



Different Constant Voltage Anodization on the Corrosion Behavior of Ti-6Al-4V Alloy

Warittha Asumpinwong [a], Kanokwan Saengkiattiyut [b], and Viritpon Srimaneepong*[c]

[a] Prapokklao Hospital, Chantaburi 22000, Thailand

[b] Metallurgy and Materials Science Research Center, Chulalongkorn University, Bangkok 10330, Thailand.

[c] Department of Prosthodontics, Faculty of Dentistry, Chulalongkorn University, Bangkok 10330, Thailand.

*Author for correspondence; e-mail: viritpon.s@chula.ac.th

Received: 7 January 2013

Accepted: 13 March 2014

ABSTRACT

The objective of this study was to investigate the corrosion behavior of titanium alloy after anodization. Ti-6Al-4V alloy specimens were anodized in a 0.5 M phosphoric acid solution for 30 minutes using constant voltages of 100, 150, 200 and 300 volt. After anodization, the surface morphology, surface roughness, and crystal structure were observed under scanning electron microscopy (SEM), scanning probe microscopy (SPM), and x-ray diffraction (XRD), respectively. To determine the corrosion behavior of as-received or anodized Ti-6Al-4V alloy, all specimens were investigated using a potentiodynamic polarization technique in a 0.9% saline solution at 37°C. The results indicated that the E_{corr} of the as-received material was statistically lower than that of the anodized groups. The E_{corr} of anodized Ti-6Al-4V alloy increased as the voltage of anodization increased. There was no significant difference in corrosion rates between the as-received material and Ti-6Al-4V alloy specimens anodized using 100 or 150 V. Titanium alloy anodized using 300 V had the highest mean corrosion rate. It can be concluded that anodization can improve the corrosion potential of Ti-6Al-4V alloy, but increased voltage in the anodization of Ti-6Al-4V alloy led to an increased corrosion rate implying that higher voltage does not provide good corrosion resistance with Ti-6Al-4V alloy. The appropriate applied anodization voltage is necessary to generate the optimum titanium surface.

Keywords: anodization, corrosion, voltage, titanium, Ti-6Al-4V

1. INTRODUCTION

There has been an increasing trend of using implants in dental and orthopedic treatment. The most important properties required for these materials are that they should be biocompatible, promote bone cell response, and have the least adverse effect on the body. A biocompatibility of materials is

also closely related to its corrosion behavior. When corrosion occurs, metal ions released from the material can react with surrounding tissue, leading to chronic irritation or hypersensitivity, which may bring about treatment failure [1].

Titanium and its alloys are widely used

as implant materials because of their many suitable properties. They have excellent corrosion resistance due to their stable surface oxide layer which spontaneously forms when they contact air [2]. One of the most common titanium alloys used as implant material is Titanium-6Aluminum-4Vanadium (Ti-6Al-4V) alloy. Ti-6Al-4V containing 5.5 to 6.75 percent by weight of aluminum and 3.5 to 4.5 percent by weight of vanadium, is commonly used in medical and dental applications. However, the safe use of Ti-6Al-4V is still controversial because of concerns about aluminum and vanadium ions being released during its corrosion [3]. To improve osseointegration (i.e. the growth of bone around surgical implant without fibrous tissue formation at the interface) and biocompatibility, the surface of titanium and titanium alloy implants have been investigated and developed. This surface treatment could possibly reduce toxic effect from metal substrate. Various modification methods have been attempted, including thermal annealing, anodization, plasma spraying, grit blasting, and acid etching. Of these methods, anodizing, which is an electrolytic process used to form a compound substrate layer coating on the metal surface by oxidation, is a simple and inexpensive application [4]. By technique of anodization, the roughness with porosities on titanium surface could also be created and this could enhance bone-implant formation. Clinical study has proved that anodized titanium with porous oxide layer and rough surface could promote stronger and faster bone growth onto titanium implant [5]. An oxide layer formed by anodization is thicker than that formed naturally [6,7]. Not only is the oxide layer increased in thickness, but the mechanical properties of the treated metal can also be improved [8]. The characteristics of the oxide layer can be altered by adjusting the

