UNIVERSITI TEKNIKAL MALAYSIA MELAKA

CHARACTERIZATION OF HYDROXYAPATITE COATING DEPOSITED ON GLASS, STAINLESS STEEL AND TITANIUM ALLOY SUBSTRATE VIA SOL-GEL TECHNIQUE

This report submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Engineering Materials) (Hons.)

by

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2013

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

BORANG PENGESAHAN STATUS LAPORAN PROJEK SARJANA MUDA

TAJUK: **Characterization of Hydroxyapatite Coating Deposited on Glass, Stainless Steel and Titanium Alloy Substrate via Sol-gel Technique**

SESI PENGAJIAN: 2012/13 Semester 2

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UTeM as a partial fulfillment of the requirements for the degree of Bachelor of Manufacturing Engineering (Engineering Materials) (Hons.). The member of the supervisory is as follow:

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(DR.ZULKIFLI BIN MOHD ROSLI)

ABSTRAK

Ketika ini, bahan ‘bio’ berlogam seperti *keluli tahan karat* dan logam campuran *titanium* digunakan sebagai bahan implan. Walau bagaimanapun, ayunan pergerakan kecil pada pertemuan antara implan dan tulang menghasilkan penggeselan yang mengauskan. Selain itu, logam *ion* implan dilepaskan ke dalam sel badan manusia semasa proses pemulihan disebabkan oleh kejadian pengaratan. Sebahagian daripada itu, salutan hidroksiapatit (HA) digunakan pada bahan implan untuk mengurangkan permasalahan dan untuk meningkatkan kadar penumbuhan tisu. Malah, HA mempunyai kebolehan untuk menumbuhkan tulang secara terus menerus pada tulang dan mengurangkan masa pemulihan. Dalam kajian ini, pencirian salutan HA pada *keluli tahan karat* dan logam campuran *titanium* telah dilakukan dalam pada masa sama juga pada substrat gelas kaca untuk menguji penyalutan. Substrat dikeringkan pada suhu 100^0C dan rawatan suhu pada 400^0C untuk mendapatkan lapisan *apatit* pada salutan. Analisa dari XRD dan EDX menunjukkan intensiti fasa HA dan kemunculan unsur kalsium dan fosforus. Hasil keputusan SEM menunjukkan bahawa ketidaksamaan pada salutan HA permukaan morfologi disebabkan kekasaran permukaan dan ketebalan salutan. Ketebalan bagi satu lapisan dari salutan HA adalah dalam purata 1.5µm. Seperti dijangka, ketebalan yang diperoleh untuk purata dalam 1µm.

ABSTRACT

Nowadays, the metallic biomaterials for instance the stainless steel and titanium alloys are used as the implant materials. However, the oscillatory micromovements at the interface between the implant and the bone exhibit the fretting wear. Besides, the metal ion of the implants is being released to the vivo in the healing process due to the corrosion phenomenon. Apart of that, the hydroxyapatite (HA) coating is utilizing to the implant materials in order to reduce the difficulty and to increase the growth rate of tissue. On the contrary, HA have the ability to bond directly to the bone and reduce the healing time. In this study, the characterization of the HA coating on the stainless steel and titanium is done as well as to the glass substrate for the testing of the coating. The substrate is dried at the 100^0C and heat treatment at the 400^0C to obtain the apatite layer of the coating. The analysis of XRD and EDX shows the intensity of the HA phase and the emerging of the element of calcium and phosphorus respectively. The SEM results shows the surface morphology obtained that the HA coating sustain the non homogeneity due to the surface roughness and the thickness of the coating. The thickness of the one layer of the HA coating is in the average of the 1.5µm. As expected, the thickness gained for the average is in the range of 1µm.

DEDICATION

To my beloved parents, Mohamad Aminallah and Sapinah without their supports and carings in life, this work will hardly to be accomplished. This work is dedicated to my dear friends, thanks for sharing their opinions and experiences in doing my project.

ACKNOWLEDGEMENT

Alhamdulillah, first and foremost, I would like to express my gratitude and appreciation to my supervisor, Dr Zulkifli Bin Mohd. Rosli. I am so appreciate that he is scarifying his time to give me guidance and advice during the process of project. All the advices given are precious and beneficial for me to complete my final year project. I am so grateful to him for giving me an opportunity to take this chance to handle such interesting and challenging project. He is helpful and professional in his field of work. I would like to convey my deepest appreciation to Universiti Teknikal Malaysia Melaka (UTeM) in allowing me to experience the final year project. Last but not least, I wish to acknowledge to my beloved family for spiritually supporting me during the process of project.

