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Effect of Ethanol on Hydrophilicity of the Anodized Films Performed by Two-Step Anodization at Low Current Density

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Abstract

Dental implants are usually made from commercially pure titanium or its alloys. The aim of this research was to evaluate the influence of the ethanol addition in 1 M H_3PO_4 as an electrolyte on hydrophilicity of the anodized films. Ti-6Al-4V alloy plates were modified using two-step anodization at a low current density of 2 mA cm^{-2} in 1 M H_3PO_4 with addition of used as an electrolyte. Surface oxide properties were characterized by using various surface analytic techniques, including Field Emission Scanning Electron Microscope (FE-SEM), Atomic Force Microscope (AFM), X-ray photoelectron spectroscopy (XPS) and contact angle measurement. The non-treated Ti-6Al-4V and the anodized films formed by one-step anodization were used as control samples. A significant increase in hydrophilicity ($p<0.05$) was observed on the anodized films formed in H_3PO_4 with addition of 80%v/v ethanol via two-step anodization due to the formation of rough surface, hydroxyl groups (OH^-) and adsorbed molecular water (H_2O). The enhanced hydrophilicity could be explained by both the surface chemistry and surface topography of the anodized films.

1. Introduction

Ti-6Al-4V has been increasingly used in dental implant applications due to its good mechanical properties and biocompatibility [1,2]. However, surface modification is usually required to improve the osseointegration between the implant surface and bone [3].

Recently, many works have been focused on the surface modification of Ti-6A-4V to permit its chemical composition and the topography of surface layers to improve hydrophilicity. It is believed that the use of high surface roughness and hydroxyl group rather than low surface roughness and hydroxyl group has some beneficial effects on hydrophilicity [2]. This is beneficial for dental implant applications. Moreover, the more hydrophilic surface of the anodized films is much more cell adhesion, spreading, proliferation and differentiation on the surface [4] because of their hydroxyl group on the surface. The hydroxyl group may guide the adhesion of proteins by mediating the integrins signaling pathway which promote cell adhesion and responses [5].

The anodization was used in this work, since it produces the uniform titanium dioxide films on the surfaces of Ti-6Al-4V. Moreover, it is a simple technique and can coat on the complex shapes. However, conventional method based on one-step anodization generally leads to oxide nanotubes comprising of bundled top surfaces. Therefore, the two-step anodization was used to solve this problem. The two-step anodization technique can produce the highly ordered and perfectly aligned oxide nanotubes with clear and open top morphology [6,7].

The aim of this study was to investigate effects of an addition of the ethanol in phosphoric acid used as an electrolyte on chemical species, surface morphology, surface roughness and formation of hydrophilic groups on the anodized surfaces. To achieve these, the two-step anodization at a low current density of 2 mA cm^{-2} in 1 M H_3PO_4 with addition of 20, 40 and 80%v/v C_2H_6O was employed to fabricate the anodized films on Ti-6Al-4V.

2. Experimental

The Ti-6Al-4V plate with dimensions of 10 x 20 x 1 mm^3 was polished by using SiC paper, and then washed in deionized water. A Pt electrode was used as a counter electrode. Ag/AgCl was used as a reference

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electrode. The working electrode (Ti-6Al-4V plate) was immersed in 1 M HF for a minute and rinsed with distilled water. The anodized films were fabricated using a two- step anodization process in phosphoric acid with various ethanol additions. The concentration of phosphoric acid was 1 M and the volume proportions of ethanol were chosen as 0, 20, 40 and 80%v/v. The anodizing current density was 2 mA cm^{-2}. The first anodization step lasted for 30 minutes. The highest hydrophilicity films were selected as the working electrode in the second anodization step. The second anodization step was carried out under the same condition as the first one. The hydrophilicity of the anodized films was investigated using contact angle measurement. Three samples of every condition were measured three times. The data expressed as the mean plus standard deviation (SD). Statistical analysis was performed by Origin software. Statistical significance was evaluated by one- way analysis of variance (ANOVA) and multiple comparisons were performed by Bonferroni post hoc tests. A p-value of < 0.05 was considered to be statistically significant. An X-ray photoelectron spectroscopy (XPS; AXIS ULTRADLD, Kratos analytical, Manchester UK.) was used to detect the surface species of the anodized films surfaces. In the XPS experiment, a monochromatic Al $K_{\alpha\ 1,2}$ radiation at 1.4 keV was used. The measured binding energies were calibrated by the C 1s peak at binding energy = 285 eV. Field Emission Scanning Electron Microscope (FE-SEM; Carl Zeiss Auria, German) was used to observe the surface morphology of the anodized films. Atomic Force Microscope (AFM, XE-120 Park System) was used to characterize the surface roughness of the anodized films. The value of surface roughness (R_a) was calculated.

