

Surface Analysis of Anodic Oxide Films Containing Phosphorus on Titanium

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Purpose: To examine the effect of phosphoric acid solution on the anodic oxide film of titanium. **Materials and Methods:** Commercially pure grade 2 titanium specimens were prepared and anodized in phosphoric acid solution at a constant current density (70 A/m²). Specimens were evaluated by means of scanning electron microscopy, x-ray diffraction analysis, electron probe microanalysis, energy-dispersive spectroscopy, profilometry, and atomic force microscopy. **Results:** The anodic oxide film was observed to consist of a porous or non-uniform layer and a dense or uniform layer. X-ray diffraction and energy-dispersive spectroscopic analyses indicated that the film consisted of a mixture of anatase and amorphous oxide, with the incorporation of phosphorus. **Discussion:** The degree of oxide crystallinity was observed to increase with an increase in voltage but decreased as the electrolyte concentration was increased. In addition, the concentration of phosphorus also increased as the electrolyte concentration and voltage increased. **Conclusions:** Electrolyte concentration and voltage play an important role in governing the anodic oxide thickness, composition, and degree of oxide crystallinity. (INT J ORAL MAXILLOFAC IMPLANTS 2002;17:331–336)

Key words: anodic oxide, surface properties, titanium

Titanium (Ti) is widely used as a metallic biomaterial for dental and orthopedic implants. It has good biocompatibility, which is attributed to the stable oxide film formed on its surface.^{1,2} Researchers have indicated that the stable oxides of Ti and its alloys provide surfaces for favorable biologic integration.^{3,4} It is also known that the stability of the oxide depends strongly on the composition, struc-

ture, and thickness of the film.⁵ A thin amorphous, but stoichiometrically defective, titanium dioxide (TiO₂) passive film can be spontaneously formed in many aqueous environments or air. However, interactions between Ti implants and the surrounding biologic environment do occur by releasing metallic ions and compounds into the tissues and allowing oxygen diffusion into their surface structure. It has been reported that the passive oxide film grows with time by dissolution and reprecipitation in vivo.^{1,6} Since biocompatibility and bone-implant interaction are governed by the implant surface, an increase in the oxide thickness can be optimized, thereby improving the biologic response.

Anodic oxidation is one process for increasing oxide thickness. Anodization has been reported to enhance oxide thickness of Ti and its alloys, thereby increasing corrosion resistance.^{7,8} However, not all electrolytes resulted in a thick oxide layer. In Na₂HPO₄/KH₂PO₄ (disodium hydrogen phosphate and potassium dihydrogen phosphate) buffer solutions, Ti and Ti alloys were found to form anodic oxide layers with low thickness (the thickest was about 180 nm).⁹ In previous work, a relatively thick anodic oxide layer of 2 µm had been produced using

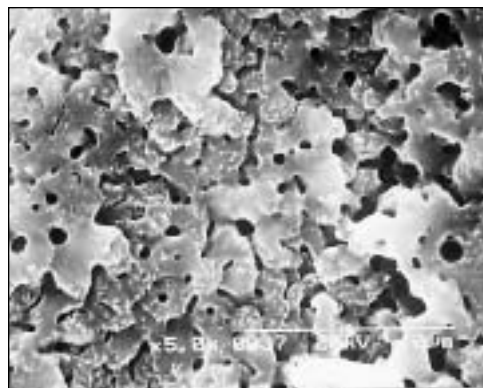
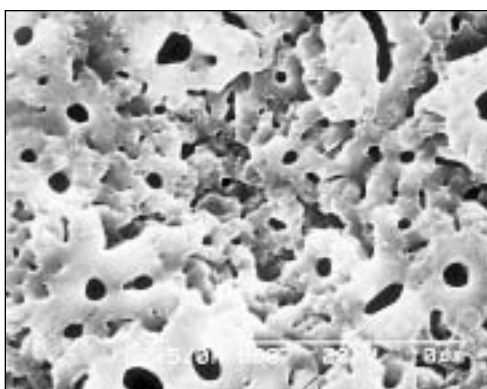
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Fig 1a to 1c Morphologies of anodic oxide films of titanium at 70 A/m² in H₃PO₄ solution.**Fig 1a** 0.15 mol/L, 320 V.**Fig 1b** 0.15 mol/L, 380 V.**Fig 1c** 0.3 mol/L, 380 V.

phosphoric acid (H₃PO₄) solution.¹⁰ However, further characterization of the oxide layer formed using H₃PO₄ solution needs to be done. In this study, the effect of electrolyte concentration on the microstructure of thick anodic oxide film of Ti produced using aqueous H₃PO₄ was investigated.

MATERIALS AND METHODS

Specimens (size 30×10×1 mm) were cut from commercially pure Ti plates (grade 2). Three parallel specimens were prepared for each processing condition. The specimens were then abraded with silicon carbide sandpaper (no. 1500), ultrasonically rinsed in acetone for 180 seconds, subsequently pickled by a mixture of aqueous hydrofluoric acid and nitric acid (the molar ratio HF/HNO₃ equaled 1:3), and finally rinsed with distilled water and dried. Galvanostatic anodization was employed in aqueous H₃PO₄. The electrolyte varied from 0.05 to 0.30 mol/L and cur-

rent density was 70 A/m². The temperature was maintained at 20°C by water bath during anodizing. After being anodized, specimens were rinsed with deionized water several times and dried.

The morphologies of anodic oxide films were observed by scanning electron microscopy (SEM) (Model S-2300, Hitachi, Tokyo, Japan). The structures and compositions of anodic oxides were analyzed by X-ray diffraction (XRD) with copper potassium α radiation (30kV and 40mA, X'pert-APD, Philips, Hilversum, The Netherlands); electron probe microanalysis (EPMA) (Shimadzu EPMA 1600, Kyoto, Japan); and energy-dispersive spectroscopy (EDS). The thickness was qualitatively analyzed by comparing the height of the XRD peak of titanium and by SEM measurement of each individual cross section. The surface roughness was measured by SurfTest SV-402 (Mitutoyo Instruments, Tokyo, Japan) in profile and the results of measured roughness were presented by the following parameters: R_a = arithmetic mean deviation of the roughness profile; R_z = mean peak-to-valley height; and R_y = maximum height of the roughness profile. The topography of anodic oxide films was imaged by atomic force microscopy (AFM) (NanoScope IIIa, Digital Instruments, Santa Barbara, CA) in tapping mode.

RESULTS

The anodic oxide films in aqueous H₃PO₄ were observed to have overlapping micro-domains consisting of pores (Fig 1a). The size of the micro-domains on the oxide film increased with an increase in the electrolyte concentration and voltage (Fig 1b). At a concentration of 0.3 mol/L, cracks were observed in the oxide film of a layered structure (Fig 1c).

Fig 2 XRD patterns of anodic oxide films at 70 A/m² in 0.15 mol/L H₃PO₄ solution. (a) 263 V; (b) 324 V; (c) 358 V.

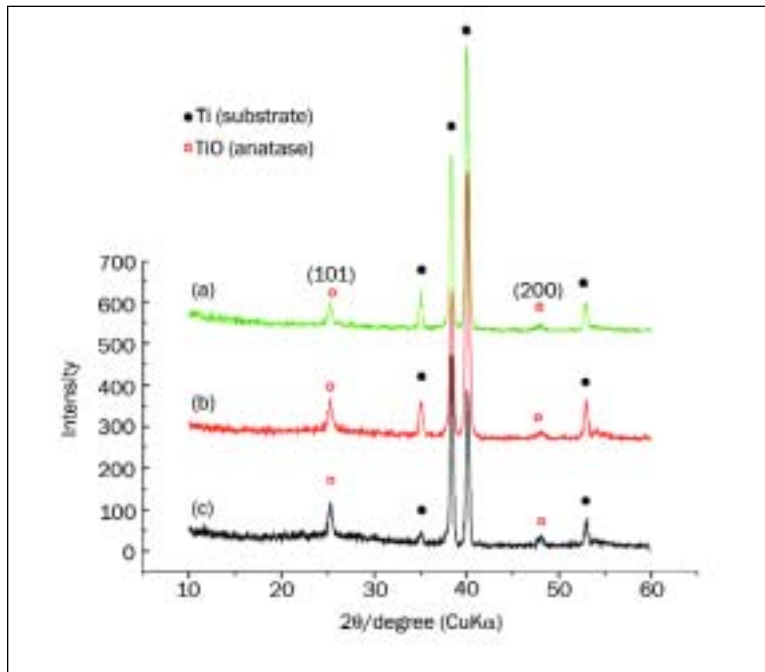
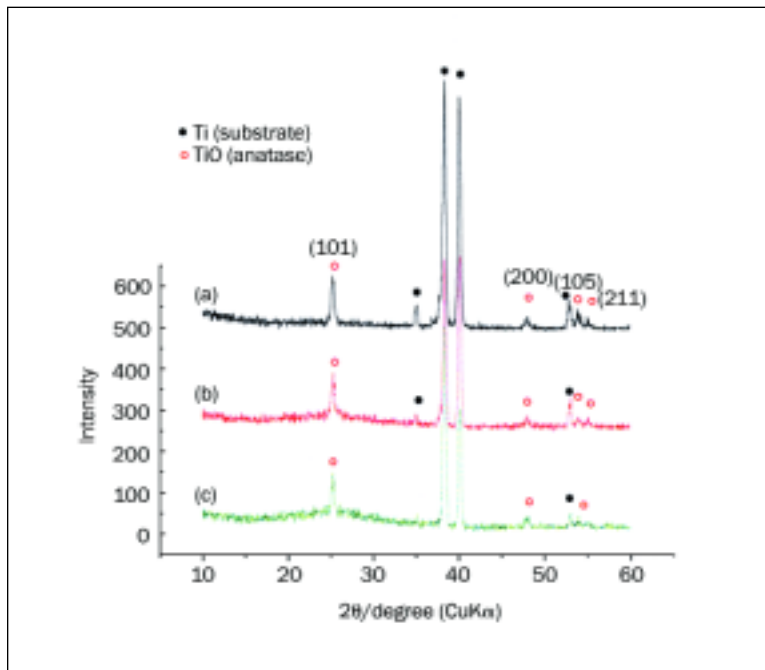


Fig 3 XRD patterns of anodic oxide films at 70 A/m² in H₃PO₄ solution. (a) 0.05 mol/L, 300 V; (b) 0.15 mol/L, 380 V; (c) 0.3 mol/L, 380 V.



XRD patterns indicated that the anodic oxide consisted of a mixture of amorphous and anatase oxide. As the final voltage was increased, the degree of oxide crystallinity also increased (Fig 2). However, as the electrolyte concentration was increased, the degree of oxide crystallinity decreased (Fig 3). Using the peak heights of the Ti substrate as references, the thickness of the oxide film was observed to increase as the electrolyte concentration increased. From the baseline of the spectra, it was seen that an increase in the electrolyte concentra-

tion resulted in an increase in the amorphous oxide. The anodic oxide film was its most crystalline at a final voltage of 325 V in 0.05 mol/L H₃PO₄ and had a great number of shallow or deep pores (Fig 4).

As shown in Table 1, the surface roughness was significantly higher than that of the original surface before anodized, ie, $R_a = 0.340 \pm 0.01 \mu\text{m}$, $R_z = 1.866 \pm 0.057 \mu\text{m}$, and $R_y = 2.400 \pm 0.200 \mu\text{m}$. As voltage and/or electrolyte concentration was increased, an increase in the roughness of anodic oxide films was observed.

Results of the EDS analysis of the anodic oxide films are shown in Table 2. As the electrolyte concentration and voltage were increased, an increase in P concentration and a decrease in Ti concentration were observed. Similarly, as electrolyte concentration and voltage were increased, the O/Ti ratio was observed to approach 2. As shown in Fig 5, SEM-EPMA analysis of a representative cross section indicated the incorporation of P into the oxide film, with the highest P concentration observed at the interface of the porous or non-uniform layer and the uniform or dense layer.

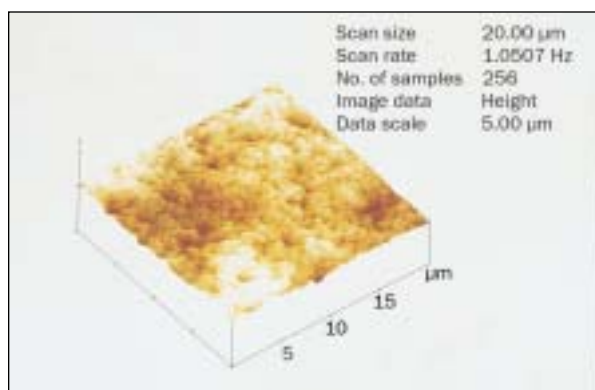


Fig 4 AFM tapping mode image of anodic oxide film of titanium at 70 A/m², 325 V in 0.05 mol/L H₃PO₄.

DISCUSSION

It is known that the surface oxide is responsible for the biologic response to Ti implants. The anodic oxide films formed using different electrolyte concentration and voltage differ in composition, structure, thickness, roughness, and topography. The morphology, thickness, and structure of the anodic oxide film of Ti depend primarily on preparation procedures, anodizing variables, and electrolytes.

Using H₃PO₄ solution, the anodic oxide film was observed to contain P, suggesting that the P-

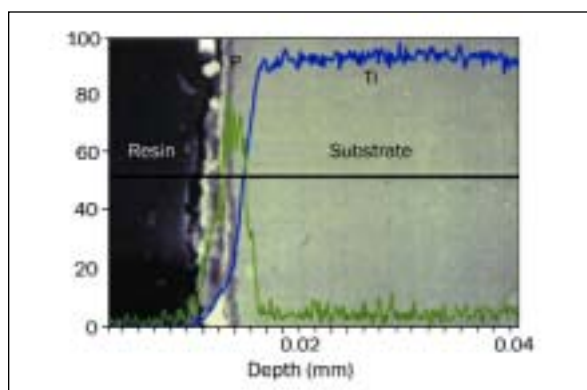


Fig 5 SEM-EPMA analysis of cross section of anodized titanium at 70 A/m², 325 V in 0.05 mol/L H₃PO₄.

Table 1 Roughness of Anodic Oxide Films with Phosphorus on Titanium

Electrolyte concentration (mol/L)	Final voltage (V)	Roughness (μm)		
		R _a	R _z	R _y
0.05	315	0.356 ± 0.005	2.533 ± 0.251	3.033 ± 0.251
0.05	325	0.466 ± 0.021	3.100 ± 0.264	3.900 ± 0.700
0.10	325	0.350 ± 0.010	2.200 ± 0.100	2.666 ± 0.351
0.15	342	0.383 ± 0.020	2.533 ± 0.231	2.933 ± 0.152
0.15	380	0.386 ± 0.020	2.800 ± 0.200	3.200 ± 0.100
0.15	391	0.516 ± 0.037	4.700 ± 0.500	5.966 ± 0.152
0.30	380	0.450 ± 0.010	2.566 ± 0.152	2.733 ± 0.208

Table 2 Composition of Anodic Oxide Films of Titanium by EDS Analysis

Electrolyte concentration (mol/L)	Final voltage (V)	Composition (mol%)			
		Ti	P	O	O/Ti
0.05	325	38.857 ± 1.494	2.376 ± 0.126	58.760 ± 1.569	1.51
0.10	325	41.023 ± 0.896	2.346 ± 0.059	56.630 ± 0.888	1.38
0.15	342	35.580 ± 1.089	4.556 ± 0.302	59.863 ± 1.151	1.68
0.15	380	34.707 ± 0.648	4.697 ± 0.191	60.600 ± 1.155	1.75
0.30	342	30.297 ± 0.648	7.347 ± 0.480	62.353 ± 1.109	2.06
0.30	380	30.453 ± 1.188	8.333 ± 0.206	61.263 ± 1.262	2.01

containing anodic oxide film enhances the absorption of P and uptake of calcium from the biologic environment to form calcium phosphate.¹¹ As the electrolyte concentration and voltage were increased, an increase in P concentration and a decrease in Ti concentration were observed. Similarly, as electrolyte concentration and voltage were increased, the O/Ti ratio was seen to approach 2. The anodic oxide was O-deficient or O-excessive and the controversy is probably related to mixed forms such as TiO, TiO₂, and Ti₂O₃.¹² A rapid increase of P in the oxide cannot be caused by a single diffusion mechanism for the concentration slope of phosphate ions, but by the migration of phosphate ions into anodic oxide films under the electric field during anodization.

The anodic oxide film produced in this study indicated a mixture of anatase and amorphous oxide. This was in agreement with past studies, suggesting that rutile was not present in the anodic films formed in aqueous solutions.¹³ The degree of crystallinity was observed to increase as the final voltage was increased. However, as the electrolyte concentration was increased, the degree of oxide crystallinity decreased. This suggests that the voltage plays a positive effect on the degree of crystallization. The results further confirmed that the degree of crystallization on the surface oxide cannot be purely thickness-dependent.¹⁴ As the electrolyte concentration was increased, the amount of P in the oxide film also increased. This suggested that the negatively charged P ions migrated into the oxide under the electric field during anodization and thus resulted in a more rapid oxide growth.

It is known that as a general trend, low thickness and rapid growth rate of the oxide favor the formation of oxide films of an amorphous structure.^{15,16} Since the low-crystalline oxide easily dissolves and reacts with chemical species in physiologic fluids, it is preferable that titanium implants be anodized in dilute H₃PO₄. Nevertheless, high concentration of the electrolyte has been observed to result in an oxide film of lower crystallinity and the occurrence of micro-cracks. The low-crystalline oxide suggests that lowering of the oxide stability and micro-cracks might be caused by mechanical or thermal stress produced in the rapid growth of the oxide by reason of the high concentration of the electrolyte. Through investigation of the effects of TiO₂ passive film crystal structure, thickness, and crystallinity on complement C3 surface absorption from diluted human plasma, it was found that anatase and rutile C3 surface concentrations increased with increased oxide thickness and crystallinity, and oxide crystallinity is more influential in C3 adsorption than

oxide thickness.¹⁷ However, the effect of oxide crystallinity on bone responses needs to be evaluated in future studies.

It was also observed from this study that the thickness of the oxide film is higher than that of untreated Ti. With an increase in oxide thickness, the corrosion resistance of the anodized Ti has also been reported to increase.^{7,18} The enhancement of corrosion resistance, in turn, suggests an increase in the biocompatibility of Ti.⁶ In addition, it has been reported that alterations of implant surface topography affect the biologic response.¹⁹⁻²¹ The microstructure in the porous anodic oxide film may influence the biologic response through surface roughness. As such, the effect of microstructure and oxide crystallinity on bone cell responses will be evaluated in future studies.

CONCLUSIONS

The anodic oxide film of Ti produced using H₃PO₄ solution was observed to consist of a porous or non-uniform layer and a dense or uniform layer. X-ray diffraction and EDS analyses indicated that the film consists of a mixture of anatase and amorphous oxide, with the incorporation of phosphorus. The degree of oxide crystallinity was observed to increase with an increase in voltage, but decreased as the electrolyte concentration was increased. In addition, the concentration of P also increased as the electrolyte concentration and voltage were increased. As such, it was concluded that the electrolyte concentration and voltage play an important role in governing the anodic oxide thickness, composition, and degree of oxide crystallinity.

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