EFFECT OF POST TREATMENT PARAMETERS ON CORROSION RESISTANCE OF Ti-13Nb -13Zr COATED WITH HYDROXYAPATITE VIA ELECTROPHORETIC DEPOSITION

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A project report submitted in partial fulfilment of the
requirements for the award of the degree of
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I would like to dedicate this project report to my ***God*** *Almighty who has been eternal rock and source of refuge*

Also this project report is dedicated to my beloved parents ***Amal*** *and* ***Najm*** *as well as my sisters and brothers who have supported me during my study period*

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ABSTRACT

Recently, applications of Ti-13Nb-13Zr alloy have been widely increased in biomedical fields due to its excellent biocompatibility and mechanical properties. However, its corrosion resistance is still a matter of concern when it is implanted inside human body. Many attempts have been done to enhance its corrosion resistance by using hydroxyapatite coating. This study includes two major directions; firstly calcium phosphate was electrophoretically coated on Ti-13Nb-13Zr surface in order to improve its corrosion resistance. Sintering post treatment was then conducted to the coated samples in order to transform the deposited layer from dicalcium phosphate dehydrated (DCPD) phase to the hydroxyapatite crystalline (HA) phase. The effect of two different sintering post-treatment parameters including time and temperature have been experienced on the corrosion potential of calcium phosphate coated substrate. Full factorial experimental designs followed by Response Surface Methodology (RSM) were employed for planning and analyzing the experimental results. Time and temperature of sintering post-treatment were considered as independent variables while corrosion potential is accounted as a response variable. Empirical models were successfully developed to predict amount of corrosion potential by using design of experiment (DOE) software. Experimental results show that the effect of sintering temperature is more significant than the sintering time. Moreover the results indicate that high corrosion potential is obtained under sintering conditions at (Time = 90 minutes, Temperature = 700° C). Finally, the electrophoretic deposition method exhibits a relatively uniform HA coating layer and free of crack.

ABSTRAK

Kebelakangan ini, aplikasi aloi Ti-13Nb-13Zr telah meningkat secara meluas dalam bidang bioperubatan kerana keserasian-bio dan sifat-sifat mekaniknya yang sangat baik. Walau bagaimanapun, ketahanan kakisannya masih menjadi perhatian apabila ia diimplankan ke dalam badan manusia. Banyak usaha telah dilakukan untuk meningkatkan rintangan kakisan dengan menggunakan salutan hydroksiapatit. Kajian ini merangkumi dua halatuju utama; pertama kalsium fosfat di salutkan ke atas permukaan Ti-13Nb-13Zr secara elektroforesis bagi meningkatkan ketahanan kakisannya. Pasca rawatan pensinteran telah dijalankan kepada sampel bersalut untuk mengubah lapisan daripada fasa dikalsium fosfat dehidrasi (DCPD) kepada fasa kristal hydroksiapatit (HA). Kesan dua parameter selepas rawatan pensinteran yang berbeza termasuk masa dan suhu telah di kaji berdasarkan kepada keupayaan kakisan ke atas substrat kalsium fosfat bersalut. Rekabentuk ujikaji faktoran penuh diikuti oleh Kaedah Respon Permukaan (RSM) telah digunakan untuk merancang dan menganalisis keputusan ujikaji. Masa dan suhu pensinteran selepas rawatan dianggap sebagai pembolehubah bebas manakala potensi hakisan diambil kira sebagai pembolehubah respon. Model empirikal telah berjaya dibangunkan untuk meramalkan jumlah potensi kakisan dengan menggunakan perisian reka bentuk ujikaji (DOE). Keputusan ujikaji menunjukkan kesan suhu pensinteran adalah faktor yang lebih signifikan berbanding masa pensinteran. Selain itu, keputusan menunjukkan bahawa potensi kakisan yang tinggi diperolehi dalam keadaan pensinteran pada (Masa = 90 minit, Suhu = 700 °C). Akhir sekali, kaedah pemendapan elektroforetik menunjukkan bahawa lapisan salutan HA yang disebabkan oleh pensinteran selepas rawatan adalah agak seragam dan bebas daripada retakan.