3. Results and discussion

3. 1 Surface hydrophilicity of the anodized films performed by one-step anodization

The contact angle was measured for studying the hydrophilicity of the anodized films. The contact angles of Ti-6Al-4V without anodization and Ti-6Al-4V treated by anodization in different concentration of ethanol are shown in Figure 1. A contact angle of Ti-6Al-4V without anodization is 75° and Ti-6Al-4V treated by one- step anodization with ethanol addition of 0, 20, 40 and 80%v/v in 1 M H_3PO_4 is 65. 79°, 70. 27°, 69. 57° and 45°, respectively. Only 80%v/v ethanol significantly decreases the contact angle, while the others (0, 20, and 40%v/v) do not. Therefore, after anodization using 80%v/v ethanol, the hydrophilicity is enhanced. Therefore, based on the wettability tests, 80%v/v ethanol in 1 M H_3PO_4 was chosen as an electrolyte to fabricate anodized films which function as working electrode in second anodization step.

3. 2 Surface hydrophilicity of the anodized films performed by two-step anodization

Figure 1 shows the hydrophilicity of each sample investigated by measuring the contact angle of a distilled water droplet on the sample surface. Compared with the anodized films with one- step anodization, the anodized films with two- step anodization (0, 20, 40 and 80%v/v ethanol addition) substantially change the hydrophilicity, the contact angle significantly decreases from 45° to 28. 83°, 25.73°, 26.84° and 21.29°, respectively. It is clear that two-step anodization at low current density of 2 mA·cm^{-2} in 1 M H_3PO_4 with 80%v/v ethanol can play an important role in enhancing the hydrophilicity of the anodized films. On the other hand, the anodized films performed by two- step anodization in 1 M H_3PO_4 with 20 and 40%v/v ethanol additions exhibit a similar contact angle as that of 0%v/v ethanol addition.

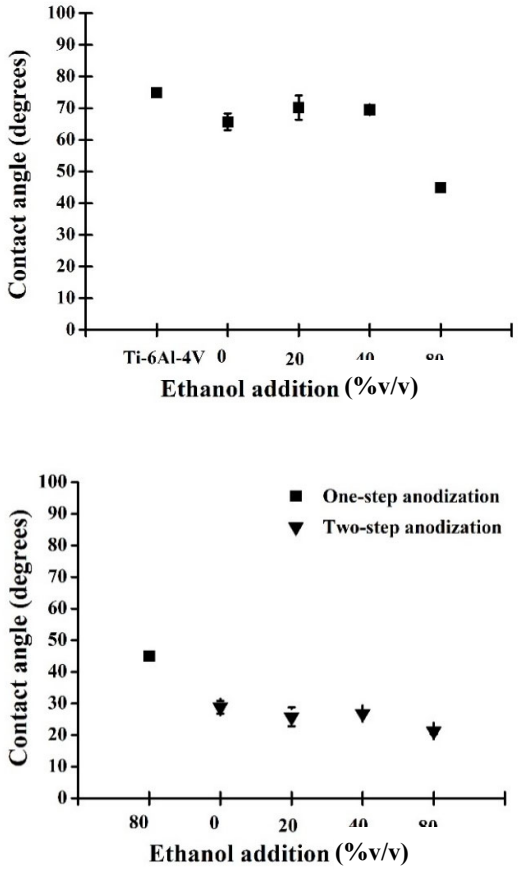

Figure 1. Contact angle of Ti-6Al-4V and the anodized films formed by one- step and two-step anodization under different ethanol additions in 1 M H_3PO_4.