anodizing conditions, such as the type and concentration of the electrolyte, temperature, current density, voltage, and additives [4]. Anodizing with a low voltage typically generates a thin dense amorphous oxide layer, while anodizing with a high voltage, over the breakdown limit, results in a thick porous crystalline oxide layer with the thickness of the oxide layer proportional to the voltage employed [9]. Another advantage of anodization is that the electrolyte ions can diffuse into, and combine with, the oxide layer [10]. Moreover, biologically active species such as phosphate ions, which can activate cell proliferation on anodized surfaces, may be incorporated into the oxide layer [11].

Several studies have shown that the corrosion resistance of commercially pure titanium improved after anodization and increased thickness of oxide layer tended to reduce corrosion rate [6,7,12]. While there are different findings among studies on anodization treated Ti-6Al-4V alloy [9,13,14]. However, most previous studies concentrated on low voltage or current and used different electrochemical techniques either galvanostatic or potentiostatic anodization. Therefore, the present study aimed to investigate the corrosion behavior of Ti-6Al-4V alloy after being anodized using a range of high voltages above dielectric breakdown of metal in order to create the rough titanium alloy surface. The surface morphology was also observed.

2. MATERIALS AND METHODS

2.1 Specimen Preparation

Seventy specimens, 10 mm in diameter and 1 mm thick, were prepared from wrought Ti-6Al-4V alloy rods (KVM Heating Element, Thailand). The chemical composition was 6.2% Al; 4.1% V; 0.18% Fe; 0.03% C; 0.027% N; 0.008% H; 0.12% O; balance Ti. All Ti-6Al-4V alloy specimens were polished

by a polishing machine using silicon carbide paper from No. 400 up to 1200 with water coolant, and then degreased with acetone in an ultrasonic bath for 5 minutes, followed by rinsing with deionized water.

2.2 Anodization Treatment

Potentiostatic anodization was performed in a 0.5% H_3PO_4 solution for 30 minutes using commercially pure titanium grade 2 as a counter electrode. All Ti-6Al-4V alloy specimens except the as-received specimens were divided into 4 groups. Each group contained fourteen specimens and the group was treated with an anodization voltage of 100 V, 150 V, 200 V, or 300 V. The Ti-6Al-4V alloy specimens were anodized in the group's assigned voltage condition for 30 minutes with the electrolyte temperature maintained at $25 \pm 1^\circ\text{C}$ in a water-cooling bath. A magnetic stirrer used to eliminate bubbles generated during the anodization treatment.

2.3 Surface Characteristics of the Anodized Film

The surface morphology of the anodized specimens was observed by scanning electron microscopy (SEM; JSM-6480LV, JEOL, Munich, Germany) prior to the corrosion test. The thickness of the oxide layer was measured from a cross-sectional SEM image. The roughness of the anodized surface was evaluated from one randomly selected specimen from each group using scanning probe microscopy (SPM; Nanoscope IV, Veeco, California, United State) with a Si probe in tapping mode. The crystalline structure of the anodized surface of the Ti-6Al-4V alloy specimens was examined by x-ray diffraction (XRD; D8 Discover, BRUKER AXS, Karlsruhe, Germany) in grazing incidence mode. The grazing angle was 3° and the range of

2-THETA was 20° to 80° .

