Comparison of Corrosion Behaviors of Bare Ti and TiO$_2$

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Abstract

In this study, titanium (Ti) surface was anodized by applying 60 voltages for two hours to form titanium dioxide (TiO$_2$) with anodization method. After anodization procedure, comparison of corrosion behaviors of the bare titanium and TiO$_2$ coated titanium was examined in 1 M KOH solution by using electrochemical methods such as anodic and cathodic current-potential curves and electrochemical impedance spectroscopy (EIS). Cyclic voltammetry (CV) and energy dispersive X-ray (EDX) were used to characterize bare Ti and anodically formed TiO$_2$ surfaces. According to obtained results, Ti surface was smooth and compact. However, surface structure of TiO$_2$ coated titanium was porous and nanotubes formed on the surface. This porous structure which has protective layer contributed to increase the corrosion resistance. Higher polarization resistance was obtained on porous TiO$_2$ than that of bare titanium. Besides, this protective layer bore well against the alkaline corrosion during long-term immersion.

Keywords:
Corrosion; Titanium; Alkaline Solution.

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1- Introduction

Titanium and its alloys are widely used in many applications, from chemical industry to medical application due to its excellent corrosion resistance which is explained to the thin, stable and protective layer that forms spontaneously on its surface when expose to the natural environment [1]. Its other important properties are good mechanical strength and high biocompatibility. Recently, many researchers have been investigating the optimization of Ti surface, particularly increasing the thickness of the oxide layer and modifying the surface morphology and crystal structure by using different methods to improve its corrosion resistance and to change chemical structure. Anodic oxidation is one of the most used methods to build anodic films which are long, homogeneous, good electrical properties and porous at high voltages. This protective layer obtained by using anodic oxidation method prevents rapid dissolution of the underlying metal. In addition, Ti possesses a wide potential window during which metal remains in the passive range for this reason, many researchers are interested in anodic oxidation method. Wide passive range is observed not only in acid environment but also in alkaline environment [2]. Growing of TiO$_2$ layer which is the most homogenous and best results has been extensively investigated and well established in acid electrolytes [3-5]. However, produced TiO$_2$ layer tends to dissolve in strong acid electrolytes such as hydrogen fluoride (HF) [6], nitric acid (HNO$_3$) [7] and hydrogen peroxide (H$_2$O$_2$) [8]. To the best of our knowledge, weak acids such as organic acids gave the best results to grow TiO$_2$ layer [9-13]. Although there is much information of anodic oxidation of metals, up to now less attention is available about corrosion of Ti metal or TiO$_2$ in strong alkaline solution. In addition, not many systematic works can be found regarding the comparison of corrosion behaviors Ti and oxide layer in alkaline electrolyte until now. When its importance is concerned in many applications, in this study, corrosion behaviors of bare Ti and TiO$_2$ obtained by using anodization method at high voltage were compared with a series of electrochemical techniques in alkaline electrolyte.
2- Materials and Methods