TABLE OF CONTENT

APPENDIX

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Au	-	Aurum
AISI	-	American Iron and Steel Institute
ASTM	-	American Society for Testing and Materials
Ca	-	Calcium
Cr	-	Chromium
CVD	-	Chemical Vapour Deposition
DDH_2O	-	Double Distilled Water
DNA	-	Deoxyribonucleic acid
EDX	-	Energy Dispersive X-Ray
Fe	-	Iron/ Ferum
HA	-	Hydroxyapatite
JCPDS	-	Joint Committee Powder Diffraction Standard
Ni	-	Nickel
P	-	Phosphorus
Pd	-	Palladium
pH	-	Potential of Hydrogen
PVD	-	Physical Vapour Deposition
SEM	-	Scanning Electron Microscopy
SiC	-	Silicon Carbide
TEP	-	Triethyl phosphate
Ti	-	Titanium
XRD	-	X- Ray Diffraction Analysis

CHAPTER 1

INTRODUCTION

1.1 Background

This project is mainly executed to characterize hydroxyapatite coatings particularly on stainless steel and titanium alloy. The most important property of materials used for fabricating implants is biocompatibility, followed by corrosion resistance (Elias et al., 2008). Moreover, stainless steel and titanium alloys are the most common metallic orthopedic materials (Yeung et al., 2007).

Stainless steel is a widely used orthopaedic implant material for internal fixation because of its mechanical strength and the capability to bend and shape the implant to create a custom fit in the operating room (Monika et al.,2011). The main advantage of the SS material is its low cost in comparison with other metallic implant materials such as titanium or cobalt alloys. However, upon prolonged contact with human tissue (37 ^{0}C, pH 5.4–7.4) corrosion phenomena takes place on the stainless steel surface resulting in the undesirable release of transition metal ions, such as chromium, iron and nickel (Herting et al.,2006).

Titanium and its alloys have been widely used as implant materials in orthopaedic and dental prosthesis for their excellent biocompatibility, high corrosion resistance, lightweight and good mechanical properties. However, the bone in-growth properties and implant fixation behaviour need to be improved in order to shorten the implant-tissue osseointegration time (Sam Zhang et al., 2006)

Although biocompatible metallic implants are strong,their bonding ability to bone tissue is very low (bioinert materials) (Hench & Andersson,1993), so coatings have drawn attention as a method to improve their adherence. In order to enhance bone-inducing effect and to reduce healing time of the implanted hard tissues, the metallic implants are typically coated with biocompatible hydroxyapatite (HA, Ca10 (PO4)6(OH)2) by means of a sol-gel coating.

The sol-gel, being one of the methods provides some benefits such as chemical homogeneity, fine grain structure, and low processing temperature (Brinker et al., 1990). Moreover, when compared with other methods, it is simple and cost efficient, as well as effective for the coating of complex shaped implants. Sol–gel protective coatings on metal and alloy surfaces can improve metal alloy corrosion resistance in various corrosive mediums and practical applications. Sol–gel coatings can also provide high oxidation, abrasion, water resistant, and many other useful properties. Consequently, the technique used of the sol-gel coatings on metal alloy substrates is the dip coating.

The dip-coating process is used mainly for the production of coatings on things such as flat glass plates, but can be used for complex objects, such as tubes, rods, pipes and fibres (Dislich, 1988). Apart of that, the coating substances that selected to use is hydroxyapatite due to its biocompatibility to natural bone. One of the considerable in using the hydroxyapatite is it can accelerates the rate of bone bonding thus; act as a fence between the body and metal parts.

On the other hand, several parameters will be apply to characterize the sol-gel coating on the metal alloy substrates such as the type of the substrate, thickness of coating, surface roughness, phase and adhesion. In this project, the characterization will be done on the metal alloy substrate and on the hydroxyapatite coating. In addition, the analysis will be determined the optimization of the coating layer's number. Therefore, the characterization test will be carried out by scanning electron microscope (SEM), X-ray diffraction analysis (XRD) and energy dispersive X-Ray (EDX).

1.2 Problem Statement

Stainless steel and titanium alloys themselves commonly used in the implant fields due to their biocompatibility to the human body. However, stainless steel and titanium alloys encounter the problem of lack of corrosion resistance and osseointegration time respectively. In order to reduce the crisis, the coating is one of the ways to improve the metal implant.

Hydroxyapatite (HA) coating is preferred to be one of the methods to prevent the problem of stainless steel and titanium alloys. HA coated titanium alloy implants integrate the bioactivity of HA and the mechanical properties of metal alloy for a perfect combination. In addition, HA coating provides protection to the metal alloy substrates against corrosion in the biological environment, and acts as a barrier against the release of toxic metal ions from the substrates into the living body (Cavalli et al., 2001).