2.4 Evaluation of Corrosion Behavior

Ten specimens of each anodized group, and the as-received group, were subjected to a potentiodynamic polarization test. The polarization was carried out in a 0.9% saline solution with pH 5.7, using a platinum rod counter electrode and a saturated calomel reference electrode. The exposed area of the working electrode was 0.5 cm^2 . The electrodes were connected to a potentiostat machine (μ Autolab type III, Metrohm Autolab, Utrecht, Netherlands). The test cell was deaerated with nitrogen gas during the measurement and water temperature was maintained at 37°C . The open circuit potential (OCP) was measured for 60 minutes and was used as the starting potential. Polarization began at 500 mV below the OCP at a scan rate of 1 mV/s and terminated at 2,000 mV above the OCP. The corrosion parameters were obtained by Autolab NOVA software version 1.7, which systematically establishes two linear extrapolations from the Tafel polarization curves. The intercepts of the extrapolations yield the determination of corrosion potentials, corrosion currents, and corresponding corrosion rates.

2.5 Statistical Analysis

The results of the corrosion rate assay were analyzed using the Brown Forsythe and Tamhane multiple comparison tests. Statistical analysis was performed using the Statistics Package of Social Sciences (SPSS) version 17.0 for window (SPSS Incorporation, Illinois, USA) with statistical significance at $p \leq 0.05$.

3. RESULTS

Figure 1 shows the surface morphology of the anodized Ti-6Al-4V alloy as observed by SEM. While polishing scratches were

seen on the as-received surface, they were otherwise unmarked. In contrast, scattered small pores were seen on the polished surface of the samples treated with an anodizing voltage of 100 V (Figure 1b). The specimens from the 150 V and 200 V groups showed a similar surface morphology, but a greater number of pores were observed with each increased voltage (Figure 1c and d). When the voltage was increased up to 300 V, distinct pores with raised boundaries were observed covering the surface (Figure 1e). This marked change in structure may have resulted because the voltage in this group was over the dielectric breakdown limit. It was observed that anodization with an applied voltage of 300 V produced pores 0.6-4.3 μm in size, which were larger

in comparison to the other groups whose pores were approximately 0.7 μm in size. The surface roughness as investigated by SPM (right side of Figure 1) corresponded to the SEM observations. Increased voltage resulted in an increase in surface roughness. The average thicknesses of the oxide layers observed by SEM are presented in Figure 2. It was found that the thickness of the oxide layers of the as-received, 100 V, and 150 V groups were not clearly identified by this technique, and could not be measured (Figure 2a, b, and c). However, the average oxide layers of the titanium specimens anodized at voltage of 200 V and 300 V were approximate 0.9 and 1.9 μm in thickness, respectively (Figure 2d and e).

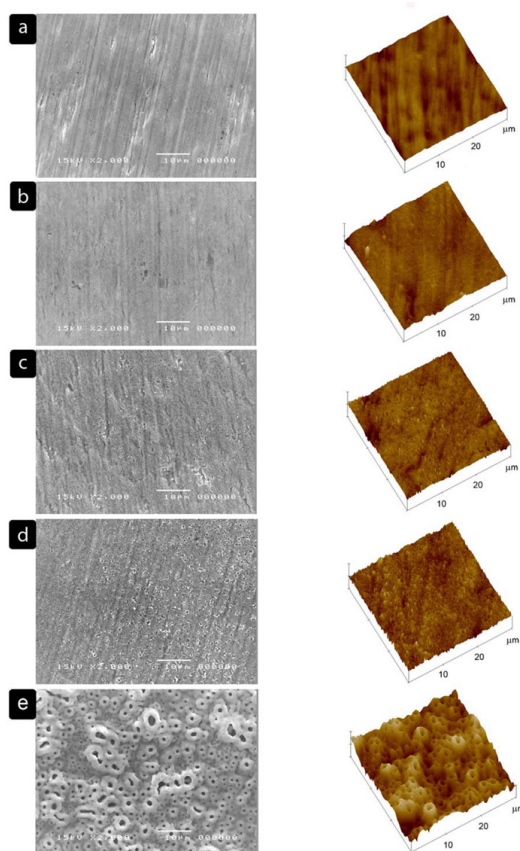


Figure 1. SEM and SPM images of (a) as-received, (b) anodized sample in 0.5 M phosphoric acid at 100 V, (c) 150 V, (d) 200 V and (e) 300 V.

