HYDROXYAPATITE COATING ON MAGNESIUM BASED ALLOY FOR BIOIMPLANT BY COLD SPRAY DEPOSITION TECHNIQUE

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UNIVERSITI SAINS MALAYSIA

2012

HYDROXYAPATITE COATING ON MAGNESIUM BASED ALLOY FOR BIOIMPLANT BY COLD SPRAY DEPOSITION TECHNIQUE

by

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Thesis submitted in fulfillment of the requirements
for the degree of
Master of Science

July 2012

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "Hydroxyapatite Coating on Magnesium Based Alloy for Bioimplant By Cold Spray Deposition Technique". I also declare that it has not been previously submitted for the award for any degree or diploma or similar title of this for any other examining body or University.

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ACKNOWLEDGEMENT

First and foremost, all praises to Allah S.W.T for giving me the strength, patience and good health to successfully complete my mixed mode project in one semester. I would like to dedicate my gratitude to Universiti Sains Malaysia for all the supports to this research work. Also, I would like to extend my gratitude to School Materials and Mineral Resources Engineering USM for providing me the facilities in order to conduct my research. My special thanks to Prof. Ahmad Fauzi Mohd Noor for constant encouragement during the work.

I would like to express my profound thankfulness to the main supervisor, Professor Brij Kumar Dhindaw for his tremendous efforts and kindness in helping and guiding me throughout my research. He is more than just a supervisor. He was there at every step on the way with the experienced insights and enthusiastic encouragement. I admire his integrity, professionalism, and the commitment to excellence. Besides, I would like to thank my co-supervisor, Associate Prof. Dr Zuhailawati Hussain for the support and great help given. Her supervision has given me enthusiasm in learning and carrying out research.

A million thanks to all the technical staff for their various contributions and assistance during the work. Besides, I am also grateful to the Universiti Sultan Zainal Abidin (UniSZA) and Ministry of Higher Education (KPT) for the financial support provided to pursue my masters degree.

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LIST OF ABBREVIATIONS

Al	Aluminium
AFM	Atomic Force Microscope
Ca	Calcium
Cl	Chlorine
CS	Cold spray
DSC	Differential Scanning Calorimetric
EDX	Energy Dispersive Spectroscopy
FESEM	Field Emission Scanning Electron Microscope
K	Kalium
HAP	Hydroxyapatite
ICPOES	Inductively Couple Plasma Optical Emission Spectroscopy
Mg	Magnesium
Mn	Manganese
Na	Natrium
O	Oxygen
P	Phosphorus
SBF	Simulated Body Fluid
SEM	Scanning Electron Microscope
Ti	Titanium

TTCP	Tetracalcium phosphate
TG	Thermagravinometric
XRD	X-ray Diffraction

SALUTAN HIDROKSIAPATIT ATAS MAGNESIUM ALOI BAGI KEGUNAAN BIOIMPLAN OLEH TEKNIK ENDAPAN SEJUK

ABSTRAK

Dalam penyelidikan ini, kaedah semburan sejuk ringkas telah direka bagi menyaluti AZ51 dengan hidroksiapatit. Maklumat terperinci mengenai pemasangan dan rekabentuk semburan sejuk telah dibentangkan. Didapati, kualiti salutan hidroksiapatit telah dipengaruhi oleh suhu pemanasan substratum magnesium, kekasaran permukaan substratum magnesium dan juga jarak kedudukan. Salutan yang terhasil didapati padat dan mempunyai lekatan yang baik pada substratum. Ketebalan salutan adalah berbeza antara 20 sehingga 30 mikrometer. Ujian analisis kimia mendapati salutan tersebut adalah hidroksiapatit. Ciri-ciri mekanikal salutan telah diuji melalui ujian nano pelekukan. Kekerasan dan modulus anjal salutan adalah masing-masing 0.1 GPa dan 9 GPa. Seterusnya, keserasian dan kebolehuraian AZ51 yang telah disalut serta AZ51 yang tidak disalut diuji di dalam ujian in vitro yang menggunakan larutan cecair badan tiruan. Spektroskopi pancaran optikal plasma terganding beraruhan dan spektroskopi serakan tenaga sinar – x menunjukkan salutan hidroksiapatit mula melarut selepas satu hari, walaubagaimanapun menunjukkan tanda pembentukan semula selepas 10 hari rendaman. Ujian karatan terpecut di dalam 3.5 wt% NaCl menunjukkan salutan hidroksiapatit tetap melindungi AZ51 magnesium substratum sehingga 10 hari rendaman. Keadaan ini berterusan sehingga 21 hari sehingga keseluruhan hidroksiapatit digantikan dengan magnesium hidroksida dan di akhir ujian, didapati ion klorida hadir di atas permukaan yang menunjukkan pembentukan magnesium klorida.

