INFLUENCE OF ULTRASONIC VIBRATION ON TiN COATED BIOMEDICAL TI-13Zr-13Nb ALLOY

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ABSTRACT

Biomedical grade of titanium alloys are prone to undergo degradation in body fluid environment. Surface coating such as Physical Vapor Deposition (PVD) can serve as one of the alternatives to minimize this issue. Past reports highlighted that coated PVD layer consists of pores, pin holes and columnar growth which act as channels for the aggressive medium to attack the substrate. Duplex and multilayer coatings seem able to address this issue at certain extent but at the expense of manufacturing time and cost. In the present work, the effect of ultrasonic vibration parameters on PVD-Titanium Nitride (TiN) coated Ti-13Zr-13Nb biomedical alloy was studied. Disk type samples were prepared and coated with TiN at various conditions: bias voltage (-125V), substrate temperature (100 to 300 °C) and nitrogen gas flow rate (100 to 300 sccm). Ultrasonic vibration was then subsequently applied on extreme high and low conditions of TiN coated samples at two different frequencies (8 kHz, 16 kHz) and three set of exposure times (5 min, 8 min, 11 min). Encouraging results of PVD coating are observed on the samples coated at higher polarity of nitrogen gas flow rate (300 sccm) and substrate temperature (300 °C) in terms of providing better surface morphology and roughness, coating thickness and adhesion strength. All TiN coated samples treated with ultrasonic vibration exhibit higher corrosion resistance than the untreated ones. Microstructure analysis under (Field Emission Scanning Electron Microscopy (FESEM) confirms that the higher ultrasonic frequency (16 kHz) and the longer exposure time (11 minutes) produce the most compact coating. It is believed that hammering effect from ultrasonic vibration reduces the micro channels' size in the coating and thus decelerates the corrosion attack. Nano indentation test conducted on the ultrasonic treated samples provides a higher Hardness/Elasticity (H/E) ratio than untreated ones. This suggests that the ultrasonic vibration treated samples could also have a lower wear rate.

ABSTRAK

Gred bioperubatan aloi titanium lebih cenderung mengalami kakisan dalam persekitaran cecair badan. Salutan permukaan seperti *Physical Vapor Deposition* (PVD) boleh digunakan sebagai salah satu alternatif untuk mengurangkan masalah ini. Hasil kajian sebelum ini menunjukkan bahawa lapisan salutan PVD terdiri daripada liang-liang, lubang pin, dan pertumbuhan kolumnar yang bertindak sebagai salah satu saluran untuk cecair menyerang substrat. Substrat yang disalut dengan dua lapisan atau lebih dilihat dapat mengatasi masalah ini pada kadar tertentu tetapi ianya melibatkan kos pembuatan yang tinggi dengan masa yang panjang. Dalam kajian ini, kesan parameter getaran ultrasonik ke atas PVD- *Titanium Nitride* (TiN) yang disalut ke atas aloi bioperubatan Ti-13Zr-13Nb telah dikaji. Sampel berbentuk cakera disediakan dan disalut dengan TiN pada voltan pincang (-125V), suhu substrat (100 hingga 300 °C) dan kadar aliran gas nitrogen (100-300 sccm). Getaran ultrasonik kemudiannya dikenakan ke atas sampel yang disalut dengan TiN dalam keadaan dua frekuensi yang berbeza (8 kHz, 16 kHz) dan tiga masa pendedahan (5 min, 8 min, 11 min). Hasil kajian salutan PVD yang menggalakkan diperolehi ke atas sampel yang dikenakan pada kadar aliran gas nitrogen dan suhu substrat yang tinggi dari segi morpologi dan keserataan permukaan, ketebalan salutan dan kekuatan lekatan yang lebih baik. Semua sampel yang dirawat dengan salutan TiN menggunakan getaran ultrasonik menunjukkan ketahanan kakisan yang tinggi jika dibandingkan dengan sampel tanpa rawatan. Analisis struktur mikro menggunakan *Field Emission Scanning Electron Microscopy* (FESEM) mengesahkan bahawa ultrasonik frekuensi yang tinggi dengan masa yang lama menghasilkan lapisan yang paling padat. Ini adalah disebabkan kesan ketukan yang dihasilkan oleh getaran ultrasonik yang mana dapat mengecilkan saiz saluran pada salutan tersebut dan dengan itu mengurangkan serangan kakisan. Ujian lekukan nano yang dijalankan ke atas sampel yang dirawat dengan getaran didapati menghasilkan nilai nisbah *Hardness/Elasticy* H/E yang tinggi jika dibandingkan dengan sampel tanpa rawatan. Ini menunjukkan bahawa sampel yang dikenakan rawatan getaran ultrasonik juga boleh menghasilkan kadar kehausan yang lebih rendah.