Ti disc (grade 2) which is surface area of 0.283 cm$^2$ is used as a working electrode. All surfaces of Ti electrode is covered with polyester resin except worked surface. Before the anodization procedure, Ti surface was polished by using emery paper (the grid of 320 – 1200). After the polishing, worked surface was washed with deionized water and degreased in acetone, ethanol and deionized water for 10 min, respectively, then dried in air to prepare electrochemical measurements. Ti surface was modified by using anodization solution at constant potential of 60 V for 2 h. Anodization solution consists of 0.5 g NH$_4$F, 2% (vol.) H$_2$O and ethylene glycol rest [14]. During the anodization procedure, two-electrode electrochemical cell was used. Pt foil (with 2 cm$^2$ surface area) as the counter electrode and Ti disc as the working electrode were placed in the cell. The anodization experiment was performed using a direct current (DC) power supply for the fabrication of the TiO$_2$. After anodization procedure, Ti electrode with oxide layer was washed with deionized water and was immersed in 1 M KOH solution for electrochemical measurements. Same experiments were done for bare Ti. Three electrode set-up was used for electrochemical measurements which contain Pt and Ag/AgCl as counter and reference electrodes, respectively. Anodic and cathodic current-potential curves were obtained separately after one-hour immersion at $E_{ocp}$ with the scan rate of 1 mV s$^{-1}$. Polarization resistances of electrodes were determined with EIS method at $E_{ocp}$ after one hour and long-term immersions (30 days). EIS measurements were conducted in the frequency range from 100 kHz to 0.003 Hz and applied amplitude was 0.005 V. Nyquist diagrams obtained from EIS were fitted by using Zview software. Characterization of bare Ti and oxide electrodes were analyzed by cyclic voltammetry (CV) with the scan rate of 100 mV s$^{-1}$ and energy dispersive X-ray (EDX). Electrochemical measurements were carried out by Ivium vertex (model no: V55600) electrochemical analyzer under computer controlled. Nuve BS 30 type water bath was used for controlling the electrolyte temperature (~ 25 °C). Analytical grade chemical substances were used in the experiments and all the experiments were also repeated at least three times.

3- Results and Discussion

Cyclic voltammogram of TiO$_2$ is given in Figure 1. The cyclic voltammogram of bare Ti is also given in the same figure as the inset. According to the inset, the peak appeared at -1.7 V (Ag/AgCl) is related to the oxidation of hydrogen and transformation of Ti$^{+3}$/Ti$^{+4}$ [13,15]. No oxygen evolution reaction is observed between 0 and 1.0 V (Ag/AgCl) [16]. In the backward scan, the peaks appeared at -1.4 and -1.75 V (Ag/AgCl) indicate the reduction of O$_2$ and Ti$^{+4}$/Ti$^{+3}$, respectively [15]. For cyclic voltammograms of TiO$_2$, the current values of anodic and cathodic peaks are significantly higher than that of obtained on bare Ti and peak potentials shifted to the more positive values. It can be explained that existence of the TiO$_2$ on the Ti surface greatly enhance its surface area [17]. As it can be seen from Figure 1, characteristic peaks of Ti are clearly observed and no peaks of other metals are seen. In addition to measurements of CV for characterization, EDX analysis of TiO$_2$ layer on Ti surface is carried out and elemental analysis is found as % 56.52 for oxygen, 27.61 for Ti and 15.87 for F atoms (the spectrum of EDX is not given here). Result of EDX is supported the results of CV.

![Figure 1. Cyclic voltammogram of TiO$_2$ obtained by applying the anodization potential of 60 V for 2h. Inset shows the cyclic voltammogram of bare Ti (electrolyte: 1.0 M KOH and scan rate $\nu$: 100 mV s$^{-1}$).](image-url)
Anodic(a) and cathodic(b) current-potential curves of bare Ti and anodized Ti electrode were given in Figure 2. In the cathodic branch, only hydrogen evolution is seen on both electrodes. When Ti surface is modified with TiO₂, open circuit potential shifted more positive values and higher hydrogen evolution current density is obtained. According to anodic branch, same behaviors are seen for both electrodes. TiO₂ formed naturally on bare Ti dissolved initial stage for bare Ti, after that, anodic current was constant until -0.584 V (Ag/AgCl). Very protective TiO₂ layer formed between these potentials [2,18]. When compared with anodized Ti (TiO₂), anodized Ti reduced the anodic current values. This reducing can be explained with existence of protective TiO₂ layer. This protective oxide layer prevented the Ti surface against attacking of the corrosive alkaline solution. EIS is useful method to understand the metal/solution or oxide/solution interface [19]. For this purpose, EIS analysis is performed for bare Ti and TiO₂. Nyquist diagrams of bare Ti and anodized Ti are given in Figure 2c. Nyquist diagrams are fitted and parameters are given in Table 1. Two-time constant were obtained on bare Ti and anodized Ti after one hour immersion due to capacitive and typical passive response. Two-time constant shows the existence of bi-layered oxide structures which one is porous outer layer and another is barrier inner layer on the electrode surface [20, 21]. Higher polarization resistance (R_p=Rs, porous layer resistance + R_b, barrier layer resistance) which is nearly twofold was obtained on anodized Ti electrode. This high R_p value proved the existence of the protective passive layer on Ti.

