

# A Method for Real Time Monitoring of Oxide Thickness in Plasma Electrolytic Oxidation of Titanium

Kwon-Jong Yoo, Yong K. Lee, and Kangsoo Lee<sup>1,†</sup>

Graduate School of NID Fusion Technology, Seoul National University of Technology, Seoul 139-743, Korea  
<sup>1</sup>Xerochem Inc., #301 993-14 Yeongdeok-dong, Giheung-gu, Yongin-si, Gyeonggi-do, Seoul 446-908 Korea

(Received December 29, 2009; Revised February 9, 2010; Accepted February 10, 2010)

During PEO (plasma-electrolytic-oxidation) treatment of titanium, the relationship between the thickness of oxide film and the measured electrical information was investigated. A simple real time monitoring method based on the electrical information being gathered during PEO treatment is proposed. The proposed method utilizes the current flowing from a high frequency voltage source to calculate the resistance of an oxide film, which is converted into the thickness of an oxide film. This monitoring method can be implemented in PEO system in which an oxide film is grown by constant or pulsed voltage/current sources.

**Keywords :** PEO, coatings, titanium oxide, thickness monitoring, pulsed source

## 1. Introduction

Titanium and their alloys are getting more attentions in many fields such as aerospace, solar cells, and biomedicine, etc., due to their high corrosion resistance, high melting point and good biocompatibility. However, since these metals are deficient in wear resistance and friction coefficient, they cannot be implemented widely as expected. In addition, some properties of these metals may not be fully compatible in applications such as dental implants and artificial heart valves.<sup>1-2)</sup> In order to overcome these limitations and supply properties required in specific applications, protection and/or functional coating on these metals is required.<sup>3-4)</sup> A titania, titanium dioxide, is one of the most favorite oxide coatings for these metals and their applications due to its low wear resistance and good biocompatibility.<sup>5)</sup> Anodizing and thermal oxidation methods have been used to coat these metals with oxide films, but films are not well-adhered onto the metal surface.<sup>6-7)</sup>

PEO combines electrochemical oxidation of metal and dielectric breakdown of the produced metal oxide in an aqueous electrolyte to produce oxide films onto metal surface.<sup>8)</sup> Due to its simple equipment and non-hazard electrolyte, PEO is a relatively convenient and ecologically friendly technique compared with the conventional coating methods.<sup>9-11)</sup> In principle, PEO is the same as the conventional anodizing method and produces an oxide film on

metal substrate. However, beyond a certain point where the voltage drop across the oxide film is high enough to break and/or melt the defect points across the oxide film, micro-discharge occurs on the oxide film, which can be observed as spark on the oxide film surface. The temperature around them has been reported be around and beyond 3000 K, which is more than enough to melt oxide film and/or change its phase. The oxide material property, such as a low thermal conductivity, may enhance these thermal processes to occur under and/or on the oxide film surface. Since PEO takes metal ions from metal substrate to produce an oxide film, it gives an excellent adhesion property between the oxide film and the anode material. In addition, it has been reported that an oxide film can be uniformly grown even on complex geometries and can be remarkably hard and resistive to corrosion and wear.

Since the electrochemical oxidation and dielectric breakdown occur concurrently during the oxidation process, it is not easy to characterize/monitor the growing oxide film in real time. Thus, PEO has been executed based on the pre-configured operation conditions. So far, research has been paid attention on the effect of electrolyte and physical configuration of experimental set-up to find the optimum process regime,<sup>12-13)</sup> which help us to understand the process. However, it does not provide any real time information on the amount of oxide film growth, which is quite useful for monitoring a mass production because a post-process characterization is not cost effective, and time-consuming.

<sup>†</sup> Corresponding author: kslee@xerochem.com

A real time monitoring system can be built to PEO and consists of an impedance meter with software running for calculation on a computer. In this study we present a simple method to monitor the growth of a titania film by interpreting the electrical data during the oxidation process in real time.

