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Characteristic and microstructure of the microarc oxidized TiO_2-based film containing P before and after chemical- and heat treatment

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ABSTRACT

Chemical- and heat treatment was performed to modify the surface of the microarc oxidized TiO_2-based (TOB) film containing P to produce nano-scale compounds containing Na, Ti and O elements. In the TOB film, anatase and rutile nanocrystals were randomly distributed in P-doped matrix. On the surface of the chemically treated TOB (C-TOB) film, amorphous titanium oxide containing Na shows nano-scale ribbonlike morphology. Na, Ti and O show uniform distribution in the outer layer of the C-TOB film along surface depth. Chemical treatment did not alter the surface roughness of the TOB film obviously; however, it improved its hydrophilic property. Heat treatment has no influence on the chemical states of Ti, Na and O, as well as wetting ability, elemental composition and atomic concentration in the outer layer of the C-TOB film. However, the phase compositions and surface morphology of the C-TOB film after heat treatment are dependent on the heat treatment temperature.

1. Introduction

In recent years, TiO_2-based (TOB) films have gained much attention [1–10]. These films can be easily formed on titanium and its alloys by a relatively convenient and effective technique of microarc oxidation (MAO) [1–10]. TOB films on titanium alloys are effective as chemical barriers against the release of metal ions from the substrates and can enhance the corrosion resistant of titanium alloys [11].

However, most of TOB films have low apatite-forming ability according to the previous researches [6,9,12–14]. Therefore, subsequent modifications such as sol–gel [15] and hydrothermal treatment [16,17] have been used to form hydroxyapatite phase or other bioactive surfaces, which can induce apatite formation. Also, these studies suggest an interesting fact that the structure and properties of the TOB films can be altered by subsequent modifications. In the previous work, alkali treatment was performed on the surface of the TOB film containing Ca and P forming specific surface structure favorable for the apatite deposition [12]. Amorphous titanium oxide containing Ca was formed on the surface of alkali-treated TOB film containing Ca and P. Further investigation indicated that chemically treated TOB film was crystallized to form calcium titanates ($CaTiO_3$, $CaTi_{21}O_{38}$) after subsequent heat treatment [13].

Enhanced ability to induce apatite formation was observed not only on the surface of the Ca- and P-doped TOB film, but also on the surface of the TOB film containing P after alkali treatment [14]. However, the structure of the newly formed compounds on the surface of the chemically treated TOB (C-TOB) film containing P is not fully understood. In this work, structure of the C-TOB film containing P after chemical and heat treatment was investigated. The current results indicated that nano-scale amorphous titanium oxide containing Na was formed on the surface of the C-TOB film, and crystalline compounds containing Na, Ti and O were obtained by heat treatment of the C-TOB film. In fact, researchers pay much attention to the amorphous titanium oxide containing Na [14,18,19], since they show interests in the potentials for biomedical application.

2. Materials and methods

2.1. Sample preparation

2.1.1. Preparation of the TOB film

In this work, the TOB film was formed on the surface of Ti6Al4V by MAO technique. In the MAO process, Ti6Al4V plates (10 mm × 10 mm × 1.5 mm) were used as anodes, and stainless steel plates were used as cathodes in an electrolytic bath. The

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Table 1
The sample labels of the initial and treated TOB films.

Sample	Microarc oxidation	Chemical treatment	Heat treatment
TOB	√	–	–
C-TOB	√	√	–
C6-TOB	√	√	600 °C
C7-TOB	√	√	700 °C

"√": with treatment; "–": without treatment.

Ti6Al4V plates were ground with abrasive papers, ultrasonically washed with acetone and distilled water, and dried at 40 °C. An electrolyte was prepared by dissolving reagent-grade chemicals of $(NaPO_3)_6$ (20 g/l) and NaOH (10 g/l) into deionized water. The applied voltage, frequency, duty cycle and oxidizing time were 300 V, 600 Hz, 8.0% and 5 min, respectively. The temperature of the electrolyte was kept at 40 °C by a cooling system.

2.1.2. Chemical and heat treatment of the TOB film

After MAO treatment of the titanium alloy, the TOB film was formed on its surface. To obtain C-TOB film, the TOB sample was treated in 10 mL NaOH solution with concentration of 5 mol/L and temperature of 60 °C for 24 h, and then gently washed with deionized water and dried at 25 °C.

The C-TOB film was heat-treated at 600 and 700 °C for 1 h in air, with a heating rate of 10 °C/min and furnace cooling. The sample labels and the parameters for the treatment conditions are shown in Table 1. In this way, amorphous titanium oxide containing Na on the surface of the C-TOB film was crystallized to form crystalline compounds.

