Effect of microstructural evolution on wettability and tribological behavior of TiO₂ nanotubular arrays coated on Ti–6Al–4V

M. Sarrafa,b,1, E. Zalnezhadb,c,*, A.R. Bushrooa,b,*, A.M.S. Hamoudad, A.R. Rafieera,b,1, B. Nasiri-Tabrizia,e

aDepartment of Mechanical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia
bCenter of Advanced Manufacturing and Material Processing, Department of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia
cDepartment of Mechanical Engineering, Hanyang University, 222 Wangsimni-ro, Seongdong-gu, Seoul, 133-791, Korea
dMechanical and Industrial Engineering Department, College of Engineering, Qatar University, P.O. Box 2713, Doha, Qatar
eDepartment of Biomedical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

Received 12 January 2015; received in revised form 20 February 2015; accepted 23 February 2015
Available online 5 March 2015

Abstract

Self-organized TiO₂ nanotubular arrays were fabricated by electrochemical anodization of Ti–6Al–4V plates in an NH₄F/H₃PO₄ electrolyte. The effect of microstructural evolutions on the wettability and tribological behavior of the TiO₂ nanotubes was investigated. Based on the XRD profiles of the fabricated material, the characteristic TiO₂ peaks were not recognized after anodization; however, highly crystalline TiO₂ (anatase and rutile) was formed due to crystallization during annealing at 500 °C for 1.5 h. The nanotube arrays were converted entirely to rutile at 700 °C. From a microstructure point of view, a highly ordered nanotube structure was achieved when the specimen was annealed at 500 °C, with a length of 0.72 μm and a pore diameter of 72 nm. Further increasing the annealing temperature to 700 °C resulted in the complete collapse of the tubular structure. The results indicate that the improved wettability of the anodized specimens was due to the combination of the effects of both the surface oxide layer and the increased surface roughness achieved after anodization. Moreover, the wear resistance and wettability of the sample annealed 500 °C were improved due to the high hardness (435 HV) and low coefficient of friction (0.133–168) of the highly crystalline structure of the TiO₂ nanotubes.

© 2015 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: Ti–6Al–4V; TiO₂ nanotube; Tribological behavior; Wettability; Anodization

1. Introduction

Due to its excellent mechanical, physical and biological performance, TiO₂ is widely used in biomedical devices. However, the mechanical behavior of biomedical-grade commercial-purity titanium is generally considered to lie below that desired for total joint replacement [1]. This low quality is caused by introduction of annealed Ti–6Al–4V alloy, which today remains the largest single titanium alloy used for biomedical applications [2]. Increased use of Ti–6Al–4V as a biomaterial stems from its lower modulus, superior biocompatibility and better corrosion resistance compared to those of more conventional stainless and cobalt-based alloys [3]. However, titanium and its alloys cannot meet all clinical requirements, and thus, to enhance the functionality of the material, namely its biological, chemical and mechanical properties, surface modification is often performed [4].