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LIST OF ABBREVIATIONS

ANOVA		Analysis of variance
DCPD	-	Dicalcium phosphate dihydrated
DF	-	Degree of freedom
DOE	-	Design of Experiment
E_{corr}	-	Corrosion potential
EDS	-	Energy dispersive spectrometer
EPD	-	Electrophoretic deposition
HA	-	Hydroxyapatite
MS	-	Mean square
RSM	-	Response surface methodology
SBF	-	Simulated body fluid
SEM	-	Scanning electron microscope
SS	-	Sum of square
XRD	-	X-ray Diffraction

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Biomaterials have a long history as orthopaedic implants and bone graft substitutes due to their well-known strength (elastic modulus larger than 100 GPa), particularly in load-bearing areas. The advantages of biomaterials include excellent mechanical properties such as fatigue, reasonable corrosion resistance, biocompatibility, suitable density, high strength and biocompatibility. The heat treatment and manufacturing method also affect these properties. Their use is however associated with several limitations, which comprise permanence, cracking, low volumetric porosity, relatively high modulus of elasticity, low osseointegration with bone tissues and the potential of releasing metallic ions which in turn resulting in a corrosion within the body. Most metals have ability to produce a complete tissue replacement for bone defects due to their biodegradable properties.

Corrosion is a great concern for use of metallic implant when it exposed in hostile electrolytic environments because the corrosion products have been implicated in causing infections, local pain, swelling, and loosening. It can, therefore, severely limit the fatigue life and ultimate strength of the material, leading to the in vivo failure of implants [42]. The human body shows natural reaction against prosthetic devices causing the osteolysis and has the tendency to isolate from the surrounding live tissues.

In order to improve corrosion resistance, biodegradation and bioactive properties, bio-ceramic coatings on metallic substrates have been widely used in bone substitutes because of their biocompatibility, bioactivity, and osteoconductivity. Surface engineering processes can be used increasingly either to modify existing surfaces or to apply coatings. Coating can be applied for a diversity of reasons. As the corrosion of metal surface is an electrochemical reaction between the metal and external agents (for example, oxygen and/or water). Coating can act as a barrier and preventing this reaction.

Hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$, is composed primarily of calcium and phosphorous with hydroxide ions that are eliminated at elevated temperatures. HA and other related calcium phosphate minerals have been utilised extensively as implant materials for many years due to its excellent biocompatibility and bone bonding ability and also due to its structural and compositional similarity to that of the mineral phase of hard tissue in human bones [43]. HA coatings have good potential as they can exploit the biocompatible and bone bonding properties of the ceramic, while utilising the mechanical properties of substrates such as Co-Cr alloys, Ti based alloy and other biocompatible alloys. While the metallic materials have the required mechanical properties, they benefit from the HA which provides an osteoconductive surface for new bone growth, anchoring the implant and transferring load to the skeleton, helping to combat bone atrophy have been extensively used for the purpose of bone graft substitute and bone tissue engineering. Because of their similarity to bone mineral, calcium phosphorous (Ca/P) based materials are biocompatible, osteoconductive and bone-bonding.

In orthopaedic field, hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) coated metal implants have been studied extensively due to their outstanding biological responses in the physiological environment and surface protection against body fluid [44]. Several coating methods have been introduced for coating of HAp on the metallic substrates: plasma spraying, sol–gel, RF magnetron sputter, ion beam dynamic mixing, pulse laser deposition, biomimetic coating, electrophoretic deposition, and electrolytic deposition. Among the various fabrication methods, electrophoretic deposition (EPD) is a promising technique, with advantages including short

formation time, simplicity in instrumentation, and capability of coating complex-shaped implants. Electrophoretic deposition is a colloidal processing technique that allows not only shaping free standing objects but also allows depositing thin films and coatings on substrates. EPD is known to be one of the most effective and efficient techniques to assemble fine particles. This technique has received significant attention due to its simplicity in setup, low equipment cost, and capability to form complex shapes and patterns. EPD is also a potentially attractive process for obtaining bioceramic. The application of EPD in the biomaterials area, in particular for obtaining HAp and bioactive glass coatings on metallic implants, has been demonstrated [45].

Electrophoretic deposition (EPD) was used in the current work as the coating technique due to its efficiency, flexibility, and economy. In general, a short deposition time is required for electrophoretic forming or coating (a few seconds to a few minutes). The deposition rate of electrophoresis can be as high as 1 mm/min. Uniform coatings of complex shapes can be easily formed by using appropriately shaped electrodes, such as wire, coil or plate. A high degree of control of coating deposit morphology can be obtained by adjusting the deposition conditions, the ceramic powder size and shape. However with increasing deposition time and voltage, the thickness of the coating increases.