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LIST OF ABBREVIATIONS

A	-	Area
a-C	-	Amorphous carbon
CA-PVD	-	Cathodic arc physical vapour deposition
C_{dl}	-	Double layer capacitance
Cp-Ti	-	Commercial pure titanium
CVD	-	Chemical vapour deposition
DLC	-	Diamond like carbon
E_{corr}	-	Corrosion potential
EIS	-	Electrochemical vapour deposition
FESEM	-	Field emission scanning electron microscope
FRA	-	Frequency response analyser
H/E	-	Hardness/Elasticity
HFCVD	-	Hot filament chemical vapour deposition
I_{corr}	-	Corrosion current density
IGC		Intergranular corrosion
OCP	-	Open circuit potential

PVD	-	Physical vapor deposition
R_{ct}	-	Charge transfer resistance
SCE	-	Saturated calomel electrode
sccm	-	Standard cubic centimetres per minute
SiC	-	Silicon carbide
TiN	-	Titanium nitride
TiAlN	-	Titanium aluminum nitride
UBM	-	Unbalanced magnetron sputtering
USM	-	Ultrasonic machining
XRD	-	X-ray Diffraction Spectroscopy

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CHAPTER 1

INTRODUCTION

1.1 Background of the problem

The field of biomaterial has caught attention of researchers because it can increase the length and quality of human life. Natural and artificial biomaterials are used to make implants or structures that replace biological structures lost to diseases or accidents. The application of biomaterial in musculoskeletal implants include dental implants, artificial hips, and knees prostheses and incorporate the screws, plates, and nails in these devices [1]. The materials used in surgical implants include stainless steel (316LSS), Co-Cr-based alloys, and Ti alloys. Titanium based alloys are preferable due to their excellent biocompatibility, outstanding corrosion resistance, relatively good fatigue resistance, and lower elastic modulus [2, 3].

Several types of titanium alloys have been developed and one of them is Ti-6Al-4V. Ti-6Al-4V was the first standard alloys employed as a biomaterial for implants. Although this alloy has an excellent reputation in terms of its biocompatibility and corrosion resistance, studies have shown that the release of aluminium and vanadium ions from this alloy causes long term problem, such as peripheral neuropathy, osteomalacia, and Alzheimer diseases [4]. Consequently other titanium alloys group have been developed as alternatives to the Ti-6Al-4V

alloy. Among them, Ti-13Zr-13Nb is the most attractive biomaterial due to its low Young's modulus and non-toxic composition. It has been reported that Ti-13Zr-13Nb alloy is preferred for biomedical applications due to its superior corrosion resistance and biocompatibility. The good biocompatibility of this alloy is due to the corrosion products of the minor alloying elements (niobium and zirconium) that are less soluble than those of aluminium and vanadium. This material also has good tensile and corrosion resistance compared to Ti-6Al-4V and Ti-6Al-7Nb alloys [5].

Although the Ti-13Zr-13Nb alloy has excellence corrosion resistance and biocompatibility under normal conditions, it is still subject to corrosion, especially when it is in contact with body fluids. The environment found in the human body is very harsh owing to the presence of chloride ions and proteins. As an implant corrodes, it releases toxic ions and causes inflammation, which may require further surgery [6]. This issue can be addressed by using a surface coating or surface modification techniques. Several studies have been conducted that attempt to increase of Ti-13Zr-13Nb. Techniques including thermal oxidation [2, 7-12], anodic oxidation [13-16], thermal spray [17], laser nitriding [18], plasma spray [19, 20], Chemical Vapour Deposition (CVD) [21], and Ion Implantation [22] have all been investigated. The processing temperature of surface modification techniques in these studies are relatively high (600 – 2000 °C), which restricts the type of substrates that can be used, as well as causing unexpected phase transitions and excessive residual stresses. Nevertheless, a few studies use surface modification techniques with low processing temperatures. Other surface modification techniques such as Physical Vapour Deposition (PVD) offer promising results using low processing temperatures (<500° C) over a wide range of coating thickness. In this thesis, PVD coating on Ti-13Zr-13Nb was proposed as a way to improve the corrosion resistance of medical implants.

