The field of biomaterials is not new and as early as 4000 years back the Egyptians and Romans have used linen for sutures, gold and iron for dental applications and wood for toe replacement. Nylon, teflon, silicone, stainless steel and titanium are some of alternative materials that are put into use after World War II (Geetha et al., 2010).

A biomaterial is different from a biological material, such as bone, that is produced by a biological system. Biomaterials consist of interdisciplinary research area that require adequate information of three primary field: (1) materials science and engineering processing structure property interrelationship of synthetic and biological materials including metals, ceramics, polymer, composites and tissues (2) biology and physiology cell and molecular biology, anatomy, animal and human physiology and (3) clinical sciences dentistry, ophthalmology, orthopaedic, plastic and reconstructive surgery, cardiovascular surgery, neurosurgery, immunology, histopathology, trial surgery, veterinary pharmaceutical and surgery (Shi et al., 2006).

The ideal biomaterial must meet a variety of different criteria, depending upon the application. The first and foremost requirement for the choice of the biomaterial in orthopaedic replacements used in load-bearing situations such as total hip replacements or dental applications is its acceptability by the human body. The implanted material should not bring any unfavourable effects like hypersensitivity, irritation and toxicity either immediately after surgery or under post-operative conditions. Also, biomaterials should have adequate mechanical strength to support the forces to which they are subjected so that they do not undergo fracture. Thirdly, a bioimplant should have high corrosion and wear resistance in highly corrosive body environment and differing loading conditions, aside from fatigue strength and fracture toughness. The success of a biomaterial or an implant is exceedingly subject to three main considerations (i) the properties (mechanical, chemical and tribological) of the biomaterial ii) biocompatibility of the implant and (iii) the health condition of the recipient and the competencies of the surgeon (Geetha et al., 2010).

The present trend of developing bioactive materials has caused an expanding requirement for developing biomaterials in an assortment of uses. In fact, it is clear that to achieve exceptionally bioactive and mechanically compatible artificial materials for load-bearing application, it is important to look for novel synthesis routes by which ideal materials can be developed with required microstructure, mechanical properties and bioactivity. In the past, great efforts have been focused around developing metallic, ceramic and polymer materials that could interfacially and bioactivity bond to hard tissues (Donglu, 2005).

2.2.1 Desired properties of implantable biomaterials

First of all, a biomaterial must be biocompatible. It should not bring an adverse response to the body and the other way around. Moreover, it should be nontoxic and noncarcinogenic. These requirements have caused the elimination of numerous engineering materials that are available. Next, the biomaterial should have adequate physical and mechanical properties to serve as augmentation or replacement of body tissues. For practical use, a biomaterial should be agreeable to being formed or machined into different shapes, have relatively low cost and be promptly accessible (Davis, 2006). The ideal material or material combination should exhibit the following properties:

(a) A biocompatible chemical composition to avoid adverse tissue reactions

(b) Excellent resistance to degradation (e. g., corrosion resistance for metal or resistance to biological degradation in polymers)

(c) Acceptable strength to sustain cyclic loading endured by the joint

(d) A low modulus to minimize bone resorption

(e) High wear resistance to minimize wear debris generation

Synthetic materials currently used for biomedical applications include metals and alloys, polymers, and ceramics. Since the structure of these materials different, they have different properties and therefore, different uses in the body. Since the focus of this research is to produce a good coating HAP on Mg substrate, only metallic and bioceramic material are reviewed in this chapter.

2.2.2 Metallic biomaterials

Metallic materials continue to play an essential role as biomaterials to assist with the repair or replacement of bone tissue that has become diseased or damaged (Niinomi, 2002). Metals are more suitable for load-bearing applications compared with ceramics or polymeric materials. This is because of their combination of high mechanical strength and fracture toughness as polymeric and ceramic materials tend to be relatively weak or brittle. Titanium and titanium alloys, stainless steels and cobalt-chromium alloys are all used in joint replacement procedures and generally provide suitable mechanical support to restore orthopaedic function (Park, 2008). The ability of metal implants to be incorporated into natural bone structure, however, has some limitation and posed problems. One restriction of these present metallic biomaterials is the possible release of toxic metallic ions and/or particles through corrosion or wear processes (Puleo et al., 1995; Jacobs et al., 1998) that prompt to inflammatory cascades which reduce biocompatibility and cause tissue loss (Lhotka et al., 2003).