![Graph](image_url)

**Figure 2.** Anodic (a) and cathodic (b) current-potential curves and Nyquist diagrams (c) of bare Ti (●) and anodized Ti (□) in 1 M KOH solution.

To investigate the effect of immersion time on the corrosion behaviors of bare Ti and anodized Ti, EIS measurements are also performed. Figure 3 shows the Nyquist diagrams obtained different immersion times of bare Ti (a) and anodized Ti (b) in 1 M KOH solution. Suggested electrical circuits and fit parameters were given in the same figures as the inset and Table 1, respectively. Since anodized Ti had more porous structure than bare Ti, parallel connected electrical circuit was used [22]. It is seen from Table 1, R_p of bare Ti reduced with increasing immersion time according to 2.day, however R_p values of anodized Ti increased firstly and decreased then increased at 30.day due to protective passive layer. Here, CPE corresponds to constant phase element, CPE is used during fitting instead of double layer capacitance (C_{dl}) as the double layer is not an ideal capacitor [23]. n is phase shift.
Figure 3. Nyquist diagrams obtained 2(●), 12(△), 22(■) and 30(○) days immersion time of bare Ti (a) and 2(△), 12(■), 22(■) and 30(○) days immersion time of anodized Ti (b) in 1 M KOH solution. Suggested electrical circuits were given as the inset.

Table 1. Fit parameters determined from EIS

| Immersion time | Ti | Anodized Ti (TiO₂) |
|----------------|----|---------------------|
|                |   Rᵣ (Ω) | CPE₁ | n₁ | CPE₂ | n₂ |  Rᵣ (Ω) | CPE₁ | n₁ | CPE₂ | n₂ |
| 1.hour         | 36942 | 26.15 | 0.70 | 5.62 | 0.99 | 63414 | 21.45 | 0.47 | 1.38 | 0.95 |
| 2.day          | 34391 | 18.23 | 0.69 | 4.63 | 0.94 | 155158 | 4.84 | 0.73 | 8.73 | 0.75 |
| 12.day         | 20332 | 19.29 | 0.71 | 2.40 | 0.98 | 388928 | 10.07 | 0.65 | 7.21 | 0.75 |
| 22.day         | 214704 | 20.64 | 0.71 | 1.24 | 0.98 | 180854 | 3.14 | 0.72 | 11.10 | 0.71 |
| 30.day         | 263924 | 20.71 | 0.72 | 1.02 | 0.99 | 255563 | 1.94 | 0.59 | 12.58 | 0.73 |

4- Conclusion

Naturally formed TiO₂ on Ti electrode can prevent the metal against the alkaline corrosion, but this thin layer dissolved in strong alkaline solution. Porous TiO₂ layer was formed on commercial Ti with the anodization method at potential of 60 V for 2 h. Synthesized TiO₂ was characterized by CV and EDX. Appearance of characteristic peaks of Ti confirmed the porous TiO₂ layer on the Ti surface. Anodically formed TiO₂ layer reduced the anodic current and improved the polarization resistance of bare Ti due to existence of porous and protective TiO₂ layer in strong alkaline solution. Anodically formed TiO₂ layer should be used in industrial applications to prevent bare Ti against corrosion.

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6- Conflict of Interest

The authors declare no conflict of interest.

7- References

[1] Aladjem, A., M. Aucouturier, and P. Lacombe. “Anodic Oxidation and Stress Corrosion Cracking (SCC) of Titanium Alloys.” Journal of Materials Science 8, no. 6 (June 1973): 787–792. doi:10.1007/bf02397908.

[2] Prusi, A., Lj. Arsov, Bala Haran, and Branko N. Popov. “Anodic Behavior of Ti in KOH Solutions.” Journal of The Electrochemical Society 149, no. 11 (2002): B491. doi:10.1149/1.1510134.