3.3 Spectroscopic investigation of the anodized films surface

XPS was used to analyze chemical species of the anodized films and the binding energies of O 1s. Figure 2 shows XPS high resolution spectra of O 1s of (a, b) Ti-6Al-4V, (c, d) 0, 80%v/v ethanol by one-step anodization, (e, f) 0, 80%v/v ethanol by two-step anodization. The asymmetry feature of the curve reveals the variation of oxidation number of oxygen. The spectra of O 1s can be separated by fitting the data with Gaussian/ Lorentzian lineshape. The binding energy for O 1s around 529-530 eV represent oxide species (O^{2-}) related to titanium oxide. A higher binding energy around 531-532 eV assigned to OH groups adsorbed on the surface. The peak located at around 533-534 eV attributed to the adsorbed molecular water (H_2O) on the surface [8-13].

Table 1 shows the comparison of peak area for oxide species (O^{2-}), hydroxyl groups (OH^-) and the adsorbed molecular water (H_2O) with a mixture of 1 M H_3PO_4 and ethanol used as an electrolyte in both one-step and two-step anodization. The peak area of titanium oxide (O^{2-}) decreases, while that of hydroxyl groups (OH^-) and adsorbed molecular water (H_2O) increases, compared to those samples without ethanol addition. The increase in hydroxyl groups (OH^-) and adsorbed molecular water (H_2O) which have high surface energy leads to the increasing hydrophilicity of the anodized surface. Therefore, the addition of ethanol in 1 M H_3PO_4 electrolyte helps enhance hydrophilicity of the anodized films.

