Accepted Manuscript

Statistical optimization and fretting fatigue study of Zr/ZrO$_2$ nanotubular arrays coating on Ti-6Al-4 V


PII: S0257-8972(14)00645-8
DOI: doi: 10.1016/j.surfcoat.2014.07.046
Reference: SCT 19583

To appear in: Surface & Coatings Technology

Received date: 11 February 2014
Revised date: 13 July 2014
Accepted date: 16 July 2014


This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.
Statistical optimization and fretting fatigue study of Zr/ZrO₂ nanotubular arrays coating on Ti-6Al-4V


⁸ Department of Mechanical Engineering, Faculty of Engineering University of Malaya, 50603 Kuala Lumpur, Malaysia.
⁷ Department of Chemistry, Faculty of Science, University of Malaya, Kuala Lumpur 50603, Malaysia.
⁹ Department of Physics, Faculty of Science, University of Malaya, Kuala Lumpur 50603, Malaysia.
⁴ Mechanical and Industrial Engineering Department, College of Engineering, Qatar University, P.O. Box 2713, Doha, Qatar.
⁹ Nanotechnology & Catalysis Research Centre (NanoCat), University Malaya, 50603 Kuala Lumpur, Malaysia.

Abstract

Herein, the fretting fatigue behavior of zirconium nanotube arrays on the surface of Ti-6Al-4V is studied. Initially, a thin film of pure zirconium (Zr) was deposited onto a Ti-6Al-4V substrate using physical vapor deposition (PVD) magnetron sputtering for the primary layer at varying DC power, temperature and substrate bias voltage values. To obtain higher adhesion strength, the Taguchi optimization method was used to estimate the optimum coating parameters,
while a Pareto ANOVA was employed to determine the significant parameters. The strongest coating adhesion, as determined by a scratch force test, was achieved at 300 W DC power, 200°C and a 75 V bias voltage. Consequently, nanotubes were produced via Zr anodization in an NH₄F electrolyte solution (95 glycerol: 5 water) at different times and at a constant potential of 60 V (second layer). The fretting fatigue behavior of anodized samples annealed at 400°C and 800°C was investigated. The results indicate that the fretting fatigue life of the ZrO₂ nanotube-coated samples was significantly improved at low and high cyclic fatigue at an annealing temperature of 400°C compared to the uncoated samples.

**Keywords:** PVD magnetron sputtering; Zirconium nanotube array; Fretting fatigue; Taguchi method; Pareto ANOVA.

1. **Introduction**

Metallic biomaterials used to replace and repair human body parts have attracted tremendous amounts of attention over the past two decades [1-3]. A large number of implant materials, such as bone plates, screws, dental implants, and artificial joints, which are utilized to a large extent in various medical applications, are made of titanium and its alloys because of titanium’s excellent biocompatibility, low elastic modulus, and high corrosion resistance [4-7]. Unfortunately, the inferior wear resistance of such implants has motivated researchers to increase their focus on overcoming this issue [8, 9]. Different aspects of biomedical applications and the mechanical properties of biomaterials are crucial with respect to materials being applied as long-term in vivo implants [10-12]. The nonconformity between bone and the implant surface layer is...
among the reasons for mechanical failure, particularly in relation to the deteriorating modulus of elasticity [13]. Therefore, it is very important to consider the mechanical properties of implant materials, especially those used in orthopedic applications. Orthopedic implant instruments are often manipulated under fatigue conditions and occasionally fail due to monotonic loads, fatigue, and corrosion fatigue [14]. Thus, investigating the mechanical performance of titanium alloys, particularly plain and fretting fatigue life, is a significant factor regarding their use in biomedical applications [15, 16].

Fretting fatigue is a phenomenon that can occur between two bodies, such as bone plates and screws [17, 18]. According to a previous assessment, 74% of implants that fail in the femoral neck region and in the modular junctions do so as a result of fretting fatigue [19-22]. Throughout the past two decades, the fretting fatigue of titanium alloys has been significantly improved using surface modifications with various nitride coatings (TiN, ZrN and TiAlN) [21-24]. Nanostructured metal oxides, such as TiO$_2$ and ZrO$_2$ nanotubes, are hard and wear-resistant, which is why the use of nanostructured TiO$_2$ and ZrO$_2$ coatings is becoming the surface modification method of choice [25, 26]. Zirconia nanotubes have several advantages, among which are their chemical and dimensional stability, good fracture toughness, Young’s modulus similar to that of stainless steel, bending strength, excellent biocompatibility, and high resistance to corrosion by bodily fluids. Thus, zirconia coatings on titanium alloys result in a high adhesion strength and are widely used in medical applications [27, 28].

Over the last few decades, various coating methods have been implemented by numerous researchers. The mechanical properties of coatings play a considerable role in biomedical implants, which is why selecting the best coating methods is a very important issue. To date, a
A variety of coating methods have been implemented, such as pulsed laser deposition (PLD) [29], chemical vapor deposition (CVD) [30], electrophoretic deposition (EPD) [29], electrochemical deposition (ECD) [32], ion beam deposition [33], and plasma sprays [34]. However, certain constraints, such as micro-cracks, phase changes at high temperatures, non-uniformity, and, especially, poor adhesion, have prompted many researchers to use physical vapor deposition (PVD) magnetron sputtering as the preferred coating technique [35]. This choice is also mainly made for a number of perceived advantages, such as high deposition rates, high-purity film formation, great adhesion to substrates, and the ability to form dense coatings [36]. Moreover, to obtain nanostructured metal oxides for diverse applications, various techniques have been employed, such as hydrothermal techniques, electrodeposition, and above all, anodization for its apt mechanical and biological integrity [37, 38].