## 2. Experimental procedure

Commercially pure Ti (Grade 2, Hyundai Titanium Co., Incheon, South Korea) plate (10×40×1 mm) was used as a substrate metal. A Ti plate and a stainless steel bath were electrically biased and worked as an anode and a cathode, respectively. Electrolyte was prepared from disodium hydrogen phosphate (Na<sub>2</sub>HPO<sub>4</sub>, Extra Pure Grade 99.0%, JUNSEI CHEMICAL Co., LTD. SAITAMA, JAPAN) solution with 20 g/L concentration, which was dissolved in the magnetically stirred de-ionized water on the hot plate at 35 °C. Ti specimens were polished with silicon carbide abrasive paper (#600 grit) and were cleaned in the ultrasonic cleaner for 10 minutes using acetone, ethanol, de-ionized water sequentially, and followed by blow-drying with the compressed air gun. PEO was conducted for Ti with a power supply (input voltage 220 V AC 3-phase). The pulsed output voltage was controlled less than 0.2% rating output accuracy at various constant applied voltages (200, 230, 270 V) at the frequency of 30 kHz for 3 minutes, and the pulse current was measured during the PEO. The ramp time to reach up to the set voltage was fixed at 1,000 ms. PEO was executed for 3 min. The arc detection control was set to a minimum such that the setting values of arc voltage, increment current level, detection sensitivity were disable, 15 A (maximum value allowed), disable, respectively.

After the PEO treatment, the specimens were blow-dried with the compressed air gun and then the surface microstructures were examined at the magnification of 2,000 using the optical microscope (PSM1000SH, Motic Inc. Hong Kong) with the digital camera (Moticam 2300 Attachable Camera 1/2" CMOS 3.0 Mega pixels with USB 2.0 PC output, Motic Inc. Hong Kong). The film thickness grown was measured by a profiler. The part of the titania film was etched by BHF (Buffered HF) completely to cre-

ate the step, the height of which was measured by a profiler.

## 3. Results and discussion

After applying pulse voltages to the electrodes, a titania film is formed on the surface of the Ti substrate. As reported in the literature, the current increased rapidly and reaches a peak at an early stage of the process with sparks on the metal surface.<sup>14)</sup> The current, then, decreases gradually with time. This indicates the surface of the metal is oxidized and the electrical resistance of the titania film is increasing due to the increase in the film thickness. After a certain amount of time, the current seems to be constant and is referred to as a stabilized current. In our experiments the current stabilizes within 1.5 minutes after the current reaches a peak. As shown in Fig. 1, the peak current was obtained within a second and then decreased gradually with time then, stabilized in 3 minutes. Thus, the total process time was limited to 3 minutes. It should be noted that even after the current is stabilized minor sparks on the surface can be observed in visual. Since most of the surface has been oxidized at an early stage, these sparks will not make a contribution to grow the film.

The peak currents and the stabilized currents, measured at about 3 minutes after the current peak, are given in

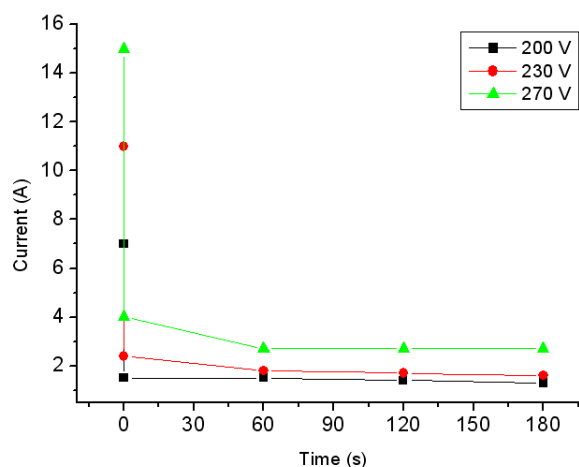


Fig. 1. Plot of the current vs time with 200,230, and 270 constant voltage applied.