HYDROXYAPATITE COATING ON MAGNESIUM BASED ALLOY FOR BIOIMPLANT BY COLD SPRAY DEPOSITION TECHNIQUE

ABSTRACT

In this study simple cold spray set up has been designed to coat AZ51 with hydroxyapatite. The details of the set up and design of the spray process has been presented. It was found that the qualities of hydroxyapatite coating were influenced by the heating temperature of magnesium substrate, surface roughness of magnesium substrate and also standoff distance. The coatings formed were compact and had good adherence to the substrate. The coating thickness varied between 20 to 30 micron meters. The chemical analysis identified the coatings as hydroxyapatite. Mechanical properties of the coatings were evaluated by nanoindentation test. The hardness and the elastic modulus of the coating were 0.1GPa and 9 GPa respectively. Further, the biocompatibility as well as biodegradation of the hydroxyapatite coated AZ51 along with uncoated AZ51 samples, were tested by subjecting them to in vitro test with simulated body fluid solutions. The inductively couple plasma optical emission spectroscopy and energy dispersive x-ray spectrometry analysis indicated that hydroxyapatite coating started dissolving after one day but showed signs of regeneration after 10 days of holding. Accelerated corrosion test in the 3.5% NaCl solution showed that the HAP coating remarkably protected the AZ51 magnesium substrate till 10 days. This continued till 21 days when most of the hydroxyapatite was replaced with magnesium hydroxide and at the end chloride ions were also detected on the surface indicating formation of magnesium chloride.

CHAPTER 1

INTRODUCTION

1.1 Research background

Orthopedic bioimplant required for the support and fixation of bone fractures are conventionally metallic as they need to maintain mechanical integrity and biocompatibility for the duration of the bone healing period. Currently titanium and stainless steel implants are mostly used. Metallic alloys of cobalt, chromium and nickel base are also utilized as biomaterials. These metallic implants meet the criteria mentioned earlier: however, there are still issues in regard to their use. The permanence of these materials is one of the key properties that add to the limitations of such a material (Shadanbaz and Dias, 2012).

The major concern on the existence of these implants in human body is regarding release of toxic elements to impair human body's health for long period of their use. For example, metal ions are released from the Ti–6Al–4V implant to the bloodstream and these may cause local irritation of the tissues surrounding the implant (Shadanbaz and Dias, 2012). Persistence irritations often result in the requirement for a second surgery for implant removal. In addition it also increases the financial burden on both the patient and/or the healthcare system. In the case of craniofacial device removal, a second

surgery may additionally have detrimental aesthetic effects in the form of increased scarring and thus psychological consequences for the patient.

The application of biodegradable implants can solve the toxicity problem. The biodegradable implants can gradually be dissolved, absorbed, consumed or excreted after the bone tissue healing. Magnesium has been suggested as an alternative. The strong points in favor of using magnesium as implant are strongly fortified by the superior biodegradability of metal magnesium in body fluid by corrosion. Magnesium and its alloy are potential biodegradable materials due their attractive biological performances; (1) metal magnesium is biodegradable in body fluid by corrosion; (2) Mg^{2+} is harmless to human body, in fact, Mg^{2+} is essential element to the human body (the daily intake of Mg^{2+} for a normal adult is 300-400mg). Redundant Mg^{2+} is harmless and can be excreted in the urine; (3) Magnesium can accelerate the growth of new bones tissues; (4) Density, elastic modulus and yield strength of magnesium are closer to the bone tissue than that of the conventional implants (Song et al., 2008). Thus, magnesium and its alloys are potential biodegradable materials due to their attractive biological performances.

Degradation occur in magnesium, and thus if corrosion rates are controlled the material would slowly degrade, removing the necessity for second removal surgeries, thereby decreasing health risks, costs and scarring, this is in contrast to the metals such titanium and stainless steel, the wear products of which can be potentially toxic or otherwise harmful to the patient. The corrosion products of magnesium have been shown to be potentially beneficial to the patient (Shadanbaz and Dias, 2012).

However, magnesium and its alloy were found susceptible to suffer attack in chloride containing solution, e.g. the human body fluid or blood plasma (Song, 2005). If the implants being made of magnesium alloys are used to repair the diseased bone tissue, they can lose the mechanical property before the healing of bone tissue due to the rapid corrosion.

In order to control the degradation rate that can be extremely rapid to Mg alloy, it is useful to coat with hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$. HAP is the natural form of calcium apatite and is the major component that composed of same ions responsible to construct the mineral part of bone and teeth. The synthetic stoichiometric structure of HAP displays hexagonal symmetry. HAP has been established to be stable up to a temperature of 1300ºC in the air (Shadanbaz and Dias, 2012). HAP shows excellent biocompatibility not only with the hard tissue, but also with soft tissue, such as skin and muscle. Moreover, HAP is bioactive mineral which promote the osseointegration when directly implanted to bone (Shi, 2006).

Recently, the techniques were performed to slow down the biodegradation rate of magnesium alloys, was electrodeposition (Shadanbaz and Dias, 2012). The plasma spraying of magnesium alloys has not been investigated possibly due to the low melting temperature of magnesium. Additionally, when HAP is plasma sprayed, it may be converted into other calcium phosphate phases such as α- or β- tricalcium phosphate, tetracalcium phosphate (TTCP) or calcium oxide (CaO) and the crystallinity of HAP may also be lowered due to rapid solidification. These alterations in chemistry and crystallinity often deteriorate the novel bioactive properties of HAP as well as its adhesion to the implant.

