Journal of Alloys and Compounds 509S (2011) S478–S481

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Effect of electrolyte on surface properties of pure titanium coated by plasma electrolytic oxidation

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ARTICLE INFO

Article history:
Received 4 July 2010
Received in revised form 10 February 2011
Accepted 10 February 2011
Available online 17 February 2011

Keywords:
Pure titanium
Plasma electrolytic oxidation
Electrolyte
Surface
Anatase

ABSTRACT

The present study investigated the surface characteristics of pure titanium subjected to a plasma electrolytic oxidation (PEO) process using two different electrolytes containing either potassium pyrophosphate or potassium triphosphate. For this purpose, a series of PEO coating were carried out at ambient temperature with a current density of 200 mA/cm^2. The surface structures of the oxide films were observed via scanning electron microscopy and the volume fractions of constitutive phases were determined based on X-ray diffraction analysis. The surface roughness of the PEO-coated sample in the electrolyte with potassium pyrophosphate was more complicated than that with potassium triphosphate. The volume fraction of metastable anatase phase in the sample coated with potassium pyrophosphate was relatively higher than that with potassium triphosphate, which was mainly attributed to different electrochemical reactions between the substrate and electrolytes during PEO coating. It was also found that the oxide film coated in the potassium pyrophosphate containing electrolyte showed the easy formation of biomimetic apatite in a simulated body fluid solution.

1. Introduction

Since the late 1960s, titanium and its alloys have been used in the fields of orthopedics and dentistry due to their abilities to exhibit high specific strength, high corrosion resistance, and chemical inertness particularly in biological circumstances [1–4]. Despite these attractive properties, their passive films were somewhat bioinert in nature so that sufficient adhesion of bone cells to implant surface was delayed after surgical treatment [5]. To enhance the capability of rapid bone-to-implant anchorage, previous investigations showed that the surface roughness of titanium implants played a favorable role in promoting osseointegration [6–8]. In addition to surface roughness, Kokubo et al. [9] reported based on SBF solution tests that, when metastable anatase phase was present in the titanium oxide film, the formation of biomimetic apatite was triggered to a greater extent than rutile phase. In order to use the two beneficial effects related to the surface roughness and anatase phase, a surface treatment with a high energy state would be applied. In this regard, plasma electrolytic oxidation (PEO) coating could be used to modify the surface structure as well as the constitutive phase of the titanium oxide film by controlling electrolytes, current density, coating time, waveform, etc. [10–13]. Among these parameters for PEO coating, the selection of the appropriate electrolytes was of great significance since different electrochemical reactions of ionized chemical elements influenced the occurrence of micro arcs and temperature of plasma bubbles which are the factor determining surface characteristics of the oxide film as could be seen from Fig. 1 [14–16].

Here, two different electrolytes containing either potassium triphosphate (K_3PO_4) or potassium pyrophosphate ($K_4P_2O_7$) were chosen due to their harmlessness to human body [17]. Then, PEO coatings were carried out to investigate their roles of electrolytes on the surface roughness and the constitution of anatase and rutile phases in the oxide films of titanium and to observe the propensity of biomimetic apatite formation in a simulated body fluid (SBF) solution.

2. Experimental procedures

The substrate sample used in this study was commercially pure titanium (Grade II) plates with dimensions of 20 mm × 10 mm × 2 mm. Prior to the PEO coating, the flat titanium plates were gradually ground with # 200–1000 abrasive papers and ultrasonically cleaned in acetone. The electrolytes tabulated in Table 1 were prepared. For both electrolytes, the values of pH and electric conductivity were approximately ~13 and ~23 mS/cm, respectively. PEO coating was carried out using a 20 kW AC power supply equipped with stirring and cooling systems. The AC power supply had an electrolyte cell consisting of a glass-vessel container with a sample holder and a cathode composed of stainless steel in the electrolyte. The temperature of the electrolyte was maintained at 293 K to stabilize the electrochemical reactions accompanying plasma arcs. A current density of 200 mA/cm^2 was applied for 300 s.

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doi:10.1016/j.jallcom.2011.02.056

Table 1
Compositions of two electrolytes used for the present PEO coating of pure titanium.