Table 1. The applied voltage, the electrical parameters, and the measured and calculated thickness of a titania film

$V_{applied}$ (V)	$I_{peak}$ (A)	$I_{stabilized}$ (A) at 3 min.	$R_{total}$ ( $\Omega$ )	$l_{titania}$ ( $\mu\text{m}$ ) measured	$l_{titania}$ ( $\mu\text{m}$ ) calculated
200 V	7	1.3	154	1.3	1.34
230 V	11	1.6	144	1.2	1.24
270 V	15	3.2	84	0.6	0.64

Table 1. The magnitude of the currents increases with the applied voltage. The thickness of the titania films are characterized by profiler and given in Table 1. Since this study focus on the relation between the electrical information and the thickness of a titania film, the thickness of a titania film is plotted against the total resistance calculated with the stabilized current in Fig. 1. The thickness of a titania film increases linearly with the total resistance.

When the current is stabilized the total resistance of the system is equal to the sum of the resistance of electrolyte, anode and cathode:

$$R_{total} = R_{electrolyte} + R_{anode} + R_{cathode} \quad (1)$$

Since the resistance of the titanium plate is very small compared with the resistance of a titania film, the resistance of anode can be approximated to that of a titania film. The equation can be rewritten as follows:

$$R_{total} = R_{electrolyte} + \rho_{oxide} \frac{l_{oxide}}{A_{oxide}} + R_{cathode} \quad (2)$$

where  $\rho_{oxide}$  and  $l_{oxide}$  are the resistivity and the thickness of a titania film respectively, and  $A_{oxide}$  is the area of the specimen. Thus, if the resistances of the electrolyte and the cathode are known, the thickness of a titania film can be calculated from the Eq (3).

$$l_{oxide} = \frac{A_{oxide}}{\rho_{oxide}} (R_{total} - R_{electrolyte} - R_{cathode}) \quad (3)$$

The intercept with x-axis in Fig. 2 is  $R_{electrolyte} + R_{cathode}$  but actually represents the resistance of the system before a titania film forms. This includes the resistance of the titanium specimen. Since the current decrease is caused by a titania film on the titanium surface, we can take the point when current reaches a peak is when a titania film

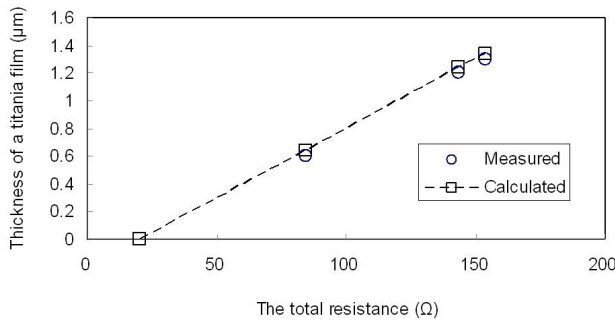


Fig. 2. Plot of the thickness of a titania film vs. the total resistance of the PEO system.

starts form on the surface by anodizing. Thus, the resistance of the system without a titania film can be obtained by dividing the applied voltage by the peak current. For applying voltages of 200, 230, and 270 V, the resistance of the system is approximately 20 Ω (Table 1).  $l_{oxide}$  is calculated for those applying voltages along with  $\rho_{oxide}$  and  $A_{oxide}$ .  $\rho_{oxide}$  has been found to be 6 MΩcm for sub micron range thin titania film from the literatures<sup>15)</sup> and  $A_{oxide}$  is measured to be around 6 cm<sup>2</sup>. Fig. 1 shows the relationship between  $l_{oxide}$  and  $R_{total}$ . The calculated thicknesses agree well with those measured by a thickness profiler, indicating this simple calculation provides real time information on the thickness of a titania film. The oxide film thickness has been measured by a thickness profiler that scans across the coated and uncoated Ti surfaces.