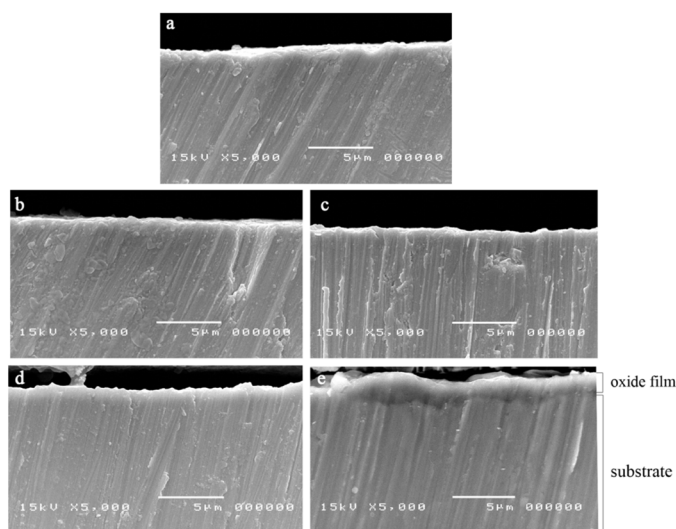


Figure 2. Cross-sectional SEM images of (a) as-received, (b) anodized sample in 0.5 M phosphoric acid at 100 V, (c) 150 V, (d) 200 V and (e) 300 V.

XRD patterns of the anodized and non-anodized (as-received) specimens are shown in Figure 3. No crystalline forms of titanium oxide could be detected on the as-received specimens (Figure 3a), while the anatase form of TiO_2 was found on the specimens anodized at voltage of 200 V and 300 V. However, it should be noted that the peak x-ray intensity for crystalline structures of these two groups was triple the baseline level which represents only a small amount of each crystalline type (Figure 3d and e), especially peak x-ray intensity of 200 V group which is much lower than that of 300 V group. This would be a consequence of thinner oxide layer. In addition, no aluminum oxide or vanadium oxide on any of the samples could be observed, however, it could be due to limitation of XRD to be able to detect if the amount of aluminium or vanadium is very low. The absence of aluminium or vanadium oxides could not however be implied in the study.

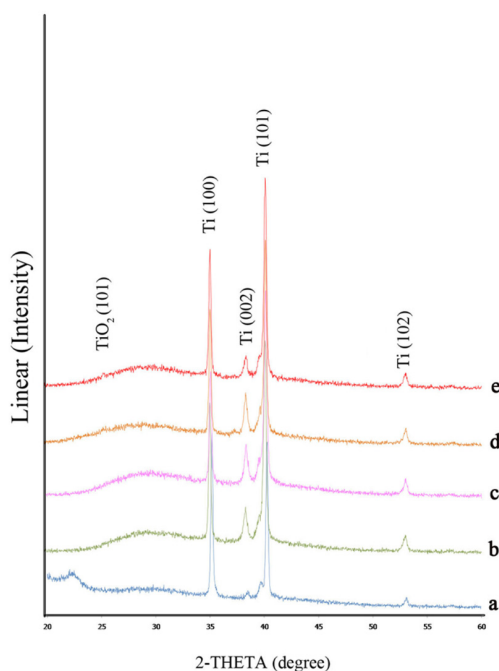


Figure 3. XRD patterns of (a) as-received, (b) anodized sample in 0.5 M phosphoric acid at 100 V, (c) 150 V, (d) 200 V and (e) 300 V.

