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Development and characterization of MAO bioactive ceramic coating grown on micro-patterned Ti6Al4V alloy surface

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ABSTRACT

In this paper, we describe a strategy for growing bioactive ceramic coatings on a micro-patterned Ti6Al4V alloy substrate using microarc oxidation (MAO) combined with fine particle shot-peening (FPSP) process, for the purpose to obtain the bio-activated titanium alloy with improved wear resistance and fatigue properties. The microstructure and phase composition of FPSP-MAO coating and simple MAO coating were examined using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The bioactivity, tribology and fatigue properties of FPSP-MAO and simple MAO coated samples were evaluated comparatively. The results indicate that the FPSP-MAO5 coating with a rougher dimple surface interspersed by fine pore structure has better inducing capacity of biomimetic apatite compared with simple MAO5 coating. FPSP-MAO5 and FPSP-MAO10 coated samples exhibit an improved fatigue life, increasing by 12.6% and 8.4% in comparison to that of the simple MAO5 and MAO10 coated ones, which is possibly attributed to residual compressive stress induced in the substrate near the coating/substrate interface. The wear resistance of FPSP-MAO5 and MAO10 coatings was significantly improved caused by the alleviated three body wear due to the debris container effect of dimples structure.

1. Introduction

Titanium and its alloys have been widely used for orthopedic and dental implants due to their good biocompatibility, excellent corrosion resistance and high strength-to-weight ratio. However, the bio-inert nature restricts their wider clinical applications. How to improve the bioactivity of titanium implants always keeps a challenge, while the wear resistance and fatigue lifetime of titanium implants are another two considering issues. The bio-activated titanium alloys with good wear resistance and improved fatigue properties can guarantee a safe operation of the implants during the expected period of use [1].

To meet the bioactivity challenge, microarc oxidation (MAO), also commonly called plasma electrolytic oxidation (PEO) [2,3], has been extensively developed to improve the bioactivity by incorporating Ca and P into TiO_2-based coatings using the electrolytes containing calcium salts such as calcium acetate, calcium glycerophosphate and calcium dihydrogen phosphate [4–7]. MAO coatings formed on titanium alloys can lower the friction coefficient and reduce wear between sliding pairs. The TiO_2 dominated coatings formed on titanium alloys in phosphate or silicate electrolyte reduce the friction coefficient down to 0.1–0.2 against steel in light loads condition, which is possibly attributed to the low friction nature of nanocrystalline TiO_2 material and also depends on the surface roughness [8–11]. However, the previous attempts mostly focused on exploring wear resistance of MAO coating for industry engineering applications, the tribological behaviors of MAO bio-activated titanium alloys are scarcely considered.

MAO treated metal samples have a very low resistance to cycling load. Yerokhin et al. [12] reported that MAO coatings with thicknesses 7 μm and 15 μm reduced bending fatigue limit of AZ21 Mg alloy by not more than 10%, which was substantially lower than the influence from conventional anodizing. Lonyuk et al. [13] made a comparative study on the axial fatigue strength of 7475-T6 aluminum alloy coated with hard anodizing and MAO coatings. While hard anodic coating with 60 μm thick reduced the fatigue strength of the alloy by 75%, MAO coating with 65 μm thick reduced the fatigue strength of the alloy only by 58%. Thus some attempts have been performed to improve the fatigue property of MAO coated metals such as Al alloy by MAO combined conventional shot-peening process. Asquith et al. demonstrates that the loss in fatigue life can be recovered to a certain extent by the application of a suitable surface cold-working process prior to treatment [14]. In their study, shot-peening was employed as such a cold-working

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process and was demonstrated to recover fatigue life of MAO treated aluminum by approximately 85%.

Unfortunately, the researches on effect of MAO on fatigue and wear resistance properties of bio-activated titanium alloys and their improving strategies were rarely reported. The fine particle shot-peening (FPSP), as a new surface cold-working process, has been developed in Japan mainly to obtain better fatigue properties compared with conventional shot-peening process for automobile industries and aerospace application [15,16]. The features of FPSP process are using a smaller ceramic media with particle diameter <50 μm (conventional shot-peening >600 μm), and having a higher velocity >200 m s^{-1} of the media flow (conventional shot-peening >50 m s^{-1}). It has been confirmed that fatigue life of aluminum alloy obtained by FPSP is around one order of magnitude longer than that by conventional shot-peening [15]. FPSP cannot only introduce compressive residual stress into the surface layer, but also induce a micro-patterned texture with rough ball pit like surface. In this work, we developed a strategy for growing bioactive ceramic coatings on a micro-patterned Ti6Al4V alloy substrate using MAO combined with FPSP process.

The FPSP was used as the pretreated process of titanium alloy, followed by the MAO treatment, in this way the specially modified layers (FPSP-MAO coating) structure with a controllable surface roughness was designed. How the modified coating structures affect bioactivity, fatigue and wear resistance property is not clear. Thus, this work focuses on the relationships between the specially modified layers microstructure and bioactivity, fatigue and wear of the combined FPSP-MAO treated titanium alloy.