Therefore, the characterization of the HA deposited on the stainless steel and titanium alloys will be carried out to investigate whether the problem arise is reconcile. In order to analyse the characterization of the HA coating, several parameters is used. The parameters that will take in account are type of the substrate, surface roughness, thickness, adhesion and the phases.

1.3 Objective

The objectives of this project are:

i. To characterize the hydroxyapatite coating deposited on the glass, stainless steel and titanium alloy substrate via sol-gel technique
ii. To observe the coating morphology, chemical composition and the phases of the sol-gel coating
iii. To seek the optimization number of the coating layer on the glass, stainless steel and titanium alloy substrate

1.4 Scope

The prominence is on the study and characterization of the hydroxyapatite coating on the stainless steel and titanium alloy substrate via sol-gel technique. Only the characterization of hydroxyapatite coating will be included in this project. Typical test method that relates to this type of coating characterization is dipping coating followed by the SEM, EDX, and XRD. Moreover, the corrosion analysis testing will not be included in this paper.

CHAPTER 2

LITERATURE REVIEW

2.1 Stainless Steel

Stainless steels are iron-base alloys that contain a minimum of approximately 11% chromium,the amount needed to prevent the formation of rust in unpolluted atmosphere. Other elements added to improve particular characteristics include nickel, molybdenum, copper, titanium, aluminium, silicon, niobium, nitrogen, sulfur, and selenium. Carbon is normally present in amounts ranging from less than 0.03% to over 1.0% in certain martensitic grades (Davis,1994).

Over the years, stainless steels have become firmly established as materials for cooking utensils,fasteners,cutlery,flatware,decorative architectural hardware, and equipment for use in chemical plants, dairy and food-processing plants, health and sanitation applications (Davis, 1994). The interest for stainless steel in the medical field is due to its mechanical properties, its mechanic resistance, corrosion resistance and its excellent biocompatibility.

In the case of stainless steel, the metal surface was unable to tolerate with the environment and hence the release of iron (Fe), chromium (Cr) and nickel (Ni) ions are evidenced in the human body (Sivakumar et al.,1992). The Cr and Ni ions thus released have shown to be powerful allergens and are demonstrated to be carcinogenic (Prabakaran et al, 2006) .Therefore, it is evident that the reduction in metal ion release is preferred to avoid the deleterious effect caused by the corrosion products in the normal bone formation. The Figure 2.1 shows the feature of the metal implant.

Figure 2.1: Feature of metal implant

(Source: http://www.nih.gov/researchmatters/january2012/01232012hip.htm)

According to the American Iron and Steel Institute (AISI), the stainless steel is designated based on the grades that have 3 digits which are 200 and 300 series for austenitic stainless steel, whereas 400 series are either ferritic or martensitic. Some of the grades have one or two letter suffix that indicates a particular modification of the composition.

Most surgical equipment is made out of martensitic steel where it is much harder than austenitic steel, and easier to keep sharp. Depending on the type of equipment, the alloy recipe is varied slightly to get more sharpness or more strength. Implants and equipment that are put under pressure (bone fixation screws, prostheses, body piercing jewellery) are made out of austenitic steel, often 316L and 316LVM compliant to American Society for Testing and Materials (ASTM) F138, because it is less brittle.

In the galvanic series, shown in the Figure 2.2, the metals are arranged according to their tendency to corrode. This series can be used to determine whether galvanic corrosion is likely to occur and how strong the corrosion reaction will be.

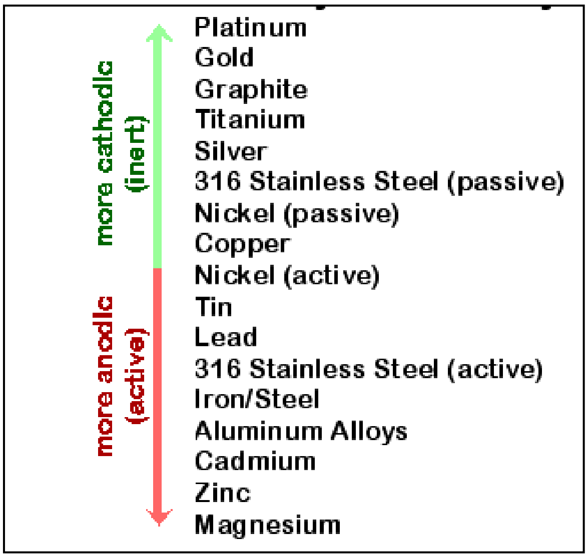

Figure 2.2: Electromotive force series of reactivity of metals/alloy in seawater

(Source:*http://www.ecr6.ohiostate.edu/mse/mse205/lectures/chapter18/chap18_slide8.gif)*