[3] Cheshideh, Hamed, and Farzad Nasirpouri. “Cyclic Voltammetry Deposition of Nickel Nanoparticles on TiO₂ Nanotubes and Their Enhanced Properties for Electro-Oxidation of Methanol.” Journal of Electroanalytical Chemistry 797 (July 2017): 121–133. doi:10.1016/j.jelechem.2017.05.024.
[4] He, Xiaoshan, Chengu Hu, Bin Feng, Buyong Wan, and Yongshu Tian. “Vertically Aligned TiO[sub 2] Nanorod Arrays as a Steady Light Sensor.” Journal of The Electrochemical Society 157, no. 11 (2010): J381. doi:10.1149/1.3486078.

[5] Shaddad, M.N., Al-Mayouf, A.M., Ghanem, M.A., AlHoshan, M.S., Singh, J.P., Al-Suhbyani, A.A. “Chemical Deposition and Electrocatalytic Activity of Platinum Nanoparticles Supported on TiO2 Nanotubes.” International Journal of Electrochemical Science 8 (2013) 2468 – 2478.

[6] Han, Jingsong, Liming Yang, Lixia Yang, Wenjing Jiang, Xubiao Luo, and Shenglian Luo. “PtRu Nanoalloys Loaded on Graphene and TiO2 Nanotubes Co-Modified Ti Wire as an Active and Stable Methanol Oxidation Electrocatalyst.” International Journal of Hydrogen Energy 43, no. 15 (April 2018): 7338–7346. doi:10.1016/j.ijhydene.2018.02.176.

[7] Xing, Li, Jianbo Jia, Yizhe Wang, Bailin Zhang, and Shaojun Dong. “Pt Modified TiO2 Nanotubes Electrode: Preparation and Electrocatalytic Application for Methanol Oxidation.” International Journal of Hydrogen Energy 35, no. 22 (November 2010): 12169–12173. doi:10.1016/j.ijhydene.2010.07.162.

[8] Allam, Nageh K., Karthik Shankar, and Craig A. Grimes. “Photoelectrochemical and Water Photoelectrolysis Properties of Ordered TiO2 Nanotubes Fabricated by Ti Anodization in Fluoride-Free HCl Electrolytes.” Journal of Materials Chemistry 18, no. 20 (2008): 2341. doi:10.1039/b718580d.

[9] Macak, Jan M., Hiroaki Tsuchiya, Luciano Taveira, Saule Aldabergerova, and Patrik Schmuki. “Smooth Anodic TiO2 Nanotubes.” Angewandte Chemie International Edition 44, no. 45 (November 18, 2005): 7463–7465. doi:10.1002/anie.200502781.

[10] Paulose, Maggie, Karthik Shankar, Sorachon Yoriya, Haripriya E. Prakasam, Oomman K. Varghese, Gopal K. Mor, Thomas A. Latempa, Adriana Fitzgerald, and Craig A. Grimes. “Anodic Growth of Highly Ordered TiO2Nanotube Arrays to 134 Mm in Length.” The Journal of Physical Chemistry B 110, no. 33 (August 2006): 16179–16184. doi:10.1021/jp060420k.

[11] Shankar, Karthik, Gopal K. Mor, Adriana Fitzgerald, and Craig A. Grimes. “Cation Effect on the Electrochemical Formation of Very High Aspect Ratio TiO2Nanotube Arrays in Formamide–Water Mixtures.” The Journal of Physical Chemistry C 111, no. 1 (January 2007): 21–26. doi:10.1021/jp066352v.

[12] Baran, Evrim, and Birgül Yazıcı. “Effect of Different Nano-Structured Ag Doped TiO 2 -NTs Fabricated by Electrodeposition on the Electrocatalytic Hydrogen Production.” International Journal of Hydrogen Energy 41, no. 4 (January 2016): 2498–2511. doi:10.1016/j.ijhydene.2015.12.028.

