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The effect of low current density on the hydrophilicity and surface properties of the anodized films performed by two-step anodization

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Abstract

The anodized films were performed by two-step anodization. The main objective of this study was to investigate the effect of different low current density by two-step anodization on the anodizing behavior, surface morphologies, surface roughness, surface species and hydrophilic property of the anodized films. The surface roughness can interlock the implant and biological tissues resulting in improve the osseointegration and the stability of dental implant materials. The hydroxyl groups can form hydrogen bond with water molecules resulting in increased the hydrophilicity to the anodized films. The FESEM and AFM were used for the analysis of the surface morphology and roughness of the anodized films. The surface roughness was obtained after anodization. The XPS was used for study the surface species of the anodized films. Hydrophilic property was measured by contact angle measurement. It was seen that the anodized films surface became hydrophilicity. The anodized films formed at low current density of 0.50 mA cm^{-2} in 1 M H_3PO_4 + 80% V/V C_2H_5OH under two-step anodization showed highest hydrophilicity. Moreover, the surface roughness and OH groups also increased. Therefore, the increase in both OH groups and surface roughness could enhance the hydrophilicity to the anodized films. Therefore, OH groups and surface roughness are two important factors may improve osseointegration in order to apply to dental implant application.

Keywords: hydrophilicity; low current density; two-step anodization

1. Introduction

The titanium alloys has favorable properties such as good biocompatibility [1], high corrosion and high strength [2]. These properties make it valuable in a number of applications such as dental implant applications. Nevertheless, titanium and its alloys are bioinert material. Therefore, developing an osseointegration is important for utilizing the advantages of the titanium alloy. Anodization is a useful technique for forming the anodized films on titanium and its alloys. The chemical composition and the topography of structure modification of TiO_2 can improve the hydrophilicity [3]. The highly porous films, the surface roughness are important physical properties on hydrophilic behavior. Therefore, not only chemical properties but also physical properties have some beneficial effects on the hydrophilicity on the films surface [1, 4, 5], which are two important factors for improving protein adsorption, cell attachment and cell behaviors including proliferation and differentiation [2, 6, 7]. Therefore, the surface roughness, surface species and hydrophilicity were investigated to help understanding about how the surface properties affect the osseointegration and providing the optimal condition for dental implant surface. The main objective of this study was to investigate the effect of different low current density by two-step anodization on the anodizing behavior, surface morphologies, surface roughness, surface species and hydrophilic property of the anodized films. The advantages of the anodized films preparation with low current density are save energy, save cost and safety. The surface roughness can interlock the implant and biological tissues resulting in improve the osseointegration and the stability of dental implant materials. The hydroxyl groups can form hydrogen bond with water molecules resulting in increased the hydrophilicity to the anodized films. Moreover, both OH groups and surface roughness could enhance the hydrophilicity to the films. The anodized films with hydrophilicity were found to be beneficial for improving osseointegration.

2. Materials and methods

The Ti-6Al-4V specimens used in electrochemical experiment were polished by silicon carbide paper from No. 400 up to 1,200. Before anodization, all samples were immersed in 1 M HF for a minute and then rinsed thoroughly by deionized water and dried in air. For the first step anodization, Ti-6Al-4V, Pt and Ag/AgCl were used as working electrode, counter electrode and reference electrode, respectively. From my previous work, the anodized films were prepared by one-step anodization at 2 mA cm^{-2} in mixture of different C_2H_5OH concentration with 1M H_3PO_4, the result showed that the anodized films formed at 2 mA cm^{-2} in 1M H_3PO_4 with 80% V V^{-1} C_2H_5OH showed highest hydrophilicity. Therefore, this condition was selected as the working electrode in this work. The anodized films were performed using 2 mA cm^{-2} in 1M H_3PO_4 + 80% V V^{-1} C_2H_5OH solution for 30 minutes on Ti-6Al-4V. For the second step anodization, the anodized films from the first step anodization, Pt and Ag/AgCl were used as working electrode, counter electrode and reference electrode, respectively. The anodized films were carried out under different current densities from 0.50 mA cm^{-2} to 1.50 mA cm^{-2} in 1M H_3PO_4 + 80% V V^{-1} C_2H_5OH for 30 minutes as shown in Fig. 1.