Electrolyte	K_3PO_4	$K_4P_2O_7$	KOH
Cell A	0.02 M	–	0.1 M
Cell B	–	0.02 M	0.1 M

The PEO-coated samples were rinsed with distilled water, dried in warm air, and immersed in a SBF solution for 7, 14, and 21 days. The ion concentrations of the SBF solution were similar to those of human blood plasma [18]. Each sample was immersed in a polyethylene beaker containing 50 ml of the SBF solution. The SBF solution was refreshed every day to maintain the ionic concentrations. The surface morphologies of each sample were observed by field-emission scanning electron microscopy (HITACHI, S-4800). A non-contact 3D surface measurement system (U-surf, NANOFOCUS) was also used for topographical observation of the PEO-coated samples. Surface roughness was commonly characterized by arithmetic mean roughness (R_a) and root mean square roughness (R_q). In general, the surface area became roughened as both values increased. The phase structure and relative volume fractions of the anatase and rutile phases were elucidated by X-ray diffraction (RIGAKU, D-MAX 2500).

3. Results and discussion

Fig. 2 shows voltage–time curves during the PEO process of pure titanium under Cells A and B conditions. The plasma bubbles occurred initially and the responding voltage steeply increased up to ~250 V, resulting in the formation of thin oxide films due to the passivating effect of the electrolytes [19]. Once dielectric breakdown started, micro arcing was initiated on the surface of the samples. For Cells A and B conditions, the final voltages were measured to be ~340 and ~370 V. This was attributed to the different electrochemical reactions which depended on the composition of electrolytes. As the responding voltage was directly proportional to the reciprocal reaction of the ions, the electrochemical resistance of Cell B was somewhat higher than that of Cell A.

Fig. 3 shows SEM images revealing surface morphologies of the PEO-coated samples under Cells A and B. The surface of oxide films contained many micro-pores with uniform distributions, which was typical of samples after PEO coating. Two important things can be drawn from Fig. 3. First, the average size of pores found in Cell A was twice as large as that found in Cell B. Second, the pit-like pores existed on the surface of the oxide film from Cell A (Fig. 3(a)), while crater-like pores appeared in the case of Cell B (Fig. 3(b)). It has been established that the formation of micro

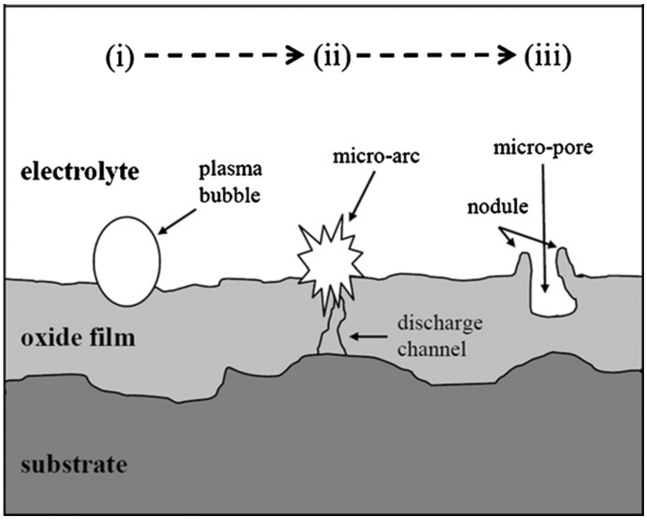

Fig. 1. Schematic diagram of the PEO coating to form the oxide film by plasma bubble implosion: (i) plasma bubbles take place on surface, (ii) micro-arcs, which are generated through the narrow discharge channels, lead to the implosion, and (iii) this implosion makes micro-pores in the oxide film.

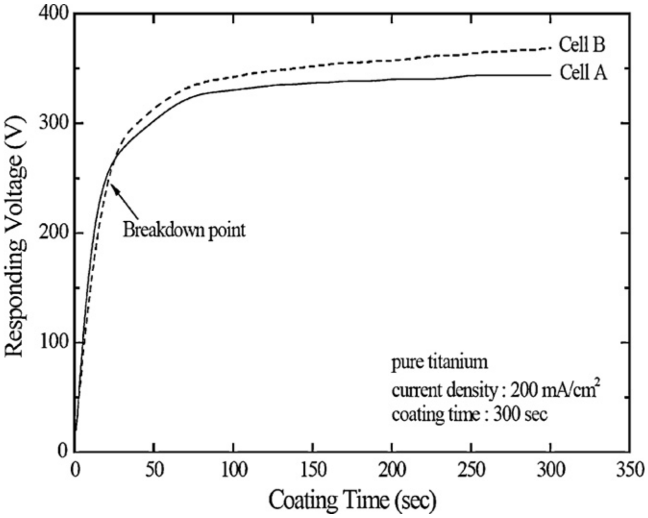

Fig. 2. Typical voltage–time curves of pure titanium samples during the PEO coating in two different electrolytes.