In this study, we demonstrate a novel approach to synthesize the HAP coating on AZ51 magnesium alloy by the modified cold spray deposition technique. AZ51 was chosen as experimental alloy to investigate the biocompatibility and biodegradation of magnesium coated with HAP. Magnesium aluminium alloy was used as experimental alloys to investigate the biocompatibility and biodegradation in the simulated body fluid solutions. Frank white et al. (2008) mentioned that the aluminum containing magnesium alloys should not be implanted into human because the aluminium was found not compatible with the human body. However a lot of data from various in vitro and in vivo experiments are available today to support the research.

To investigate the effect of HAP coating by above technique, in vitro dissolution study was conducted to study the bioactivity when subjected to the physiological medium. The biodegradation rate of AZ51 coated with HAP by cold sprayed coating technique was evaluated in the simulated body fluid. In addition accelerated corrosion behavior of HAP coated AZ51 alloy was also investigated by immersion in 3.5wt% NaCl solution.

1.2 Problem statement

Commonly the existing techniques to coat HAP on magnesium alloy was electrodeposition. However, electrodeposition process requires accurate control of variables. The failure to control the process variables caused the base material intrusion into the deposit precipitating new phases.

The plasma spray technique has been not investigated for possibly due to low melting point of magnesium. In addition, the plasma spray process requires high energy consumptions and complex unit.

Therefore the purpose of this study is to design a simple HAP coating technique that would produce acceptable coating of HAP on magnesium alloys. This involves development of a cold spray coating technique and characterization of the coating with respect to mechanical and bio chemical properties.

1.3 Objective

1. To formulate synthesis route to coat HAP powder on the magnesium metal by cold spray technique to obtain good adhering dense HAP coatings.

2. To study the physics of interface between coated HAP and the base magnesium metal implant in the cold sprayed condition using different characterization techniques.

3. To investigate compatibilities of HAP coating on magnesium alloys bio-implant in the simulated body fluid and biodegradability in the accelerated corrosion test.

1.4 Outline of study

This study basically consisted of five main parts.

I. Formulate synthesis route to coat HAP powder on the magnesium metal by low temperature method like cold spray technique.

II. Characterization of HAP coating.

III. Mechanical testing of HAP coating

IV. Biocompatibility test in simulated body fluid (SBF) solution.

V. Biodegradability test in 3.5 wt% NaCl solution as accelerated corrosion test.

In part I, a modified cold spray deposition technique was introduced as a synthesis route to coat the HAP powder on the magnesium alloy metal. The trial runs were performed to calibrate the process and equipment set up. The process parameter set up included the heating temperature of the magnesium substrate, surface roughness and pressure while equipment parameter set up included the standoff distance. In part II, the synthesized HAP coating on the magnesium alloys substrate was characterized to study the morphology, phase, surface roughness, chemical composition and thermal properties of the coating. In part III, the mechanical properties which are hardness and elastic modulus of the HAP coating was tested by nanoindentation testing. Part IV implies the biocompatibility test so called 'In Vitro' whereas the coated magnesium and uncoated magnesium samples were immersed in the SBF solution for various immersion periods. The final part of this study focused on the biodegradability test in order to investigate the protectiveness of HAP coating in the 3.5wt% NaCl solution towards various immersion time intervals. The concentration of NaCl at 3.5 wt% was chosen as corrosive medium for the accelerated corrosion test.

CHAPTER 2

LITERATURE REVIEW

2.1 Biomaterials

Biomaterial is defined as synthetic material used to replace part of living system or function in intimate contact with living tissue (Shi, 2006). In order to achieve the purpose, a biomaterial must be in contact with living tissues or body fluids promoting an interface between living and nonliving substance (Sujata, 2005). A biomaterial is different from a biological material, such as bone, that is produced by a biological system. Biomaterials can be categorized into different types in terms of their structural, chemical, biological characteristic for the example as in ceramics, glasses and polymers with the varied degree of bioactivity. Biomaterials consist of interdisciplinary research area that require sufficient knowledge of three main 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, orthopedic, plastic and reconstructive surgery, cardiovascular surgery, cardiovascular surgery, neurosurgery, immunology, histopathology, experimental surgery, veterinary medicine and surgery (Shi, 2006).

2.2 Metallic biomaterials

The advantage of metallic biomaterials in terms its property such as can endure

the tensile stress made the metallic biomaterial differ from other biomaterial ceramic and polymer. The high modulus and yield point coupled with ductility of metals make them suitable for bearing large load without leading to large deformation and permanent dimensional changes.

Metallic implants are used for two primary purposes. Implant has been used as prostheses serve to replace a portion of body such as joints, long bone and skull plates. On the other hand, fixations devices are used temporarily join two pieces of tissues together, and normally they are removed after healing.

