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Characterization of plasma electrolytic oxidation film on biomedical high niobium-containing β-titanium alloy

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ABSTRACT

The plasma electrolytic oxidation (PEO) film on Ti-39Nb-6Zr alloy was successfully prepared in KOH solution. The electrochemical corrosion and wear behaviors of bare and coated alloys in phosphate buffer saline (PBS) were investigated. The biocompatibility was evaluated by culturing osteoblast cells on the bare and coated alloys. The results showed that corrosion resistance and wear resistance of Ti-39Nb-6Zr alloy in PBS solution were significantly improved after PEO surface treatment. In addition, the PEO film had higher zeta potential at pH 7.4, which resulted in a higher protein adsorption amount. The PEO film promoted osteoblast cell proliferation and differentiation into the polygonal shape. The PEO film on Ti-39Nb-6Zr alloy showed excellent corrosion resistance, wear resistance and osteogenic properties.

1. Introduction

The new β-type titanium alloys with non-toxic elements such as Nb, Zr, Ta and Mo have excellent biocompatibility and high mechanical strength, which has shown great prospect in biology [1–3]. At present, Ti-Nb-Zr alloys have drawn much attention for their high yield strength and low Young's modulus close to bone due to the addition of Nb element, furthermore, the alloying element Zr also benefits the blood compatibility [4]. As a result, Ti-Nb-Zr alloys have been developed as good bone graft materials.

The surface topography, chemistry and properties of implant materials have great influence on their biological properties. It has been suggested that the porous structure and roughness surface can facilitate the adhesion and growth of cells [5]. The surface potential affects the protein absorption [6]. In addition, the bare Ti-Nb-Zr alloys have the poor wear performance, which limits their service life and application in biomaterials [7].

Plasma electrolytic oxidation (PEO) is an efficient method to fabricate porous ceramic films on valve metals such as Ti, Al, Mg, Zr, and the PEO films usually have good adhesion strength, corrosion resistance and wear performance [8–10]. Some papers about PEO surface modification of pure Ti and its alloys for biology application have been published [11–13]. Recently, the β-type alloy titanium alloys with high content of alloying elements such as Ti-39Nb-6Zr have drawn a great attention for their biological prospect [14,15]. In our previous work, it was found that the compact films on Ti-39Nb-6Zr alloy could be fabricated by plasma electrolytic oxidation at different voltages [17]. And it's interesting to investigate the biological properties of PEO films on Ti-39Nb-6Zr alloy, such as corrosion and wear resistant in PBS solution and the biocompatibility.

In this work, electrochemical and wear behaviors in PBS solution and in-vitro bioactivity of PEO film on Ti-39Nb-6Zr alloy were evaluated. Moreover, the relationship between surface zeta-potential, protein adsorption and cell proliferation were analyzed.

2. Experimental procedure

The Ti-39Nb-6Zr alloy with the dimensions of 25 mm × 12 mm × 1 mm was set as an anode, while the cathode was a stainless steel container. The Ti-39Nb-6Zr samples were polished by emery paper and ultrasonically cleaned in acetone, ethanol and deionized water, respectively. A pulsed power supply was employed for the PEO treatment in 2.5 g/L KOH solution. The electrical parameters were + 350 V of positive voltage, −60 V of negative bias voltage and 75 Hz of frequency. The treating time was 10 min.

The surface and cross-section morphologies of PEO film were observed by field emission scanning electron microscopy (FESEM, Hitachi S-4800), and its surface roughness (R_a) was measured by a profilometer

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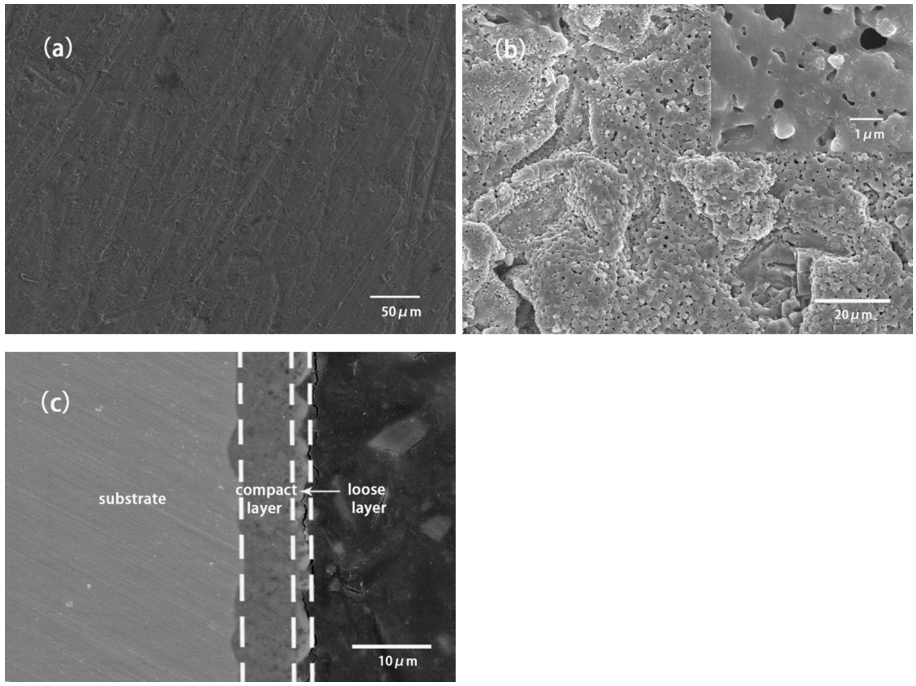

Fig. 1. (a) bare alloy and (b) PEO film surface morphology, and (c) cross-sectional microstructure of PEO film.