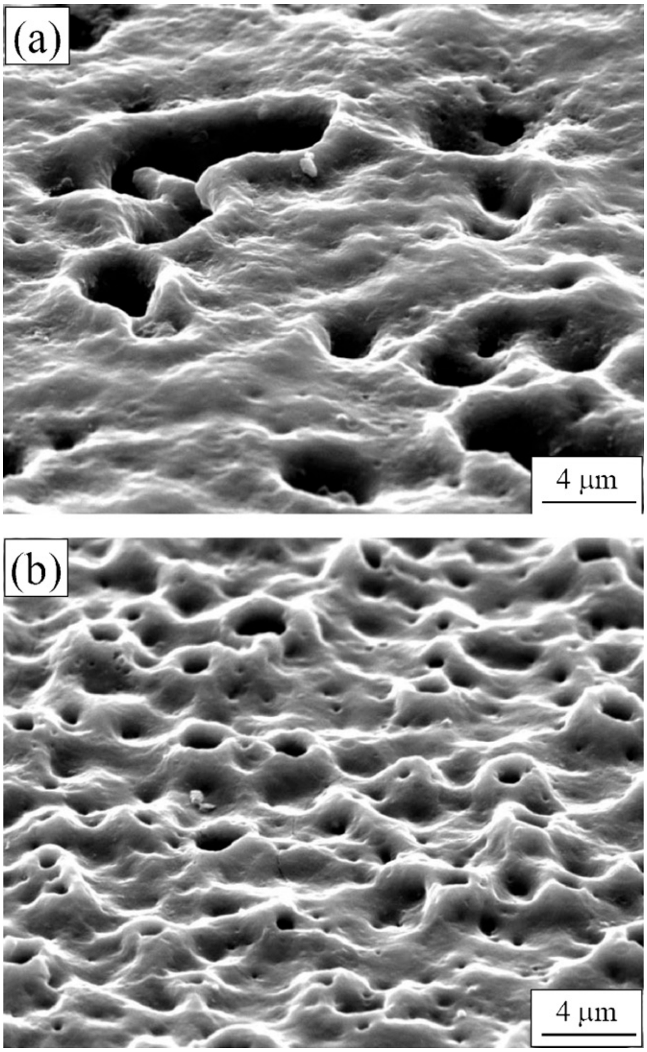

Fig. 3. Surface structures of the oxide films of pure titanium samples via PEO coating in (a) Cells A and (b) B electrolytes.

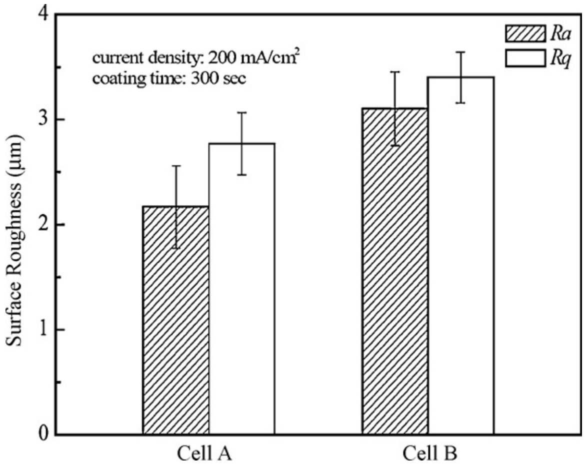

Fig. 4. Surface roughness of the oxide films of the PEO-coated titanium samples. (R_a: average arithmetic roughness, R_q: root mean square roughness).