From a corrosion point of view, materials implanted in vivo initially come in contact with extracellular body fluids such as blood
and interstitial fluids. It has been observed that the chloride ion concentrations in blood plasma and interstitial fluid, 113 mEq/l and 117 mEq/l [5], respectively, are sufficiently high to corrode metallic materials. In addition, body fluids contain amino acids and proteins that tend to accelerate corrosion [6,7]. However, the pH level decreases to about 5.2 in hard tissue after implantation and recovers to 7.4 within 2 weeks [8]; consequently, corrosion due to an abrupt change in body fluid pH appears to be negligible. Toxicity and allergy may occur in vivo if implant materials are corroded by body fluid, leading to the release of metal ions into the body fluid for a prolonged period and the combination of ions with biomolecules such as proteins and enzymes [3]. On the other hand, wear in mechanical parts is important which is needed to assess the reliability of a material in medical implant applications because an implant has to withstand not only onetime peak stresses but also the several million load cycles that it typically experiences throughout its lifetime [9]. Ti–6Al–4V alloy is reported to have notoriously poor wear resistance due to its low resistance to plastic shearing and the low level of protection imparted by surface oxides [10]. Recently, research on the tribological properties and mechanisms of Ti–6Al–4V alloy under different sliding speeds and loads was conducted [11,12]. According to these studies, a transition from oxidative wear to delamination wear occurred with an increase in sliding speed and that low wear resistance was due, in part, to the weak protection afforded by surface oxides. Qiu et al. [13] examined the effect of friction heat on the friction and wear performance of Ti–6Al–4V alloy under high sliding speeds. The authors observed that TiO, TiO2, and V2O4 oxides were formed on the worn surfaces as the friction temperature increased. This behavior originated from the rapid decrease in the wear resistance of Ti–6Al–4V alloy with an increase in sliding speed, which led to the formation of a loose oxide layer. It is clear that loose oxides do not provide a protective effect because of the unfavorable Pilling-Bedworth ratio and the internal stresses owing to the mismatch in thermal expansion between the oxide and the subsurface alloy [14]. In other comparative studies, Ohidul Alam and Haseeb [15] investigated the tribological properties of Ti–6Al–4V and Ti–24Al–11Nb alloys subjected to dry sliding wear against hardened steel and reported that severe delamination was responsible for the low wear resistance of Ti–6Al–4V. The authors suggested that the lower wear rate of Ti–24Al–11Nb was linked to the ability of this alloy to form a Ti-Nb oxide-based protective layer. Thus improving the wear resistance and corrosion behavior of metallic implants by various surface treatments is a challenging task but one that can help expand the use of titanium and titanium alloys in biomedical applications [3]. According to the literature [16–20], the fabrication of self-organized oxide nanotube layers as a suitable surface treatment can improve the fundamental specifications of titanium alloys. In terms of corrosion resistance, TiO2 nanotube layers on titanium exhibit better corrosion resistance in simulated biofluids than does smooth-Ti [21]. In addition, recent work has shown that, on TiO2 nanotube layers, hydroxyapatite growth can be further enhanced [22]. A promising biomedical application of these nanotubular arrays has been reported recently by Park et al. [23], who studied cell responses to a highly defined spacing variation involving vertically aligned TiO2 nanotubes with six different diameters ranging between 15 and 100 nm. The findings support those reported in recent studies on cells reacting sensitively to nanoscale roughness on silicon or silica substrates [24,25], indicating that cell responses to biomimetic surfaces depend not only on the chemistry of a biomaterial but also on the geometry of the nanoscale microenvironment. Cell interactions with extra-cellular surfaces are mediated by the clustering of integrins into focal adhesion complexes and the activation of intracellular signaling cascades in the nucleus and the cytoskeleton.

In this work, the surface modification of Ti–6Al–4V alloy by anodizing in NH4F/H3PO4 to enhance implant integration was studied in conjunction with the effect of subsequent thermal treatment on the microstructural features, wettability and tribological behavior of self-organized TiO2 nanotubular arrays. To clarify the reactions occurring during anodization, the formation and growth mechanism of TiO2 nanostructures was discussed in detail. Efforts were made to clarify the mechanism responsible for differences in functional properties with respect to the microstructural features of the TiO2 nanotube arrays.

2. Materials and methods

2.1. Substrate preparation

Ti–6Al–4V plates (15 mm × 15 mm × 2 mm, E Steel SDN. BHD, Malaysia) were used as substrates. Specimens were polished using SiC emery paper (800–2400 grit), followed by wet polishing in a diamond slurry. Afterwards, the polished samples were sonicated in acetone for 10 min at 40 °C. Finally, all specimens were washed three times with distilled water and dried at 100 °C for 1 h.

2.2. Preparation of self-organized TiO2 nanotubular arrays

Electrochemical anodization was conducted in a two-electrode electrochemical cell in which, a graphite rod (D=7 mm) was joined to the cathode and the sample was fastened to the anode (Fig. 1). The distance between the electrodes was fixed at 20 mm in all experiments. Anodizing was carried out using a direct current (DC) power source (Model E3641A, Agilent Technologies, Palo Alto, USA) at various potentials for 4 h with a magnetic stirring speed of 150 rpm. The anodization electrolyte was a mixture of 0.2 M H3PO4 and different concentrations of NH4F (0.3–0.5 M). Details regarding the anodization and annealing conditions are summarized in Table 1. After anodization, samples were washed with de-ionized water to move residual materials from their surface. Finally, to form the crystalline phases, the anodized specimens were annealed at 500, 600 or 700 °C for 1.5 h under a normal atmosphere at a heating and cooling rate of 10 °C/min.