Common engineering materials presently used for implants include stainless steel, Co- based alloy, Ti alloys, Ta, Pt and Ir metals. These alloys contain some of following metals: Aluminium, Cobalt, Chromium, Iridium, Iron, Manganese, Molybdenum, Nickel, Niobium, Palladium, Platinum, Titanium, Vanadium, Tungsten, Yttrium and Zirconium. Most metals used for manufacturing implants such as Fe, Cr, Co, Ti, Ta, Mo and W can be tolerated by the body in minute amounts but cannot be tolerated in large amount (Sujata, 2005). Due to the possibility of corrosion in the hostile environment of the body and the release of corrosion products into the surrounding tissue, the biocompatibility of metal implant is of considerable concern. Resistance to corrosion in aqueous chloride containing environment is therefore a primary requirement for metallic implants.

Traditional metallic biomaterials have been found to be suitable to be used in implant. These metallic biomaterials are stainless steel and titanium based alloys. However, pure magnesium and its alloy became current potential metallic biomaterials.

Metallic biomaterial such as 316L stainless steel, titanium alloys and cobalt based alloys, have been used as because it's excellent mechanical and corrosion properties. However, their release of nickel traced element can cause toxicity of corrosion product and fretting debris to human body, fracture to the corrosion fatigue, lack of biocompatibility and inadequate affinity for cells and tissue (Sumita et al., 2004).

Presently, biodegradable metals are breaking the current paradigm in biomaterial science to develop only corrosion resistant metal. Witte et al. (2008) reported that metals which consist of trace elements existing in human body are promising candidates for temporary implant materials. These implants would be temporarily needed to provide mechanical support during the healing process of injured or pathological tissue. Magnesium has been investigated recently by many authors as a suitable biodegradable biomaterial.

2.2.1 Magnesium as potential biomaterial for orthopedic implant

The proper function of orthopedic 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 bone.

The implant material is expected to withstand applied physiological forces without substantial dimension change, catastrophic brittle fracture, or fracture in 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).

Based on that critical demand, magnesium alloys were first introduced as orthopedic in the first half of last century. However, because of its corrosion resistance, a large amount of hydrogen accumulates around the implant during the in vivo corrosion process, confining the widespread use of magnesium based materials as biomaterial. Despite, magnesium still possesses many attractive characteristic that make magnesium based material potential candidate to serve as implant for load bearing application.

Magnesium has a much lighter density than other implant materials. It also has greater fracture toughness as compared to HAP (Staiger et al., 2006). Furthermore, it was shown that the elastic modulus and compressive yield strength values are more comparable to that of natural bone than the other commonly used metallic implants.

Magnesium ion present in human body, whereby approximately 1 mol of magnesium is sorted in 70kg adult human body and estimated amount of half of total

physical magnesium in the bone tissue. Magnesium also consists in human metabolic reactions and is nontoxic to the human body. Magnesium has good biocompatibility and it is biodegradable in human body fluid by corrosion, thus eliminating the need for another operation to remove the implant. Based on these desirable features had made magnesium as promising implant material (Staiger et al., 2006).

Table 2.1 Summary of physical and mechanical properties of implant materials in comparison to natural bone (Grenoble D et al., 1972).

Properties	Natural bone	Magnesium	Synthetic hydroxyapatite
Density (g/cm^3)	1.8–2.1	1.74–2.0	3.1
Elastic modulus (GPa)	3–20	41–45	73–117
Compressive yield strength (MPa)	130–180	65–100	600
Fracture toughness ($MPa.m^{1/2}$)	3–6	15–40	0.7

White et al. (2008) mentioned that the recent advances in magnesium alloys have been in understanding the interface and interaction of magnesium alloys and their biological environment. In contrast to previous technical alloys development aiming on the improvement of mechanical properties, corrosion resistance and production costs, the main focus is shifting to the influence of the alloying elements on the formation of corrosion protective interfaces and on the surrounding biological environment in vitro and in vivo. However, currently available magnesium alloys were investigated in different biomedical application. Magnesium alloy were also investigated as bone implant and can be applied in various design e.g. as screws, plates and other fixture devices. Magnesium chips have been investigated for vertebral fusion in spinal surgery

of sheep and open porous scaffolds made of magnesium alloys have been introduced ad load bearing biomaterials for tissue engineering.

2.2.2 Magnesium and its alloys

Magnesium and its alloy have been investigated recently by many researchers as a suitable biodegradable biomaterial. The magnesium alloy currently under investigation as implant materials are mostly commercial alloys that have been developed for the needs in transportation industry. The designation system of magnesium alloy is generally following the nomenclature of America Society for Testing and Materials (ASTM) and uses typical letter figure combination (Table 2.2).

Magnesium alloys can be divided into three major groups: pure magnesium (Mg) with traces of other elements aluminium (Al) containing alloys and those alloys which are free of Al (Frank Witte et al., 2008). Typical Al containing magnesium alloys are AZ91, AZ31, AE21, calcium (Ca) modified AZ alloys, and LAE442. AZ31 and AZ 91 have been used over decades in technical application. In addition to the given elements Al and Zn, these alloys contain small amount of manganese (Mn). LAE442 is based on the alloy AE42 and contain AL, RE, Mn and additionally lithium (Li). LAE442 has been developed recently as density reduced magnesium alloy with improved ductility and enhanced corrosion properties (Witte et al., 2008).