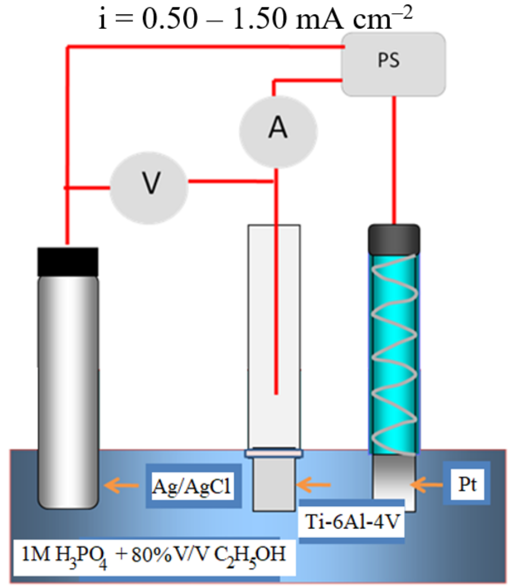


Fig. 1 Electrochemical experiment using low current density

The surface roughness (R_a, R_q, R_z, R_p) of the Ti-6Al-4V and the anodized films was examined by atomic force microscopy (AFM, XE-120 Park Systems). Field Emission Scanning Electron Microscope (FE-SEM; Carl Zeiss Auria, German) was used to observe the surface morphology of the anodized films. X-ray photoelectron spectroscopy (XPS; AXIS ULTRADLD, Kratos analytical, Manchester UK.) was used for surface species analysis for example TiO_2, OH groups on the anodized films surface. The spectra were collected using a monochromatic Al K_α 1, 2 radiation at 1.40 keV. The C1s line at 285 eV was used for calibrating the binding energy. The surface hydrophilicity of Ti-6Al-4V and the anodized films was examined by measuring contact angles using a sessile drop of deionized water on each specimen surface. Statistical analysis was performed by Origin software. Significant differences in the contact angles were determined by one-way analysis of variance (ANOVA) and followed by Bonferroni post hoc tests for multiple comparisons. A p-value of < 0.05 was considered to be significant.

3. Results and Discussion

The Growth of the Anodized Films under Two-Step Anodization

The anodic growth kinetic curves are shown in Fig. 2, which show the different behaviors on the Ti-6Al-4V surface during anodizing process using a range of current densities between 0.50 – 1.50 mA cm^{-2} in 1 M H_3PO_4 + 80% V V^{-1} C_2H_5OH as an electrolyte. The growth of anodized films under anodizing process, the oxygen and hydroxyl ions migrated from the electrolyte through the Ti-6Al-4V surface when the constant current flowed through the three electrode cell. In this process, the titanium dissolved and formed titanium oxide at the surface. Moreover, the hydrogen ions formed hydrogen gas bubbles at the cathode [8]. These bubbles are a significant factor in the formation of pores during anodizing process [9]. The growth of anodized films consists of two processes; the first process, the anodic potential increases to the breakdown potential resulting in the dissolution of the anodized films. The slope of the potential of two-step anodization is much faster than one-step anodization. Moreover, the increased current density causes an increased voltage [10] due to the growing electric energy [11]. It is indicated that the increment of current density could enhance the incorporation of metal oxide leading to an increase in the electrical resistance in the anodized films [12]. The second process, the voltage drop increases because of the increased oxide thickness [13]. The final voltage increased with the increase in current density. Therefore, the improvement of current density is beneficial for the formation of anodized films on Ti-6Al-4V surface. On the contrary, the voltage become stable until the end of the process. It is due to the oxide growth and dissolution of the anodized films in the same time. This result is similar to our previous works [14, 15], Wu, Z. et al.'s result [13] and Ping, W. et al.'s result [11].