Nevertheless, to the best of our knowledge, the fretting fatigue of ZrO$_2$ nanotubular arrays grown on Ti-6Al-4V has not been reported. Consequently, in this study, a pure zirconium (Zr) thin film was coated onto a titanium substrate using a PVD magnetron sputtering technique followed by anodization to grow zirconia (ZrO$_2$) nanotubular arrays as the second layer. The PVD coating process parameter settings for obtaining higher zirconium coating adhesion to the substrate were examined and investigated using Taguchi’s experimental design method. Orthogonal Taguchi arrays and signal-to-noise (S/N) ratios were analyzed to determine the optimal levels. A confirmation test was performed on the optimal coating parameter levels to illustrate the effectiveness of the Taguchi optimization. For further analysis, the Pareto ANOVA method was utilized to obtain optimum coating-to-substrate adhesion strength conditions. Highly ordered and self-organized anodic ZrO$_2$ nanotubes were electrochemically fabricated at 60 V over different
time periods via anodization using an electropolished Zr metal substrate in a water and glycerol solvent mixture containing ammonium fluoride (NH₄F) electrolytes. The stability of the Zr coating on the substrate and the fretting fatigue life of the ZrO₂-nanotube-coated substrate were evaluated using a micro-scratch tester and a rotating bending fretting fatigue test machine to explore their potential application as implant materials.

2. Experimental methods

2.1. Preparation of Zr thin film coating

Titanium alloy plates with dimensions of 20 × 10 × 5 mm were used as the zirconium coating substrate. The titanium surfaces were polished with SiC emery paper (200-2000 grit) and subsequently wet-polished. The titanium substrates were sonicated in ethanol and acetone to remove organic dirt and subsequently rinsed with distilled water and dried at 100°C for 10 min. After cleaning, the coated samples were electropolished in a mixed electrolyte solution of 60% perchloric acid (40 ml) and methanol (160 ml) at 10 V for 150 s under constant stirring. Subsequent to electropolishing, the substrates were washed with deionized (DI) water and dried at 100°C for 10 min. In the second step, PVD magnetron sputtering (TF450 Sputtering System, SG Control Engineering, Singapore) was used to deposit a thin film of zirconium onto the titanium substrates. A pure zirconium target (99.995% purity, 101.5 mm disk and 3 mm thickness) was used in this investigation. The system had a vertical configuration with dual switchable services of DC and RF targets placed at a distance of 150 mm above a rotatable substrate holder. The target was pre-sputtered in an argon atmosphere to remove the oxide layer. The chamber was evacuated to below 2×10⁻⁵ Torr before introducing argon gas for the sputtering
process. The working pressure was maintained at $5.2 \times 10^{-3}$ Torr, and the argon gas flow rate was fixed at 20 sccm for a deposition time of 3 hours.

2.2. Zirconium anodization

The highest adhesion strength was obtained for the Zr-coated samples anodized in ammonium fluoride (NH$_4$F, Sigma-Aldrich CO., 0.5 wt%) electrolyte dissolved in a 95:5 glycerol (Sigma-Aldrich CO., 99 wt%) and DI water solvent mixture at room temperature. Anodization was carried out in a two-electrode electrochemical cell with a graphite rod (D = 5 mm) as the counter electrode. The distance between the counter and the working electrodes was fixed at approximately 15 mm. The electrochemical treatment was performed using a direct current (DC) power source (Model E3641A, Agilent Technologies, Palo Alto, USA) at a constant potential of 60 V for different anodization times of 20, 40, and 60 minutes. Thermal annealing was performed in an argon gas furnace at 400$^\circ$C and 800$^\circ$C for 2 hours with heating and cooling rates of 3$^\circ$C min$^{-1}$.

2.3. Design of experiment (DOE)

The most important experimental design aspect lies in the control factor selection [39]. Design of experiment (DOE) is a statistical method used to determine the minimum number of experiments needed to provide comprehensive information on the factors influencing performance parameters. It is also used to design a set of experiments whereby all related factors are systematically varied. The Taguchi method is the best DOE for this purpose because it
involves all possible affected factors; hence, the non-significant variables are easy to determine. To reduce the number of experiments, the coating procedure was intended to utilize an orthogonal array (OA), which serves to systematically vary and test the different levels of each of the control factors. The control factor and experimental condition levels applied are shown in Table 1. It should be noted that the selection of PVD coating parameters intervals was based on some preliminary tests and the knowledge attained by previous works [A-D]. The control parameters were the DC power, temperature and DC bias voltage. In this experiment, the fractional factor design was a standard L₉ (3⁴) orthogonal array, which was selected for its ability to verify the interactions among the parameters presented in Table 2.

In the next step, the S/N ratio, which is a statistical measure for choosing control levels, was analyzed using all the data obtained from the OA. The data were generated from three repetitive measurements to determine the amount of variations and to identify the shift in the mean response. Moreover, the S/N ratio, or the ratio of the mean (signal) to the standard deviation (noise), accounted for the mean and the variations. The S/N equation relies on its optimization of quality characteristics. In the course of this study, the quality characteristic selected was “the larger is superior.” The results were analyzed using a statistical analysis of variance (ANOVA) with a Pareto chart to demonstrate the influence of process parameters on the adhesion strength between the coating and the substrate. The Pareto chart was combined with analysis of variance to determine the reason behind applying the principle of “90 percent of problems are derived from 10 percent of causes.” This method is quick and simple, and it determines which parameters are significant in determining the predicted value be appraised in a confirmation experiment.
2.4. Fretting fatigue

The cylindrical test specimens (ISO 1143) were examined using a ring-type load cell and bridge-type fretting pads in a rotating bending fretting fatigue machine. Figure 1 presents the fretting fatigue specimen (Fig. 1a), fretting pad (Fig. 1b), and fretting ring (Fig. 1c). To apply a normal contact load (fretting load) between the friction pads and the specimen, load adjusting screws on a proving ring were used. The pads’ contact surfaces were polished using four grades of silicon carbide emery paper (from 800 to 2000 grit) and cleaned using ethanol prior to each test. Plain and fretting fatigue tests were carried out in air (approximately 40-70% relative humidity) at room temperature under two-point loading conditions at a constant average contact pressure of 100 MPa and using a rotating bending fatigue test machine (R=-1) under working stress amplitudes of 150-500 MPa and a rotational speed of 3000 rpm. The nominal maximum cyclic stress was set at a value expected to produce a fatigue life of between 10⁴ and 10⁷ cycles, and the experiments were stopped if the specimen did not fail at 1×10⁷ cycles.

Figure 2 shows the schematic of the strain gauges connections with electrical rotating connector accompany with Wheatstone bridge circuits.

