Surface characteristics and electrochemical corrosion behavior of a pre-anodized microarc oxidation coating on titanium alloy

W.F. Cui [a,*], L. Jin [a], L. Zhou [b]

[a] Key Laboratory for Anisotropy and Texture of Materials, Northeastern University, Shenyang 110004, China
[b] Institute of Northwestern Nonferrous Metal Research, Xi'an 710016, China

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ABSTRACT

A porous bioactive titania coating on biomedical β titanium alloy was prepared by pre-anodization followed by micro arc oxidation technology. The effects of pre-anodization on the phase constituent, morphology and electrochemical corrosion behavior of the microarc oxidation coating were investigated. The results show that pre-anodization has less influence on the phase constituent and the surface morphology of the microarc oxidation coating, but improves the inner layer density of the microarc oxidation coating. The decrease of plasma discharge strength due to the presence of the pre-anodized oxide film contributes to the formation of the compact inner layer. The pre-anodized microarc oxidation coating effectively inhibits the penetration of the electrolyte in 0.9% NaCl solution and thus increases the corrosion resistance of the coated titanium alloy in physiological solution.

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1. Introduction

As one of the surface modification technologies, microarc oxidation (MAO) has been suggested to prepare a porous, adherent and rough titania coating which enhances bioactivity, hydrophilicity, cellular reaction and corrosion resistance of the implants in body [1–4]. However, the surface bioactivity of the MAO coating on titanium metal is strongly associated with apatite (or hydroxyapatite) content incorporated within titania coating. High applied voltage during MAO process can accelerate electromigration process of the ions in electrolyte, which attracts the more Ca^{2+} and PO_4^{3-} ions to incorporate into the oxide layer by the redox reactions in the electric field on the surface of the electrode and promotes the formation of apatite [5,6]. On the other hand, the strong discharge phenomenon generated by high applied voltage increases the pore size and decreases the density of the coating [7]. It has been proved that long-time immersion in simulated body fluid or fluoric physiological solution brings corrosive ions to penetrate through the porous layer and even thin inner layer, resulting in the serious corrosion of the coated magnesium alloy or titanium alloy [8–11]. Moreover, cracks and poor adhesion easily arise from high applied voltage. Therefore, it is a key issue how to improve the corrosion resistance of the porous MAO coating with high bioactivity so as to alleviate toxicity and allergic reactions inside a living creature due to the release of metal ions to the adjacent tissue. By adjusting MAO parameters, e.g. applied voltage, time and electrolyte component, the thickness and chemical composition of the coating can be well controlled [6,12]. But the rational

distribution in thickness between dense inner layer and porous outer layer is difficult to achieve. It has been reported elsewhere that pre-anodization on aluminum enabled the faster establishment of the micro-discharges regime that facilitated to increase the density of the coating [13]. As the inner layer of MAO coating is a barrier layer to decrease the corrosion rate of the substrate, it is especially expected to increase the thickness or density of the inner layer by pre-anodization treatment. Up to date, to the author's knowledge, the characteristics of the pre-anodized MAO coating and the effect of pre-anodization on the corrosion resistance of MAO coating are seldom investigated in details. The present study aims to examine the surface and inner layer morphology of the pre-anodized MAO coating on titanium alloy and to clarify the electrochemical corrosion properties of the pre-anodized MAO coating after long-time immersion in physiological solution.

2. Experimental

2.1. As-received material

A biomedical β titanium alloy was chosen to be the substrate of the MAO coating. The microstructure and mechanical properties of the alloy have been described in another publication [14]. The material was remelted for three times in cold crucibles by vacuum electromagnetic suspension smelting. The chemical compositions of the material are (wt.%) 30.5Nb, 8.83Zr, 0.82Fe, 0.026O and balance Ti. The ingot was hot forged to square billet at 1000 °C. The small specimens with dimension of $30 \times 30 \times 2$ (mm) were cut from the forged billets and solution-treated at 810 °C for 60 min to homogenize the microstructure. Before pre-anodization treatment, the specimens were ground
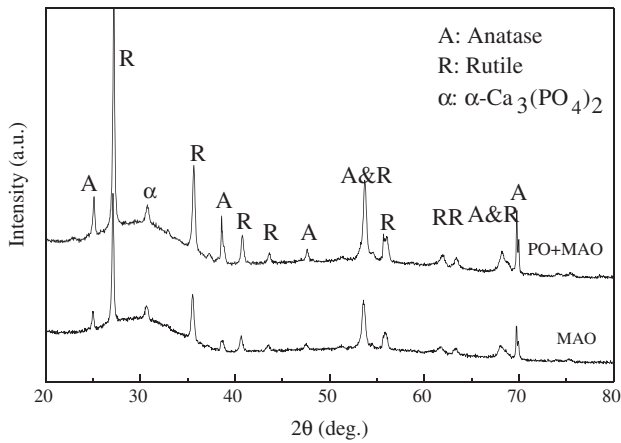
Fig. 1. XRD results of the MAO coatings with and without pre-anodization. The phase compositions consisted of rutile TiO_2, anatase TiO_2 and small amount of α-$Ca_2(PO_4)_3$ compounds.

using SiC waterproof abrasive paper and ultrasonically cleaned with acetone, ethanol and distilled water in sequence.

