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Ceramics International 32 (2006) 527–531

CERAMICS
INTERNATIONAL

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Hydroxyapatite formation on oxide films containing Ca and P by hydrothermal treatment

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Received 27 August 2004; received in revised form 25 February 2005; accepted 15 April 2005
Available online 1 June 2005

Abstract

Oxide films were formed on titanium by means of microarc oxidation (MAO) using a direct current power supply. The oxide films containing Ca and P were obtained in an electrolyte containing β-glycerophosphate sodium salt pentahydrate (β-GP) and calcium acetate (CA). The surfaces of the oxide films were rough and porous, and the concentration of Ca and P were 7.3 mol% and 6.4 mol%, respectively, when MAO was performed in an electrolyte containing 0.04 M β-GP and 0.10 M CA at 200 A/m^2 current density and 430 V final voltage. The oxide film consists of anatase, rutile and an amorphous phase. After hydrothermal treatment at 190 °C, the hydroxyapatite crystals were precipitated on the oxide film surfaces. The amount of hydroxyapatite crystals increased by increasing the hydrothermal treatment time and the Ca/P ratio in the oxide film.

Keywords: D. TiO_2; Microarc oxidation; Hydroxyapatite

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1. Introduction

Titanium and its alloys are widely used for dental and orthopaedic implants under load-bearing conditions because of excellent biocompatibility, mechanical properties and high resistance [1,2], but cannot directly bond to bone. Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (HA) is an important active material to chemically bond to living bone. Owing to the lower mechanical properties of HA, its application has been limited in clinics. Therefore, coating HA on titanium and its alloy is a popular method to provide a composite with both active material and excellent mechanical properties. For this purpose, various coating methods have been developed [3–8]. Currently, the hydroxyapatite plasma spray coating is widely used in cementless hip replacement surgery [9]. The hydroxyapatite coating, however, gives rise to problems including composition and structure control, and tightly bonding to the substrate [10,11]. The purpose of the present study is to form hydroxyapatite coating on titanium. Oxide films containing Ca and P were obtained by microarc oxidation on a Ti substrate. After hydrothermal treatment, the hydroxyapatite crystals were precipitated on the surfaces of films.

2. Experimental

Commercially pure Ti metal plates (sample size 10 mm × 10 mm × 1 mm) were abraded with SiC sandpaper no. 800, then rinsed by a mixture of hydrofluoric and nitric acids (HF/HNO_3) at 1:3 ratios, and finally washed with acetone and distilled water in an ultrasonic cleaner. The oxide films were obtained by MAO on a Ti substrate in an electrolyte containing 0.04 M β-glycerophosphate sodium salt pentahydrate and 0.10 M calcium acetate. The MAO was performed at 200 A/m^2 current density. The oxide films were hydrothermally treated in water solution adjusted to pH 11.0–11.5 by adding NaOH solution at 190 °C in an autoclave.

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doi:10.1016/j.ceramint.2005.04.006

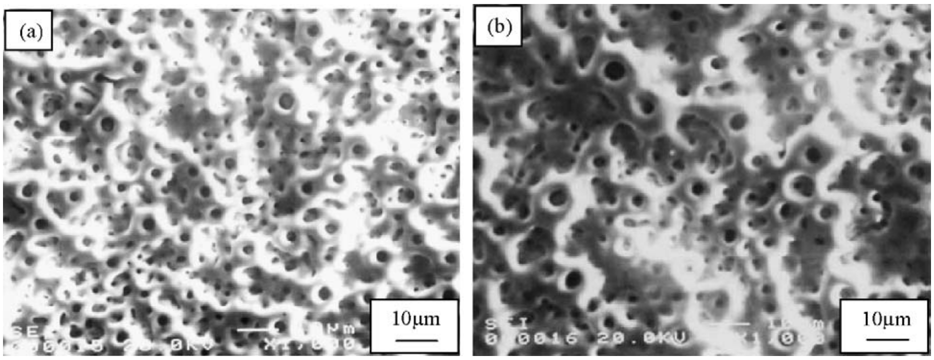

Fig. 1. SEM micrographs of oxide films formed in the electrolyte of 0.04 M β-GP and 0.10 M CA at 200 A/m^2: (a) 350 V and (b) 430 V.

