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The improvement of wettability, biotribological behavior and corrosion resistance of titanium alloy pretreated by thermal oxidation

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ABSTRACT

The thermal oxidation process was performed on biomedical titanium alloys to improve surface properties for the application in artificial cervical disc. The pretreated Ti6Al4V was characterized with XPS, XRD and SEM. The wettability, biotribological behavior and corrosion resistance were evaluated under distilled water and 25 wt% bovine serum lubricant. Rutile TiO_2 as the main compound was formed with the increase in hardness. The wettability was improved significantly after oxidation. Compared with the untreated, the friction coefficients and wear volumes of treated samples all decreased with about 50% reduction in both dry sliding and lubrication conditions. Corrosion resistance for oxidized samples was also enhanced with a big reduction of corrosion current density and a shift in corrosion potential towards the positive direction.

1. Introduction

Ti6Al4V alloys are widely used as bio-implant materials, particularly for orthopedic applications due to their low density, excellent biocompatibility and mechanical properties [1,2]. They are also used as the preferred endplate materials for artificial cervical intervertebral disc implant because of the imaging requirements (e.g. MRI/CT) [3]. However, the main limit of titanium alloys is their poor tribological behavior, characterized by high coefficients of friction, severe adhesive wear and low abrasion resistance [4]. It is believed that thermal oxidation (TO) is a relatively simple and cost-effective method to improve the tribological properties of Ti6Al4V, which forms a thick and hard oxide film on the surface [5]. In addition, in situ ceramic coatings, mainly based on rutile, are of higher bonding strength and relatively higher thickness compared to the naturally formed oxide layer (about 4–6 nm) [6,7]. Therefore, rutile TiO_2 coating formed on titanium alloys has attracted extraordinary attention due to their potential application in artificial joint such as artificial cervical disc.

According to the previous research [6–8], oxidation temperature and time are the main parameters to obtain excellent rutile TiO_2 coating. However, high temperature and prolonged durations result in the debonding stratification between oxide scales and interface, while insufficient temperature and durations may form discontinuous oxides [6]. In our previous investigations [9], the water vapor oxidizing atmosphere has been adopted to ensure the continuous formation and consistent growing of oxidized layer with the temperature changing from 600 to 800 °C and the time from 0.5 to 8 h and the optimal parameters are found to be 700 °C for a duration time of about 4 h.

In order to apply this technique in artificial joint products, especially artificial cervical discs, evaluations of biotribological and corrosion behaviors are necessary. However, the previous literature mainly focus on the wear and corrosion resistance in industrial application [10–13] such as aerospace, ship, metallurgy, chemical industry and environmental protection, in which the material of ball or pin used is mostly alumina [10,11], steel [12,13] etc. Ultra-high molecular polyethylene (UHMWPE), the most important and commonly used polymer joint material, is seldom studied in the wear experiments. In addition, bovine serum, the most common and versatile simulating body fluid [14], is also seldom involved. Furthermore, the modification technique has still not been widely applied in biomedical devices, especially in orthopedics and joint products.

In this study, thermal oxidation under optimal parameters was performed on biomedical titanium alloys. The surface composition and micro-structure of oxidized titanium alloy were characterized using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and scanning electron microscopy (SEM). Then, the

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wettability, biotribological behavior and corrosion resistance of oxidized Ti6Al4V alloy and the untreated specimen were investigated under distilled water and 25 wt% bovine serum lubricant.

2. Materials and experimental details

2.1. Thermal oxidation

Before oxidation, cylindrical samples with the thickness of 5 mm were cut from the medical grade titanium alloy (Ti6Al4V) bar with the diameter of 30 mm. Then, the samples were successively ground using 60–1200 mesh Al_2O_3 abrasive papers. Final polishing was made with diamond paste to achieve a mirror-like surface finish with an average surface roughness value of 0.06 μm and then the substrates were cleaned in ethanol and dried with dry air. Isothermal oxidation treatments were carried out in a laboratory type air circulated furnace (GSL-1200X) under flowing water vapor atmosphere at 700 °C for 4 h followed by natural cooling in the furnace. The heating rate was 5 °C/min in the heating process. The operation details have been reported in our previous investigation [9].