However, almost none of the above mentioned alloys have been developed to be a biodegradable implant material. The reason is perhaps due to the complex alloy

Table 2.2 Influence of alloying elements and impurities on properties and processing of Mg alloys at ambient temperatures (Witte et al., 2008).

Alloying element/ impurities	ASTM	Effect of the alloying element/impurity on									
		UTS	Ductility	UCS	Hardness	Notch sensitivity	Creep resistance	High temperature strength	Corrosion resistance	Grain refinement	Castability
Aluminium	A	+	+		+					+	+
Calcium	X	+				–	++		–	+	+
RE	E						++	+		+	
Copper	C	–	+	–					– –	–	
Iron	F		+						– –		
Lithium	L	–	+	–					–		
Manganese	M	+	+			+	+		+[b]	+	
Nickel	N								– –		
Silicon	S		–	+	+		+	+	–		–
Strontium	J	+	+	+			+	+		+	
Yttrium	W	+				–	++	+		+	+
Zinc	Z	+	–[a]								
Zirconium	K	+	+					+		++	

UTS = ultimate tensile stress, UCS = ultimate compressive stress, effect coding: ++ = excellent, + = good, – = bad, – – = detrimental.
[a] At high Zn concentration.
[b] Only in combination with Al.

composition it is not certain. If the observed in vivo degradation can be truly connected to a chemical element, an intermetallic compound or microstructure effect based on the processing route.

2.2.3 AZ51 Magnesium alloy

In order to improve the magnesium, some alloying elements were added into the magnesium. Compared to the high purity magnesium, magnesium alloys are most suitable for load bearing application due to their excellent mechanical properties. The low corrosion resistance of magnesium alloys the major limitation for its use in musculoskeletal surgery has been improved by appropriate alloy composition.

Aluminum containing magnesium alloys are investigated by research groups in biomedical application. White et al. (2008) mentioned that the aluminum containing magnesium alloys should not be implanted into human; however a lot of data from

various in vitro and in vivo experiments are available today. Therefore, it is recommended that the Mg-Al alloys system should just be used as experimental alloys to investigate the improvements of processing and surface modification technologies (i.e. coatings) in biomedical application. Magnesium is rarely use in its pure state. Instead it is usually alloyed with other element like aluminium, zinc and zirconium to improve its properties like corrosion resistance. However, for the use in human body, high purity of magnesium was strictly recommended.

In this experiment, AZ51 alloys have been used as experimental alloys in order to investigate the physical properties of this alloy to be used as bioimplant material. AZ51 alloy is a new magnesium alloy that have been synthesized by adding 1 wt% and 2wt% of Aluminum into AZ31B matrix respectively by using an innovative disintegrated melt deposition technique followed by hot extrusion. Alam et al. (2011) reported that the microstructural characterization studies revealed that equiaxed grain morphology, reasonably uniform distribution of intermetallics in the matrix and minimal porosity.

2.2.3.1 Physical properties

This magnesium alloy was found to have excellent physical properties compared to pure metal after adding with the aluminum at respective percentage. The higher percentage of aluminum have assisted in improving the overall mechanical properties including microhardness, modulus of elasticity 0.2% yield strength, ultimate tensile strength and work of fracture of this alloy.

Alam et al. (2011) also reported by adding 2 wt% of aluminum, slightly increased in theoretical density which is 1.792 g/cm^3 as compared to the normal density that is about 1.791 g/cm^3. The porosity was obtained at 0.08%. In term of mechanical properties, the Vickers microhardness test that has been conducted on the sample shows the addition of Al increased the microhardness value of AZ31 matrix. Around 29 % microhardness value was increased when 2% of aluminum was added into AZ31B in order to develop AZ51 alloy. Moreover AZ51 magnesium alloy exhibit 37% higher hardness when compared to commercial AZ61A alloy.

Table 2.3 Results of room temperature microhardness and modulus of elasticity tests (Alam et al., 2011).

Materials	Microhardness (HV)
AZ 31	66 ±2
AZ 41	77±3
AZ 51	85±3
AZ 61A	62

2.3 Bioceramic materials

Ceramic are refractory polycrystalline compounds, usually inorganic including silicates, metallic oxides, carbides and various hydrides, sulphides and selenides. Oxides such as Al_2O_3, ZrO_2, and SiO_2 contain metallic and non-metallic elements while others are ionic salts: NaCl, CsCl, ZnS etc. Covalently bonded ceramics are diamond and carbonaceous structure like graphite and pyrolyzed carbons. Important factors

influencing the structure and property relationship of the ceramic materials are the radius ratio and relative electronegatively between the positive and negative ions (Shi, 2006).