The pressure needed to create fretting is transmitted to the contact region by a calibrated proving ring and a pair of loading pads. Each pad has two flat bases (contacting surfaces) through which load are exerted on the specimen. The pads were made of stainless steel 410 with σ₅₅₅ = 700MPa and σₚ = 420MPa. The pads are revolved accompany with the sample as this may affect the sliding fluctuations between sample and pads.
The normal load is applied by an adjusting screw and is measured utilizing a Wheatstone bridge circuit. Four strain gauges were bonded to the proving ring and wired to make a Wheatstone bridge circuit to measure the elastic strains induced by loading the ring through the load adjusting screw. The load calibration curve versus strain was attained by 10N standard weights for the fretting ring (see Fig. 3 (a)). The normal contact load can be gaged from the curve presented in Fig. 3 (a).

The friction force, generated by sliding movement between the specimen and pads and normal contact load, was calibrated before testing. Four strain gauges, two in direction of friction and two at right angle to this direction, were bonded to the friction pads to measure the elastic strain applied by friction force. This type of strain gauge configuration would abrogate the effect of temperature rise owing to the fatigue loading in contact region. The pads were clamped to the specimen by the same normal loads as was to be utilized in real experiments. The specimen was then pulled by constant load using INSTRON universal tensile testing apparatus. The strain induced by this load was measured by Wheatstone Circuit Bridge appended to the friction pads. This procedure was repeated for various loads and the calibration curve of friction force versus strain was attained. The calibration curve is depicted in Fig. 3 (b). The friction coefficient ($\mu$) can be specified by dividing the maximum measured friction force at a friction pad foot by the contact load at that foot.

2.6. Characterization

The surface coating morphology and cross-sections were observed under a high-resolution FEI Quanta 200F field emission scanning electron microscope (FESEM). Micrographs
for a quantitative analysis were produced for at least two different locations on each sample. This was done to ensure that the measurements were representative of the overall microstructure as well as to gauge the degree of sample variability. The coating thickness was directly measured from the FESEM micrographs. At least six measurements were taken from different areas of the cross-section to ensure that the measurements reflected the actual coating thickness. The coating cross-section was also studied using a relatively non-destructive method. A focused ion beam (FIB) with a high-resolution FESEM (FEI Quanta 200F) was used for ion milling and ZrO2/Zr cross-section characterization. Ion milling was conducted at 30 keV with milling and cleaning cross-section currents of 2 nA and 10 pA, respectively. The adhesion strength was measured using a Micro Materials NanoTest (Wrexham, U.K.) with a diamond indenter, sliding velocity of 5 µm s⁻¹, and a gradual rate of increase of the load of 9.2 mN s⁻¹. The critical load at which coating adhesive failure occurred was detected by optical microscopic examination of the scratch tracks after the test. Three scratches were produced for each sample. A Ti/Zr/ZrO₂ cross-section was prepared using a rather destructive method using a diamond cutting tool machine. An X-ray diffraction (XRD) (for the as prepared and annealed samples) measurement was performed using an Empyrean X-ray diffractometer with Cu Kα radiation (λ = 1.54178 Å) operating at 45 kV and 30 mA, with a step size of 0.026°, scanning rate of 0.1°s⁻¹, and 2θ range from 10 to 80°. The coatings’ mechanical properties were investigated using a microhardness Vickers test (HMV Micro Hardness Tester Shimadzu). The source of variations gathered from five test sites was within the limit for each sample. Indentation experiments were conducted for three samples per the processing condition.

3. Results and discussion
3.1 Data analysis for high adhesion strength

Implant tissue materials are required to be stable and durable because they will be placed inside living bodies for long periods of time [40, 41]. However, because of the application specificity, the characterization and improvement of the adhesion strength between the coating and the implant are imperative. This is because the adhesion strength is directly related to the coating’s performance and reliability. After characterization, the significant process parameters are to be identified and optimized. An adhesion strength analysis for the coating parameters was performed using an S/N response analysis and a Pareto ANOVA.

In the S/N ratio calculation (eq. 1), the “larger-the-better” characteristic formula was used to identify the combination of optimum factors to enhance the coating adhesion.

\[
S / N = -10 \log \left( \frac{1}{n} \sum_{i=1}^{n} \frac{1}{Y_i} \right),
\]

where S/N is the signal-to-noise ratio and the adhesion strength response; \( n \) is the number of experiments (scratch test) performed for each sample, which is three; and \( Y \) is the measured response value of the \( i^{th} \) experiment. The S/N function shown in Eq. 1 is a performance measurement parameter involved in developing an incentive-to-noise factor. Tables 3 and 4 indicate the calculated (S/N) ratio and the (S/N) response values for adhesion strengths that are plotted in Fig. 4. As shown in Table 4 and in Fig. 4, the significant parameters affecting deposition and the surface quality rate are the DC power and the DC bias voltage, because they determine the best adhesion strength, followed by temperature. The optimum parameter
combination for the scratch adhesion strength was determined by the maximum mean S/N ratio, which was 300 W, 200°C, and a DC bias of 75 V (A_2B_2C_3).

Figure 4 shows that the 300 W DC power resulted in the highest adhesion strength compared to 200 W or 400 W. The DC power source produced a plasma, which caused the Zr target to sputter Zr atoms onto the substrate surface and subsequently bond with other atoms to form a zirconium coating. When the DC power was increased from 200 W to 300 W, the ionized and sputtered particles became more energetic, increasing the sputtering rate, a phenomenon that may cause the distance between the energized atoms to decrease and render the surface more adhesive. However, a further increase in the DC power would result in very-high-energy bombardments, adding many defects to the growing film and lowering the coating adhesion to a certain level. Therefore, the best condition for the surface scratch force was achieved at a medium DC power (A_2).

The DC bias voltage is another significant parameter in the Zr coating process, which helps the coating to obtain higher surface adhesion. It is clear that the coated sample adhesion increased when the substrate bias voltage was increased from 25 to 75 V. Ions with sufficient energy are capable of penetrating the surface layer and inducing local compression while simultaneously enhancing percolation into the substrate’s surface to form a compact network microstructure, which results in a strengthening of the bond between the film and the substrate. However, if the atoms in the film are loosely bonded on the substrate, they will easily become dislodged by incoming atoms. Thus, strong adhesion to the substrate is of paramount importance. The best condition for the surface scratch force was achieved at a maximum DC bias voltage (point C3). In addition, the temperature did not significantly affect the Zr coating adhesion. The
effect of the temperature was related to the DC bias voltage. High adhesion was attained at 200°C with a DC bias voltage of 75 V. This is mostly due to the motion of energized atoms, which produces a homogenous surface. It is also believed that the substrate temperature influences the dilution of atoms in the course of the growth of the Zr. It was observed that the maximum coating adhesion obtained in this study was at a critical load of 2,200 mN.