2.2. Surface characterization and wettability

The treated samples were examined by X-ray photoelectron spectroscopy (XPS) by using a spectrometer (Thermo Scientific ESCALAB 250Xi, USA) fitted with monochromatic Al-Kα X-ray radiation (150 W, $h\nu = 1486.6$ eV). The details of the fitting method for XPS and FWHM results were as follows. The software used for fitting was XPS Peak. Firstly, the ASCII type data was imported in the software and the Shirley type background was selected. Secondly, several peaks were added to the original curve. At this time, the position of added peak, FWHM, peak area and other constraints such as peak spacing and peak area ratio could be selected. In this study, two peaks were selected near the initial peaks and the peak spacing of binding energy between the two selected peaks was fixed as 5.8 eV for Ti_{2p}, which is a fixed value. However, the FWHM and peak area were not selected. Then, the fitting and optimization were performed by several times until the satisfactory results appeared. Finally, the parameters of the final peaks could be checked according to the NIST database. X-ray diffraction (XRD) analysis was performed on D8 ADVANCE X-ray diffractometer system made by BRUKER with Cu-Kα radiation by scanning in the 2θ range 10°–90° to evaluate the crystal structure of untreated and thermal oxidized (TO) samples. Hardness of thermal oxidized samples was measured by a micro hardness tester under an indentation load of 4.90 N with the loading time of 15 s. The static-water contact angles were measured by a contact angle instrument under distilled water and 25 wt% bovine serum, respectively. Such measurements were repeated five times for each sample, and the average value was regarded as hardness or contact angle.

2.3. Biotribological test

Since the majority of artificial cervical discs are designed as the ball (mainly made of UHMWPE) and socket (mainly made of titanium alloy) joint structure [15], the ball and socket articulating surfaces are subjected to the action of sliding and rubbing, resulting in serious surface wear during their operation in the body. This structure can be simplified as a friction pair including a UHMWPE pin (the radius of 20 mm) with a spherical crown (the radius of 14 mm) and an articulated Ti6Al4V disc [9]. In this study, the UHMWPE pin with the spherical crown was made from

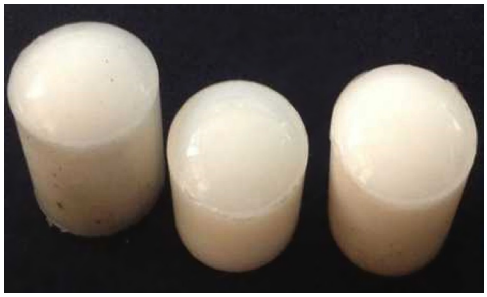

Fig. 1. The UHMWPE pin with the spherical crown.

powders in a hot-pressing furnace (Fig. 1) and the average surface roughness (R_a) was 0.88 ± 0.09 μm.

The biotribological tests were performed between untreated/TO titanium with UHMWPE samples using a universal multi-functional tester (UMT) developed at CETR (Campbell, California) with pin-on-disc reciprocating sliding style in distilled water, bovine serum lubrication and dry friction condition. Since it was hard to observe obvious wear scars for both titanium alloys and implanted alloys with a normal contact stress of the joint for a long time according to ISO 18192-1 and ASTM F2423 [16], the tests were performed with a load of 90 N, equivalent stress of 49.8 MPa to accelerate the wear failure of the samples. The constant sliding time was about 6 h and a steady-state condition could be obtained at an average sliding speed of 0.05 m/s with a stroke of 8 mm. The temperature was maintained at 37 ± 1 °C during the wear process to simulate the physiological medium around the contact area of the prostheses in vivo. Bovine serum used in this study was diluted by ultrapure water without any preservative to the concentration of 25 wt%.

The two-dimensional interface damages were studied using cross-sectional view of worn surfaces parallel to the sliding direction using high speed digital microscope system (VW-9000 made by KEYENCE in Japan) and scanning electron microscopy (FEI Quanta 200 FEG) under the condition of high vacuum mode (80.0 Pa, $h\nu = 15.0$ keV), respectively. The three-dimensional interface damage, maximum wear depth and the wear volume of wear scars on titanium alloys were measured by a 3D surface profiler.

2.4. Corrosion resistance test

The corrosion resistance of untreated and thermally oxidized samples was evaluated by potentiodynamic polarization studies in distilled water and 25 wt% bovine serum, respectively. All the corrosion experiments were performed at 37 ± 1 °C. Before performing corrosion studies, the untreated and thermally oxidized samples were thoroughly rinsed in distilled water and dried using a stream of compressed air. The cleaned samples, either untreated or thermally oxidized, were used as the working electrode while a saturated silver chloride electrode and a platinum wire served as the reference and auxiliary electrodes, respectively. There was only one side of the working electrode sample (the area was about 7.07 cm^2) exposed to the electrolyte solution. The tests should not be started until the open circuit potential (OCP) was stable. The scan range was firstly settled from the initial potential (OCP − 0.5 V) to the final potential (OCP + 0.5 V). However, if the corrosion system was still not stable or satisfying, the scan range could be reduced and settled from the initial potential (OCP − 0.25 V) to the final potential (OCP + 0.25 V). These process could last several times until the stable potentiodynamic polarization curves were obtained. During the potentiodynamic polarization measurements the scan rate was settled as 0.01 V/s. The corrosion potential (E_{corr}) and the corrosion current density (I_{corr}) were determined from the polarization curves using the Tafel