2.3. Characterization of TiO2 nanotubular arrays

2.3.1. Phase analysis and microstructural characterization

The phase composition and purity of the samples were examined by powder X-ray diffraction (XRD) analysis using a PANalytical Empyrean X-ray diffractometer (Cu–Kα radiation) over a 2θ range from 20° to 80°. To clarify the phase structure, the XRD patterns were compared to standards compiled by the Joint Committee on
Powder Diffraction and Standards (JCPDS), namely JCPDS005-0682 for Ti, JCPDS01-071-1167 for TiO₂ (Anatase) and JCPDS01-072-1148 for TiO₂ (rutile). The size and morphology of the anodized samples were characterized using a field emission scanning electron microscope (FESEM; SU8000, Hitachi, Japan) operated at an acceleration voltage of 1–2 kV. Furthermore, an atomic force microscope (AFM, Nanoscope IIIA scanning probe) in tapping mode was used to identify the topographical texture of the surfaces and wear scars. To examine the wear scars and roughness profiles, a three-dimensional scanning system (Alicona Infinite Focus) was employed.

2.3.2. Evaluation of microhardness

The Vickers microhardness of the anodized samples was estimated using microhardness measurement equipment (Shimadzu Newage Micro Hardness Tester HMV-2T). The indentation-duration and applied load were 15 s and 98.07 mN. In addition, five indentations per specimen were carried out to determine the average microhardness values.

2.3.3. Surface roughness and hydrophilicity

The surface hydrophilicity (wettability) of the specimens was examined by measuring contact angles using a sessile drop of deionized water deposited on each specimen surface. A video-based optical contact angle measuring system (OCA 15EC) was utilized to inspect the optical wettability. In this experiment, the liquid volume was kept constant (10 μl) for all contact angle assessments of the specimens. The wettability of the specimens was assessed using a drop velocity of 2 μl/sec at a temperature of 26 ± 1 °C. To analyze the specimens’ surface roughness, AFM images were recorded using a Nanoscope IIIA scanning probe in tapping mode.

2.3.4. Tribological behavior

To examine the wear resistance of the anodized samples, a pin-on-disc tester (DUCOM pin-on-plate reciprocating friction monitor TR-282) was utilized. In this mode, the dry-sliding test began as the pin slid against a stationary counterpart plate. Cylindrical pins with a length of 8 mm and diameter of 6 mm were used in all experiments. Before the analysis, both the pins and samples were cleaned thoroughly in distilled water and degreased with acetone. During testing, the reciprocating motion was generated by an electro-motor. Three normal loads, i.e., 5, 10, and 15 N, were applied to the disc. During the wear test, the tangential frictional force was continuously recorded using a load cell sensor attached to the pin-holder arm and reported as a root mean square value. The kinetic coefficient of friction (μk) was displayed in the instrumentation output which was calculated by dividing the recorded frictional force by the normal load. A weight balance (Denver Instrument) with a high precision of 0.1 mg was used to determine the wear rate.

3. Result and discussion

3.1. TiO₂ nanotube self-ordering

Generally, the formation of TiO₂ nanotubular arrays in F⁻-containing electrolytes is a result of the following competing electric field-assisted processes:

(i) hydrolysis of Ti metal to form TiO₂,
(ii) dissociation of NaF and
(iii) chemical dissolution of TiO₂ at the oxide/electrolyte interface [26].

Moreover, the following TiO₂ tube growth stages are proposed based on the results of previous reports [26]:

(i) Initial barrier layer formation – there is an exponential decrease in the anodic current density until it reaches a steady state. A current drop occurs due to the formation of a compact oxide film, which enhances the resistance and reduces the current density [27].
(ii) Formation of uniformly distributed pores – the chemical dissolution of the barrier oxide layer occurs, and the current density increases. During this step, nanopores are generated by random local dissolution of the TiO₂ surface, as indicated in previous studies [28]. Raja et al. [29] proposed that the ordering of pores occurs due to local surface perturbations, in which the strain energy increases, causing the migration of F⁻ ions to regions with higher strain energy and the migration of hydrogen ions to maintain electrical neutrality, and leading to the dissolution of Ti⁺⁺ ions.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Anodization potential (V)</th>
<th>Electrolyte composition</th>
<th>Thermal treatment (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>10</td>
<td>0.2 M H₃PO₄/0.3 M NH₄F</td>
<td>500, 600, 700</td>
</tr>
<tr>
<td>S2</td>
<td>10</td>
<td>0.2 M H₃PO₄/0.4 M NH₄F</td>
<td></td>
</tr>
<tr>
<td>S3</td>
<td>10</td>
<td>0.2 M H₃PO₄/0.5 M NH₄F</td>
<td></td>
</tr>
<tr>
<td>S4</td>
<td>20</td>
<td>0.2 M H₃PO₄/0.3 M NH₄F</td>
<td></td>
</tr>
<tr>
<td>S5</td>
<td>20</td>
<td>0.2 M H₃PO₄/0.4 M NH₄F</td>
<td></td>
</tr>
<tr>
<td>S6</td>
<td>20</td>
<td>0.2 M H₃PO₄/0.5 M NH₄F</td>
<td></td>
</tr>
</tbody>
</table>

