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# Investigation of nano-structured Zirconium oxide film on Ti6Al4V substrate to improve tribological properties prepared by PIII&D



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#### ABSTRACT

Plasma immersion ion implantation and deposition (PIII&D) is the most attractive and efficient technique used in the medical field to tailor materials for biomedical applications. In the present study zirconium oxide nano-structured thin films were deposited on surface of Ti6Al4V alloy for bias voltages of 15, 20 and 25 kV. The chemical composition, surface roughness and thickness of deposited films were characterized by the x-ray photoelectron spectroscopy (XPS), atomic force microscope (AFM) and ellipsometry respectively. The XPS results confirm the formation of a dense zirconium oxide film of the treated specimens. AFM results exhibit a smooth film with maximum roughness of about 8.4 nm is formed. The thickness of the film is increased with the increase in bias voltages and is maximum at 25 kV. The effect of bias voltages on wear characteristics was further investigated by pin-on-disk test. It is observed that the friction coefficient is reduced, whereas wear resistance is enhanced and it is found to be maximum at 25 kV compared to the other bias voltages. Nanohardness is improved up to twice compared to untreated specimen at the maximum bias voltage. Therefore, it is concluded that deposition of zirconium oxide using the PIII&D is produced a dense layer on the substrate surface, which can be used as a promising candidate for the improved tribological properties of Ti6Al4V.

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#### 1. Introduction

The demand of biomaterials in various applications such as dental roots, stents, joint replacements and orthopedic fixation has been increased in recent era. It is difficult and time-consuming to design new biomaterials and therefore the most economical way is to modify surface properties of existing biomaterials to fulfill the modern requirements [1–3]. The surface of implanted material can be altered using thin film deposition techniques. Different deposition techniques have appeared in the available literature. However among these, plasma immersion ion implantation and deposition (PIII&D) is becoming the versatile technique to modify the surface properties of the materials over the last decade [4–6]. PIII&D has the potential to alter the surface properties of without any change in bulk [5]. Moreover, ions can be incorporated into the

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http://dx.doi.org/10.1016/j.apsusc.2016.09.091 0169-4332/© 2016 Published by Elsevier B.V. materials approximately up to the depth of hundreds of nanometer using PIII&D which has been widely used in the medical field to improve the bio-medical properties of polymers, metals and there alloys [5–7].

Ti6Al4V alloy is the most suitable material for biomedical implants as compared to the pure Ti and some of its other alloys due to its high mechanical strength, modulus of elasticity comparable to the bone, good biocompatibility and excellent corrosion resistance [8,9]. However, Ti6Al4V alloy exhibits the poor tribological properties, limiting its use in load-bearing applications [10,11]. Liang et al. [12] reported that degradation of artificial implants like knee, elbow and hip joints were occurred after 10-15 years of use. The main causes behind this degradation were wear failures. Moreover, it was observed that wear particles promoted the corrosion process resulting in genetic damage [13]. Therefore, it is imperative to make these implant materials wear and corrosion resistant. The wear resistance of implant material can be enriched by improving the hardness of substrate to inhibit defections and ploughing due to counter load [14]. This can be achieved by coating the different materials on the surface of Ti and its alloy.



Full Length Article

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Fig. 1. Survey Scan spectrum of (a) untreated Ti6Al4V (b) ZrO<sub>2</sub> deposited specimen.

Ganapathy et al. [8] deposited the Al<sub>2</sub>O<sub>3</sub> and 8mole% of Yttriumstabilized ZrO<sub>2</sub> composite coating on Ti6Al4V which exhibited a superior wear resistance. The wear rate was found to be 253 times lower as compared to the Ti6Al4V alloy. The decrease in wear rate was due to the formation of dense structure, improving the hardness of the substrate. Similarly, Narvaez et al. [14] observed the wear mechanism of TiAlN coating at different bias voltages and concluded that the film grown at -40V exhibited the best tribological properties. In another study Obadele et al. [15] coated Ti6Al4V with ZrO<sub>2</sub> in Ti matrix and observed decrease in the friction coefficient with enhanced wear resistance. More recently, Liu et al. [16] observed that the friction coefficient of texture surface decreased after the nitrogen ion implantation improving the wear resistance was improved. Although many researchers have made the considerable efforts to improve the wear behavior of Ti6Al4V alloy but to the best of our knowledge, no one has prepared the nano-structured zirconium oxide film at various voltages by PIII&D technique. Therefore the aim of present study is to explore the effect of nano-structured zirconium oxide film on tribological properties of Ti6Al4V alloy.

#### 2. Experimental details

Ti6Al4V samples  $(10 \text{ mm} \times 10 \text{ mm} \times 2 \text{ mm})$  were mechanically grinded to mirror polished with SiC papers grit (200-1200), ultrasonically rinsed in acetone, ethanol and distilled water (10 min each) and then dried in air before its exposure to plasma. Plasma immersion ion implantation and deposition (PIII&D) was carried out in the plasma ion implanter housed in plasma laboratory,



Fig. 2. Deconvoluted XPS spectrum of (a) Ti 2p (b) Zr 3d (c) O1s.

City University of Hong Kong. The details of PIII equipment and implanter are mentioned elsewhere [17]. The base pressure of  $1.3 \times 10^{-2}$  Pa was achieved in the vacuum chamber by mechanical and turbo molecular pumps. Argon gas was used for cleaning the specimens by means of sputtering. Zirconium cathode was used to produce zirconium ions to deposit Zirconium oxide thin film. High purity argon (Ar 99.99% pure) and oxygen (O<sub>2</sub> 99.99% pure) gases were fed into the chamber to generate the plasma at 30 sccm and

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