In addition, a Pareto ANOVA was employed in the optimization process to analyze the effects of control parameters in the Zr coating process. It showed the percentage of factor influence for each parameter in a straightforward manner. The main reason for employing the Pareto ANOVA was to analyze the zirconium coating parameters to obtain higher adhesion to the substrate, which in turn leads to superior surface integrity and longer specimen fretting fatigue life. Table 5 presents the Pareto ANOVA analysis for the adhesion of the coating using the S/N response data. The sum of the squares of the differences between the levels of A and S_a, for instance, is as follows:

$$S_a = (A_1 - A_2)^2 + (A_1 - A_3)^2 + (A_2 - A_3)^2.$$  \hspace{1cm} (2)

Similarly, $S_b$ and $S_c$ were also calculated. The contribution ratio for each parameter was calculated from the percentage of the sum of the squares of the differences for each parameter to the total sum of the squares of the differences. Table 5 presents the adhesion strength analysis, where the important factors are chosen from the left-hand side of the Pareto diagram. The best-level factor combination for the highest adhesion strength is the following: DC power (A) - 33.70%, bias voltage (C) - 9.19% and temperature (B) - 5.32%. It is obvious that the DC power (69.90) is the main parameter and that it significantly affects the coating-to-substrate adhesion.
strength. From the Pareto ANOVA, response table, and response graph, the maximum coating adhesion strength could be achieved under the conditions of high DC bias voltage and middle DC power and temperature. It is emphasized that the optimal levels obtained from these experimental results are only near optimal, having taken the parameters and their levels into consideration.

As mentioned earlier, the scratch test was performed to evaluate the interfacial adhesion between the coating and the substrate. The scratch test is a means of assessing adhesion strength and should be performed under the same conditions due to the effect of intrinsic parameters related to the testing conditions, such as the loading rate, scratching speed, and indenter shape, as well as extrinsic parameters that are relevant to the substrate and coating properties, friction coefficient, surface condition, and testing environment for the critical load value [42]. The profiles of the residual scratch tracks in terms of the load and the depth as a function of distance were recorded. It was confirmed that the scratch tracks were at a critical load value, as indicated by a small change in the depth profile (Fig. 5). The critical loads were determined based on the scratch track of the load-displacement graph, which is defined as (a) $L_{e-p}$, the elastic-to-plastic transition; (b) $L_{c1}$, the cohesive failure, which results in edge or trackside cracking; (c) $L_{c2}$, the mixture of adhesive and cohesive failure, which indicates film delamination on the trackside and tensile cracking from its substrate; and (d) $L_{c3}$, the total coating failure by the entire display of the substrate surface. In the current work, several failure mode types were identified to indicate the critical loads required to break the bond between the Zr coating and its substrate. As illustrated in Figs. 5 and 6 and in the insets, the Zr coating was initially in an elastic-to-plastic transition mode. $L_{c1}$, the first critical load, appeared as some cracking on the trackside followed
by mild tensile cracking along the scratch tracking. By increasing the scratch load, the
delamination trackside gradually became clear and was marked by $L_{c2}$. As the load increased,
several types of failures, such as trackside cracking, delamination, and chipping, occurred, and
the spacing between tensile cracks appeared greater than before until coating delamination
occurred along the scratch path recorded as $L_{c3}$ [43].

3.2. Microstructure characterization

Figure 7 shows FESEM top view images of ZrO$_2$ nanotube arrays synthesized using
anodic oxidation of a Zr-coated sample in a glycerol solution containing 0.5 wt% NH$_4$F and 5
vol% H$_2$O at 60 V for different anodization times. Fig. 7(a and b) indicates the growth in ZrO$_2$ at
30 and 45 minutes. Evidently, the surface is not smooth, and it is partially covered by loose, solid
matter. The top end of the nanotubes adheres in clusters, with few precipitates or intermediate
reaction products and with some parts of the surface becoming covered by patches of thin, coherent layers; however, the majority of nanopores remain uncovered. Figure 7c shows a lower
magnification image of the top surface of nanotubes at an anodization time of 60 minutes. It is
obvious that the tube openings are very smooth and homogeneously distributed all over the
nanotube surface. Figure 7d is a higher magnification image, showing a much clearer view of the
top part of the nanotubes.
Figure 8 and the inset show the cross-sectional morphology and a higher magnification view of the anodized Zr from the FESEM and FIB. The anodic layer has a thickness of approximately 1.6 μm. Figure 8a and the inset show that the oxide layer has a wire-like structure with an average diameter of 50 nm. The inset of Fig. 8a is a higher magnification image, showing a much clearer view of the length and outer diameter of the nanotubes. Figure 8b shows a FESEM micrograph of the cross-section of a ZrO$_2$ sample produced using the FIB milling technique. The FIB facilitates the production of smooth surfaced nanotubes.

3.2 ZrO$_2$ growth mechanism

The exact mechanism of the ZrO$_2$ nanotube formation remains unknown, but the growth and formation of ZrO$_2$ nanotube arrays via anodization is discussed below. ZrO$_2$ nanotube formation in fluoride containing electrolytes is the result of three competing processes: (1) the electric-field-assisted oxidation of the Zr substrate to form ZrO$_2$, (2) the electric-field-assisted dissolution of zirconium ions in electrolyte, and (3) the chemical dissolution of ZrO$_2$ by fluoride ion etching. These processes can be expressed by the following possible reactions:

\[
\begin{align*}
\text{Zr}^{4+} + 2\text{O}^{2-} & \rightarrow \text{ZrO}_2 \quad (1) \\
\text{H}_2\text{O} & \rightarrow 2\text{H}^+ + \text{O}^{2-} \quad (2) \\
\text{Zr}^{4+} + 4\text{OH}^- & \rightarrow \text{Zr(OH)}_4 \quad (3) \\
\text{Zr}^{4+} + 2\text{H}_2\text{O} & \rightarrow \text{ZrO}_2 + 4\text{H}^+ \quad (4) \\
\text{ZrO}_2 + 6\text{F}^- + 4\text{H}^+ & \rightarrow [\text{ZrF}_6]^{2-} + 2\text{H}_2\text{O} \quad (5) \\
\text{Zr}^{4+} + 6\text{F}^- & \rightarrow [\text{ZrF}_6] \quad (6)
\end{align*}
\]
According to the above reactions, H\(^+\) is produced (reaction 4) once anodization takes place, leading to a decreasing pH inside the pores, thus accelerating the chemical dissolution process (reaction 5). Chemical dissolution produces zirconium fluoro-complexes, which are a key factor in achieving regular pore formation by enlarging and deepening the pores. It has been reported that the voltage in the anodization process is vital to the control of the pore dimension and the shape. It is also acknowledged that there are two interfaces inside the tubes: oxide/metal and oxide/anodizing solutions. With higher electric fields, the movement rates of the cations and/or anions (O\(^2-\) and Zr\(^{4+}\)) as interstitial ions or vacancies would increase, which could precipitate greater movement rates of O\(^2-\) and Zr\(^{4+}\) via the oxide layer toward the metal/oxide interface, thus inducing the progression of the barrier layer (reaction 4). At the same time, the metal ions migrate from the metal to the solution/oxide interface and become dissolved in the solution [42-44]. However, the F\(^-\) ions also cause electric field dissolution (reaction 6), completely removing the oxide layer. It is also known that a total of three processes can be assumed to occur via growth: (1) the formation of an initial barrier oxide layer, (2) the formation of uniformly distributed nanopores, and (3) the separation of the pores’ interconnections in the nanotubes [19–21].

3.3 Crystal properties

It is recognized that the crystallinity and microstructure of zirconia play a significant role in different properties and potential applications. The mechanical properties of zirconia nanotube arrays annealed at different temperatures were investigated. From the results above, the crystallization transformation of the nanotube arrays were assessed using samples that were annealed in highly purified argon gas at 400\(^\circ\)C and 800\(^\circ\)C for 2 hours. The XRD patterns of the
titanium, titanium-coated zirconium, and annealed anodized samples are shown in Fig. 9. It is apparent from Fig. 9b that the coated zirconium is crystalline. The main sharp peak observed at 34.85° is attributed to the (0 1 1) tetragonal phase (JCPDS 050-1089) of zirconium. The annealed ZrO2 nanotubes exhibit some obvious sharp peaks, which correspond to a crystallized ZrO2 structure, such as the tetragonal and monoclinic phases. When the coated sample was annealed at 400°C, the majority of the diffraction peaks could be indexed as the tetragonal phase because they were identified as (101), (110), (112), (103) and (211) diffractions of tetragonal ZrO2 according to JCPDS 080-0784. This is in agreement with previous results for fabricated ZrO2 nanotube arrays. At 800°C, the diffraction peaks of tetragonal zirconia disappeared and were recognized as (011), (11-1), (111), (200), (220), (022), (003), (-203) and (-312) diffractions of monoclinic ZrO2 according to pdf 037-1484. Thus, based on previous reports, it is clear that the nanotube structure does not undergo any obvious alteration when the annealing temperature is below 600°C; therefore, heating to higher temperatures to obtain F-free nanotubes resulted in the nanotubes’ crystallization and collapse [44, 46]. Guo et al. [48] reported that the transformation phase of tetragonal ZrO2 to monoclinic ZrO2 occurs at 600°C, but in this study, the morphology of the annealed zirconia nanotubes did not change at high-temperature calcinations. This is most likely because the argon prevented the destruction of the nanotube morphology. According to Guo et al. [46], at an annealing temperature of 800°C, the nanotube structure showed less collapse and cracking, with some bubble-like particles observed on the walls. These may be attributable to the phase transformation and volume expansion of the nanotubes during heat treatment.
As observed in Fig. 9(c and d) of the as-calcined XRD pattern, a peak attributed to the titanium substrate and the zirconium coating can be detected. The high peak at 34.89° is due to zirconium, and the weak peaks at 39.87° and 40.95° correspond to the titanium phase. Guo et al. stated that a mixture of crystallized tetragonal phase (t-ZrO2) and a monoclinic phase ZrO2 (m-ZrO2) could be observed at an annealing temperature of 400°C. Although the pattern in the present study differs from Guo’s results owing to the varying sample preparation conditions, it is clear that the conversion of amorphous ZrO2 nanotubes and crystallized ZrO2 after annealing had taken place.

3.4 Microhardness of ZrO2 coating

In general, the ZrO2 nanotube phase transformation leads to a significant change in the mechanical and biological properties. It is notable that tetragonal zirconia is more stable at room temperature compared to the cubic and monoclinic forms of zirconia. The hardness of the ZrO2 nanotubular arrays was evaluated using a microhardness tester (HMV Micro Hardness Tester Shimadzu) to obtain information about the local hardness (HV), which serves in the investigation of fretting fatigue life in the next section. The microhardness values of the ZrO2 nanotubular arrays coated using Ti-6Al-4V at different annealing temperatures (400°C and 800°C) were 363 HV and 296 HV, respectively. The results indicate that the surface hardness decreases with increasing annealing temperature from 400°C to 800°C. In this regard, Catledge et al. [50, 51] and M. Cattani-Lorente et al. [52] also found a strong correlation between the tetragonal-monoclinic phase transformation and diminution of surface hardness in explanted femoral heads.
The enhanced mechanical properties of nanotubular arrays are caused by two main deformation behaviors. One is the densification of tubular arrays as a result of the nanotubes collapsing, whereby the buckling of the nanotubes might play an important role. The second reason is related to the wear of the dense surface that occurs under the indenter tip. Essentially, the areas under the indenter tip are densified, and the other sides of the indenter are subjected to a shear stress that induces both densification and wear. Therefore, as the indenter penetrates the coating surface, the modulus increases as a result of the increasing contribution of the substrate to the overall layered material strength.