The electric field strength across a titania film, when the process is stabilized, is calculated with the stabilized current, the extracted resistance, and thickness of a titania film for those applying voltages:

$$E_{oxide} = \frac{V_{oxide}}{l_{oxide}} = \frac{I_{stabilized} \times R_{oxide}}{l_{oxide}} \quad (4)$$

$$= \frac{I_{stabilized} \times (R_{total} - R_{cathode} - R_{electrolyte})}{l_{oxide}}$$

$E_{oxide}$  built across a titania film are 129, 156, and 318 V/μm for the applying voltages of 200, 230, and 270 V. Those values are not strong enough to break a titania film found in the literature and, thus, the titania film is in steady state when the parameters are extracted for the calculation.

## 4. Conclusions

A proposed simple monitoring method turns out to be useful to get some idea on the oxide film thickness growth in real-time. Its simple implementation in PEO system in which an oxide film is grown by constant or pulsed voltage/current sources<sup>16)</sup> has been demonstrated. The same voltage/Current applied for the oxide film growth during PEO has been utilized to obtain the electrical information to calculate the oxide film thickness. The resistance of electrolyte can be measured in real time together with the proposed method in order to improve the accuracy of the calculation.

## References

1. T. Kitsugi, T. Nakamura, and M. Oka, *J. Biomed. Mater. Res.*, **32**, 149 (1996).
2. Y. X. Leng, J. Y. Chen, and Z. M. Zeng, *Thin. Solid.*

- Films.*, **377**, 573 (2000).
3. Y. Han, S.H. Hong, and K.W. Xu, *Surf. Coat. Technol.*, **154**, 314 (2002).
  4. S. V. Gnedenkov, P. S. Gordienko, O. A. Khisanfova, T. M. Scorobogatova, and S. L. Sinebrukhov, *J. Mater. Sci.*, **37**, 2263 (2002).
  5. J. C. Keller, C. M. Stanford, J. P. Wightman, R. A. Draughn, and R. Zaharias, *J. Biomed. Mater. Res.*, **28**, 939 (1994).
  6. J. Pouilleau, D. Devilliers, F. Garrido, S. Durand-Vidal, and E. Mahe, *Mater. Sci. Eng.*, **B47**, 235 (1997).
  7. A. Bloyce, P. Y. Qi, H. Dong, and T. Bell, *Surf. Coat. Technol.*, **111**, 172 (1999).
  8. T. B. Van, S. D. Brown, and G. P. Wirtz., *Am. Ceram. Soc. Bull.*, **56**, 563 (1977).
  9. A. L. Yerokhin, V. V. Lyubimov, and R. V. Ashitkov, *Ceram. Int.*, **24**, 1 (1998).
  10. X. Nie, A. Leyland, H. W. Song, A. L. Yerokhin, S. J. Dowe, and A. Matthews, *Surf. Coat. Technol.*, **116**, 1055 (1999).
  11. W. Xue, Z. Deng, R. Chen, and T. Zhang, *Thin Solid Films.*, **372**, 114 (2000).
  12. V. S. Rudnev, I. V. Lukiyanchuk, D. L. Boguta, V. V. Kon'shin, A. S. Rudnev, and P. S. Gordienko, *Russ. Prot. Met.*, **38**, 191 (2002).
  13. S. V. Gnedenkov, O. A. Khisanfova, A. G. Zavidnaya, S. L. Sinebryukhov, V. V. Kon'shin, S. B. Bulanova, and P. S. Gordienko, *Russ. J. Appl. Chem.*, **76**, 23 (2003).
  14. I. Han, J. H. Choi, B. H. Zhao, H. K. Baik, and I. S. Lee, *Curr. Appl. Phys.*, **7S1**, 23 (2007).
  15. G.-R. Gu, Z. He, Y.-C. Tao, Y.-A. Li, J.-J. Li, H. Yin, W.-Q. Li, and Y.-N. Zhao, *Vacuum*, **70**, 17 (2003).
  16. Y. M. Wang, D. C. Jia, L. X. Guo, T. Q. Lei, and B. L. Jiang, *Mater. Chem. Phys.*, **90**, 128 (2005).