*Anodization time (4 h) and stirring speed (150 rpm) were identical in all experiments.
(iii) Separation of interconnected pores into nanotubes – the current density again stabilizes. Nanotube formation is the consequence of the simultaneous growth of voids (regions between pores that are susceptible to field-assisted oxidation/dissolution) and pores as suggested by Mor et al. [30]. In contrast, Raja et al. [29] claim that the separation of pores into individual nanotubes may be a result of repulsive forces between cation vacancies. After 1 h, nanotubes are grown, as confirmed by Crawford [26].

3.2. Phase compositions

Fig. 2 displays the XRD profiles of the samples anodized for 4 h at 20 V in an electrolyte containing 0.2 M H₃PO₄ and 0.4 M NH₄F before and after annealing at 500 and 700 °C for 1.5 h. As shown in Fig. 2a, no characteristic peaks of TiO₂ were identified after anodizing, whereas Ti (JCPDS005-0682) was detected as the main phase. During annealing at 500 °C for 1.5 h, highly crystalline mixed phases of anatase (JCPDS01-0711167, crystal system: tetragonal; space group: I41/amd; space group number: 141) and rutile (JCPDS01-0721148, crystal system: tetragonal; space group: P42/mnm; space group number: 136) TiO₂ were developed as a consequence of crystallization. With a further increase in the annealing temperature to 700 °C for 1.5 h, the nanotube arrays were entirely converted to rutile, as indicated by the magnified XRD patterns over the range of 27° ≤ 2θ ≤ 28° (Fig. 2b). Hence, several typical peaks of rutile, including those due to the (1 1 0) plane at 2θ=27.44°, the (0 0 1) plane at 2θ=36.09°, the (1 1 1) plane at 2θ=41.25°, the (2 1 1) plane at 2θ=54.32°, and the (2 2 0) plane at 2θ=56.63° were identified after reaching a temperature of 700 °C. Based on the XRD data, it is clear that the phase composition of the anodized samples was notably affected by the subsequent thermal treatment, which played an important role in determining the functional properties of the specimens. In addition, the volume fraction of rutile increased when the annealing temperature rose to 700 °C. This phase transition could improve the mechanical properties and tribological behavior of the specimens.

3.3. Microstructural evaluations

Fig. 3 shows FESEM images of the sample anodized for 4 h at 20 V in an electrolyte containing 0.2 M H₃PO₄ and 0.4 M NH₄F before thermal treatment. As shown in the figure, it is clear that a porous structure formed after the anodization. According to the higher-magnification FESEM image shown in Fig. 3b, the anodized sample exhibited an average inner diameter of 55 nm and a mean tube wall thickness of 12 nm.