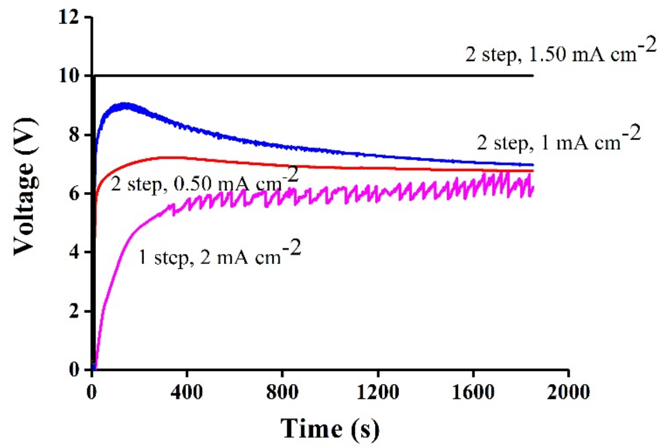


Fig. 2 Voltage vs. Time curves of the anodized films under one-step anodization at 2 mA cm^{-2} and two-step anodization at low current density of 0.50 – 1.50 mA cm^{-2} in 1M H_3PO_4 + 80% V V^{-1} C_2H_5OH.

Hydrophilicity of the anodized films

The contact angles of the untreated Ti-6Al-4V, the anodized films under one-step anodization at 2 mA cm^{-2} and the anodized films performed at 0.50, 1 and 1.50 mA cm^{-2} were 64.20°, 43.40°, 12.63°, 16.10°, 16.80°, respectively as shown in Fig. 3. The untreated Ti-6Al-4V showed the largest contact angle and the anodized films formed at 0.50 mA cm^{-2} had the lowest contact angle. The contact angle of the anodized films significantly decreased after two-step anodization. It is indicated that the hydrophobic Ti-6Al-4V was changed to hydrophilic surface by two-step anodization.

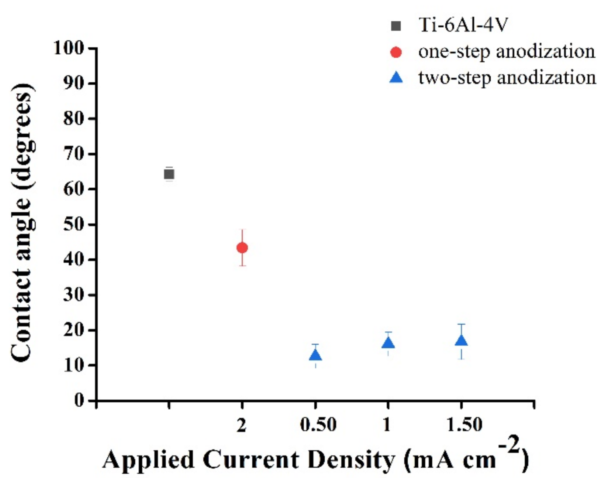


Fig. 3 The contact angle of the untreated Ti-6Al-4V, the anodized films under one-step anodization at 2 mA cm^{-2} and two-step anodization at low current density of 0.50 – 1.50 mA cm^{-2} in 1M H_3PO_4 + 80% V V^{-1} C_2H_5OH.

Surface Roughness of the Anodized Films

The hydrophilicity, surface roughness and surface morphology of the anodized films were measured using contact angle measurement, AFM and FE-SEM as shown in Fig. 3, Fig. 4 and Fig. 5. Table 1 showed the R_a (the roughness average), R_q (the root-mean-squared roughness), R_z (the ten-point average roughness) and R_p (the peak-to-valley of the line) of the untreated Ti-6Al-4V and the anodized films performed at 0.50 and 1.50 mA cm^{-2} in 1M H_3PO_4 + 80 V/V C_2H_5OH. The R_a and R_q of the anodized films performed at 0.50 and 1.50 mA cm^{-2} were significantly higher than that of the untreated Ti-6Al-4V (Table 1). The roughness in Table 1 showed different value because the parameters of surface roughness were calculated from different formula and showed different definitions; R_a is Roughness Average calculated from $R_a = \frac{1}{n}\sum_{i=1}^{n}|y_i|$, R_q is Root Mean Square (RMS) Roughness calculated from $R_p = \sqrt{\frac{1}{n}\sum_{i=1}^{n} y_i^2}$, R_z is the ten-point average roughness and R_p is the peak-to-valley of the line calculated from $R_p = \max_i y_i$. Moreover, the results showed that the effect of current densities on the surface roughness is not obvious. This result is similar to E. Vermesse et al.'s report [16]. Therefore, no effect of the anodic current densities was noted on the roughness. The images from atomic force microscopy are shown in Fig. 4. The roughness (R_a) of the films prepared under two-step anodization in different current densities is approximately 162 – 202.50 nm.