1.2 Problem statements

Surface coatings, such as PVD, can minimize the corrosion rate of titanium alloys that are exposed to body fluids. Past reports indicated that coated PVD layers have pores, pin holes, and columnar growths that act as channels for aggressive mediums to attack the substrate [23-26]. Duplex and multilayer coatings address this issue but at the expense of manufacturing time and cost. Therefore, an alternative method is needed to reduce the penetration of body fluids and react with bare substrate. One of possible surface modifications to PVD coatings uses a mechanical treatment. Several studies have demonstrated that sand blasting PVD coatings increases the compactness and hardness of the coating, which leads to lower wear rates [27-34]. However, very limited literature exists on surface mechanical treatment especially on the application of ultrasonic vibration to reduce corrosion attack of TiN coated Ti based implants. Most researchers have reported the behaviour of mechanical treatment on wear rate mechanism only. Therefore, a detailed study is needed to evaluate the effect of ultrasonic treatments on PVD-TiN coated Ti-13Zr-13Nb alloys in terms of corrosion resistance.

1.3 Objectives of the study

The objectives of this study were:

i. To analyse the effect of PVD coating parameters on the surface morphology, coating thickness, and adhesion strength of TiN coated biomedical grade Ti alloys.

ii. To investigate the effect of ultrasonic vibration treatment on the hardness and coating thickness of TiN coated samples.

iii. To compare the corrosion performance of ultrasonic treated and untreated TiN coating samples under simulated body fluids.

1.4 Scopes of the study

The study was conducted using the following limits:

i. Ti-13Zr-13Nb was used as the substrate material.

ii. The variable CAPVD parameters included nitrogen gas flow rates (100-300 sccm) and substrate temperature (100-300° C). The bias voltage was fixed at -125V.

iii. An ultrasonic machine (Sonic mill AP-10001X) was used to hammer the TiN coated samples using micro steel balls.

iv. Ultrasonic parameters varied from 8 to 16 kHz for 5, 8, and 11 minutes of exposure time.

v. FESEM was used to characterize surface morphology and coating thickness. A nano-indenter was used to determine TiN hardness.

vi. Tafel plot and EIS were used to evaluate corrosion on untreated and treated TiN coated samples.

vii. A Kokubo solution was used to simulate body fluids during corrosion resistance testing.

1.5 Significance of the study

The use of ultrasonic vibrations as a post treatment on TiN coated layers was expected to reduce corrosion when the implant was subjected to body fluids. The hypothesis was that ultrasonic vibration would provide micro-steel ball impingement that would result in a TiN coated layer with higher hardness and less porosity. The technique applied was less expensive than the multilayer and duplex coatings suggested by other researchers. The application of TiN coated Ti-13Zr-13Nb is appropriate for orthopaedic plates that are commonly used in bone surgery. The success of this method will improve the life of prosthesis and reduce implant revision costs. In addition, this study will help manufacturers produce more

sustainable biomedical implants by increasing the surface hardness of the implant and thus providing better wear resistance capabilities. This study will also add to the knowledge and understanding of the behaviour of TiN coatings on biomedical implants.

1.6 Thesis organization

This thesis consists of five chapters. Chapter 1 is the introduction, which covers the background of research, the problem statement, and the objectives, scope, and significance of study. Chapter 2 provides an overview of general implant materials, a review of surface modification techniques, PVD, ultrasonic vibration, and an evaluation of coating performances. At the end of this chapter, the literature is summarized and gaps in the research are discussed.

In Chapter 3, the experimental approach adopted in this study is discussed including the substrate material and its preparation, and an explanation of the procedure for testing CAPVD and ultrasonic treatments. The analytical equipment used in this study is also discussed in this chapter, including a corrosion test, adhesion strength, nano indenter, FESEM, and XRD.

In Chapter 4, the results of Experiment Stages I, II and III are described and discussed. Experiment Stage I discusses the preliminary trials conducted before the actual experiment began. In Stage II, the effects of CAPVD parameters on surface morphology, coating thickness, and adhesion strength are discussed. Stage III describes the effect of ultrasonic treatments under extreme PVD conditions on corrosion resistance and hardness. Chapter 5 presents the conclusions from this study and recommendations for future work.