3.5 Fretting fatigue analysis

To investigate the fretting fatigue life of the Zr/ZrO₂-coated specimens, some experiments were carried out, the results of which are shown in Figs. 10-12. The experiments were conducted for a stress ratio of R=-1, frequency of 50 Hz, constant contact force of 100 MPa, and working stress amplitudes of 150-500 MPa. Figure 10 (a) presents a comparison of the number of cycles to failure versus bending stress for plain fatigue and for fretting fatigue of uncoated specimens. It is clear from Fig. 10 (a) that the fatigue and fretting fatigue lives of uncoated specimens diminish with increasing bending stress. Fretting had a deleterious effect on the fatigue life of the coated and uncoated specimens. The reduced percentage of the fretting fatigue life of uncoated vs. stress in comparison to plain fatigue is illustrated in Fig. 10 (b). As the figure suggests, the reduction in fretting fatigue life is due to the increasing applied bending stress. For example, at a stress of around 150 MPa, the reduction is nearly 53% while at 500MPa
it is around 18%. Figure 11 (a) presents a comparison of the number of cycles to failure versus bending stress for fretting fatigue of uncoated and Zr/ZrO$_2$-coated specimens (at annealing temperature of 400°C (tetragonal)). It is evident from Fig. 11 (a) that the fretting fatigue life of Zr/ZrO$_2$-coated specimens with a higher surface hardness (Tetragonal phase) significantly improves at low and high cyclic fatigue regimes, which is attributed to the higher [49] surface coating hardness and to the smaller friction between the fretting pads and the substrates in the presence of the nanotube array. Reduction in fretting fatigue life percentage of uncoated vs. stress compared to Zr/ZrO$_2$-coated specimens (400°C (tetragonal)) is depicted in Fig. 11 (b), which shows that the improvement in fretting fatigue life is higher at lower bending stress. As an example, the improvement percentage at stresses of around 150 and 300 MPa are 40% and 12% respectively.

The effect of the annealing monoclinic phase (800°C) on the fretting fatigue life of the Zr/ZrO$_2$-coated specimens was also investigated. As demonstrated in Fig. 12 (a), the fretting fatigue life of the coated specimens was enhanced compared to the uncoated specimens under low cycle fatigue (at bending stresses of 350-500 MPa) while at high cycle fatigue the results are reversed. By studying Fig. 12 (b) it can be understood that the fretting fatigue lives of Zr/ZrO$_2$-coated specimens (800°C) only improved 8% at high bending stress, while at low bending stress, the fretting fatigue life reduction of 12% can be seen (compared to the fretting fatigue lives of uncoated specimens). The decreased fretting fatigue life in the high cyclic fatigue regime can also be attributed to the removal of the hard coating (ZrO$_2$ nanotube ceramics debris) from the coated specimen’s surface. This is caused by the fretting pads and by the fluctuating load trapped between the friction pads and the specimens, who may remove the thin hard coating, form the
substrate and this crashed ceramic film can behave as abrasive particles on the micro- and nano scales. These crashed, hard particles change the friction conditions to others similar to those produced in uncoated specimens. A stress concentration is subsequently generated (under the friction pads on the specimen’s surface). The stress concentration on the bare surface may initiate cracks, and because there is enough time for cracks to propagate inside the specimen at high cyclic fatigue, fracture and failure occur.

A comparative study of the S/N curves of the coated specimens at various heat treatment temperatures (monoclinic and tetragonal phases) indicates that an annealing temperature of 400°C causes the generation of a tetragonal phase, which has a significant effect on the fretting fatigue life of Zr/ZrO₂-coated Ti-6Al-4V at high and low cyclic fatigue compared to coated specimens with a lower hardness (monoclinic phase). This phenomenon can be potentially attributed to the high hardness and density of tetragonal ceramic ZrO₂ nanotubes [49, 50]. Cracks initiated in contact areas (fretting pads and ZrO₂ nanotube coating) due to high stress concentrations and continuous cyclic loads will result in crack propagation toward the zirconium coating. Because the Zr coating-to-substrate adhesion is strong and because the Zr also penetrates the substrate (which is the nature of the PVD magnetron sputtering technique), the cracks are transferred and subsequently propagate toward the substrate [52-55].

The Coulomb friction law, \( F = \mu P \) was used to calculate the coefficient of friction, \( \mu \). \( P \) and \( F \) are the contact normal and tangential loads, respectively. The fretting load was measured using the proving ring. The strain from the Wheatstone bridge mounted on the proving ring was monitored by a strain unit. \( F \) was then measured from the proving ring calibration curve [56]. The contact load, \( P = 1000N \), was kept constant throughout the experiments.
Coefficient of friction evaluation versus number of cycles to failure for an uncoated, a Zr/ZrO$_2$-coated (at annealing temperature of 400°C) and a Zr/ZrO$_2$-coated specimens (at annealing temperature of 800°C) specimen are depicted in Figs. 13 a-c, respectively. As the figures suggest, the coefficient of friction varies during the tests. Furthermore, all coefficient of friction curves present almost the same pattern. After the first short period, they rise to a maximum value and then begin to decline up to the point of fracture.

At first cracks grow slanting to the normal force direction. As soon as a fatigue crack begins in the contact area, at some angle to the contact surface, under the contact loads effect, the conditions for its continued development are dictated by the local mode I and mode II stress intensity factors amplitudes, Δ$k_1$ and Δ$k_2$, respectively. The angle approximation at which a fatigue crack begins at the fretted surface and the direction along which continued crack propagation takes place needs a fracture criterion [57].

As a supplementary analysis, FESEM images from a top view of Zr/ZrO$_2$-coated samples with different surface hardness values are shown in Fig. 14. Figure 14a displays the cracks, scars, and detached part of the specimen coated at an annealing temperature of 400°C before fracturing at a bending stress of 250 MPa after 3.1×10$^6$ cycles. Two distinct layers (ZrO$_2$ nanotubes and the Zr coating) and the substrate surface can be easily recognized. Deep scars produced by the fretting pads at high cyclic fatigue may cause the sample’s surface to become vulnerable. Figure 14b presents the detached and crashed coating form of the specimen surface (at an annealing temperature of 800°C) under the fretting pads at a bending stress of 200 MPa after 4.2x10$^6$
cycles. The cracks and detaching may be attributed to the low modulus of elasticity and microcracks of the Zr/ZrO₂ coating (monoclinic phase) under fretting pads and cyclic bending loading made by the rotating bending fatigue test machine.