Fig. 4 shows typical cross-sectional and bottom-view FESEM images of the TiO₂ nanotube arrays anodized for 4 h at 20 V in an electrolyte containing 0.2 M H₃PO₄ and 0.4 M NH₄F. As demonstrated in the cross-sectional image shown in Fig. 4a, a highly ordered nanotubular structure with an average individual length of 1 μm was formed after the anodization. In addition, this figure shows that the TiO₂ nanotubes possessed a bamboo-shaped structure with good density, which could lead to enhanced chemical activity and stronger interactions. Indeed, this feature is a crucial parameter...
contributing to good mechanical properties [17,19]. On the other hand, it is clear that the bottom of the TiO2 nanotubes showed a series of evenly spaced “bumps” (Fig. 4b) due to the pore tips of individual nanotube. Because the electric field across the electrode is very high during the early stages of anodization, field-assisted dissolution dominates over chemical dissolution. As anodization progresses and the oxide layer thickens, chemical dissolution dominates over field-assisted dissolution. This behavior enhances the size and density of the pores. In the next step, the growth and propagation of the pores occur by internal motion at the oxide/metal interface, which causes the formation of hollow cylindrical oxide particles that develop into nanotubular structure. Besides, as the oxide layer at the bottom of the pore is subjected to chemical dissolution, it becomes thinner with time. If anodization is conducted in a concentrated fluorine solution, the attack rate would be faster and thus the decrease in thickness would be faster. As the thickness declines, electric-field-assisted dissolution would occur again in this region, and consequently, the pores would penetrate into the substrate and the nanotubes would become increasingly longer. However, as a voltage is constantly applied, anodization would occur again at the bottom of the pores, which would lead to the development of nanotubes with closed bottoms. It should be noted that the growth of the nanotubes is thus affected by the amount of fluoride in the bath and the degree of electric field dissolution such that the rate of electric field dissolution at the barrier layer inside the nanotubes would be high at a very high anodization voltage. Accordingly, longer nanotubes would be produced in this manner. This finding is in good agreement with the results reported in a previous study [31].

In the case of the sample anodized after being annealed at 500 °C (see Fig. 5a and b), the average inner diameter and wall thickness were 50 and 20 nm, respectively. As shown in Fig. 5c, further increasing the annealing temperature to 600 °C caused to the significant changes in the microstructural features of the specimen such that the nanotubular arrays collapsed completely and adopted a nanorod morphology. Similar trend was observed in the case of the sample annealed at 700 °C (Fig. 5d). Furthermore, in accord with the FESEM observations, the level of coarsening increased as the annealing temperature was increased from 600 to 700 °C. This behavior demonstrates that coarsening of the TiO2 nanotube arrays may occur after annealing at high temperatures (>500 °C). A similar observation of the collapse of the tubular structure of TiO2 after annealing was previously reported for a Ti-based substrate. Jaroenworaluck et al. [32] reported that no significant changes in the morphology of TiO2 nanotubes were observed up to 500 °C, whereas the nanotubular arrays partially collapsed after annealing at 550 °C. With a further increase in temperature, the tubular structure was completely removed at 600 °C; indeed, at this temperature, nanoparticles were sintered together. Recently, Mohan et al. [33] also observed that TiO2 nanotubes annealed at 450 °C had a tubular morphology, whereas those annealed at 600 °C completely collapsed. To control the phase stability, Arbiol et al. [34] and Tryba et al. [35] found that introducing alloying elements such as Nb and C into TiO2 increases the anatase-to-rutile transition temperature, and also increases the temperature at which the tubular structures collapse. In addition to the anatase–rutile transition, Ghicov et al. [36] reported that mixed oxide nanotubes are more stable against thermal treatment at 650 °C in Ti–45Nb than pure TiO2 is. This finding suggests that controlling the phase and microstructure of self-organized TiO2 nanotube arrays after annealing is a challenging task.

![Image](https://example.com/image.png)

**Fig. 4.** FESEM images of TiO2 nanotube arrays anodized for 4 h at 20 V in an electrolyte containing 0.2 M H3PO4 and 0.4 M NH4F (a) cross-sectional view and (b) bottom view of nanotubes.

**Fig. 6** shows a high-resolution FESEM image of a sample anodized for 4 h at 20 V in an electrolyte containing 0.2 M H3PO4 and 0.4 M NH4F after annealing at 500 °C. As shown, the wall thickness of the nanotubular structure increased after thermal treatment. It is generally well established that the properties of nanotube arrays are dependent on their structural properties, including their length, wall thickness, wall roughness, pore diameter, and tube-to-tube spacing. As shown in the figure, thickening of the TiO2 nanotubes wall occurred at 500 °C due to mass transport involving Ti4+ diffusion at the bottom and along the walls of the TiO2 nanotubes. In fact, the change in the morphological features of the nanotubular arrays with annealing temperature can be ascribed to the excessive diffusion of Ti ions along the nanotube walls, which induced oxidation and thus thickened the oxide walls [37].