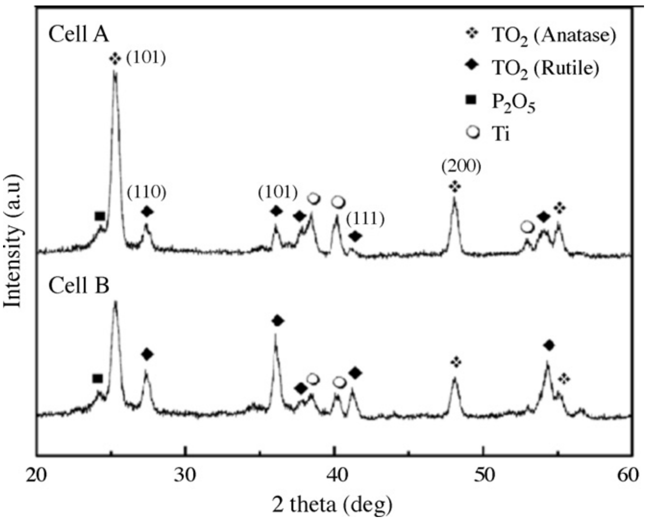

Fig. 5. XRD patterns of the oxide films of the PEO-coated titanium samples.

pores was closely related to chemical interactions during plasma electrolysis [10]. Since the ionized plasma bubbles of Cell A were more thermally pronounced than of Cell B as aforementioned, they were imploded to form lager pores in Cell A than in Cell B. Such crater-like pores suggested that the roughness of the oxide film coated under Cell B appeared to be higher from the SEM images, which was confirmed by direct surface roughness measurements. This explanation was consistent with the observations where the values of R_a in the oxide films in the Cells A and B were estimated to be ~2.2 and ~2.8 μm, and R_q to be ~3.1 and 3.4 μm, respectively, as clearly shown in Fig. 4. In the community, the relationship between the ideal pore size and osseointegration (or apatite formation) was still under debate [20,21]. Nashimoto et al. [21] have postulated that the fine pore size as low as 1.2 μm was the most suitable for cell anchoring. Thus, it was thought that the surface of the oxide film coated in the Cell B might lead to the formation of apatite with ease.

Fig. 5 shows the XRD patterns of the PEO-coated samples under Cells A and B. The anatase, rutile, titanium, and P_2O_5 were detected from the individual peaks. The compound of P_2O_5 was normally a by-product of the electrochemical reaction between the electrolytes and the titanium substrate. Thus, the anatase and rutile phases were important as constituent phases present in the oxide films. According to qualitative FWHM analysis, the volume fraction of the anatase phases under Cell B was relatively higher than under Cell A. This was still insufficient to provide information on the volume ratios of each phase. Thus, the volume fraction of rutile phase (X_R) is measured using the following equation [22]:

$$X_R = \frac{1}{1 + (0.8 I_A / I_R)} \qquad (1)$$

in which I_A and I_R denote integrated intensity values of the anatase (1 0 1) plane and rutile (1 1 0) plane peaks, respectively. The volume fractions of anatase and rutile were determined to be