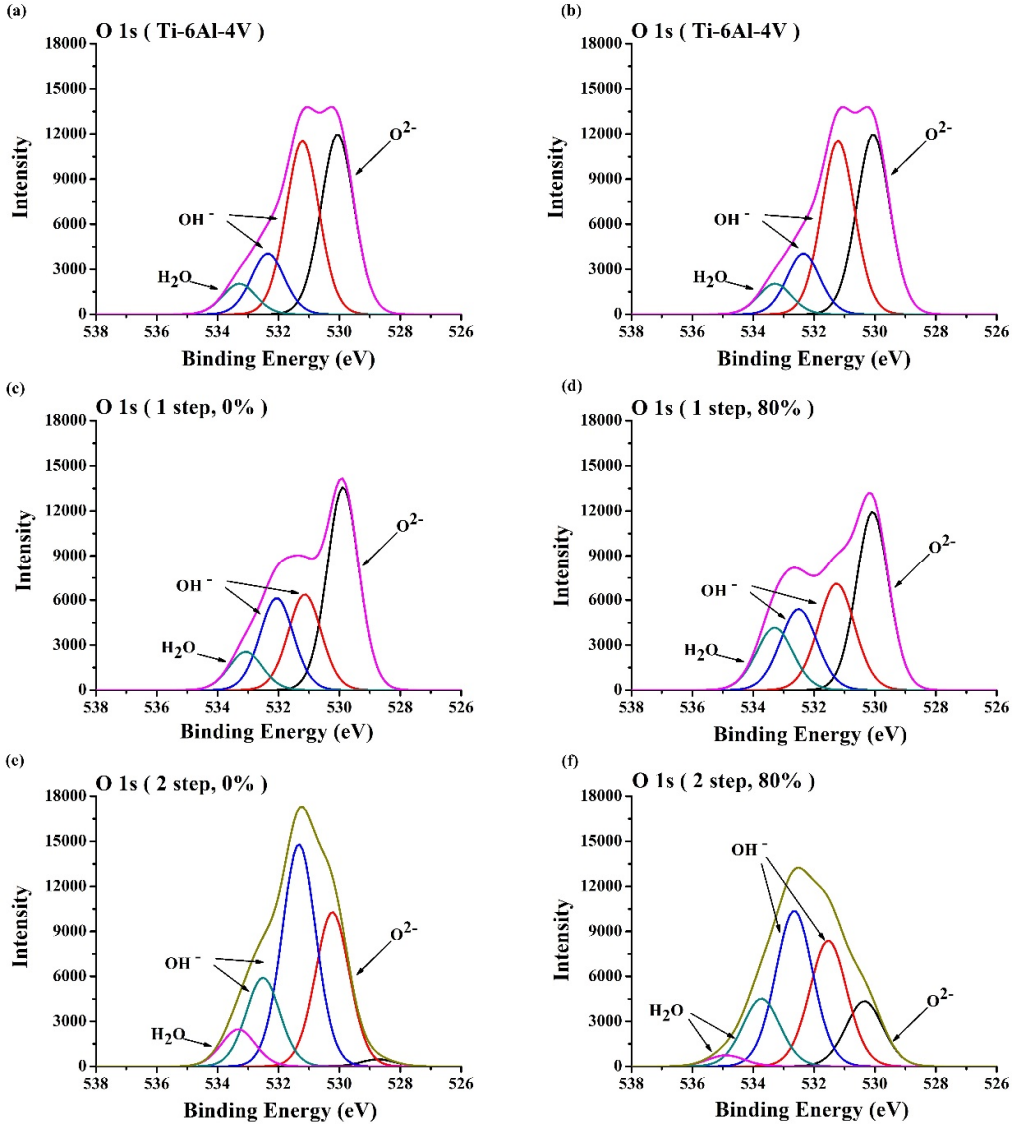

Figure 2. XPS high resolution spectra of O 1s of (a, b) Ti-6Al-4V, (c, d) 0, 80%v/v ethanol by one-step anodization, and (e, f) 0, 80%v/v ethanol by two-step anodization.

Table 1. Comparison of peak area for oxide species (O^{2-}), hydroxyl groups (OH^-) and adsorbed molecular water (H_2O)

Sample	Peak area (%)		
	Oxide species (O^{2-})	**Hydroxyl groups (OH^-)**	**Adsorbed molecular water (H_2O)**
Ti-6Al-4V	40.5	52.7	6.8
1 step, 0%	46.1	44.7	9.2
2 step, 0%	31.7	61.0	7.3
1 step, 80%	38.8	45.9	15.3
2 step, 80%	15.3	66.1	18.6

For two-step anodization, the peak area of titanium oxide (O^{2-}) decreases but hydroxyl group (OH^-) and adsorbed molecular water (H_2O) increases. In contrast, the hydroxyl group (OH^-) decreases for samples prepared by one-step anodization. Therefore, the anodized films formed by two-step anodization are more hydrophilic than those formed by one-step anodization. The contact angle measurement clearly suggests the successful enhancing hydrophilicity on the anodized films via two-step anodization using 2 mA·cm^{-2} in 1 M H_3PO_4 with 80%v/v ethanol electrolyte.

3.4 Surface morphology and surface roughness

Figure 3 shows the surface morphology of Ti-6Al-4V before and after modifications. Ti-6Al-4V before modification shows a flat surface as shown in Figure 3(a), when compared to those surfaces of the modified Ti-6Al-4V. Surface roughness was observed on Ti-6Al-4V before and after modifications as shown in Figure 3 (b-f). Figure 3 (b), the anodized films performed by one-step anodization displays a rough surface. However, after anodizing process by two-step anodization, the morphology shows rougher surface.

Figure 4 shows three-dimensional AFM images and average roughness (R_a) derived from the AFM analysis of the recorded area (5 µm x 5 µm) of Ti-6Al-4V before and after modifications. The anodized films surface performed by two-step anodization became very rough as compared to Ti-6Al-4V and the anodized films surface performed by one-step anodization. The surface roughness of the anodized films performed by two-step anodization in a mixture of 1M H_3PO_4 and 20, 40 and 80%v/v ethanol are similar according to the AFM image. R_a represents the arithmetic mean value of the deviations of a rough profile relative to the average line profile over the entire length measured [14]. The R_a of the anodized films performed in 20, 40 and 80%v/v ethanol were 337, 411 and 301 nm, respectively. The R_a of the anodized films performed by two-step anodization in a mixture of 1 M H_3PO_4 and 20, 40 and 80%v/v ethanol is higher than that of Ti-6Al-4V and the anodized films performed by one-step anodization. Therefore, addition of ethanol in electrolyte could enhance surface roughness to the anodized films.