### 3.4. Microhardness assessment

**Fig. 7** displays the disparity in the Vickers hardness values of the substrate, the un-annealed TiO2 nanotubular arrays, and the arrays heat treated at 500 and 700 °C. The hardness value of the substrate was 269 HV. During anodization, an amorphous TiO2 phase was formed, which dominated the hardness of the entire specimen. In this case, the hardness value was 373 HV. After thermal annealing at 500 °C, crystallization of TiO2 (transition from amorphous to a highly crystalline structure) occurred and as a result the surface hardness was enhanced and reached a value of 435 HV. Moreover, a
considerable decrease in the amount of chemisorbed water occurred when the anodized samples were annealed at 500 °C, which led to the densification of the nanotube films [38]. For the anodized sample crystallized by further annealing at a temperature of up to 700 °C, the fraction of the rutile structure increased notably; this effect increased the surface hardness value to 489 HV because among three types of TiO₂ oxides (rutile, anatase and brookite), the rutile structure exhibits the highest hardness and lowest friction coefficient [39]. However, based on microstructural observations (see Fig. 5), the nanotubular arrays collapsed completely after thermal annealing at 700 °C which suggests that annealing at 500 °C in a normal atmosphere is the optimum condition for the thermal treatment of TiO₂ nanotube arrays on Ti67.

3.5. Surface wettability

Anodization processes form nano-pore films with microscopic coarse structures [40,41]. These structures have
different surface wettabilities (hydrophilicities) depending on the processing parameters applied. In general, surface wettability is a measure of surface energy and is most commonly quantified by the contact angle $\theta$ [42]. As shown in the inset of Fig. 8a, the shape of a drop of water on a material's surface is governed by forces pulling at the contact line of the drop in the plane of the solid, where the solid (S)/liquid (L), liquid (L)/vapor (V) and solid (S)/vapor (V) interfaces meet. In this context, the contact angle is defined by the equilibrium state reached between these forces acting on the contact line, separating the wetted and non-wetted portions of a homogeneous smooth solid surface such that each interface is described by a certain free energy per unit area ($\gamma_{SL}$, $\gamma_{LV}$, and $\gamma_{SV}$). Hence, the contact angle on a smooth and flat surface can be expressed using Young's model ($\cos(\theta) = (\gamma_{SV} - \gamma_{SL})/\gamma_{LV}$) [43].

It is clear that anodization can play an important role in determining the surface wettability of a material. In this study, the contact angle of the substrate was $\theta = 72.8^\circ$ (see Fig. 8a). After anodization, due to the formation of a porous structure, the hydrophilicity of the surface was improved such that the contact angle decreased to $11.6^\circ$ (see Fig. 8b). During annealing at 500 $^\circ$C, a highly ordered nanotubular array was formed due to the transition from an amorphous to a highly crystalline structure, resulting in an improvement in hydrophilicity. Accordingly, the contact angle decreased notably to $\theta = 7.5^\circ$ (see Fig. 8c). In the case of the sample annealed at 700 $^\circ$C, the nanotubular arrays collapsed completely and adopted a nanorod morphology. This behavior had an adverse effect on the surface wettability, causing the contact angle to increase to $\theta = 13.3^\circ$ (see Fig. 8d). It has been reported that the extents of cell attachment, spreading, and cytoskeletal organization are greater on hydrophilic surfaces than on hydrophobic surfaces [44]. Based on these observations, it can be concluded that the improved wettability of the anodized specimens was due to the combination of the effects induced by both the surface oxide layer and the increased surface roughness after anodization.

3.6. Tribological behavior and surface roughness

Fig. 9 shows the friction coefficient ($\mu_k$) as a function of cumulative sliding time under normal loads of 15, 20 and 25 N. It is clear that a feature common to all of the profiles is an increase in the friction coefficient with the normal load (see the tables in Fig. 9). Moreover, based on the obtained data, the wear loss increased linearly with an increase in the load from 15 to 25 N. According to this figure, the value of $\mu_k$ was clearly enhanced at the beginning and reached a steady-state within a short period. This behavior was due to the initial consecutive wear of the surfaces' micro asperities and increased conformity of worn surfaces. Hence, in the early stages, wear damage was caused by brittle micro-fractures within surface grains and by tribochemical reactions [45]. As shown in Fig. 9, the plotted friction lines of the substrate and anodized sample under a load of 15 N were very similar to each other and reached a steady-state condition within 2 s. Similar trends were also observed under applied loads of 20 and 25 N. These results demonstrate that the substrate and anodized specimen exhibited similar wear behavior over the range of loads examined. In addition, all samples remained stable under a load of 15 N and showed friction coefficient values ranging from 0.093 to 0.280; however, as the normal load was increased to 20 and 25 N, higher coefficients of friction ranging from 106 to 314 were observed. It should be noted that the sudden
increase in the friction coefficient of the anodized sample after annealing at 500 °C indicates that coating failure occurred. On the other hand, it can be observed that the values of the friction coefficient decreased significantly after subsequent annealing. This behavior can be related to the formation and crystallization of TiO₂ as well as the change in phase structure from anatase to rutile. Thus, it can be concluded that the high hardness and low coefficient of friction of the highly crystalline structure of the TiO₂ nanotubes noticeably improved the wear resistance of Ti–6Al–4 V a result that can be considered in practical applications.