2.2. Preparation and characterization of microarc oxidation coating

The specimens were firstly pre-anodized in 0.5 mol/l H_2SO_4 solution at 40 V voltage for 60 min. After rinsed by distilled water, the specimens with pre-anodized film were put in the electrolytic containing 0.2 mol/l $(CH_3COO)_2Ca\cdot H_2O$, 0.12 mol/l $NaH_2PO_4\cdot 2H_2O$ and 0.15 mol/l NaOH for the preparation of MAO coating. The frequency was 600 Hz, the duty cycle was 20% and applied voltage was 400 V, using a pulse power supply for 10 min. For comparison, MAO coating without pre-anodization was prepared under the same technological parameters. Thereafter, pre-anodized MAO coatings are abbreviated as PA + MAO. The surface and cross-sectional morphologies of the coatings were observed by SEM

(JSM-7001F, Japan). The phase constituents of the coatings were analyzed by XRD (PW3040-60 X'Pert Pro MPD, Netherland) using Cu-Kα radiation.

2.3. Electrochemical properties measurements

The electrochemical corrosion tests were performed using an electrochemical workstation (IM6ex Zahner Elektrik Co., Germany) with three electrodes: working electrode, platinum counter electrode and saturated calomel (SCE) reference electrode. The coated specimens were immersed in 0.9% NaCl (pH = 6.8–7.1) at room temperature for 24, 168 and 336 h, respectively. Then the electrochemical impedance spectra (EIS) of the coated specimens were measured to examine the permeability of electrolyte through the coating. A sinusoidal potential perturbation of 5 mV was applied at the open circuit potentials. Frequency was swept from 10^{-2} Hz to 10^5 Hz in logarithmic increment. The impedance data were analyzed using ZSimpWin software and were fit to appropriate equivalent electrical circuit. Polarization measurements were performed on the coated specimens with and without pre-anodization in 0.9% NaCl. The scanning rate was 0.2 mV/s.

3. Results and analysis

3.1. Characterization of the MAO coatings on titanium alloy

X-ray diffraction (XRD) analysis was employed to compare the phase composition of the MAO coatings with and without pre-anodization. It can be seen in Fig. 1 that the MAO coating mainly consisted of rutile TiO_2, together with small amount of anatase TiO_2 and α-$Ca_2(PO_4)_3$ compounds. Pre-anodization had less effect on the phase composition of the MAO coating. Fig. 2a and b displays the surface morphologies of the MAO coatings. The average pore-diameter and pore-distribution had little difference for the two coatings, but the pore-depth of the pre-anodized MAO coating looked to be shallower than that of the non-pre-anodized
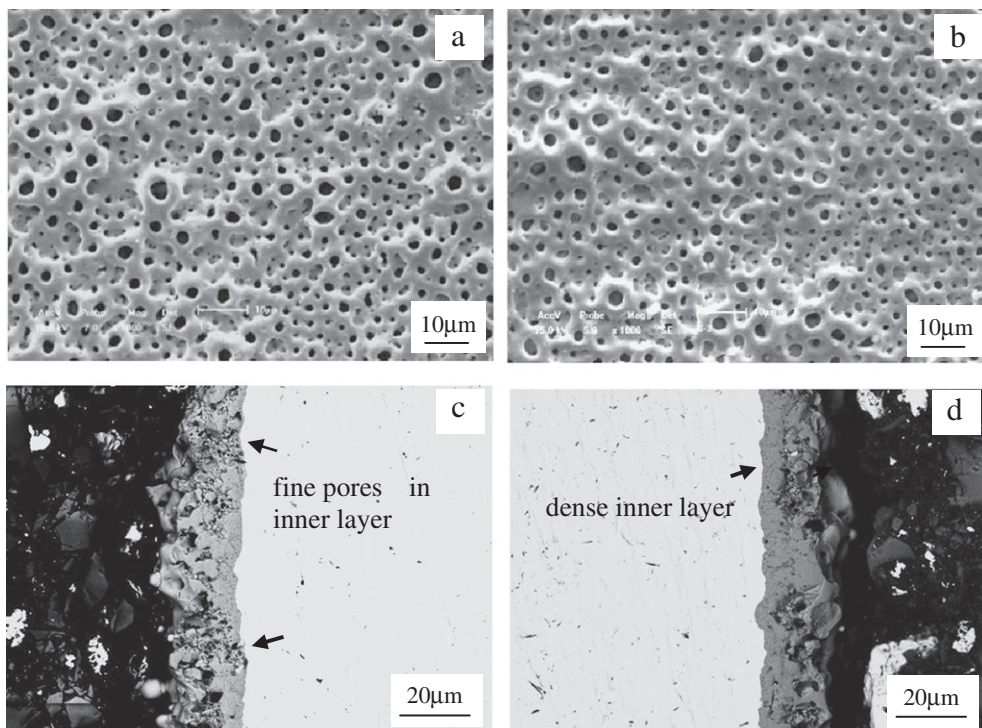

Fig. 2. The surface porous morphologies of the MAO coatings with and without pre-anodization (a, b), the cross-sectional morphologies showing aggregated fine pores in the inner layer of the non-pre-anodized MAO coating as depicted by black arrow (c) and the denser inner layer of the pre-anodized MAO coating (d).