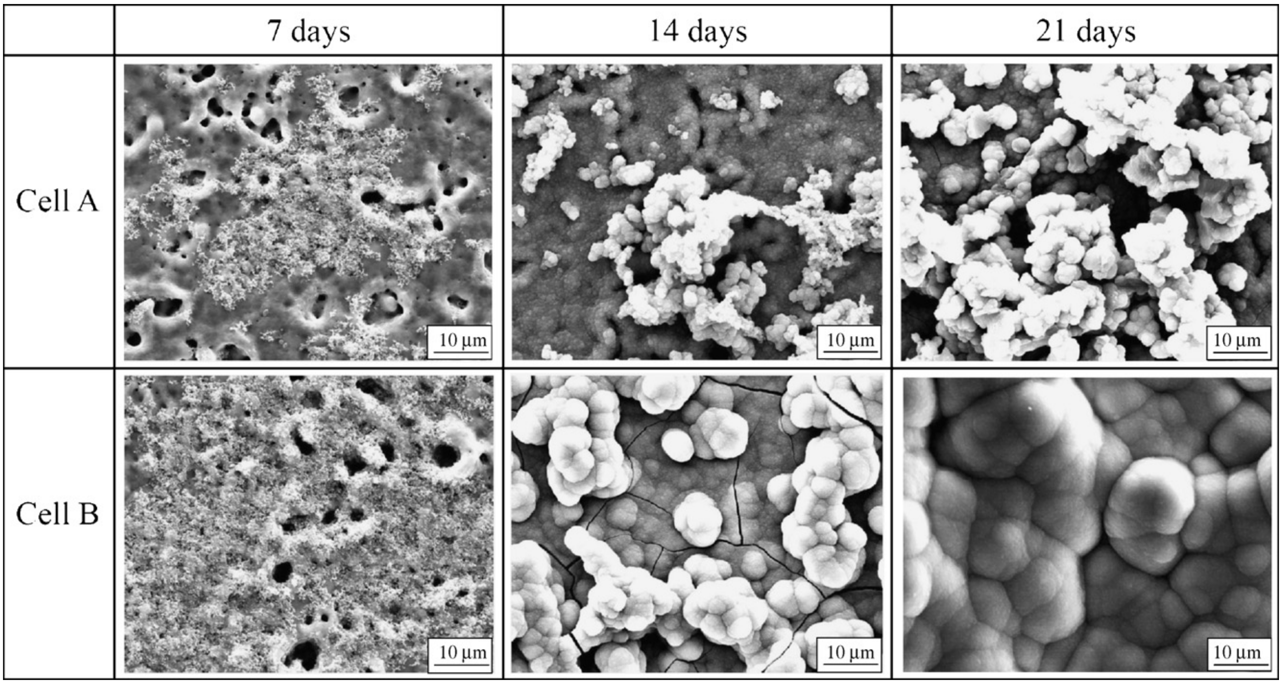

Fig. 6. Formation of the biomimetic apatite on the PEO-coated titanium samples after immersion tests in the SBF solution for 7, 14, and 21 days.

approximately ∼0.69 and ∼0.31 in the oxide films from Cell A, and ∼0.85 and ∼0.15 from Cell B, respectively. Since anatase was thermally metastable, it readily transformed into rutile phase at relatively high temperatures [23]. As noted earlier, the temperature of the plasma bubbles was somewhat high during the PEO treatment using Cell A. Hence, the anatase phase in the oxide film from Cell A changed into the rutile phase, whereas a more amount of anatase phase still existed in the oxide film from Cell B.

Fig. 6 shows surface morphologies of the PEO-treated samples subjected to immersion in a SBF solution for 7, 14, and 21 days. Fine precipitates of apatite were detected on the both oxide films in 7 days. It was found, however, that fine precipitates on the oxide film from Cell B were much denser than that from Cell A, which was in part attributed to the rough surface structure of the oxide film. Recently, Uchida et al. [24] demonstrated that the anatase phase possessed a better capability for apatite formation compared to the rutile phase. The crystallographic compatibility between the biomimetic apatite of (0 0 0 1) plane and the anatase phase of (1 1 0) plane was better than that between the biomimetic apatite of (0 0 0 1) plane and the rutile phase of (1 0 1) plane. As a result, the anatase phase was anticipated to exhibit a higher ability for apatite precipitation than what the rutile phase did. Thus, the surface of the oxide film from Cell B with abundant anatase phases showed higher density of these precipitates. After immersion in the SBF solution for 14 days or more, the surface of the oxide film from Cell B became fully covered with dense biomimetic apatite, while apatite particles were deposited on the surface in Cell A. If apatite precipitates were formed uniformly throughout the oxide film surface, their additional growth would become easier. Thus, the oxide film coated in Cell B exhibited denser biomimetic apatite structure than that in Cell A.

4. Summary

The effect of the electrolytes on the surface characteristics of pure titanium subjected to PEO coating was investigated. Comparing the surface morphologies of the oxide films from Cells A and B, a higher electrochemical resistance and an exothermal reaction under Cell B condition produced crater-like structure of micro pores, resulting in high surface roughness. The present XRD patterns showed that the oxide film from Cell B contained more abundant anatase phase than that from Cell A. From the SBF tests, the surface of the oxide film from Cell B revealed a rapid growth rate of biomimetic apatite. Consequently, it was found that, as compared to the oxide film from Cell A, the oxide film from Cell B featured rougher surface as well as higher amount of anatase phase, leading to the excellent formation of the biomimetic apatite in the SBF solution.

Acknowledgement

This work was supported by the National Research Foundation (2009-0079807).

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