In addition, the elastic modulus of current metallic biomaterials are not well matched with that of natural bone tissue, resulting in stress shielding effects that can lead to reduced stimulation of new bone growth and remodelling which decreases implant stability (Nagels et al., 2003). Current metallic biomaterials are essentially neutral in-vivo, remaining as permanent fixtures which in the case of plates, screws and pins used to secure serious fractures must be removed by a second surgical procedure after the tissue has healed sufficiently. Repeat surgery increases costs to the health care system and further morbidity to the patient.

Magnesium has been investigated recently by many authors as a suitable biodegradable biomaterial and has become current potential metallic biomaterials. It also assists in numerous human metabolic reactions and is nontoxic to the human body. Magnesium has great biocompatibility and it is biodegradable in human body fluid by corrosion, thus eliminating the requirement for another operation to remove the implant. All these desirable features make the Mg-based material a promising metallic implant material (Gupta et al., 2011).

2.2.3 Bioceramics

Ceramic materials for orthopaedic applications were introduced in the 1970s, where failures of the biomaterials being use then, for example steel, cobalt alloys and poly (methacrylate) began to be detected. Subsequently, attention was directed to ceramic materials in an attempt to find good bone integration features. Ceramics used for the repair and reconstruction of diseased, damaged or worn out parts of the musculo-skeletal system are known as bioceramics (Hench et al., 1993). Bioceramics may be classified as bioinert, resorbable and bioactive (Emad et al., 2012). These main classes of bioceramics are categorized according to the response that they initiate within the body.

For instance, bioinert ceramic is one which does not react with the surrounding physiological tissue upon implantation. An example of relatively bioinert ceramics is dense and porous aluminium oxide (Al_2O_3), zirconia (ZrO_2) and single phase calcium aluminates. Bioinert ceramics is typically used for a structural-support implant or load-bearing implant. Some of these are the femoral head, bone screw and fixation plate.

Examples of non-structural implants are ventilation tubes, sterilization devices and drug delivery devices (Joyce et al., 2012).

The second type of bioceramics is resorbable or biodegradable ceramics. The idea of utilizing biodegradable ceramics as bone substitutes was presented in 1969 (Joe et al., 2012). Resorbable ceramics as the name implies, degrade upon implantation in the host. This material will be eventually replaced by endogenous tissue. Almost all resorbable ceramics are the variation of calcium phosphate except biocoral and plaster of Paris. Examples of resorbable ceramics are aluminium calcium phosphate, coralline and tricalcium phosphate. Bioceramics are widely applied to the dental and orthopaedic applications such as bone fillers after tumour surgery, a replacement for hips and maxillofacial reconstruction (Hench, 1991).

The third type of bioceramics is bioactive or surface-reactive ceramics. Upon implantation in the host, surface-reactive ceramics form a strong bond with the adjacent tissue (Best et al., 2008). Examples of this type bioceramics are dense non-porous glasses, bioglass, ceravital and HAP. One of their uses is the coating of metal prosthesis since metals tend to be toxic to the human body. This coating offers a stronger bonding to adjacent tissues which is very important for prosthesis. Hydroxyapatite is extensively used to enhance the integration of femoral implants into the hip joint. Hydroxyapatite appears as the most promising bioceramics because of its exceptional biological properties, for example non-toxicity, lack of inflammatory response and absence of fibrous or immunological reactions. Hydroxyapatite also possesses identical chemical composition and high biocompatibility with natural bone (Kehoe et al., 2008).