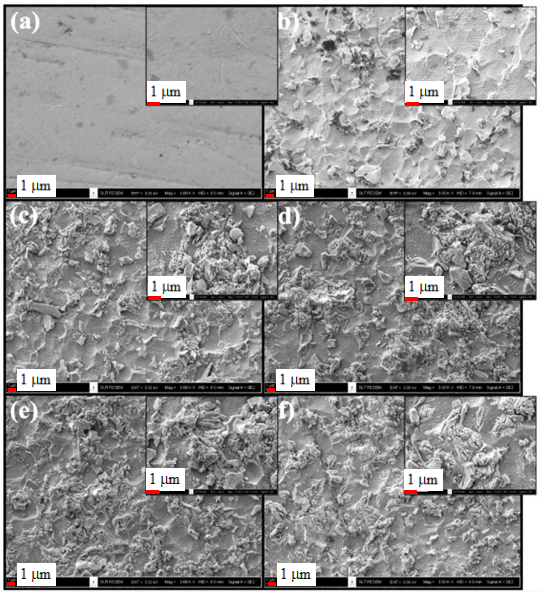

Figure 3. Surface morphology of the Ti-6Al-4V and after various treatments: (a) Ti-6Al-4V, (b) the anodized films formed by one-step anodization in 80%v/v ethanol, the anodized films formed by two-step anodization in a mix of 1 M H_3PO_4 and (c) 0%, (d) 20%, (e) 40 % and (f) 80%v/v ethanol as an electrolyte.

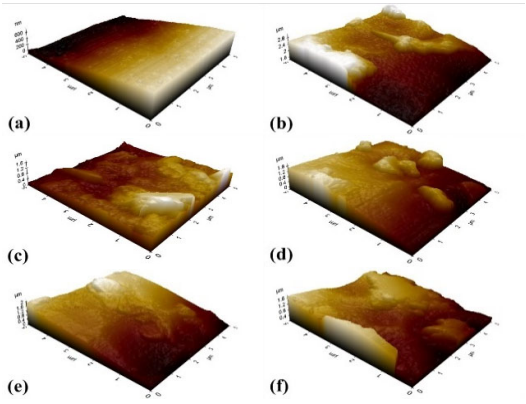

Figure 4. AFM images for Ti-6Al-4V and after various treatment: (a) Ti-6Al-4V, (b) the anodized films formed by one-step anodization in 80%v/v ethanol, the anodized films formed by two-step anodization in a mixture of 1 M H_3PO_4 and (c) 0 %, (d) 20%, (e) 40% and (f) 80%v/v ethanol used as an electrolyte.

In our research the ethanol-based electrolyte for Ti anodization at room temperature and low current density of 2 mA·cm^{-2} was used with success. The surface roughness obtained in this study has R_a between 301-411 nm. The R_a of the anodized films is independent on the concentration of the ethanol. The

obtained surface roughness of the anodized films fabricated using ethanol-based electrolyte in two-step anodization is significantly higher than that usually obtained in one-step anodization.

The results show that the significant enhancement of hydrophilicity can be achieved by the ethanol addition under low current density via two- step anodization. Qin et al. [15] reported that during the anodizing process, the ethanol could enhance the growth rate and work as a cooling agent. The ethanol can easily evaporate into the oxygen bubbles due to its low surface energy and melting point. Therefore, the evaporation of ethanol can accelerate the bubble growth resulting in an increase of ion transformation on the anodized films and also increase the surface roughness [15]. Moreover, the ethanol in electrolyte increase the OH group to the anodized films. Therefore, both surface roughness and OH group on the anodized films could enhance the hydrophilicity to the films.

Based on the results of XPS, FE-SEM and AFM, it can be concluded that the improved hydrophilicity of the anodized films was due to the combination of the oxide surface layer and the increased surface roughness after two-step anodization at a low current density of 2 $mA \cdot cm^{-2}$ in a mixture of 1 M H_3PO_4 and 80%v/v ethanol used as an electrolyte.

4. Conclusions

We performed the anodized films using 1 M H_3PO_4 with addition of ethanol at low current density of 2 $mA \cdot cm^{-2}$. It was found that the presence of ethanol in 1 M H_3PO_4 used electrolyte in two-step anodization is beneficial for increasing hydrophilicity. The highest hydrophilicity occurs on the anodized films surface formed at 2 $mA \cdot cm^{-2}$ in 1 M H_3PO_4 with 80%v/v ethanol addition electrolyte. XPS data demonstrated that a highly hydroxyl groups (OH^-) and adsorbed molecular water (H_2O) were formed on the anodized films formed at 2 $mA \cdot cm^{-2}$ in 1 M H_3PO_4 with 80%v/v ethanol via two-step anodization. FE- SEM and AFM images showed that the surface roughness of the anodized films performed by two-step anodization was increased. Therefore, both surface morphologies and chemical species are of great significance for enhancing hydrophilicity to the anodized films formed by two-step anodization at a low current density of 2 $mA \cdot cm^{-2}$ in a mixture of 1 M H_3PO_4 and 80%v/v ethanol used as an electrolyte.

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