[13] Baran, Evrim, and Birgül Yazıcı. “Fabrication of TiO2-NTs and TiO2-NTs Covered Honeycomb Lattice and Investigation of Carrier Densities in I−/I3− Electrolyte by Electrochemical Impedance Spectroscopy.” Applied Surface Science 357 (December 2015): 2206–2216. doi:10.1016/j.apsusc.2015.09.212.

[14] Jiang, Weimin, Huimin Cui, and Ye Song. “Electrochemical Corrosion Behaviors of Titanium Covered by Various TiO2 Nanotube Films in Artificial Saliva.” Journal of Materials Science 53, no. 21 (July 18, 2018): 15130–15141. doi:10.1007/s10853-018-2706-5.

[15] Liao, Wenjuan, Jingwei Yang, He Zhou, Muthu Muruganathan, and Yanrong Zhang. “Electrochemically Self-Doped TiO2 Nanotube Arrays for Efficient Visible Light Photoelectrocatalytic Degradation of Contaminants.” Electrochimica Acta 136 (August 2014): 310-317. doi:10.1016/j.electacta.2014.05.091.

[16] Kim, Choonsoo, Seonghwan Kim, Jusol Choi, Jaehan Lee, Jin Soo Kang, Yung-Eun Sung, Jihwa Lee, Wonyong Choi, and Jeyong Yoon. “Blue TiO2 Nanotube Array as an Oxidant Generating Novel Anode Material Fabricated by Simple Cathodic Polarization.” Electrochimica Acta 141 (September 2014): 113–119. doi:10.1016/j.electacta.2014.07.062.

[17] Cao, Huazhen, Zhiwei Wang, Guangya Hou, and Guoqiang Zheng. “TiO2 Nanotube-Supported Amorphous Ni–B Electrode for Electrocatalytic Oxidation of Methanol.” Surface and Coatings Technology 205, no. 3 (October 2010): 885–889. doi:10.1016/j.surfcoat.2010.08.037.

[18] Prusi, A.R., and Lj.D. Arsov. “The Growth Kinetics and Optical Properties of Films Formed Under Open Circuit Conditions on a Titanium Surface in Potassium Hydroxide Solutions.” Corrosion Science 33, no. 1 (January 1992): 153–164. doi:10.1016/0010-938X(92)90024-w.

[19] González, J.E.G, and J.C Mirza-Rosca. “Study of the Corrosion Behavior of Titanium and Some of Its Alloys for Biomedical and Dental Implant Applications.” Journal of Electroanalytical Chemistry 471, no. 2 (August 1999): 109–115. doi:10.1016/s0022-0728(99)00260-0.

[20] Souto, R. “Degradation Characteristics of Hydroxyapatite Coatings on Orthopaedic TiAlV in Simulated Physiological Media Investigated by Electrochemical Impedance Spectroscopy.” Biomaterials 24, no. 23 (October 2003): 4213–4221. doi:10.1016/s0142-9612(03)00362-4.

[21] Venugopalan, Ramakrishna, Jeffrey J Weimer, Michael A George, and Linda C Lucas. “The Effect of Nitrogen Diffusion Hardening on the Surface Chemistry and Scratch Resistance of Ti-6Al-4V Alloy.” Biomaterials 21, no. 16 (August 2000): 1669–1677. doi:10.1016/s0142-9612(00)00491-9.
[22] Pan, J., D. Thierry, and C. Leygraf. “Electrochemical Impedance Spectroscopy Study of the Passive Oxide Film on Titanium for Implant Application.” Electrochimica Acta 41, no. 7–8 (May 1996): 1143–1153. doi:10.1016/0013-4686(95)00465-3.

[23] Assis, Sérgio Luiz de, Stephan Wolynec, and Isolda Costa. “Corrosion Characterization of Titanium Alloys by Electrochemical Techniques.” Electrochimica Acta 51, no. 8–9 (January 2006): 1815–1819. doi:10.1016/j.electacta.2005.02.121.