2.2.3.1 Application of Bioceramic

Bioceramics are widely applied to the dental and orthopaedic applications such as bone fillers after tumor surgery, replacement for hips and maxillofacial reconstruction (Hench, 1991). Hydroxyapatite (HAP), and other related calcium phosphate minerals are extensively used to improve the integration of femoral implants into the hip joint. HAP appears as the most promising bioceramics due to its outstanding biological properties such as anti-toxicity, lack of inflammatory response and absence of fibrous or immunological reactions. HAP also possesses identical chemical composition and high biocompatibility with natural bone (Kehoe and Eng, 2008).

Examples of the applications of various bioceramics are given in Table 2.1. However, ceramics usage as implant is in a small range due to their inherent brittleness, micro cracks, low impact strength and low tensile strength (Hui et al., 2010).

Table 2.1: Bioceramics and its application (Robert et al., 2015)

Application	Ceramic
Coatings for chemical bonding	HAP, surface-active glasses
Artificial tendons and ligaments	poly(lactic acid) (PLA)-carbon-fibre composites
Bone filler	Al_2O_3
Joint replacement	Al_2O_3, ZrO_2
Dental Implants	HAP, Al_2O_3, surface-active glasses

2.3 Magnesium

Magnesium is the 6th most abundant element in the earth's crust, representing 2.7% of the earth's crust. Despite the fact that Mg is not found in its elemental form, Mg compounds can be discovered around the world. The most widely found compounds are magnesite ($MgCO_3$), dolomite ($MgCO_3.CaCO_3$) and carnallite ($KMgCl_3.6H_2O$). Magnesium is the third most abundant dissolved mineral in the seawater (1.1 kg/m^3) and the lightest of all structural metals. It has a density of 1.74 g/cm^3, which is approximately one-fourth the density of steel and two-thirds that of aluminium. As a result of its low density and high specific mechanical properties, Mg-based materials are effectively pursued by companies for weight-critical applications (Gupta et al., 2011).

Magnesium also has high thermal conductivity (for pure Mg at 25^{o}C = 156 W/m.K), high dimensional stability, good electromagnetic shielding characteristics, high damping characteristics, good machinability and effectively reused (Kojima, 2000, Shanghyn et al., 2013). These properties make it important in a few applications including automobile and computer parts, aviation components, mobile phones, sporting goods, handheld tools and household equipment. However, Mg has not penetrated automotive despite its good properties because of the two major disadvantages. First, they exhibit low high temperature strength especially for power train applications. Secondly, Mg has a poor corrosion resistance (Blawert et al., 2014). The step for improving the corrosion resistance of Mg was the introduction of high purity alloys. Alloying can further improve the general corrosion behaviour, but it does not change galvanic corrosion problems if Mg is in contact with another metal and an electrolyte (Blawert et al., 2004 and Maria, 2011).

Magnesium has even been recommended for use as an implanted metal because of its low weight and inherent biocompatibility (Gray et al., 2002). However, the use of Mg alloys is generally not advisable because most alloying elements (see Table 2.2) can be toxic to the human body (except for Ca alloys). Furthermore, preparation of these alloys adds to the cost of the implant without giving any distinct advantages therefore the use of pure Mg in bio implants has been seriously considered (Poinern et al., 2012).

Table 2.2: Chemical composition of pure Mg, AZ31, AZ61 and AZ91 alloys (mass%) (Michal et al., 2015).

	Mg	**Al**	**Zn**	**Mn**	**Si**	**Cu**	**Ni**	**Fe**	**Ca**	**Pb**
Pure	99.974	0.003	0.006	0.004	0.003	0.0003	0.0007	0.0047	0.001	0.001
AZ31	95.704	3.05	0.82	0.40	0.020	0.003	0.0012	0.0023	-	-
AZ61	92.546	6.56	0.61	0.26	0.020	0.002	0.0006	0.0015	-	-
AZ91	90.24	8.80	0.71	0.19	0.029	0.029	<0.001	0.001	-	-

*Magnesium(Mg) *Aluminium(Al) *Zinc(Zn) *Manganese(Mn) *Silicon(Si) *Copper(Cu) *Nickel(Ni) *Iron(Fe) *Calcium(Ca) *Lead(Pb)