Evaluation the electrochemical corrosion behaviour of HA coating layer on the Ti-13Nb-13Zr substrate is one of the goals of this project. It is expected the coating of HA layer to improve the corrosion resistance by this project's method.

1.2 Problem Statement

Nowadays corrosion of the biomaterials becomes a significant issues the corrosion behaviour of various implants and the role of the surface oxide film and the corrosion products on the failure of implants are discussed. Nonetheless, these problems would be solved by coating implants with biocompatible and corrosion resistant material like Hydroxyapatite (HA). Electrochemical deposition of HA

following by sintering post-treatment on metallic implant has unique advantages due to its capability of forming uniform coating and simple setup. But there is still lack of research and study on controlling of post-treatment parameters including time and temperature after EPD coating on Ti-13Nb-13Zr substrate.

1.3 Objectives of the Study

Based on the problem statement of the project, the objectives of this research were:

i. To evaluate the effect of post-treatment parameters (sintering time and temperature) on corrosion resistance of HA coated Ti-13Nb-13Zr alloy.
ii. To determine the optimal setting of post treatment parameters for better corrosion resistance of (Ti-13Nb-13Zr) substrate.

1.4 Scopes of the Study

The scopes of this project were:

i. The implant material used in this study was limited to one of the metallic implant material which is Ti-13Nb-13Zr alloy.
ii. Coating performances were evaluated in terms of corrosion resistance and micro-crack formed after sintering post-treatment.
iii. Electrophoretic deposition technique (EPD) was employed for coating of HA on Ti-13Nb-13Zr alloy.
iv. Design Expert 7 software (DOE) was used to analyse the experimental results.
v. Two different sintering parameters including time and temperature were used to evaluate their effects on the corrosion resistance of HA coated layer.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, biomaterials and their applications, corrosion and their types, definition of hydroxyapatite, electrophoretic deposition process, sintering post treatment, design of experiment, and response surface methodology (RSM) are defined. First, the models of biomaterials, corrosion behaviour of Ti, electrophoretic coating process, and the methods of coating are discussed. Following that, the design of experiment approach and application of DOE in behavior of sintering parameters are introduced in order to have truly comprehension of the design of experiment concept. Having discussed the design of experiment method, the integration of DOE is introduced to address the significance of it for improving the potential corrosion of coating layer. Response surface methodology (RSM) is defined in order to explain how it uses to evaluate the obtained results of conducting experiment. Finally, some of critical review HA coating on implant biomaterials using EPD.

2.2 Introduction to Biomaterials

Biomaterial has been used to make devices to replace a part or a function of the body in a safe, reliable, economic, and physiologically acceptable manner. Over the years, various definitions of the term biomaterials have been proposed. For

example, a biomaterial can be simply defined as a synthetic material used to replace part of a living system or to function in intimate contact with living tissue. According to this definition one must possess knowledge in a number of different disciplines or collaborate with individuals from a wide variety of different specialties in order to properly develop and use biomaterials in medicine and dentistry as seen in Table 2.1.

Table 2.1 : Fields of Knowledge to Develop Biomaterials [1]

Discipline	Examples
Science and engineering	Materials sciences: structure–property relationship of synthetic and biological materials including metals, ceramics, polymers, composites, tissues (blood and connective tissues), etc.
Biology and physiology	Cell and molecular biology, anatomy, animal and human physiology, histopathology, experimental surgery, immunology, etc.
Clinical sciences	All the clinical specialties: dentistry, maxillofacial, neurosurgery, obstetrics and gynecology, ophthalmology, orthopedics, otolaryngology, plastic and reconstructive surgery, thoracic and cardiovascular surgery, veterinary medicine, and surgery, etc.

Table 2.2 provides some examples of the uses of biomaterials, which include replacement of a body part that has lost function due to disease or trauma, to assist in healing, to improve performance, and to correct abnormalities. The role of biomaterials has been influenced considerably by advances in many areas of biotechnology and science. For example, with the advent of antibiotics, infectious disease is less of a threat than in former times, so that degenerative diseases assume a greater importance. Moreover, advances in surgical technique and instruments have permitted materials to be used in ways that were not possible previously [1].