Ceramics and glasses have been given a lot of attention as candidates for implant material since they posses some highly desirable characteristics for some application. The main advantage of ceramic is their inertness in aqueous condition and biocompatibility as well. Other advantages of ceramic are their brittleness and very low strength in tension. Therefore they are limited to the application that involve of compression loading conditions. The application was found used in the acetabular cup or a femoral head of total hip joint replacement. Some application do not require high loading, including HAP for artificial bone and barium sulphate ($BaSO_4$) for bone cement. Alumina, calcium phosphates, glass ceramics, zirconia and carbons are not extensively studied and are used infrequently.

There have been a number of bioceramics which are well-known for their potential in biomedical applications. Among them are alumina, zirconia, glass ceramics and HAP. Since early 1970, pure alumina (> 99%) has been used as implant material especially for artificial joint prostheses (mostly hip) and teeth because of its excellent compatibility with tissue and its good mechanical properties. However it has much lower tensile strength than compressive strength due its brittleness. These characteristics limit its use to compressive loading applications. Most alumina used for implant fabrication is either polycrystalline solid of high density and purity or an artificially grown colorless single crystal similar to sapphire or ruby (Shi, 2006).

Instead of using the alumina as biomaterial, zirconia also has potential to be used

in fabricating implant. Some of them are called “fake diamond” or “cubic zirconia” since some zirconia single crystal can be of green grade and made into jewel. Some of mechanical properties of zirconia are as good or those better than those of alumina ceramics. Zirconia is highly biocompatible, like other ceramic and can be made into such large implant as the femoral head of a hip joint replacement.

However, HAP is the most potential biomaterial that obtained special attention in developing bio-implant product. HAP, $Ca_{10}(PO_4)_6OH_2$ was the important biomaterial that has been widely used in dental and orthopaedic implants due to its chemical and crystallographic similarity to the natural bone mineral. Lack of cytotoxic effects make the HAP biocompatible with hard tissue, skin and muscle tissue.

2.3.1 Hydroxyapatite

Hydroxyapatite is an important biomaterial (with a Ca/P ratio of 1.67) present in bones and teeth. In fact, it comprises the primary mineral content of bone (43 wt %), which implies that HAP is highly biocompatible in nature. HAP is naturally occurring mineral form of calcium apatites. Because of its bioactivity, it is widely used as an implant material in clinical application (Park, 2008).

Because of its excellent properties, HAP has been used as coating on the bio-implant surface. HAP have been deposited on the metallic biomaterial such as on the titanium alloy, stainless steel and magnesium alloy in order to control the corrosion rate when implanted into human body. HAP contained lack of cytotoxic effect where it makes HAP biocompatible with the human tissue. The important part of HAP is that can

be bonded to the bone directly (Park, 2008). Despite its, its ideal bioactive properties, poor mechanical strength hinders the use of HAP as a load bearing implant. As a result, the combination of bioactive HAP coating and mechanically strong metal has become approaching approach to fabricate surgical implant for load bearing applications.

By coating with HAP, the corrosion rate can be controlled in order to prevent the sudden failure of the implants. Currently in a recent study, HAP was deposited onto the magnesium alloy to improve its biodegradable performance. In the studies performed by Song et al. (2008), the bioactive HAP coating was electrodeposited on AZ91D magnesium alloy. The biodegradable behavior of HAP coating was investigated by electrochemical test and immersion test. The experimental results indicated that as deposited coating consisting of dicalcium phosphate dehydrate (DCPD, $CaHPO_4 .2H_2O$) and β-tricalcium phosphate (β-TCP, $Ca_3(PO_4)_2$) was transformed into uniform hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) coating after immersion in 1 M NaOH solution for 2 h. The HAP coating was found slow down the biodegradable rate of AZ91D in human body environment. Besides, the HAP coating also was obviously improved biodegradation rate of magnesium alloy in simulated body fluid as well. From the corrosion morphology, indicated that the HAP coating can provide enough protection to the magnesium alloy substrate (Song et al., 2008).

2.3.1.1 Physical properties of hydroxyapatite

HAP has a specific crystallographic structure hexagonal and $P6_3/m$ space group. However pure HAP is different from biological apatite whereby biological apatite

contains important minor substituent (e.g., CO_3^{2-}, Na^+, Mg^{2+}) and more accurately described as carbonate apatite. (CHA), approximated by the formula $(Ca,Mg,Na)_{10}(PO_4,HPO_4,CO_3)(OH)_2$ (Park, 2008).

The apatite family of mineral, $A_{10}(BO_4)_6X_2$, crystallize into hexagonal rhombic prism. HAP has unit dimension of a = 0.9432 nm and c = 0.6101nm. The atomic structure of HAP projected along the c axis on the basal plane. Hyroxyl ions lie on the corners of the projected basal plane and occur at equidistant intervals [half of the cell (0.344nm)] along columns perpendicular to the basal plane and parallel to the c-axis. Six of the ten calcium ions in the unit cell are associated with hydroxyl in these perpendicular columns, resulting strong interaction between them (Park, 2008).