The chemical composition of the film was semi-quantitatively analyzed with an electron probe micro analyzer (EPMA; JAX-8800, JEOL Co., Japan). The microstructure of the sample surface was observed by scanning electron microscopy (SEM; JSM-6300, JEOL Co., Japan). The crystal structure was analyzed by X-ray diffraction (XRD; RTNT-1500, Rigaku Co., Japan) with Cu Kα radiation 40 kV 200 mA at a scanning speed of 4.00°/min, and with the scanning range (2θ) from 10° to 60°.

3. Results and discussion

Fig. 1 shows the microstructure of the oxide films in the electrolyte containing 0.04 M β-GP and 0.10 M CA. The oxide films were rough and porous, with pores well separated and homogenously distributed over the sample. As the titanium substrate surface was initially smooth, the porous surface originates from the high temperature and high pressure in the discharge channels during the MAO process.

Table 1 shows the chemical composition of the films obtained in the electrolyte containing 0.04 M β-GP and 0.10 M CA at 200 A/m^2. It was found that concentration of Ca increases with increasing final voltage, and P does not significantly change with final voltage. The concentration of Ca and P were 7.3 mol% and 6.4 mol%, respectively, when MAO was performed in the electrolyte containing 0.04 M β-GP and 0.10 M CA at 200 A/m^2 and 430 V final voltage.

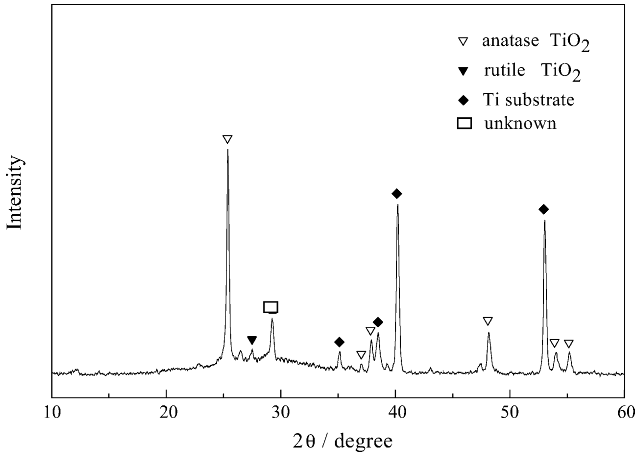

Fig. 2. X-ray diffraction patterns of surface oxide film formed in the electrolyte of 0.04 M β-GP and 0.10 M CA at 200 A/m^2 and 430 V before hydrothermal treatment.

XRD patterns of the oxide film obtained by MAO are given in Fig. 2. The oxide film is mainly composed of anatase, rutile and an amorphous phase. In addition to the phases mentioned above, an additional peak at (2θ 29.24°) is not clear. They maybe were complex compounds composed of Ca and P, existing in the oxide film through the whole voltage treatment.

The oxide film with Ca/P ratio 1.14 was treated hydrothermally in an autoclave at 190 °C for 10 h, and the pH of water was adjusted to 11.0–11.5 by adding NaOH.

Table 1
Parameters of microarc oxidation of Ti

Electrolytes (M)		CD (A/m^2)	Final voltage (V)	Composition of oxide film (mol%)					
β-GP	CA			Ti	O	Ca	P	C	Ca/P
0.04	0.10	200	250	30.9	62.2	1.3	5.6	0.0	0.23
0.04	0.10	200	300	28.4	63.1	2.4	6.1	0.0	0.39
0.04	0.10	200	350	24.6	63.8	4.9	6.6	0.1	0.74
0.04	0.10	200	380	25.3	62.7	5.2	6.7	0.1	0.78
0.04	0.10	200	400	25.2	62.5	5.7	6.6	0.0	0.86
0.04	0.10	200	430	24.2	62.1	7.3	6.4	0.0	1.14

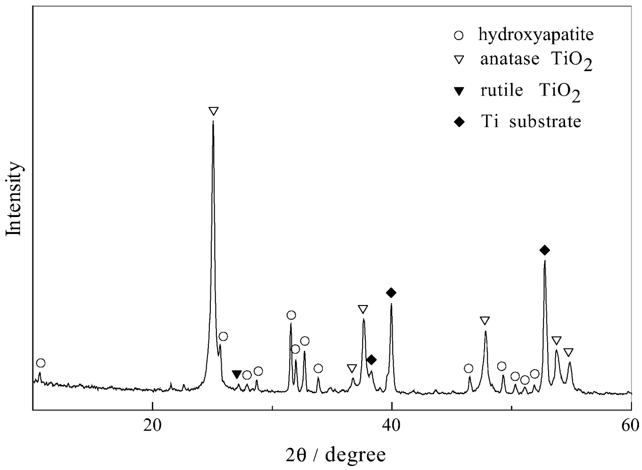

Fig. 3. X-ray diffraction patterns of surface oxide film formed in the electrolyte of 0.04 M β-GP and 0.10 M CA at 200 A/m^2 and 430 V after hydrothermal treatment.

Fig. 3 shows the XRD patterns of the oxide film after hydrothermal treatment. The unknown and amorphous phases disappeared, and the peaks corresponding to hydroxyapatite were clearly identified. Fig. 4 shows microstructures of the oxide films after hydrothermal treatment. The SEM micrographs revealed that the hydroxyapatite crystals were precipitated on the oxide film surfaces and the porous microstructure of the oxide film was retained. It also can be seen that the amount of hydroxyapatite increases with the increase of the hydrothermal treatment time and final voltage (Fig. 5). The difference in amount of hydroxyapatite crystals can be attributed to difference in Ca/P ratios. As shown in Table 1, the Ca/P ratios increased with the increase of the final voltage, and then the Ca/P ratio was too small to form large hydroxyapatite crystals when the final voltage was lower.

The formation process of HA crystals was affected by two factors: nucleation of HA and diffusion of Ca and P from inner layer towards the film surface. It is well known that Ti-OH groups induce HA nucleation [12,13], similar to Si-OH [14] and Zr-OH groups [15]. When the oxide films were hydrothermally treated at 190 °C in a water solution with a pH of 11.0–11.5, Ti-OH groups were produced on the oxide film surface. HA crystals were precipitated on the oxide film surface, which was mainly attributed to the effect of Ti-OH groups. The porous structure of the surface also plays an important role in inducing HA nucleation. Li et al. [16] showed that the porous anatase induces HA nucleation, while dense single crystal anatase does not. Yang also reported that porous anatase formed by microarc oxidation induces HA formation when immersed in a simulated body fluid containing Ca^{2+} and PO_4^{3-} ions [17].

The HA nuclei were formed due to the effects of Ti-OH groups and the porous structure of surface, and they spontaneously grow and give rise to HA according to the following reaction [18]:

$$10Ca^{2+} + 6PO_4^{3-} + 2OH^- \leftrightarrow Ca_{10}(PO_4)_6(OH)_2$$

The above reaction resulted in a Ca^{2+} and PO_4^{3-} ions deficiency as a result of Ca^{2+} and PO_4^{3-} ions diffusion from the inner layer towards the surface. Finally, a large amount

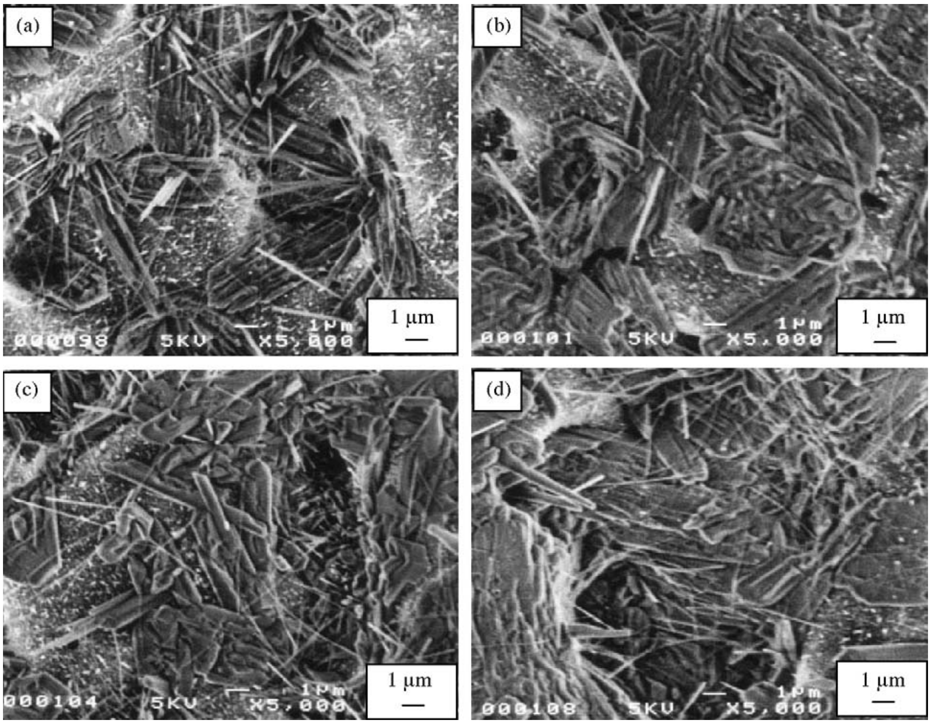

Fig. 4. (a) SEM micrographs of oxide films after hydrothermal treatment: (a) 4 h; (b) 12 h; (c) 18 h and (d) 24 h.

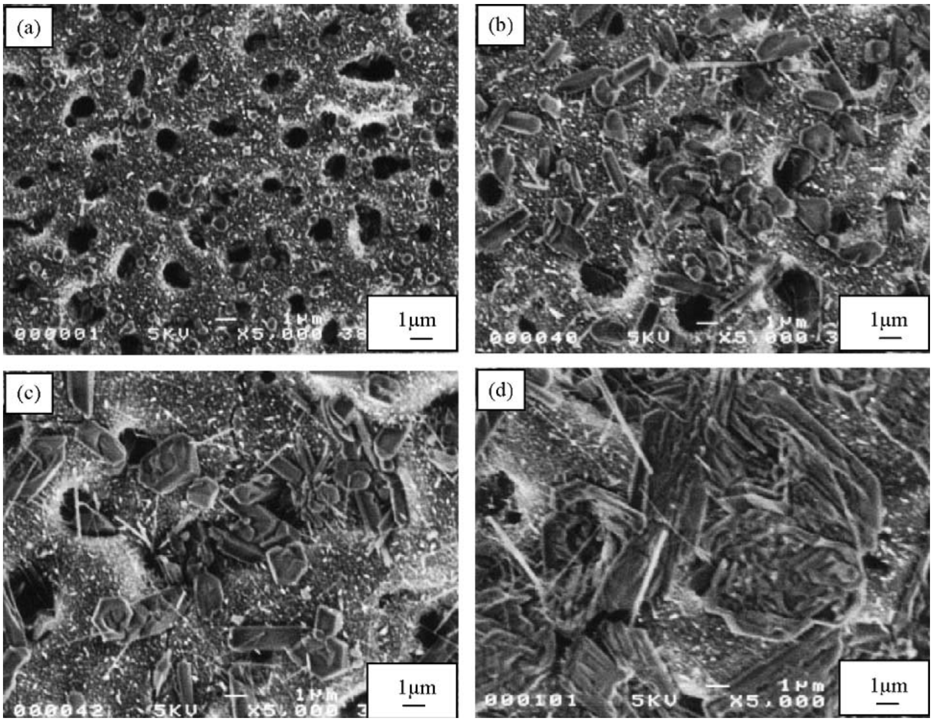

Fig. 5. SEM micrographs of oxide films after hydrothermal treatment 12 h: (a) 300 V; (b) 350 V; (c) 400 V and (d) 430 V.

hydroxyapatite crystals were precipitated on the oxide film surface.

4. Conclusions

The electrolyte containing β-GP and CA is suitable to form an oxide film containing Ca and P on titanium by microarc oxidation. The surfaces of the oxide films displayed a rough and porous structure. The concentration of Ca and P was 7.3 mol% and 6.4 mol%, respectively, when MAO was performed in an electrolyte containing 0.04 M β-GP and 0.10 M CA at 200 A/m^2 and 430 V final voltage. The oxide film consists of anatase, rutile and amorphous phase. After hydrothermal treatment, hydroxyapatite crystals were precipitated on the oxide film surfaces. The amount of hydroxyapatite crystals increased by increasing the hydrothermal treatment time and the Ca/P ratio in the oxide film.

Acknowledgements

The authors are grateful to Ryusuke Osada of Analysis Center of Material of Chiba Institute of Technology for assistance in EPMA and SEM investigation.

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