Table 2.2 : Uses of Biomaterials [1]

Problem Area	Examples
Replacement of diseased or damaged part	Artificial hip joint, kidney dialysis machine
Assist in healing	Sutures, bone plates, and screws
Improve function	Cardiac pacemaker, intraocular lens
Correct functional abnormality	Cardiac pacemaker
Correct cosmetic problem	Augmentation mammoplasty, chin augmentation
Aid to diagnosis	Probes and catheters
Aid to treatment	Catheters, drains

Biomaterials are commonly characterized as materials used to construct artificial organs, rehabilitation devices, or implants to replace natural body tissues. More specific, biomaterials are materials that are used in close or direct contact with the body to augment or replace faulty materials. In general biomaterials can be classified into living or once living materials, which fit into the division of for example tissue engineering, and materials that are of a synthetic origin. Such biomaterials can be defined as inorganic or organic materials that are biocompatible and can be implanted in the human body to replace or repair failing tissue. In 1986 the European Society for Biomaterials compiled a set of "Definitions in Biomaterials" [3]. Some definitions for biomaterials and most important terms in the field are listed in Table 2.3.

Table 2.3 : Definitions for Biomaterials

Biomaterial	A non-viable material, used in a medical device, intended to interact with biological systems
Implant	Any medical device made from one or more materials that is intentionally placed within the body. Either totally or partially buried beneath an epithelial surface
Prosthesis	A device that replaces a limb, organ or tissue of the body
Artificail organ	A medical device that replaces, in part or in whole, the function of one of the organs of the body

Especially, materials known from the field of implantology that are used for the fixation or the replacement of diseased hard tissue have run through numerous inventions. Particularly, as this class of biomaterials includes certain materials systems such as metals, ceramics and polymers, which are used for example in reconstructing bones, joints or for teeth replacement, the diversity of inventions and modifications on bulk as well as surface properties, has reached an enormous quantity[1,3].

2.3 Performance and Application of Biomaterials

The performance of materials in the body can be classified in many ways. During recent decades vast and continuously increasing numbers of biomedical implants have been introduced for continuous use in the human body. Performance of biomaterials in the body can be defined in several ways due to the rapid development and expansion of biomaterials science. Biomaterials success depend on some factors such as the material design, properties, and biocompatibility of the material used, as well as some other factors not under the control of the engineer, including the technique used by the surgeon, the health and condition of the patient, and the activities of the patient. If we can assign a numerical value (f) to the probability of failure of an implant, then the reliability can be expressed as:

$$r = 1 - f \tag{2.1}$$

If, as is usually the case, there are multiple modes of failure, the total reliability *rt i*s given by the product of the individual reliabilities *r1* = (1 – *f*1), etc.

$$rt = r1.r2\ldots\ldots rn \tag{2.2}$$

Consequently, even if one failure mode such as implant fracture is perfectly controlled so that the corresponding reliability is unity, other failure modes such as infection could severely limit the utility represented by the total reliability of the implant. One mode of failure which can occur in a biomaterial, but not in engineering materials used in other contexts, is an attack by the body's immune system on the implant. Another such failure mode is an unwanted effect of the implant upon the body; for example, toxicity, inducing allergic reactions, or causing cancer. Consequently, biocompatibility is included as a material requirement in addition to those requirements associated directly with the function of the implant [46].

Biomaterials must have mechanical and performance requirements that originate from the physical properties of the materials. The following are some categories of such requirements:

i. Mechanical Performance
ii. Mechanical durability
iii. Physical Properties

So, Table 2.4 shows some of the mechanical performances for biomaterial devices.

Table 2.4: Mechanical performances

Device	**Properties**
A hip prosthesis	Must be strong and rigid
A tendon material	Must be strong and flexible
A heart valve leaflet	Must be flexible and tough
An articular cartilage substitute	Must be soft and elastomeric
A dialysis membrane	Must be strong and flexible but not elastomer

2.4 Biomaterials Classifications

Actually, there are different common classification types of biomaterials implanted with human biological systems. These types can be classified into two main categories. The first category is based on ***natural biomaterials***, while the second category of biomaterials is based on ***synthetic engineering biomaterials***. With the advanced technology of engineering biomaterials tissues, a new third category is created, called combined of biomaterials. Figure 2.1 shows new simple block diagram of biomaterials classification [2].