2.2. Characterization

2.2.1. X-ray diffraction (XRD)

The TOB films before and after treatment, the phase composition of the sample surfaces were analyzed by a glance-angle X-ray diffraction (XRD, Philips X'Pert, Holland) using a Cu Kα radiation. In the XRD experiment, the angle of the incident beam was fixed at 1° against the sample surfaces in order to detect the phase composition of the sample surfaces and the measurements were performed with a continuous scanning mode at a rate of 2°/min.

2.2.2. Scanning electron microscopy (SEM) and energy dispersive X-ray spectrometer (EDS)

The surface morphologies of the samples were observed by a scanning electron microscopy (SEM, CamScan MX2600, CamScan Co., England). In addition, the ion concentrations of the sample surfaces were detected by an energy dispersive X-ray spectrometer (EDS, Oxford Model 7537, England) equipped on the SEM system.

2.2.3. Transmission electron microscopy (TEM)

A Philips CM-12 TEM was used for TEM work at 120 kV. The TEM sample of the TOB films was prepared by single-side cutting by ion beam sputtering. And the TEM samples of the C-TOB film was prepared by immersing the TEM sample of the TOB film in NaOH aqueous solution with concentration of 5 mol/L. In addition, the constituents of the samples were also analyzed by EDS equipped on the TEM system.

2.2.4. Atomic force microscopy (AFM)

The surface characters of the TOB and treated TOB films were also depicted by an atomic force microscopy (AFM, DI.Bioscope, Veeco, America) in an uncontacting tapping mode with curvature radius of 5–10 nm, resolution of x-, y-direction about 2 nm and z-direction about 0.5 nm and number of samples of 256. The average roughness (Ra) of the TOB and treated TOB films was calculated by analyses of AFM image.

2.2.5. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS, PHI 5700, America physical electronics) was used to detect the chemical compositions of the sample surfaces. An Al Kα (1486.6 eV) X-ray source was used to analyze the chemical state of Ti, Na and O with a hemispherical analyzer in a high-resolution mode. The XPS take-off angle was set at 45°. A region about 2 mm × 0.8 mm on each surface was analyzed. The measured binding energies were calibrated by the C 1s (hydrocarbon C–C, C–H) of 285 eV.

2.2.6. Auger electron spectroscopy (AES)

AES measurement was performed on a scanning auger nanoprobe (PHI 700, ULVAC Inc., America) to detect the concentrations of Na, P, Ti and O with increasing depth near the surfaces of the TOB and modified TOB films. The auger electron take-off angle in the AES was 40°. The sample surfaces were sputtered by Ar^+ ions with a referenced rate of 144 nm/min of SiO_2 under a voltage and a current intensity of 3 kV and 10 nA, respectively. The sputtered and analyzed areas were about 2 mm × 2 mm and 40 μm × 40 μm, respectively. The data acquisition was performed every 30 s.

2.2.7. Wetting angle

Wetting angle was measured using the liquid drop method (using distilled water) on a contact angle goniometer (CAM101, KSV Instruments Ltd., Finland).

3. Results

Fig. 1 shows the XRD patterns of the surfaces of the TOB and C-TOB film before and after heat treatment. Anatase was observed in the TOB and C-TOB films as shown in Fig. 1a and b. In Fig. 1c and d, after heat treatment at 600 and 700 °C of the C-TOB film, diffraction peaks of anatase, rutile and sodium titanate were observed.

Fig. 2 shows the surface morphologies of the TOB, C-TOB, C6-TOB and C7-TOB films. The surface morphologies of the TOB and C-TOB as shown in Fig. 2a–c were discussed in the previous study [14]. Only the outer layer of the TOB film was modified after chemical treatment [14]. On the surface of the C6-TOB film, fiber-

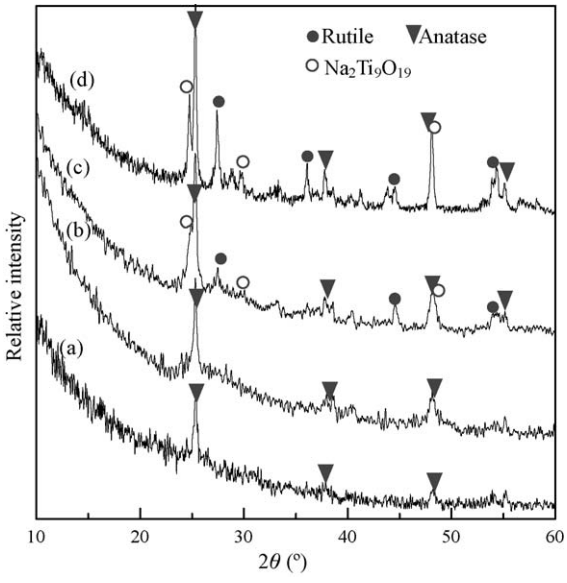

Fig. 1. XRD patterns of (a) TOB, (b) C-TOB, (c) C6-TOB and (d) C7-TOB films.