This study further assayed the samples for their corrosion behavior. The potentiodynamic polarization curves presented in Figure 4 indicated that the corrosion potential (E_{corr}) of the as-received specimens was statistically lower ($p < 0.05$) than that of all anodized groups and that corrosion potential increased with increased voltage (Table 2). The corrosion current density (i_{corr}) and corrosion rate, which was calculated from i_{corr} of all groups, are also

shown in Table 1. Unlike the corrosion potential, there was no statistically significant difference in the corrosion rate among the as-received, 100 V, and 150 V groups. The corrosion rate of 200 V and 300 V groups was also statistically different from the other groups and from each other ($p < 0.05$). Using an anodization voltage of 300 V resulted in the highest corrosion rate among all the groups, followed by 200 V group.

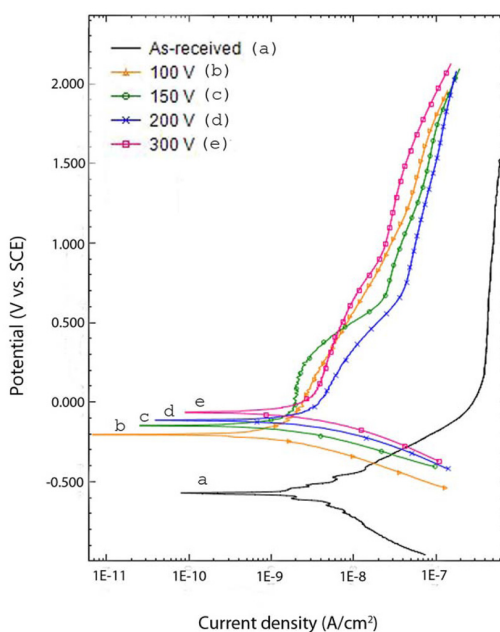


Figure 4. Representative potentiodynamic polarization curves of (a) as-received, (b) anodized sample in 0.5 M phosphoric acid at 100 V, (c) 150 V, (d) 200 V and (e) 300 V.

Table 1. Corrosion parameters of as-received and anodized groups in 0.9% saline solution ($N = 10$).

Group	E_{corr} (V vs. SCE)	i_{corr} (nA/cm ²)	Corrosion rate (mm/year)
As-received	-0.601 ± 0.064^a	4.54 ± 0.71	$7.64 \times 10^{-5} \pm 1.21 \times 10^{-5a}$
100 V	-0.199 ± 0.039^b	4.12 ± 0.83	$6.92 \times 10^{-5} \pm 1.40 \times 10^{-5a}$
150 V	$-0.148 \pm 0.040^{b,c}$	4.39 ± 0.57	$7.39 \times 10^{-5} \pm 9.71 \times 10^{-6a}$
200 V	-0.098 ± 0.032^c	19.49 ± 3.17	$3.27 \times 10^{-4} \pm 5.34 \times 10^{-5b}$
300 V	-0.038 ± 0.029^d	34.34 ± 3.32	$5.77 \times 10^{-4} \pm 5.59 \times 10^{-4c}$

* Entries are means \pm standard deviation and same letter (superscript) shows no statistically significant difference

4. DISCUSSION

In addition to osseointegration, minimal reaction and not being rejected by the body are factors in successful implant placement. However, body fluid is considered an extremely corrosive substance for metallic materials, resulting in ion release. In vivo, most metal ions can form complexes with body proteins and induce allergic reactions, or may act as allergens, which cause chronic inflammation or hypersensitivity [1]. Furthermore, corrosion products may affect the life-span of an implant, with one study indicating a relationship between the level of implant metal ions in the blood serum and movement of the prosthesis [15].

Previous studies have demonstrated that anodization improved the corrosion resistance of titanium [6,7,12] and its alloys [9,10,14]. While there was no absolute conclusion on what is responsible for the increased corrosion resistance from an anodized film, a number of factors have been suggested. Increased oxide layer thickness [9] or a surface with a low Ca/P ratio after being anodized in a calcium and phosphorus-containing electrolyte solution [16] including the presence of anatase in the passivated oxide layer [14] are among factors that may play a part of increase in corrosion resistance. Furthermore, surface morphology [12], including pore size [10,17], or oxide film composition [13], were also determined to be an effect on corrosion behavior of materials. In the present study, the corrosion potential (E_{corr}) of the anodized groups was higher than that of the as-received group. Similar to other studies [9,10,14], our evaluation of E_{corr} confirmed that the corrosion resistance of Ti-6Al-4V alloys could be improved by anodization. The surface anodized with voltage of 300 V showed the highest E_{corr} . This finding might be related to the increased thickness of