Table 1 Roughness and contact angle values

sample	R_a (nm)	R_q (nm)	R_z (nm)	R_p (nm)
Ti-6Al-4V	7.30	10.10	96.80	62.90
0.50 mA	202.50	235.60	1036.30	530.90
1.50 mA	162	193.80	897.40	462.80

After anodization, the roughness of Ti-6Al-4V was improved. Improving of roughness on the films surface will affect the growth of bone tissue [6]. This work could enhance the roughness on the Ti-6Al-4V after anodization. After anodization at low current densities of 0.50 – 1.50 mA cm^{-2}, the R_a and the R_q of the samples increase due to the dissolve and films formation on the Ti during anodizing process as shown in the anodized films formation in Fig. 2. It is indicated that the two-step anodization leads to the increase of R_a and R_q due to the formation and growth of the anodized films on Ti-6Al-4V. The hydrophilicity of the anodized films was improved significantly after anodization.

The contact angle of this work is accordance with this theory: the anodized films formed at 0.50 and 1.50 mA cm^{-2} exhibit lower contact angle compared to the Ti-6Al-4V surface since the former has significant higher roughness value compared to the latter. Therefore, the effect of roughness on hydrophilicity should be considered to understand the mechanism of hydrophilicity.

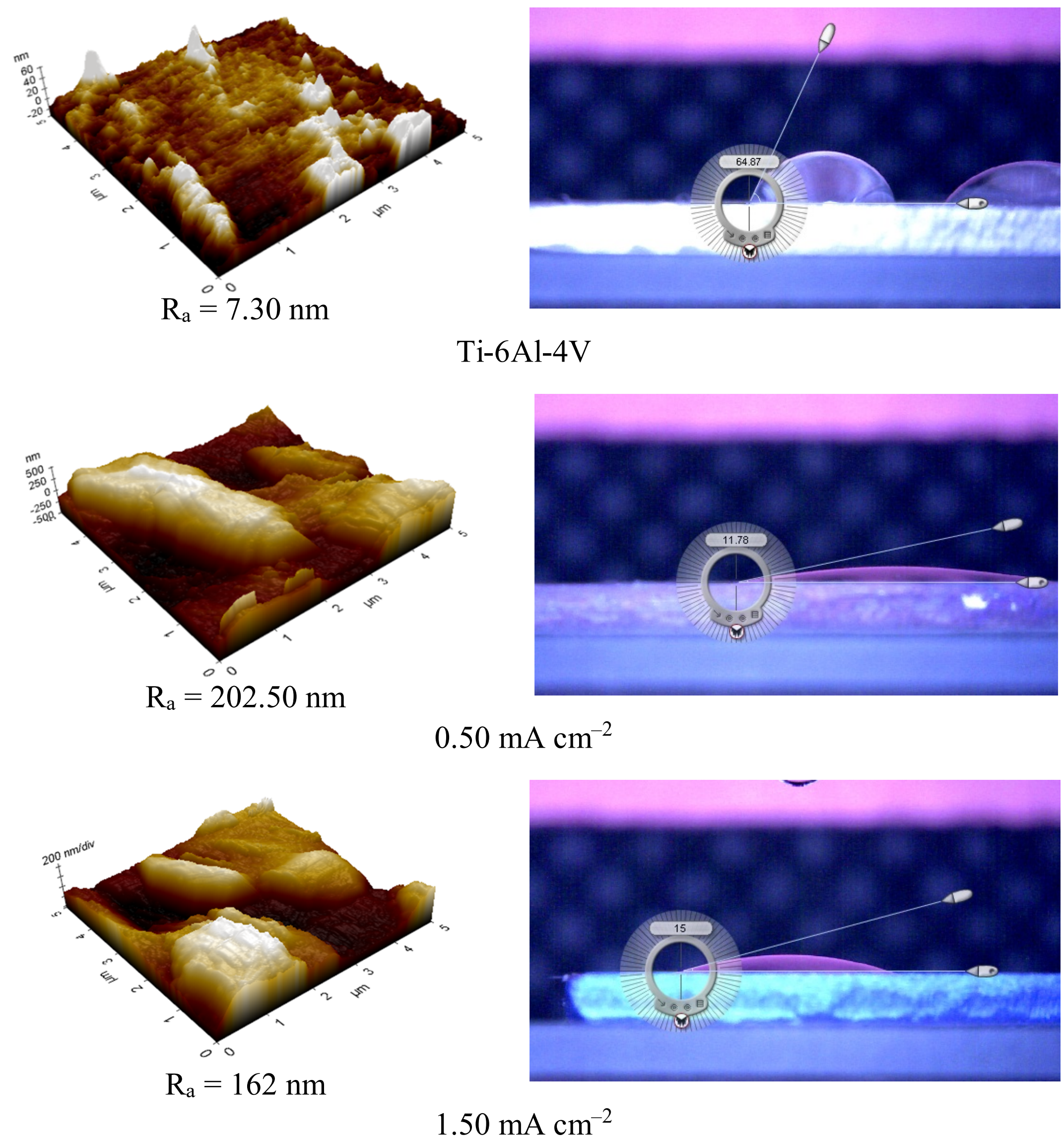
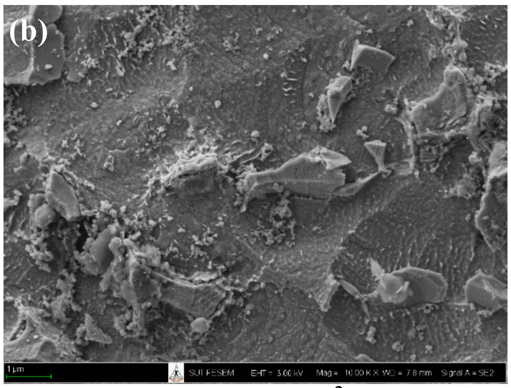
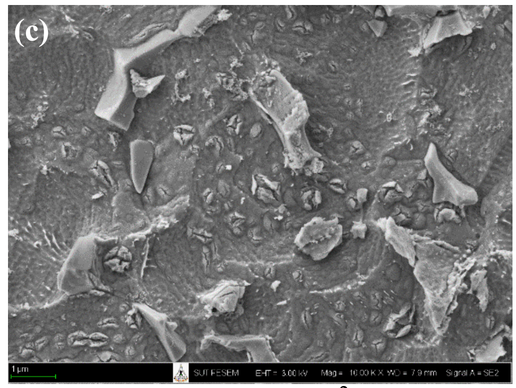


Fig. 4 AFM images and contact angle of Ti-6Al-4V and the anodized films formed at 0.50 – 1.50 mA cm^{-2}.

Ti-6Al-4V



0.50 mA cm^{-2}



1.50 mA cm^{-2}

Fig. 5 Surface morphology of the Ti-6Al-4V and after various treatment: (a) Ti-6Al-4V, the anodized films performed by two-step anodization using (b) 0.50 mA cm^{-2} and (c) 1.50 mA cm^{-2}.

Fig. 5 shows the surface morphology of the untreated Ti-6Al-4V and the anodized films formed at 0.50 and 1.50 mA cm^{-2}. The results showed that the untreated Ti-6Al-4V showed smooth surface. However, the surface of the anodized films using 0.50 and 1.50 mA cm^{-2} under two-step anodization showed more roughness than untreated Ti-6Al-4V. It is indicated that two-step anodization using low current density in 1M H_3PO_4 + 80 V V^{-1} C_2H_5OH could enhance surface roughness to the anodized films.