The ideal Ca/P ratio of HAP is 10/6, and the calculated density is 3.219g/ml. It is interesting to note that substitution of OH with F gives greater structural stability, due to the closer coordination of F than the hydroxyl to the nearest calcium. This is the reason why the resistance of enamel to dental carries is enhanced by fluoridation.

2.3.1.2 Chemical properties of hydroxyapatite

Hydroxyapatite is considered bioactive, indicating that the ceramic may undergo ionization in vivo and that the rate of dissolution may depend on many factors which are degree of crystallinity, crystalline size, processing condition (temperature, pressure and partial water pressure) and porosity. HAP was found slightly soluble in distilled water. Solubility in distilled water may increases with the addition of electrolytes. Furthermore,

in the presence of amino acids, proteins, enzymes and other organic compound may change the solubility of HAP. These solubility properties are closely related to biocompatibility of HAP with tissue and its chemical reactions with other compound. However, the solubility rate depends on differences in shape, porosity, crystal size, crystallinity and crystallite size. The solubility of sintered HAP is very low. The rate of solubility is 0.1mg/year in subcutaneous tissue. HAP reacts actively with proteins, lipid and other organic species (Park, 2008).

The most interesting property of HAP is its excellent biocompatibility, the result of its suspected direct chemical bonding with hard tissue. Hench et. al. (1971) reported that after spreading 0.254nm thick layer of amorphous calcium orthophosphate precipitate on its surface, the epitaxial HAP crystal growth on the surface of Bioglass wafers (1.23cm diam., 0.32cm thick). X-ray diffraction analysis of the crystallization of HAP showed an average crystal size of 20nm, which in the same range as observed size in vivo mineral crystals (Heughebaert et al., 1988).

2.3.1.3 Mechanical properties of hydroxyapatite

A wide variation was reported in mechanical properties of HAP. Jarcho et al. (1976) reported that fully densified polycrystalline specimen of HAP synthesized by them had average compressive and tensile strength of 917 and 196 MPa respectively. A compressive strength was 3000kg/cm^2 (294 MPa), a bending strength of 1500 kg/cm^2 (147 MPa) a Vickers hardness of 350kg/mm^2 (3.43GPa).

The elastic modulus of HAP obtained were measured by ultrasonic and resonance frequency techniques is given in Table 2.4. Although there are variations

Table 2.4 Elastic Modulus of HAP and Mineralized Tissue (Park, 2008)

Test Method	Material	Elastic modulus (GPa)
Ultrasonic interference technique	HAP (mineral) HAP (synthetic) Dentin Enamel	144 117 21 74
Destructive technique	Human cortical bone	24.6-35
Resonance frequency technique	HAP (synthetic) Canine cortical bone	39.4 -63 12-14.6

in values which depend on the measurement technique, it is significant that HAP has higher elastic modulus than mineralized tissues. Along this line of thought, it is interesting to note that relatively smaller amount of organic materials mainly collagens exist in the enamel, which has higher elastic modulus than the bone and dentine. This fact is indirect evidence that the mineral portion of hard tissue is made of HAP. Poisson ratio for the mineral or synthetic HAP is about 0.27, which is somewhat close to that bone (0.3) according to Grenoble (Grenoble et al., 1972 et).

2.4 HAP coating on magnesium alloy by difference coating technique

The main purpose of HAP coating on the magnesium alloy substrate is to improve the biodegradation. Instead of biodegradation issue, the biocompatibility also

should be considered. The HAP, Ca_{10} $(PO_4)_6(OH)_2$ coating can satisfy two properties. HAP is major inorganic component of natural bone and can accelerate the bone growth.

Several coating techniques have been reported previously to increase the biocompatibility, improve healing condition and decrease wear particle production of current orthopedic metallic implant. Due to high reactivity property of magnesium and its relative low melting temperature (650ºC) not all coating technique can be adapted for application on magnesium. Industrial application involve the use of non biocompatibility coatings and therefore inappropriate for clinical use. The requirement of coatings for clinical use must present the biocompatibility behavior. Recently, the researchers introduced electrodeposition and so gel techniques to control the biodegradation rate of magnesium alloys.

Electrodeposition technique was found to be simple and inexpensive process which can be carried out at room temperature, thickness and chemical composition of HAP coating can be controlled by adjusting the electrodeposition conditions. Song et al. (2008) has reported that electrodeposition method to coat HAP can improve its biodegradable performance.

The electrodeposition method was performed by immersed the AZ91D magnesium alloy plate in the electrolyte solution contain 0.1M $Ca(NO_3)_2$, 0.06M $NH_4H_2PO_4$, H_2O_2 10ml/l and pH 4.3. Electrodeposition was carried out at a stable cathodic potential of 4V for 2h at room temperature. Then, the as-deposited coating was immersed in 1M NaOH solution for 2h at 80ºC.

The biodegradable behavior of HAP coating was investigated by electrochemical test and immersion tests. The experimental result has shown that the as-deposited coating consisting of dicalcium phosphate dehydrate (DCPD, $CaHPO_4.2H_2O$) and β-tricalcium phosphate (β-TCP, $Ca_3(PO_4)_2$) was transformed into uniform HAP ($Ca_{10}(PO_4)_6(OH)_2$) coating after immersion in 1M NaOH solution for 2 hr. The HAP coating can obviously slow down the biodegradation rate of AZ91D magnesium alloy in stimulated body fluid (Song et al., 2008).