2.3.1 Magnesium as potential biomaterial for orthopaedic implant

The proper function of orthopaedic device depends upon numbers of factors, shortcoming in any of which may result in problem or failure: (1) device should be in proper design for sufficient strength (2) material selection is important for biocompatibility, corrosion resistance, long term stability and adequate strength. Assuming if correct surgical procedure, no infection, proper design and negligible corrosion, the most likely cause of the problem are one of the following (1) mismatch of elastic modulus between implant and bone (2) restriction of the vascular system preventing proper nutrition and causing necrosis and loss of strength leading to secondary fracture. Thus, failure may occur in the combination of these three modes (a) sufficient pain requiring surgical removal of the implant (b) mechanical failure of implant (c) secondary fracture of the bone.

The implant material is expected to withstand applied physiological forces without substantial dimension change, catastrophic brittle fracture or fracture in the longer term from creep, fatigue or stress corrosion. Thermodynamic stability can be only achieved in the ideal situation of equivalent replacement material in an identical structure to that natural tissue. Any departure from this may create a different stress state in the remaining tissue and hence the potential for bone resorption and implant joining (Bhat, 2006).

The history of biodegradable Mg implants began soon after the discovery of elemental Mg by Sir Humphrey Davy in 1808. The commercial production of Mg metal by electrolysis was acknowledged by Robert Bunsen in 1852. Edward C. Huse used some of Mg wires as ligatures to stop bleeding vessels of three human patients in 1878. He already observed that the corrosion of Mg was slower in-vivo and that the period until complete degradation was dependent on the size of the Mg wire used (Witte, 2009).

In orthopaedic applications, Mg are of interest as candidate because of its low toxicity of Mg^{2+} ions: its naturally present in human body and an estimated amount of half of the total physical Mg is present in the bone tissue, involved in many metabolic reactions and physiological mechanism, and excess Mg^{2+} can be excreted by urine (Vormann, 2003; Hermawan et al., 2010). Moreover, the fast degradability of Mg in the body; the stents in the body can be consumed and absorbed in a short period. On the other hand, the excellent mechanical properties of Mg; the density and Young's Modulus of Mg (ρ= 1.74g/cm^3, E=45GPa) are similar to that of the natural bone

(ρ=1.75g/cm^3, E=40-57 GPa) (Staiger et al., 2006). The close matching in mechanical properties, specifically the elastic modulus of Mg to those of bone is a great advantage relative to conventional implant metals in the avoidance or minimization of stress shielding and the resulting osteopenia (Chiu et al., 2007). Stress shielding is the process by which bone mass and density will decrease in the vicinity of an implant with a mismatched (usually higher) stiffness value, as it transfers the load away from the adjacent bone. This can cause serious problems and implant failure if it continues and is known to be a problem with current orthopaedic devices based on stainless steel or titanium, which have a density, elastic modulus and yield strength higher than that of bone.

Magnesium has great biocompatibility and it is biodegradable in human body fluid by corrosion, therefore help to avoid the second operation for removing and the long term stress-protection of the implants for bone repair (Witte et al., 2009). This means the implant would not remain in the body for longer than is needed to perform its task and be replaced by bone. This also means that patients would benefit from only temporary exposure to a ‘foreign’ object in their body. This is extremely crucial, as over time complications can and do occur for many implants with more issues likely to arise the longer an implant remains in vivo.

Due to functional roles and presence in bone tissue, Mg might have stimulatory effects on the growth of new bone tissue (Staiger et al., 2006). These desirable features have made Mg as promising implant material. The summary of physical and mechanical properties of natural bone and some implant materials are presented in

Table 2.3. Based on Table 2.3, it could be seen that the density between natural bone and Mg is quite similar. Moreover, Mg fracture toughness, elastic modulus and compressive yield strength are higher than the natural bone.

Table 2.3: Physical and mechanical properties of natural bone and some implant materials (Gupta et al., 2011).