the oxide film acted as protective barrier showing better corrosion resistance. Regarding to oxide thickness, few studies reported the linear relationship between anodized potential and oxide thickness [6,9]. This could also be observed in this study even though their studies used much lower potential voltages and different parameters such as electrolytes or time. It can be noticed from the obtained graphs in Figure 4 showing that anodized groups displayed the passive region of potentiodynamic polarization curves unlike the as-received group. This advises the stable oxide film after anodization compared to that of untreated one. In addition, this is well congruent with a previous study showing that even though anodization tends to increase corrosion potential (E_{corr}), high voltage would accelerate the corrosion rate of anodized titanium alloy affirmed with the increase in current density [14]. However, our findings contrast with a study by Song *et al.* which claimed that anodization could not improve the corrosion resistance of Ti-6Al-4V alloys because of the high electric conductivity and high solubility of vanadium oxide on the anodized surface [13]. The different finding between their study and this study could be due to various electrochemical application, electrolyte. Moreover, either aluminium oxide or vanadium oxide could not be observed on the anodized oxide film in the present study as a result of limitation of analysis.

Surface morphology has been described in prior studies as a factor influencing the corrosion characteristics. One study showed that rough pores formed at high potential increased the roughness average (Ra) values of surface roughness [12], and this porous structure on the anodized surface impacted its physical properties. The presence of pores wide enough for electrolytes to enter but

sufficiently narrow to create a stagnant zone can promote corrosion on that surface. While the oxide layer is a natural protective barrier giving titanium and its alloys good corrosion resistance, susceptibility to localized corrosion can occur due to high microenvironmental concentrations of chloride or hydrogen ions resulting from localized destruction of the protective film [18]. It has been reported that the presence of small sized pores generated a higher corrosion rate than did large sized pores because of the lack of free flow of metal ions [19]. Rapid metal dissolution takes place in pores and an excess of positive charges produced in this area leads to the migration of chloride ions into the pores. Increased amounts of metal chlorides in the pores hydrolyze in water to free acids that accelerate the dissolution rate of a metal and its alloys. These could explain our finding that titanium alloy anodized at 300 V presented the greatest corrosion rate followed by 200 V group compared with the other groups. Moreover, the high voltage over the dielectric breakdown limit leading to sparking could cause the anodized surface to become porous. These pores were seen to be high in number and likely promoted localized corrosion (pitting or crevice corrosion) manifested by the highest corrosion rate observed in our study. While the higher corrosion potential of anodized titanium would increase its corrosion resistance in an unfavorable environment, once corrosion occurs, it would corrode relatively faster, as found in our study.

To explain the obtained data displaying in Table 1, the few studies on the relationship between the voltage used in anodizing Ti-6Al-4V alloy and its corrosion rate [9,14] were performed at various voltages no higher than 100 V unlike this study which conducted the voltages starting from 100 V up to 300 V.

They reported that the corrosion rate was decreased with the increased voltage of anodization except the study by Paul and Yadav [14] revealing that applied higher voltage also had an unfavorable effect on corrosion rate. Corresponding to our finding, even though there is no significant difference in corrosion rate among 100 V, 150 V groups and as-received group, it is dramatically increase in current density (i_{corr}) implying higher corrosion rate when 200 and 300 V of voltage were conducted. As abovementioned, the consequent change in surface topography of more porosity formed on the anodized surfaces causing from high voltages would promote higher localized corrosion. It is noted that different voltages would produce different surface morphology of anodized titanium. Therefore, it should be taken into account that potential voltage higher than dielectric breakdown can create the porous oxide surface topography in favor of improved bone growth onto titanium implant material indicating better osseointegration [5]. Whereas, high voltage could also compromise the fatigue strength of implant material due to possible microcracks on the oxide coating of titanium implant [14] and corrosion behavior as found in this study. High voltage was, however, aimed to use in this study to produce porous titanium oxide surface.