In general, the elimination and displacement of material during wear causes changes in surface topography. In this study, AFM in contact mode was used to assess the topographical characterization of plain and worn surfaces as shown in Fig. 10. AFM images were gathered for all samples over an area of 20 μm × 20 μm. All roughness values are reported in terms of Rₐ, which represents the arithmetic mean of height deviations from the mean profile value (50 scan line). As shown in Fig. 10a, micro-pores appeared on the surface of the substrate, which could be attributed to the method used to manufacture the substrate. As shown, the dominant characteristic of the worn surface was the appearance of coarse ridges and grooves (Fig. 10b,c,d and f). Similar behavior was recently reported by Ezazi et al. [45]. According to the AFM images of the worn surfaces, lateral grooves surrounded by high peaks were formed, representing the formation of microgrooves on the surface of the samples due to the severe plastic deformation of the substrate, a ductile alloy. These results demonstrate that wear occurred by homogeneous deformation in isothermal mode, whereby material was eliminated by the extrusion and lip formation. As indicated in Fig. 10c, the anodized sample showed a coarser area with protruding hillocks. In the case of the anodized sample annealed at 500 °C (see Fig. 10d), a highly ordered nanotube structure was achieved which, resulted in the lowest surface roughness among the specimens. In addition, the deep groove configuration was not trivial in the case of the anodized sample annealed at 700 °C, in which the topographical heterogeneity in width and depth were obvious (Fig. 10f). Based on the obtained data, the average roughness value inside the wear tracks of the annealed sample at 500 °C was 14.4 nm, nearly 2 times less than the value measured for the substrate (30.7 nm). This result confirmed the important role played by the self-organized TiO₂ nanotubular arrays in reducing wear, which is very important in biomedical applications.

4. Conclusion

In summary, the effect of microstructural features on the wettability and tribological behavior of TiO₂ nanotubes coated
Fig. 10. AFM images of undamaged and worn surfaces for (a,b) substrate, (c) un-annealed TiO$_2$ nanotubular arrays and arrays heat treated at (d) 500 and (e,f) 700 °C.
on Ti–6Al–4 V was examined. XRD data demonstrated that, the characteristic peaks of TiO2 were not detected after anodization; however, a highly crystalline TiO2 phase with both anatase and rutile configurations was formed during annealing at 500 °C for 1.5 h. These nanotubular arrays were completely transformed into nanorods with a rutile structure at 700 °C. FESEM images showed that, coarsening of the TiO2 nanotube arrays occurred at higher temperature (> 500 °C) and that the level of coarsening increased as the annealing temperature was increased from 600 to 700 °C. During annealing at 500 °C, a transition from an amorphous to a highly crystalline structure occurred, and consequently, the surface hardness value was increased from 373 to 435 HV. In addition, due to the formation of a highly ordered nanotubular array after annealing at 500 °C, an improvement in hydrophilicity was observed and the contact angle noticeably declined to θ = 7.5°.

The results of tribological evaluation showed that the average roughness value inside the wear tracks of the sample annealed at 500 °C was 14.4 nm, which was nearly 2 times less than the value measured for the substrate (30.7 nm).

Acknowledgment

This research was funded by the Ministry of Higher Education, Malaysia with the high impact research grant no. UM.C/HIR/MOHE/ENG/27 and partly sponsored by UM. TNC/IPPP/UPGP/638/PPP/P9212012B and UM.TNC2/RC/AET/261/1/RPO17-2012C.

References