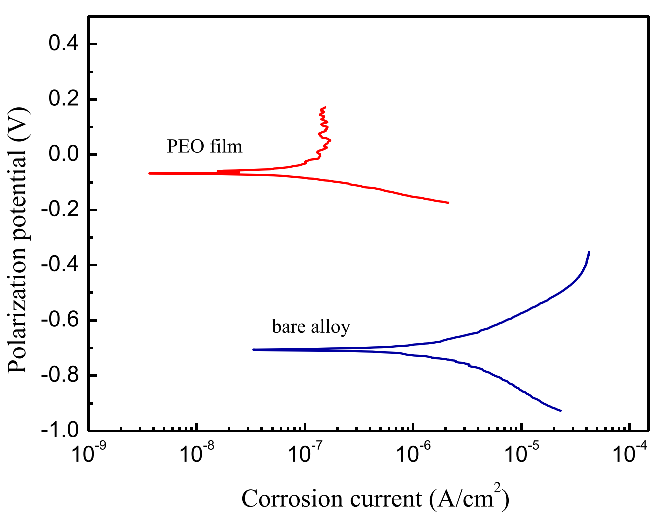

Fig. 2. Potentiodynamic polarization curves of bare Ti-39Nb-6Zr alloy and PEO film in PBS solution.

Table 1
Fitting results of polarization curves of bare Ti-39Nb-6Zr alloy and PEO film in PBS solution.

Samples	i_{corr}(A·cm^{-2})	E_{corr}(V)	R_p (Ω·cm^2)
bare alloy	2.48×10^{-6}	−0.70	1.47×10^4
PEO film	1.59×10^{-7}	−0.061	2.01×10^5

(TR-200).

The corrosion behaviors in phosphate buffer saline (PBS) solution with the composition of NaCl (8 g/L), KCl (0.2 g/L), $NaH_2PO_4{\cdot}2H_2O$ (0.14 g/L), KH_2PO_4 (0.20 g/L) were evaluated using an electrochemical workstation (PARSTAT 2273). The saturated calomel electrode (SCE) and the platinum coil was used as a reference electrode and a counter electrode, respectively. Potentiodynamic polarization was measured at a scan rate of 1 mV/s, and electrochemical impedance spectroscopy (EIS) was performed in a frequency range from 1 MHz to 0.01 Hz.

The tribological performance of bare Ti-39Nb-6Zr alloy and PEO film was evaluated by a ball-on-disk friction and wear tester (HT-1000). The samples were fixed in a stainless steel container with dimensions of Φ 50 mm × 30 mm, and the PBS solution with 20 mL was added into the container to ensure that the friction region of sample was completely immersed in PBS solution. The samples were against the Si_3N_4 ball of 5.953 mm in diameter under 3 N load and 300 rpm rotating rate with 10 min duration, and the wear track radius is 3 mm. The cross-sectional profiles of wear tracks were measured by a profilometer and their cross-sectional area was calculated, then the volumetric wear rate was obtained from the following formula.

$$\nu = \frac{Sd\pi}{Vtd\pi G} = \frac{S}{VtG}$$

where S is cross-sectional area, V is rotating rate, t is testing time and G is load.

The zeta-potential tests of the bare alloy and PEO film were performed by an electrokinetic analyzer (EKA, Anton Paar GmbH). The zeta-potential is measured by streaming potentials method from pH 2.5 to pH 9.5. The electrolyte is 0.001 M KCl solution, meanwhile 0.5 M HCl and 0.5 M NaOH solution are used to adjust the pH of electrolyte. The zeta-potential is generated when the electrolyte is forced through a narrow slit of 100 μm between two same samples.

The samples of bare alloy and PEO film were immersed in 50 mL bovine serum albumin (BSA) solution (1 mg/mL, PBS solution) for 24 h to study the protein adsorption. Mouse osteoblastic MC3T3-E1cells were cultured in a-modified essential medium (a-MEM, Hyclone) supplemented with 10% fetal bovine serum (FBS, Gibco), 1% penicillin/streptomycin, and 2 mM L-glutamine and incubated in a humidified atmosphere of 5% CO_2 at 37 °C. The cells were cultured on the bare alloy and PEO film with the dimension of 10 mm × 10 mm × 1 mm for 24 h and 48 h, respectively.