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

by

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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.

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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).