The relationship between crystal structure and corrosion behavior is still unclear. A previous study reported that during oxide crystallization, high internal compressive stress occurs. This produces electron conductive paths through the oxide layers, permitting anodic reactions causing oxide layer dissolution [20]. Other studies detected crystalline Ti_2O_3 [10] or the anatase form of TiO_2 [14] on anodized Ti-6Al-4V surfaces and these provided good corrosion resistance compared to an amorphous surface. In contrast, Narayanan et al. concluded that

crystalline structure was less influential on corrosion properties than were the thickness and self-healing pores of the oxide surface [10]. In the present study, the groups anodized at 200 V and 300 V formed anatase TiO₂ on the titanium surfaces even though very small peaks of crystalline structure could be detected. These two groups demonstrated a statistically higher corrosion rate than the other groups regardless of oxide thickness. This may imply that crystalline structure of titanium oxide has less influence on corrosion resistance than the surface morphology of an anodized titanium surface.

Notably, anodization at the highest voltages used in our study provided better corrosion resistance and created rough titanium surface for the reason of improved osseointegration but reversely resulted in higher corrosion rate. However, because the properties and surface topography of an titanium oxide layer can be modified by adjusting the conditions of the anodization process, further study defining the suitable conditions for anodization is necessary in order to obtain the optimal implant properties combining its mechanical, physical, and electrical properties, and especially its biocompatibility. This should include *in vitro* study on behavior of osteoblastic-like cell on anodized titanium in order to apply to medical applications.

5. CONCLUSIONS

It shows that anodization could improve the corrosion potential of Ti-6Al-4V alloy, while the higher voltages would have an adverse effect on corrosion behavior leading to higher corrosion rate. This study suggests that the porous surface would have an influence on the corrosion behavior of the anodized titanium alloy. The appropriate applied anodization voltage is necessary to

generate the optimum titanium surface.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support from The ASAHI Glass Foundation. The authors would also like to thanks the Metallurgy and Materials Science Research Institute, Chulalongkorn University for generously providing the use of test instruments.

REFERENCES

- [1] Singh R. and Dahotre N., Corrosion degradation and prevention by surface modification of biometallic materials, *J. Mater. Sci. Mater. Med.*, 2007; **18**(5): 725-751. DOI 10.1007/s10856-006-0016-y.
- [2] Jackson M.J. and Ahmed W., *Surface Engineered Surgical Tools and Medical Devices*, Springer, USA, 2007.
- [3] Thompson G.J. and Puleo D.A., Ti-6Al-4V ion solution inhibition of osteogenic cell phenotype as a function of differentiation timecourse *in vitro*, *Biomaterials*, 1996; **17**(20): 1949-1954. DOI 10.1016/0142-9612(96)00009-9.
- [4] Kim K.H. and Ramaswamy N., Electrochemical surface modification of titanium in dentistry, *Dent. Mater. J.*, 2009; **28**(1): 20-36. <http://dx.doi.org/10.4012/dmj.28.20>.
- [5] Schupbach P., Glauser R., Rocci A., Martignoni M., Sennerby L., Lundgren A. and Gottlow J., The human bone-oxidized titanium implant interface: A light microscopic, scanning electron microscopic, back-scatter scanning electron electron microscopic, and energy-dispersive x-ray study of clinically retrieved dental implants, *Clin. Implant. Dent. Relat. Res.*, 2005; **7**: **Suppl 1**: 36-43. DOI 10.1111/j.1708-8208.2005.tb00073.x.