Materials	**Density (g/cm^3)**	**Fracture Toughness ($MPa\ m^{1/2}$)**	**Elastic Modulus (GPa)**	**Compressive 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	50-200	189-205	170-310
Magnesium	1.74-2.0	15-40	41-45	65-100
Hydroxyapatite	3.1	0.7	73-117	600

Moreover, there are a lot of benefits of Mg as bioimplant materials. Magnesium is the lightest of all structural metals (1.74 g/cm^3). Pure Mg has strength to weight ratio of approximately 130 kN.m/kg. This is two times greater than one of the most commonly used Ti alloys (Ti_6Al_4V, 260 kN.m/kg) and as a result less material may be used to provide similar mechanical function in the body (Vormann, 2003). Moreover, Mg is unique due to its extremely high damping capacity (ability to absorb energy) the highest of any metal (Witte et al., 2008). This can be important in load-bearing applications where the shock and vibration-absorbing properties of Mg could provide significant benefit over other materials (Nicholas et al., 2013).

In the biomedical field, this can be very important in heavy load-bearing applications, where the shock and vibration absorbing properties of Mg could provide significant benefit over other materials. Current biomaterials such as pure Ti are relatively inert in the body, meaning they exhibit little host response, positive or negative. In contrast, Mg is considered biocompatible and non-toxic and has been shown to increase the rate of bone formation. Magnesium is also an important ion in the formation of the biological apatite that make up the bulk of bone mineral (Okuma, 2001).

If fully realized, functional bioresorbable implants based upon Mg would be unique to the field, giving the mechanical advantages of a metal combined with the degradable and biological advantages displayed by polymers. The key points of interest that Mg possesses over current materials, for examples, its biodegradability and low specific strength (i.e. reduced chance of stress shielding), additionally pose some of the greatest challenges to its use in the wider context. The notion that implants made from Mg from the bio perspective are designed to degrade also means that their shape and mechanical properties constantly change over the life of the implant, adding another layer of complexity to carrying out a full life-cycle design.

While investigations of bone cell response to pure Mg metal are scarce, various studies have investigated the effect of enhancing the surface of a biomaterial, for example, hydroxyapatite (HAP) with Mg ions and suggest a biochemical role for Mg in the bone system (Staiger et al., 2006). Revell et al., (2004) observed increased interfacial strength for implants with HAP surfaces enriched with Mg. Zreiqat et al.,

(2002) reported significantly increased bone cell adhesion on Mg-enriched alumina. Cells grown on Mg enriched substrates expressed a significantly enhanced level of $\alpha_5\beta_1$ integrin receptor, in addition to increased expression of collagen I extracellular matrix protein, thus suggesting a role of Mg in the cell attachment process.

Two studies done by Yamasaki et al.,(2002) and Yamasaki et al.,(2003) using Mg-enriched apatite or collagen materials reported similar beneficial effects of Mg-enriched materials on bone cell attachment and tissue growth. The precipitation of amorphous calcium phosphate or Mg calcium apatite $((Ca_{1-x}Mg_x)_{10}(PO_4)_6OH_2)$ coatings has been seen on the surface of Mg-based metals incubated in physiological electrolyte (Li et al., 2004; Kuwahara et al., 2001). Besides, a study by Myoui et al.,(2004) demonstrated an enhanced reaction of mesenchymal stem cells and MG-63 osteoblast-like cells with respect to adhesion, proliferation and metabolic activation on 1 wt. % Mg–HAP. More recently, Levingstone (2008) have demonstrated biocompatible Mg substituted HAP at 5.7 mol. % Mg.

A similar coating is observed in the corrosion layer of Mg-based metals implanted in vivo (Witte et al., 2005).In addition to the possible enhancement of cell attachment and growth, the precipitation of calcium phosphates at the surface may slow the corrosion process of Mg (Li et. al., 2004 and Kuwahara et. al., 2001). Given the achievement in the improvement of the biological response to Ti metals through the induction of a biomimetic calcium phosphate coating, the potential feature of Mg metals is an intriguing possibility, certainly worthy for further exploration.