Figure 15 illustrates the crack propagation and fracture of the uncoated specimens at higher magnification at a bending stress of 350 MPa after 3.4×10⁵ cycles. The crack begins in the contact area (substrate and contact pressure of the fretting ring) and propagates toward the substrate. Furthermore, the fractures of the Zr/ZrO₂-coated specimens at an annealing temperature of 800°C (monoclinic phase) are presented in Fig. 16. Figure 16a shows the Zr/ZrO₂-coated specimen fracturing at a bending stress of 350 MPa after 4.5×10⁵ cycles. A number of cracks and pits inside the substrate and the Zr/ZrO₂ thin-film coating are visible under FESEM, which resulted from the fretting pads and the fretting fatigue. Figure 16b presents the Zr/ZrO₂-coated specimen fracture at a bending stress of 250 MPa after 1.3×10⁶ cycles. Clearly, the coating delamination from the substrate is a consequence of the contact pressure of the fretting fatigue pads. At a lower bending stress (150 MPa) and at a high number of cycles (approximately 6.1x10⁶), the coating completely detached under the edge of the fretting pads (Fig. 16c). This implies that the brittleness, tensile residual stress concentration, and microcracks of the hard Zr/ZrO₂ coating (monoclinic phase) were responsible for the coating’s removal [55, 58]. In addition, the ZrO₂ nanotube array produced by the anodizing process is part of the pure zirconium coating; therefore, the adhesion is greater compared to that between the zirconia and the substrate. Hence, nanotubes heat treated at an annealing temperature of 800°C (which are now ceramics) cracked and detached under the fretting pad pressure. Due to their high adhesion,
they delaminated from the substrate’s surface, and thus, with further cyclic loading, the coating was gradually removed [55].

Figures 17(a and b) depict Zr/ZrO₂-coated specimen fractures at an annealing temperature of 400°C (tetragonal phase) and a bending stress of 300 MPa after 1.7×10⁶ cycles along with a bending stress of 150 MPa after 9.7×10⁶ cycles, respectively. Cracks and pits are visible in the fracture fretting fatigue specimens. A study of these images suggests that some Zr/ZrO₂ coating still remained under the fretting pads at high cyclic loads (9.7×10⁶ cycles). This is attributed to the compressive properties of the ZrO₂ nanotube coating that was heat treated at an annealing temperature of 400°C (tetragonal phase) under friction pads, thus making the coating more tolerant at even higher cyclic loads [19, 50, 55, 59].

Conclusion

In this study, a pure zirconium coating was deposited on a Ti-6Al-4V substrate as a first layer by a DC magnetron sputtering PVD technique. The Taguchi response, a Pareto ANOVA analysis and a confirmation experiment determined the most significant process parameters (DC power, temperature and bias voltage) in obtaining higher surface adhesion, as concluded from the scratch force test. The best surface adhesion obtained was at a DC power of 300 W, temperature of 200°C and bias voltage of 75 V. The scratch results indicate that the strongest adhesion was at a scratch length of 1223.31 μm, failure point of 1114.51 μm and load of 2200 mN. A series of ZrO₂ nanotubes was fabricated by varying the anodization time in a mixture of glycerol, water and fluoride containing an electrolyte. According to the FESEM results, a 60 min anodization time was sufficient to grow ZrO₂ nanotubes with a clean, smooth surface at 60 V.
Different annealing temperatures, namely, 400°C and 800°C, produced different ZrO₂ phases, which were tetragonal and monoclinic, respectively. Mechanical properties, including the microhardness and fretting fatigue life, of the ZrO₂ nanotubular arrays coated onto Ti-6Al-4V were investigated using a microhardness tester and a rotating bending fretting fatigue machine, respectively, for the different phases. The fretting fatigue life measurement of the uncoated and coated samples indicated that the tetragonal phase of the coated samples enhanced the fretting fatigue life at high and low cyclic fatigue compared to the uncoated and ZrO₂-coated (monoclinic phase) samples.

Acknowledgement

The authors wish to thank Dr. Pardis Moslemzadeh Tehrani for valuable discussions. This work has been supported by the University of Malaya, grants No: UM TNC2/RC/261/1/1/RP021C-13AET, HIR F0004-21001 and IPPP Grant: PG 129-2012B.

References


Figure and table captions

**Fig. 1** Fretting fatigue specimen (a), a drawing of the fretting pad (b), the real image of the fretting fatigue specimen (c), and the fretting ring (d).

**Fig. 2** The schematic of the strain gauges connections with electrical rotating connector accompany with Wheatstone bridge circuits.

**Fig. 3** Calibration curves for (a) fretting ring and (b) friction pads.

**Fig. 4** The $S/N$ response graph for the adhesion strength.

**Fig. 5** Scratch force (adhesion) test results for a coated sample and force and depth versus depth graphs, indicating the critical load: 300 W DC power, 200 °C and 75 V bias voltage.

**Fig. 6** Failure modes observed during scratch testing of an as-deposited zirconium coating at different stages.

**Fig. 7** FESEM images of ZrO$_2$ nanotube arrays for different anodization times: 30 min (a), 45 min (b), 60 min (c) and high magnification image of nanotubes at an anodization time of 60 min (d).

**Fig. 8** FESEM image of the cross-section with inset at high magnification (a), FIB milling images of zirconium nanotube arrays (b).

**Fig. 9** XRD patterns of the Ti alloy (a), Ti-coated Zr (b), ZrO$_2$ annealed at 400°C (c), and ZrO$_2$ annealed at 800°C (d).

**Fig. 10** (a) S/N curve of plain fatigue and fretting fatigue for the uncoated specimens and (b) the reduction percentage of fretting fatigue life vs. stress.
**Fig. 11** (a) S/N curve of fretting fatigue for the uncoated specimens and Zr/ZrO$_2$-coated samples annealed at 400°C and (b) the reduction percentage of fretting fatigue life vs. stress.

**Fig. 12** (a) S/N curve fretting fatigue for the uncoated specimens and Zr/ZrO$_2$-coated samples annealed at 800°C and (b) the reduction percentage of fretting fatigue life vs. stress.

**Fig. 13** The friction of coefficient curves versus fretting fatigue life for (a) uncoated, (b) Zr/ZrO$_2$ coated specimen (400°C) and (c) Zr/ZrO$_2$ coated specimen (800°C).