- [6] Afshar A. and Vaezi M.R., Anodizing of titanium in NaOH solution and its corrosion resistance in PBS physiologic solution, *Scientia Iranica*, 2003; 10: 361-366.
- [7] Karambakhsh A., Afshar A., Ghahramani S. and Malekinejad P., Pure commercial titanium color anodizing and corrosion resistance, *J. Mater. Eng. Perform.*, 2011; 20(9): 1690-1696. DOI 10.1007/s11665-011-9860-0.
- [8] Lewandowska M., Pisarek M., Rozniatowski K., Gradzka-Dahlke M., Janik-Czachor M. and Kurzydowski K.J., Nanoscale characterization of anodic oxide films on Ti-6Al-4V alloy, *Thin Solid Films*, 2007; 515(16): 6460-6464. DOI 10.1016/j.tsf.2006.11.074.
- [9] Karambakhsh A., Afshar A. and Malekinejad P., Corrosion resistance and color properties of anodized Ti-6Al-4V, *J. Mater. Eng. Perform.*, 2012; 21(1): 121-127. DOI 10.1007/s11665-010-9791-1.
- [10] Narayanan R. and Seshadri S.K., Phosphoric acid anodization of Ti-6Al-4V - structural and corrosion aspects, *Corros. Sci.*, 2007; 49: 542-558. DOI 10.1016/j.corsci.2006.06.021.
- [11] Kim S.E., Lim J.H., Lee S.C., Nam S.C., Kang H.G. and Choi J., Anodically nanostructured titanium oxides for implant applications, *Electrochimica Acta*, 2008; 53(14): 4846-4851. DOI 10.1016/j.electacta.2008.02.005.
- [12] Park I.I., Woo T., Lee M., Ahn S., Park M., Bae T. and Seol K., Effects of anodizing voltage on the anodized and hydrothermally treated titanium surface, *Met. Mater. Int.*, 2006; 12(6): 505-511. DOI 10.1007/BF03027751.
- [13] Song H.J., Kim M.K., Jung G.C., Vang M.S. and Park Y.J., The effects of spark anodizing treatment of pure titanium metals and titanium alloys on corrosion characteristics, *Surf. Coat. Technol.*, 2007; 201(21): 8738-8745. DOI 10.1016/j.surfcoat.2006.11.022.
- [14] Paul S. and Yadav K., Corrosion behavior of surface-treated implant Ti-6Al-4V by electrochemical polarization and impedance studies, *J. Mater. Eng. Perform.*, 2011; 20(3): 422-435. DOI 10.1007/s11665-010-9691-4.
- [15] Okazaki Y. and Gotoh E., Comparison of metal release from various metallic biomaterials *in vitro*, *Biomaterials*, 2005; 26(1): 11-21. DOI 10.1016/j.biomaterials.2004.02.005.
- [16] Narayanan R. and Seshadri S.K., Point defect model and corrosion of anodic oxide coatings on Ti-6Al-4V, *Corros. Sci.*, 2008; 50: 1521-1529. DOI 10.1016/j.corsci.2008.02.023.
- [17] Narayanan R., Mukherjee P. and Seshadri S., Synthesis, corrosion and wear of anodic oxide coatings on Ti-6Al-4V, *J. Mater. Sci. Mater. Med.*, 2007; 18(5): 779-786. DOI 10.1007/s10856-006-0007-z.
- [18] Fontana M.G., *Corrosion Engineering*, McGraw Hill, New York, 1986.
- [19] Seah K.H.W., Thampuran R. and Teoh S.H., The influence of pore morphology on corrosion, *Corros. Sci.*, 1998; 40: 547-556. DOI 10.1016/S0010-938X(97)00152-2.
- [20] Milosev I., Metikos-Hukovic M. and Strehblow H.H., Passive film on orthopaedic TiAlV alloy formed in physiological solution investigated by X-ray photoelectron spectroscopy, *Biomaterials*, 2000; 21: 2103-2113. DOI 10.1016/S0142-9612(00)00145-9.