The metals such as gold and silver are very inactive and unlikely to corrode. Hence, both of this metal, likely to be used as jewellery. The several metal that tendency to corrode is magnesium, zinc and aluminium that can be categorised as reactive metal. Stainless steel is in the position of active material that tends to corrode easily comparing to the inert material. Thus, the stainless steel will be coating in order to improve its corrosion resistance.

One of the most effective ways to prevent corrosion is to coat the base material. Coatings can protect a substrate by providing a barrier between the metal and its environment and/or through the presence of corrosion inhibiting chemicals in them. In order for a coating to provide adequate corrosion protection, the coating must be uniform, well adhered, pore free and self-healing for applications where physical damage to the coating may occur (Gray & Luan, 2002).

Sol-gel coatings have been reported to provide corrosion protection to metals (Soutar et al., 2002). Sol–gel coatings provide an additional dense barrier for corrosive species and assure good adhesion of the organic paint system to the metal substrate (Lamaka et al., 2008).

2.2 Titanium Alloy

Titanium (Ti) name comes from Greek words, Titans. Titanium is the ninth most abundant element on Earth and the sixth most abundant metal on Earth, after aluminium, iron, sodium, potassium, and magnesium. Pure titanium is lustrous, or shiny, and silvery in color. It is lightweight for a metal and very strong. It resists corrosion and can be easily shaped. It is commonly combined with other elements such as oxygen, nickel and aluminium to create other useful materials (Greg, 2008).

Although titanium has the highest strength to density ratio it is the material of choice only for certain application area because of its high price. This high price is mainly a result of the high reactivity of titanium with oxygen. The high reactivity with oxygen leads to the immediate formation of a stable and adherent oxide surface layer when exposed to air, resulting in the superior corrosion resistance of titanium in various kinds of aggressive environments, especially in aqueous acid environments (Gerd & James, 2007)

Pure titanium is nontoxic;commercially pure titanium and some titanium alloys generally are biologically compatible with human tissues and bones. The excellent corrosion resistances and biocompatibility coupled with good strength make titanium and its alloys useful in chemical and petrochemical applications, marine environments and biomaterials applications. The combination of high strength, stiffness, good toughness, low density, and good corrosion resistance provided by various titanium alloys at very low to elevated temperatures allows weight savings in aerospace structures and other high performance applications (Matthew, 2000).

Titanium alloys have four classes which are alpha, near-alpha, alpha-beta and beta due to crystallographic variations. Titanium (alpha) and the Ti-6Al-4V (alpha-beta) alloy are used for dental and orthopaedic purposes. Other titanium alloys including beta titanium alloys are being used and introduced for use as surgical implants, where strength requirements are higher than those of pure titanium. In order to attain higher strength, in commercially pure titanium, alloying elements are added (Brown & Lemons, 1996)

It is known that the highly biocompatible passivation film of Ti materials can support direct on growth of bone tissue (Williams et al., 2001) .However, based on many in-vitro experiments, it was suggested that stress and friction can lead to the corrosion of Ti materials, and the passive dissolution of the metals creates adverse effects on hard tissue formation reaction sequence (Kim & Ducheyne, 1991).

In order to prevent the foreign body reaction to the metallic implant materials, various bioceramic coating techniques have been used including ion plating, sputter coating, chemical vapor deposition (CVD), plasma spraying, electrophoretic deposition and ion implantation (Hwang & Kim, 2003)

In order to avoid the problem, low-cost and simple surface modification techniques of titanium materials were used in hence to achieve stable bone bonding at the interface between bone and titanium implant that is sol-gel coating by using hydroxyapatite precursor. The coating technique used is dip coating.

2.3 Hydroxyapatite

Hydroxyapatite (insoluble form of calcium phosphate with empirical formula of $Ca_3(PO_4)_3OH$) is particularly useful for chromatographic purification/fractionation of Deoxyribonucleic acid, DNA. Hydroxyapatite can be used for medical applications such as bone repair, augmentation, substitution and coatings of metals used as dental and orthopaedic implants (LeGeros & LeGeros, 1993). Hydroxyapatite (HA) is well established as a biocompatible ceramic capable of forming a good bond with natural bone (Jarcho, 1981). The Figure 2.3 shows the bone growth around hydroxyapatite.