Spectroscopic Investigation of the Anodized Films Surface

Fig. 6 shows the XPS spectra of the Ti-6Al-4V before and after anodization. The values of the binding energy of Ti $2p_{3/2}$ of Ti-6Al-4V surface could be fitted two components at 458.60 eV and 460 eV and Ti $2p_{1/2}$ could be fitted two components at 464.40 eV and 465.50 eV, corresponding to a chemical state of Ti^{4+} [17]. While, the values of the binding energy of Ti $2p_{3/2}$ of the anodized films formed at 0.50 mA cm^{-2} by two-step anodization could be fitted two components at 458 eV and 459.30 eV and Ti $2p_{1/2}$ could be fitted two components at 463.40 eV and 464.70 eV, corresponding to a chemical state of Ti^{4+} [17]. The O1s of Ti-6Al-4V surface could be fitted four components at 530 eV (O^{2-}), 531.20 eV (OH^{-}), 532.30 eV (OH^{-}) and 533.30 eV (H_2O), which corresponding to a chemical state of O^{2-}, OH^{-} and H_2O, respectively. while, the O1s of the anodized films formed at 0.50 mA cm^{-2} by two-step anodization could be fitted four components at 529.30 eV (O^{2-}), 530.30 eV (O^{2-}), 531.60 eV (OH^{-}) and 532.60 eV (OH^{-}), which corresponding to a chemical state of O^{2-} and OH^{-}, respectively [17 – 19]. The XRD cannot detect the peak because the anodized films are very thin films. Therefore, the XPS was selected to identify the chemical species of the anodized films. The XPS spectra showed the chemical species by binding energy. The results showed that the intensity of binding energy of Ti^{4+} decreased due to the formation of the TiO_2 films on the Ti-6Al-4V. Moreover, the intensity of binding energy of OH groups increased. It is indicated that the increasing of OH groups and decreasing of Ti^{4+} could enhance the hydrophilicity to the anodized films.

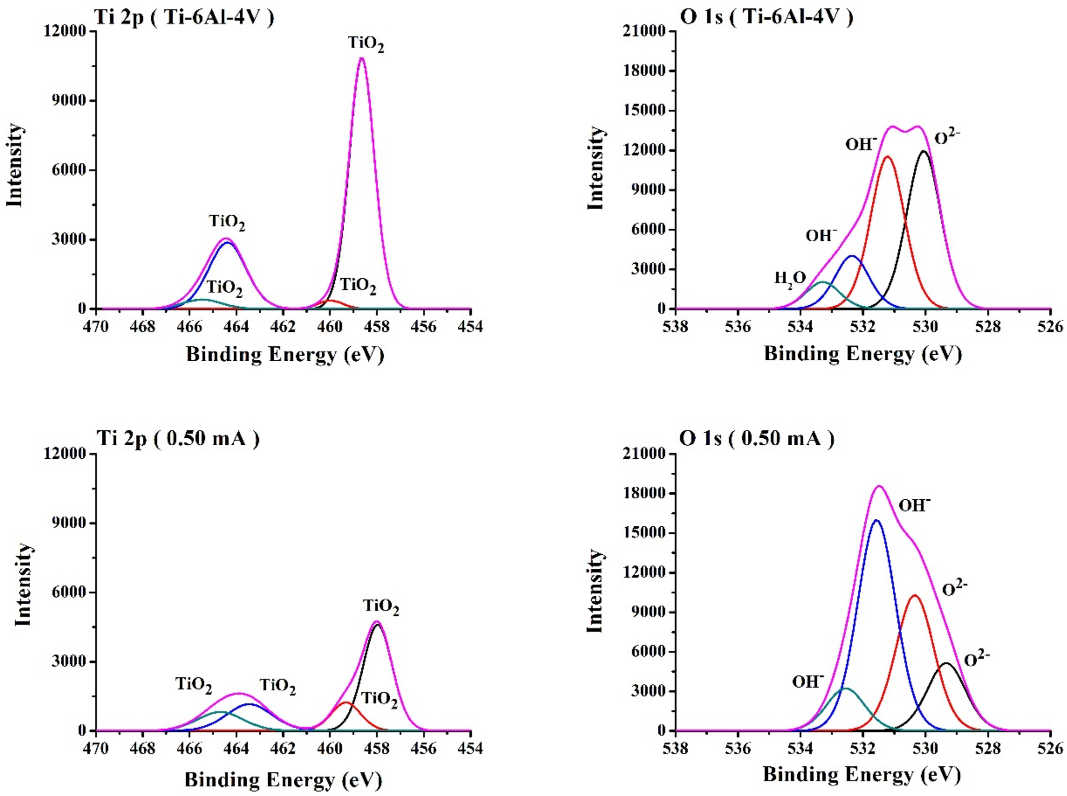


Fig. 6 Ti 2p and O 1s XPS spectra of Ti-6Al-4V and the anodized films formed at 0.50 mA cm^{-2} in 1 M H_3PO_4 + 80% V/V C_2H_5OH.