2.5 Cold spray deposition technique

Cold spray is a relatively recent spray technology and there are different approaches known by different names such as cold gas dynamic spraying, kinetic spraying, high velocity powder deposition, supersonic powder deposition etc. Cold spraying (CS) represents a radical difference from conventional thermal spraying methods. The deposition process relies mainly on kinetic energy rather than the combination of thermal and kinetic energies of spraying particles (Champagne, 2007). In this process, spraying particles (metal or ceramic) are accelerated to a high velocity by a high speed gas flow, and a coating is formed through the intensive plastic deformation of particles at room temperature. There are several factors that affect the deposition of the powder particle on the substrate which are the optimal design of geometry and configuration of the spraying nozzle, the effect of standoff distance of substrate and the placement of powder release position as well.

As with any other material processing technique, the cold spray process has its own advantages and disadvantages. The main advantages of the cold spray process that is solid state process, which results in many unique coating characteristics. Meanwhile the main advantages arising are due to the plastic deformation process, which leads to a loss of ductility of the coating (Choudhuri and Mohanty, 2008).

By cold spray technique, high deposition efficiency (DE) values have been achieved with for most metals, alloy and composites. Experimental result has shown that to obtain very high deposition efficiency by optimizing the oxygen content of feedstock material, stress relieving the powder particles and optimization of particle size distribution can obtain very high DE values for most materials.

Besides, in comparing to thermal spray processing, the substrate is heated by the flame to varying degrees that it difficult to be sustained for the low melting temperature metal such as magnesium. Furthermore, high temperature will induce warping of substrate is highlighted by thermal spray technique especially when the thickness of the specimen is too small.

2.5.1 HAP coating by cold spray deposition technique

Conventionally, bioceramic such as HAP have been deposited by plasma spray technique. However, due to the inherent high temperature in plasma spray, the deleterious effect such as phase alteration, evaporation and debonding occur by this coating technique. Many researchers have carried out extensive work on development of

cold spray deposition technique. A cold spray system established by Choudhuri and Mohanty (2008) is used to deposit HAP coatings on the titanium alloy.

The system consists of gas pressure regulator, gas heater, powder feeder or

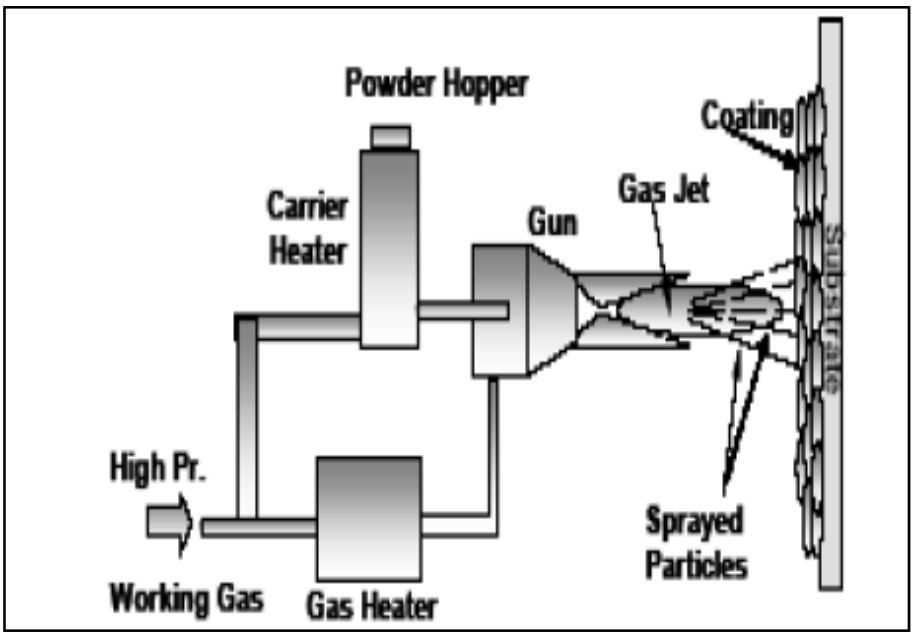

Figure 2.1 Schematic of cold spray deposition process (Choudhuri and Mohanty, 2008).

or hopper and spray gun. A premixed powder was fed up by a high pressure powder feeder into heated N_2 gas stream through a converging diverging nozzle (Figure 2.1). The gas pressure and temperature in the nozzle pre chamber varied from 25-38 bars and 400-700 ºC respectively. The nozzle was placed 25mm from the subtracted standoff distance. Robot transverse speeds at 50 – 400m/s were employed to deposit coating. Based on this method, Choudhuri and Mohanty (2008) have developed novel approach to deposit bioceramic coatings at temperature well below their melting point by cold spray by using a mixture of titanium and HAP powder.