**Fig. 14** Top view FESEM images of the Zr/ZrO$_2$-coated samples under fretting pads at an annealing temperature of 400°C and bending load of 250 MPa after 3.1x10$^6$ cycles (a) and at an annealing temperature of 800°C and bending load 200 MPa after 4.2x10$^6$ cycles (b).

**Fig. 15** Crack propagation and fracture of the uncoated specimen under fretting fatigue at a bending stress 350 MPa after 3.4x10$^5$ cycles.

**Fig. 16** The fractures of Zr/ZrO$_2$-coated specimens at an annealing temperature of 800°C (monoclinic phase).

**Fig. 17** Zr/ZrO$_2$-coated specimen fracture at an annealing temperature of 400°C (tetragonal phase) and bending stress of 300 MPa after 1.7x10$^6$ cycles.

**Table 1** The control factors and experimental condition levels.

**Table 2** L$_9$ (3$^3$) Orthogonal array.

**Table 3** Measured adhesion strength and calculated (S/N) ratio.

**Table 4** S/N response values for adhesion strength (scratch force).

**Table 5** Pareto ANOVA analysis for adhesion of coating to substrate.
Fig. 1
Fig. 2

Strain gauges for friction pads

Strain gauges for fretting ring

Electrica

Data Acquisition
Fig. 3
Fig. 4
Fig. 5
Fig. 6
Fig. 7
Fig. 8
Fig. 9
Fig. 10
Fig. 11
Fig. 12

- Reducing Percentage in Fatigue Life%
- Maximum Stress (MPa)

- Uncoated Specimens Fretting Fatigue
- Zr/ZrO2-Coated Specimens (800°C) Fretting Fatigue
Uncoated Specimen at 350°C

Friction Coefficient vs. Number of Cycles

- Friction Coefficient: 0.44 to 0.64
- Number of Cycles: 0 to 600,000

Zr/ZrO2 Coated Specimens (400°C)

Friction Coefficient vs. Number of Cycles

- Friction Coefficient: 0.341 to 0.349
- Number of Cycles: 0 to 100,000

150 MPa
Fig. 13
Fig. 14
Fig. 15
Fig. 16

48
Fig. 17
Table 1 E. Zalnezhad

<table>
<thead>
<tr>
<th>Parameters designation</th>
<th>Process parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Level 1</td>
</tr>
<tr>
<td>A DC Power (W)</td>
<td>200</td>
</tr>
<tr>
<td>B Temperature(°C)</td>
<td>150</td>
</tr>
<tr>
<td>C DC bias voltage (V)</td>
<td>25</td>
</tr>
</tbody>
</table>

Table 2 E. Zalnezhad

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>1</td>
<td>200</td>
</tr>
<tr>
<td>2</td>
<td>200</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
</tr>
<tr>
<td>4</td>
<td>300</td>
</tr>
<tr>
<td>5</td>
<td>300</td>
</tr>
<tr>
<td>6</td>
<td>300</td>
</tr>
<tr>
<td>7</td>
<td>400</td>
</tr>
<tr>
<td>8</td>
<td>400</td>
</tr>
<tr>
<td>9</td>
<td>400</td>
</tr>
</tbody>
</table>
### Table 3 E. Zalnezhad

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Scratch force (mN)</th>
<th>Calculated S/N ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1st</td>
<td>2nd</td>
</tr>
<tr>
<td>1</td>
<td>861</td>
<td>892</td>
</tr>
<tr>
<td>2</td>
<td>1267</td>
<td>1289</td>
</tr>
<tr>
<td>3</td>
<td>1385</td>
<td>1386</td>
</tr>
<tr>
<td>4</td>
<td>1648</td>
<td>1630</td>
</tr>
<tr>
<td>5</td>
<td>2110</td>
<td>2135</td>
</tr>
<tr>
<td>6</td>
<td>1538</td>
<td>1578</td>
</tr>
<tr>
<td>7</td>
<td>1022</td>
<td>1029</td>
</tr>
<tr>
<td>8</td>
<td>965</td>
<td>973</td>
</tr>
<tr>
<td>9</td>
<td>1158</td>
<td>1149</td>
</tr>
</tbody>
</table>

### Table 4 E. Zalnezhad

<table>
<thead>
<tr>
<th>Parameters designation</th>
<th>S/N response</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Level 1</td>
</tr>
<tr>
<td>A DC Power (W)</td>
<td>61,31</td>
</tr>
<tr>
<td>B Temperature(°C)</td>
<td>61,13</td>
</tr>
<tr>
<td>C DC bias voltage (V)</td>
<td>60,83</td>
</tr>
</tbody>
</table>
Table 5. E. Zalnezhad

<table>
<thead>
<tr>
<th>Factor and interaction</th>
<th>DC power (A)</th>
<th>Temperature (B)</th>
<th>Bias voltage (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summation at the level of input parameter</td>
<td>1</td>
<td>61.31</td>
<td>61.13</td>
</tr>
<tr>
<td>2</td>
<td>64.91</td>
<td>62.83</td>
<td>62.61</td>
</tr>
<tr>
<td>3</td>
<td>60.44</td>
<td>62.68</td>
<td>63.21</td>
</tr>
</tbody>
</table>

| Total of summation at factor level | 186.65 | 186.65 | 186.65 |
| Summation of squares of differences (S) | $S_a=33.70$ | $S_b=5.32$ | $S_c=9.19$ |
| Summation of squares of differences $S_t=S_a+S_b+S_c$ | 48.21 |
| Contribution ratio (%) | 69.90 | 14.03 | 19.06 |

**Pareto Diagram**

| Cumulative contribution ratio | 69.90 | 88.97 | 100 |
| Optimum combination | $A_2$ | $C_3$ | $B_2$ |
| Remarks on optimum condition | The significant factors are chosen from the left-hand side in the above Pareto diagram which cumulatively contributes up to 90%. |
| Optimum conditions for all factors | $A_2B_2C_3$ |
Highlight

- Investigate the effect of ZrO2 nanotubes on fretting fatigue life Ti-6Al-4V
- Explore the effect of different phases on microhardness of ZrO2 coated Ti-6Al-4V
- Determine the adhesion of pure Zr coating on Ti-6Al-4V
- Optimize the parameter combination for coating adhesion