Table 2 shows the comparison of peak area for oxide species (O^{2-}), hydroxyl groups (OH^-) and adsorbed molecular water (H_2O) of Ti-6Al-4V and the anodized films formed at 0.50 mA cm^{-2} by two-step anodization. Fig. 6 and Table 2 show that the binding energy of the anodized films formed at 0.50 mA cm^{-2} by two-step anodization shifted to higher binding energy and the peak area of oxide species (O^{2-}) and hydroxyl groups (OH^-) increase. Moreover, Fig. 6 show that the intensity of the Ti2p of the anodized films decrease after anodization. It is found that there is no relationship between the roughness and the current density. As is stated in Ref. [13], the anodized films growth is composed of several processes. During anodizing process using constant current density, the injection of electrons into the anodized films and the oxygen evolution cause electric breakdown on the films. According to the Pourbaix diagram, the titanium oxide has a large tendency to react with hydroxyl group to form hydrous oxide and dissolve in electrolyte solution resulting in the porous structure. The relationship between the current density and the breakdown voltage may important role in anodic breakdown as the mechanical property of the films. The increased current densities cause changing the electric filed and the adsorption of ionic species such as OH groups at the oxide/electrolyte interface. Therefore, the oxide growth behavior may be different [13]. It may be due to the formation of the anodized films on the Ti-6Al-4V surface. Therefore, the anodized films formed by two-step anodization at a low current density can increase OH groups and decrease titanium because of the formation of the anodized films. It is indicated that the increase in OH groups can improve the hydrophilicity to the films. Therefore, not only physical properties (roughness) but also chemical properties (TiO_2 and OH groups) has some beneficial effects on the hydrophilicity on the anodized films surface [1], which are two important factors may improve osseointegration in order to apply to dental implant application.

Table 2 Comparison of peak area for oxide species (O^{2-}), hydroxyl groups (OH^-) and adsorbed molecular water (H_2O) of Ti-6Al-4V and the anodized films formed at 0.50 mA cm^{-2} in 1 M H_3PO_4 + 80% V V^{-1} C_2H_5OH

Sample	Peak area (%)		
	Oxide species (O^{2-})	**Hydroxyl groups (OH^-)**	**Adsorbed molecular water (H_2O)**
Ti-6Al-4V	40.50	52.70	6.80
0.50 mA cm^{-2}	44.60	55.40	0

4. Conclusion

The anodized films formed at low current density of 0.50 – 1.50 mA cm^{-2} in 1 M H_3PO_4 + 80% V V^{-1} C_2H_5OH under two-step anodization showed different anodizing behavior and also changed the surface morphologies, surface roughness, surface species and hydrophilicity. The formation of the anodized films benefits from the increased potential breakdown resulting in the dissolution of the anodized films and the increased voltage drop due to the increased oxide thickness. The two-step anodization using low current density of 0.50 – 1.50 mA cm^{-2} in 1 M H_3PO_4 + 80% V V^{-1} C_2H_5OH leads to the increase of the surface roughness, OH groups and the decrease of titanium due to the growth of the anodized films on Ti-6Al-4V. Moreover, the anodized films formed at 0.50 mA cm^{-2} showed highest hydrophilicity due to higher OH group and surface roughness than other conditions. Therefore, the increase in both OH groups and surface roughness could enhance the hydrophilicity to the anodized films under two-step anodization, which are two important factors may improve osseointegration in order to apply to dental implant application.

5. Suggestions

Since the focus of this research is the improvement of the hydrophilicity by two-step anodization at low current density. The results showed that the two-step anodization at low current density could enhance hydrophilicity to the anodized films. These finding may enhance the biocompatibility to the anodized films. Furthermore, the research framework may study about the biocompatibility on the anodized films.

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