2. Experimental

2.1. Materials and FPSP pre-treatment

The commercial Ti6Al4V alloy was used as the substrate for the treatment. The samples were polished using 800# and 1000# abrasive paper, and cleaned in distilled water followed by acetone. To obtain the micro-patterned surface with rough ball pit, the Ti6Al4V alloy samples were subjected to the FPSP treatment.

During this present FPSP process, the ball-shape α-Al_2O_3 particles with a mean diameter 28 μm were used as the peening medium. Thus, the shot peening by fine ceramic media does not introduce the iron pollutants as the conventional shot-peening does. The pressurized pure nitrogen (1 MPa) serves as a carrier gas to accelerate α-Al_2O_3 ball particles to supersonic speeds. The gas is heated and then forced through a converging diverging nozzle, where it can be accelerated to supersonic speeds (over 600 m s^{-1}). Spray ball particles were axially injected upstream of the nozzle and collided on the surface of Ti6Al4V alloy samples surface. The strong impulse force enabled the metal surface to deform and the micro-patterned surface formed with uniformly dispersed half-ball pit structure.

2.2. Coating preparation

The electrolyte was prepared from the solution of dissolving reagent-grade chemicals of $Ca(CH_3COO)_2 \cdot H_2O$ (0.025 mol l^{-1}), $Ca(H_2PO_4)_2 \cdot H_2O$ (0.075 mol l^{-1}) and NaOH (0.045 mol l^{-1}) into distilled water. A 65 kW microarc oxidation device provides the voltage waveforms, and the main pulse parameters, such as pulse duration, voltage amplitude and duty cycle during both positive and negative biasing can be adjusted independently. The electrical parameters were fixed as follows: voltage 500 V, frequency 600 Hz, duty cycle 10.0%. In the experiments, the test samples were fabricated by simple MAO treatment and FPSP combined with MAO treatment. The coatings with 5 μm and 10 μm thick grown on polished titanium substrate were marked as MAO5 and MAO10, respectively. Similarly, the coatings with 5 μm and 10 μm thick grown on FPSP treated titanium substrate were marked as FPSP-MAO5 and FPSP-MAO10, respectively.

2.3. Coating characterization

The microstructure of the sample surface treated by FPSP, MAO, and the combination of the two methods, was investigated by X-ray diffraction (XRD) with a Philips X'pert diffractometer using Cu Kα, the measurements were performed with a continuous scanning mode at a rate of 4° min^{-1} with an incident angle of 3°. The surface and cross-section morphologies of the coatings were observed by a Hitachi S-4700 scanning electron microscopy (SEM).

2.4. Immersion of specimens in a simulated body fluid

The bioactivity of simple MAO and FPSP-MAO specimens were evaluated by observing the formation ability of biomimetic apatite in simulated body fluid (SBF). The simple MAO and FPSP-MAO specimens were soaked in 50 mL SBF with ionic concentrations (Na^+ 142.0, Mg^{2+} 1.5, K^+ 5.0, Ca^{2+} 2.5, Cl^- 147.8, $HCO_3{}^{2-}$ 4.2, $HPO_4{}^{2-}$ 1.0 and Si $O_4{}^{2-}$ 0.5 mmol l^{-1}) for 7, 14 and 28 days. The SBF was refreshed every other day. The SBF was prepared by dissolving reagent-grade chemicals of NaCl, $NaHCO_3$, KCl, $K_2HPO_4 \cdot 3H_2O$, $MgCl_2 \cdot 6H_2O$, $CaCl_2$ and Na_2SO_4 into distilled water and buffering at pH 7.4 with tris (hydroxymethyl), minomethane ($(CH_2OH)_3CNH_2$) and 1.0 mol l^{-1} HCl at 37 °C [17].

2.5. Fatigue tests

Fatigue tests of samples were conducted using MTS 810 testing machine at room temperature. The tested yield strength ($\sigma_{0.2}$) of Ti6Al4V alloy sample is 1227 MPa. We took 70% $\sigma_{0.2}$ as the cyclic stress level (834 MPa). The stress ratio was selected as 0.1, and the cycle frequency was set as 8 Hz, according to the possible stress state of the bone replacing implants. The fatigue tests were set to run up to the complete fracture.

2.6. Tribology tests

The tribological behaviors of the simple MAO and FPSP-MAO samples were evaluated using a pin-on-disk tester under the dry sliding conditions. Balls of SAE 52 100 steel (hardness HRC 61) with a diameter of 6.0 mm and a surface roughness *Ra* 0.05 μm were used as the counterface materials. The normal load was 1 N. The friction coefficient was recorded by the computer during each test. The wear tracks of the worn samples were observed and analyzed by means of a scanning electron microscopy (SEM) and energy disperse spectroscopy (EDS). The specific wear volume rate (K_s) was calculated from the following equation:

$$K_s = \frac{\Delta V}{(P \times d)} \quad (1)$$

where ΔV is the volume loss in mm^3, determined by wear scar profile. *P* the normal load in Newton and *d* is the sliding distance in metres.

3. Results and discussion

3.1. Microstructure of FPSP and FPSP-MAO coatings

The surface morphologies of before and after FPSP treatment of Ti6Al4V alloy are shown in Fig. 1a and b, respectively. A micro-patterned surface with uniformly dispersed half-ball dimple structure was formed after FPSP treatment. The supersonic