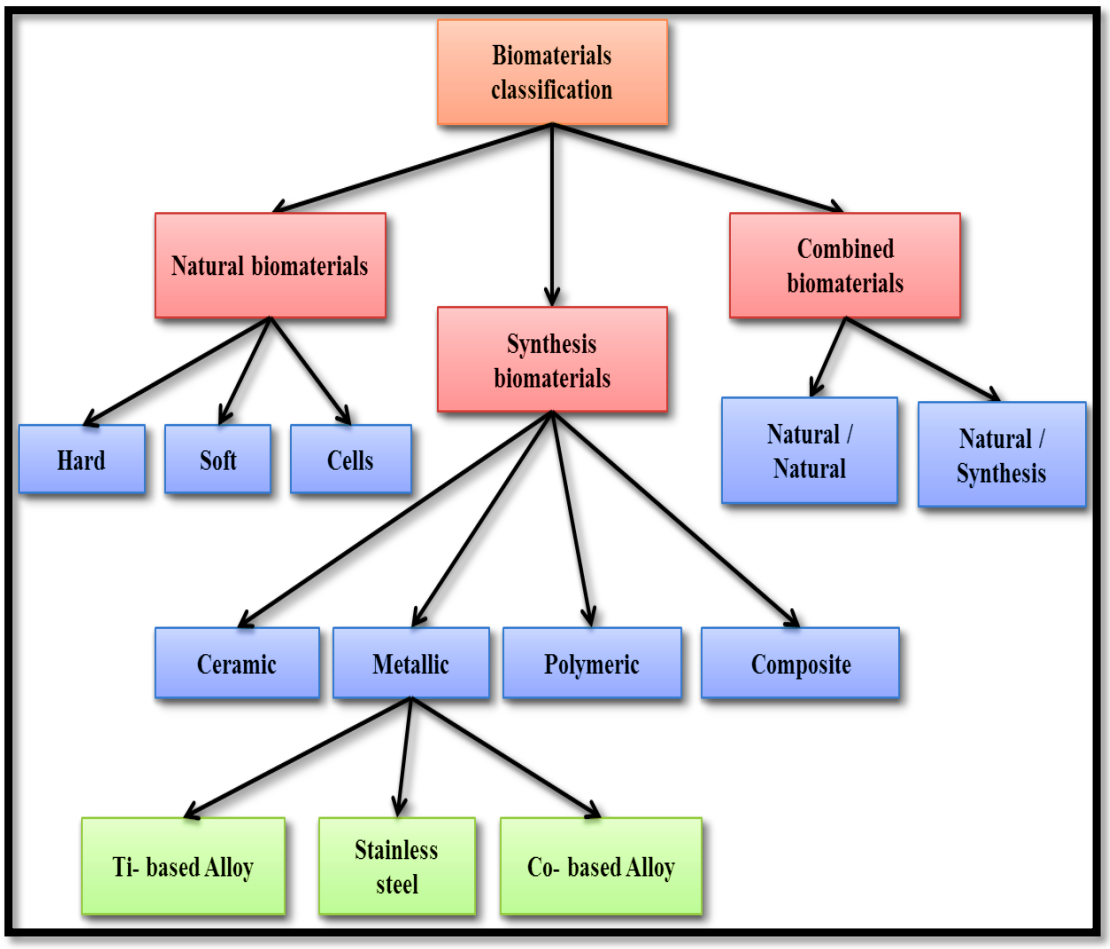

Figure 2.1 Classifications of biomaterials [2]

2.4.1 Natural Bio*materials*

Human natural biomaterials are materials that contain similar architectures to the native tissue. They are replacing with donor natural elements needed for proper tissue reconstruction. Natural biomaterials in the human biological system are classified into three types (soft, hard and cells). The natural soft tissue likes skin, tendon, pericardium, cornea, nerve, muscle and so on. The natural hard tissue is a kind of connective tissue likes bone, collagen, dentine and cuticle. While the natural blood and lymph cells are the stem cells. Natural materials (hard or soft) have important role in tissue engineering and organ regeneration. The use of natural biomaterials has typically required chemical or physical pre-treatment aimed to: