

## 양극산화에 의한 티타늄 산화피막의 전기화학적 거동과 형상

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## Electrochemical Behavior and Morphology of Anodic Titanium Oxide Films

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**요약**: 순 티타늄(공업용 순 티타늄, 2급)의 0.5M에서 0.7M 농도의 H<sub>3</sub>PO<sub>4</sub> 용액에서 0.3~1.0 A/dm<sup>2</sup>의 정전류 밀도변화에 따른 anodizing 거동을 관찰하였다. 이때 형성된 산화피막을 SEM과 XRD로 관찰, 분석하였다. 실험결과 0.05M H<sub>3</sub>PO<sub>4</sub> 용액의 조건에서 전압-시간 (V-T)곡선의 초기에는 직선적인 관계를 보였고, 전류밀도가 증가함에 따라 포물선의 형태를 나타내었다. 그리고 V-T곡선의 형태는 전해질의 농도의 증가에 따라 큰 변화가 없었지만, 최종적인 전압은 감소하였다. 티타늄의 산화피막은 전해질 농도와 전류밀도가 증가할수록 미세한 입자 형태에서 눈꽃과 같은 층을 이룬 입자들로 구성된 구조를 나타내었다. 산화막과 전해질의 계면에서의 방전에 의해 산화피막의 국소적인 침착과 용해를 동반하였다. 산화피막의 결정성은 anodizing 전압이 증가할수록 증가하였고 전해질의 농도가 증가할수록 감소하는 경향을 보였다.

**Abstract**: The galvanostatic anodization of commercially pure titanium plate (c.p.Ti, grade 2) was investigated in various concentrations of aqueous H<sub>3</sub>PO<sub>4</sub> from 0.05M to 0.7M. The surfaces of anodic oxide films, formed by the current density in the range between 0.3 and 1.0 A/dm<sup>2</sup>, were analyzed by SEM and XRD. The voltage-time (V-T) curves displayed an initial linear part and a subsequent parabolic part, and the initial slopes increased with an increase in the current density in 0.05M H<sub>3</sub>PO<sub>4</sub>. As the concentration of the electrolyte increased, the V-T curves exhibit no change but the final voltage decreased. The anodic oxide film of titanium developed from fine grains to snowflake-like grains in a layered structure with an increase in the concentration of the electrolyte and current density. Sparking at the interface of the oxide/electrolyte accompanied the local deposition and dissolution of the oxide film through discharging. The crystallinity of the anodic oxide film increased with the anodizing voltage and decreased with an increase in the concentration of the electrolyte.

**Key words**: Titanium, anodizing, oxide film, morphology

### INTRODUCTION

Titanium has been successfully used for dental and

orthopedic implants due to its superior biocompatibility and high corrosion resistance[1-5], attributable to the oxide films on its surface[6-9]. A thin oxide layer naturally forms on titanium implants in air, however, the thickness, morphology, topography, and chemical composition of this layer is quite variable over a relatively wide range. It is known that titanium implants are covered by a surface oxide that is approximately 2~5 nm thick[8],

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and this oxide layer grows slowly during implantation [3,10,11]. Eventually, a thick oxide layer on Ti implants can act as a barrier, thereby preventing metallic ions from releasing, which eventually inhibits local irritation of the tissues surrounding the implant. However, the formation of a thick porous oxide layer improves the roughness of the implant surface, which then increases the percentage of direct bone-implant contact[12]. Anodic oxidation is a superior method in terms of the characteristics of the resulting oxide films. Although considerable attention has been paid to the photoelectrochemical application of anodic oxides of titanium[13,14], no systematic research on the anodizing of titanium in aqueous phosphoric acid has been reported.

This work investigates the electrochemical behavior involved in the anodizing of titanium in an aqueous H<sub>3</sub>PO<sub>4</sub> solution and then analyzes the morphology of the resulting oxide films.

### MATERIAL AND METHODS

The experimental material was commercially available pure Ti plate (c.p.Ti, grade 2). The specimens, 30 mm×10 mm×1 mm, were polished with sandpaper #1200 and then pickled in a 25 vol.% HF solution for 20s to remove any surface oxide formed in air. Then, the specimens were degreased by acetone or other organic solvents, rinsed with distilled water, and finally dried by blowing air. The anodic oxidation was conducted in the cell using a power supply based on the constant current density mode with a current density within the range of 0.3~1.0

A/dm<sup>2</sup> in the electrolyte, i.e. an aqueous H<sub>3</sub>PO<sub>4</sub> solution. The temperature of the electrolyte was maintained at 25°C and the concentration varied between 0.05 and 0.7M.

The anodized specimen surfaces were then examined by scanning electron microscope (SEM) (Model S-2, Hitachi, Japan) and analyzed by X-ray Diffractometer with CuKα radiation (30 kV and 20 mA, Philips).

### RESULTS AND DISCUSSION

In Fig. 1, the voltage-time (V-T) curves of the anodized titanium displayed two parts, i.e. a linear part in the initial stage and a subsequent parabolic part in 0.05M H<sub>3</sub>PO<sub>4</sub>. The slope of the V-T curves initially increased with an increase in the current density and then decreased. This decrease in the V-T slope relative to the duration of the anodic oxidation resulted from a lowering of the current efficiency, i.e. gas evolution or dissolution of the oxide film. As the concentration of the electrolyte increased, the V-T curves exhibited no distinct change but the final voltage decreased (Fig. 2). The oscillation, corresponding to the sparking at the interface of the oxide/electrolyte, particularly occurred in the parabolic part. The onset of the sparking transpired earlier as the concentration of the electrolyte increased. With a longer anodizing time or higher voltage, the sparking spots gradually decreased in number and increased in size eventually scanning over the whole surface of the specimens, resulting in intense voltage oscillations. The linear part corresponded to the thickening of the barrier layer of the oxide film, and furthermore, the slope of the curve

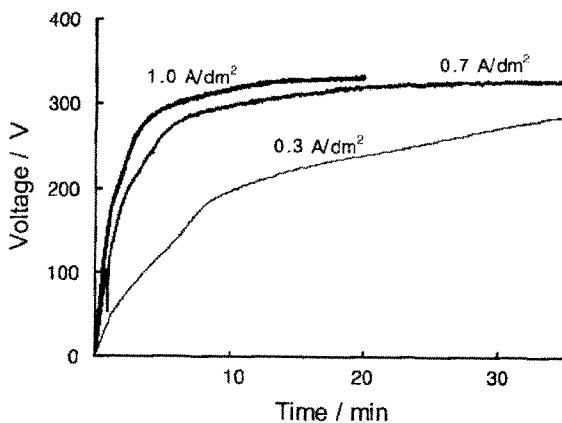


그림 1. 0.05M H<sub>3</sub>PO<sub>4</sub> 용액에서 티타늄 양극산화시 시간-전압곡선  
Voltage vs. time curves of anodizing of titanium in 0.05M H<sub>3</sub>PO<sub>4</sub> solution

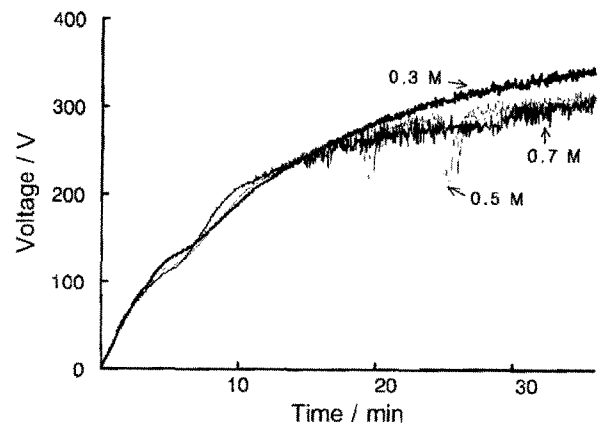


그림 2. H<sub>3</sub>PO<sub>4</sub> 용액에서 0.5 A/dm<sup>2</sup>의 정전류조건으로 티타늄 양극산화시 시간-전압곡선  
Fig. 2. Voltage vs. time curves of anodizing of titanium at 0.5 A/dm<sup>2</sup> in H<sub>3</sub>PO<sub>4</sub> solution

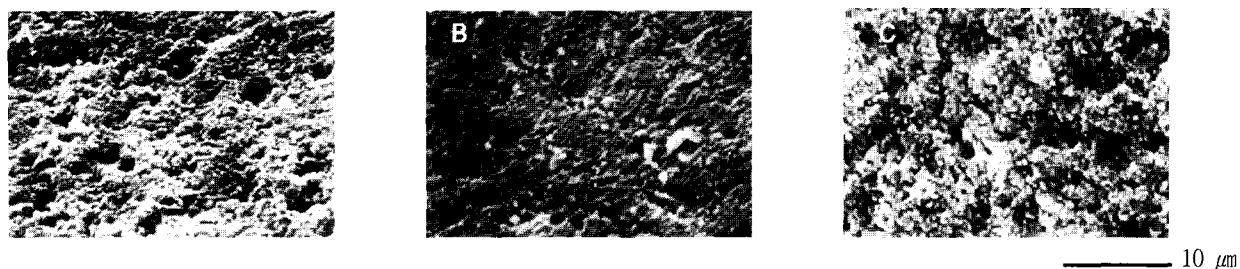


그림 3. 0.05M  $H_3PO_4$  용액에서 형성된 티타늄 양극산화막의 SEM 관찰상 (A)  $0.3 A/dm^2$ 의 정전류조건에서 35분간 양극산화, (B)  $0.7 A/dm^2$ 의 정전류조건에서 35분간 양극산화, (C)  $1.0 A/dm^2$ 의 정전류조건에서 20분간 양극산화

Fig. 3. SEM micrographs of anodic oxide films of titanium in 0.05M  $H_3PO_4$  solution (A) at  $0.3 A/dm^2$  for 35min, (B) at  $0.7 A/dm^2$  for 35min, and (C) at  $1.0 A/dm^2$  for 20min

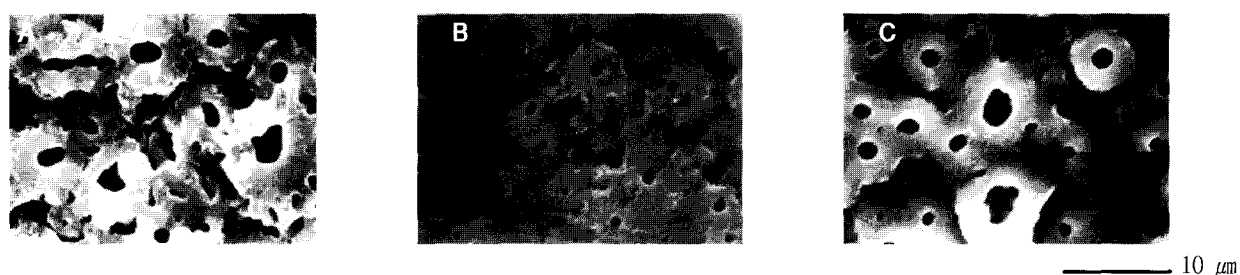


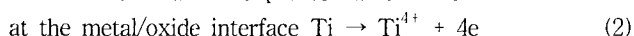
그림 4. (A) 0.3M, (B) 0.5M, (C) 0.7M  $H_3PO_4$  용액에서  $0.5 A/dm^2$ 의 정전류조건으로 15분간 양극산화시 형성된 타이타늄 산화피막의 SEM 관찰상

Fig. 4. SEM micrographs of anodic oxide films of titanium at  $0.5 A/dm^2$  for 15min in  $H_3PO_4$  solution (A) 0.3M, (B) 0.5M, (C) 0.7M

essentially reflected the rate of the thickening of the barrier layer. According to the high field law, the stationary growth of a barrier layer follows a homogeneous pattern such that thickness basically increases linearly with voltage (V)[15]:

$$\frac{dV}{dt} = \frac{M}{zF\rho} E j_F \quad (1)$$

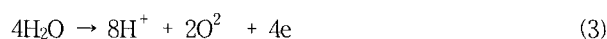
where  $M$  and  $\rho$  are the mole and density of the oxide, respectively.  $F$  is the Faraday constant,  $E$  is the anodizing electric field,  $j_F$  is the current density of the film formation (equal to the total current during anodization,  $j_{an}$ , times the efficiency of the film formation,  $\eta_F$ ), and  $z=4$  for  $TiO_2$  formation. Thickening only takes place at the metal/oxide interface, and the oxide/electrolyte and metal/oxide interfaces remain parallel. The reactions at the interfaces can be expressed as follows:



and the  $Ti^{4+}$  ions migrate into the oxide layer;

at the oxide/electrolyte interface, a water-splitting reaction[16] occurs and the  $O^{2-}$  ions migrate from the oxide/electrolyte interface to the metal/oxide interface by the electric field to form  $TiO_2$ . Meanwhile, the oxygen

ions turn into oxygen molecules at the surface of the oxide film based on losing electrons and, as a result, the reaction becomes more striking.



Accordingly, the efficiency of the anodizing decreases with an increase in the anodizing time or voltage, however, the barrier layer can also be formed at a reduced efficiency within a certain range, which only results in a decrease in the slope of the V-T line.

Fig. 3 indicates that some pores existed in the rough surface with fine grains in 0.05M  $H_3PO_4$ . The grains increased in size and the surface became rougher with an increase in the current density. With a 0.3M concentration, snowflake-like grains with a layered structure were observed, the pores increased in size from the inner to the outer layer, and the grains tended to overlap with each other as the concentration of the electrolyte increased (Fig. 4). With an increase in the anodizing voltage, pores were observed in the barrier layer of the oxide film caused by the injecting of cations, such as hydrogen ions and titanium ions, from the oxide film into

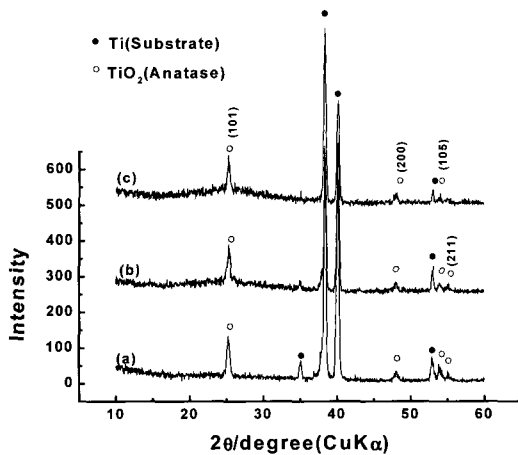


그림 5. (a) 0.05M, (b) 0.15M, (c) 0.3M H<sub>3</sub>PO<sub>4</sub> 용액에서 0.7 A/dm<sup>2</sup>의 정전류조건으로 15분간 양극산화시 형성된 티타늄 산화피막의 XRD 양상

Fig. 5. XRD patterns of anodic oxide films of titanium at 0.7 A/dm<sup>2</sup> for 15min in H<sub>3</sub>PO<sub>4</sub> (a) 0.05M (b) 0.15M (c) 0.3M

the electrolyte under the electric field. When sparking occurred, this was accompanied by the local deposition and dissolution of the oxide films, i.e. local discharging. Consequently, the oxide film thickened at the interface of the oxide/electrolyte in a non-uniform way except for a uniform thickening at the interface of the oxide/substrate.

With an increased concentration of the electrolyte from 0.05 to 0.3M, the degree of crystallization, according to the peak intensity of anatase and the baseline bulge, from an amorphous to a crystalline structure, i.e. anatase, slightly decreased, however, the amorphous fraction increased (Fig. 5). There was no distinction between the final voltages except in the case of a 0.05M concentration of the electrolyte. With an increased electrolyte concentration at a current density of 0.5 A/dm<sup>2</sup>, the crystallinity decreased as the baseline bulge appeared to be more prominent (Fig. 6). The final voltages were 348 V, 316 V, and 290 V for 0.3, 0.5, and 0.7M, respectively. This confirmed that an increase in the final voltage promoted the crystallization of the oxide layer and a higher concentration increased the amorphous fraction.

## CONCLUSIONS

(1) In 0.05M H<sub>3</sub>PO<sub>4</sub>, the voltage-time (V-T) curves display an initial linear part and a subsequent parabolic part. The initial slopes increase but the subsequent slopes decrease as increasing the current density. As the concentration of the electrolyte increases, the V-T curves shows

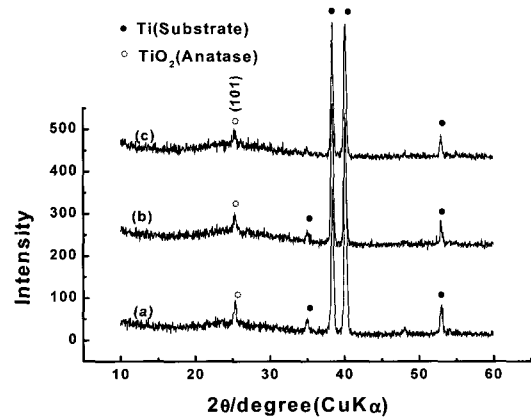


그림 6. (a) 0.3M, (b) 0.5M, (c) 0.7M H<sub>3</sub>PO<sub>4</sub> 용액에서 0.5 A/dm<sup>2</sup>의 정전류조건으로 15분간 양극산화시 형성된 티타늄 산화피막의 XRD 양상

Fig. 6. XRD pattern of anodic oxide films of titanium at 0.5 A/dm<sup>2</sup> for 15min in H<sub>3</sub>PO<sub>4</sub> (a) 0.3M, (b) 0.5M, (c) 0.7M

no change and decrease in the final voltage.

(2) With an increase in concentration of the electrolyte and current density, the oxide films of titanium develop from fine to snowflake-like grains in a layered structure with pores in the center. Sparking during anodizing is accompanied by the local deposition and dissolution of the oxide film through discharging.

(3) The crystallinity of the anodic oxide film increases with an increase in the anodizing voltage, however, it decreases with an increase in the concentration of the electrolyte.

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