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Effect of annealing temperature on the TiO_2 anodized films properties for dental implant application

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Abstract

The TiO_2 anodized films generated at low current density after annealing are good candidates for surface coating, as a hydrophilicity is a crucial characteristic that determines dental implant applications. In this study, the hydrophilicity of TiO_2 anodized films annealed at various temperatures was examined. It was found that increasing the annealing temperature during the anodization procedure improves the hydrophilicity of the TiO_2 anodized films. This is related to the evolution of the TiO_2 anodized film structure produced by raising the annealing temperature, which converts the TiO_2 anodized amorphous phase to rutile phases. Moreover, increased annealing temperature results in more oxygen vacancies, hydroxyl groups, and roughness, which further improves hydrophilicity.

1. Introduction

The TiO_2 films were used as biomaterials due to their non-toxicity and biocompatibility [1-3]. They are known for their wide range of applications, including surface self-cleaning [4], oil-water separation, and biomaterials [5-8]. The hydrophilicity of biomaterial surfaces plays a crucial role in protein adsorption and cellular adhesion. Therefore, achieving surface hydrophilicity is essential for biomaterials.

The hydrophilicity [9] of biomaterial surfaces affects protein adsorption and cellular adhesion in biological systems [10]. As a result, one of the most essential features of biomaterials is surface hydrophilicity [7,11-13]. According to certain studies, surface hydrophilicity is influenced by surface chemistry, free energy, and surface roughness [14,15]. Many approaches have been tried to improve the surface hydrophilicity of TiO_2 films, including two-step anodization, increasing the tube diameter, changing the crystal structure or thickness, surface roughness and surface species.

Annealing, a high-temperature process, transforms the amorphous phase of films into crystalline phases like anatase or rutile, affecting their hydrophilic properties. Higher annealing temperatures enhance hydrophilicity by removing impurities, increasing surface roughness, and influencing the crystalline structure and phase composition [16-20]. Different phases of TiO_2 exhibit varying hydrophilicity levels. Controlling the annealing process is crucial for optimizing the hydrophilic properties of TiO_2 anodized films, especially in dental implant applications.

This study focuses on TiO_2 anodized films produced through a two-step anodization process, followed by annealing at different temperatures. The hydrophilicity of the films is evaluated through water contact angle measurements, while exploring the relationship between film structure, chemical species, morphology, surface roughness, and the effect of annealing temperature. The results demonstrate that the annealing temperature is a critical factor in determining the hydrophilicity of TiO_2 anodized films [20] and can be adjusted to meet specific application requirements e.g., dental implants.

2. Experimental

Sandpapers were used to mechanically polish Ti-6Al-4V samples of 1 cm × 2 cm × 0.1 cm. To remove native oxide coatings, they were submerged in 1M HF for 1 min. The 1st step anodization was performed in an electrolyte solution comprising of 1 M H_3PO_4 + 85% v/v C_2H_5OH

and utilizing the Ti-6Al-4V substrate as working electrode, graphite as counter electrode, and Ag/AgCl as reference electrode for 0.5 h at room temperature, applying 0.2 mA·cm^{-2}. The treated Ti-6Al-4V from the 1st step anodization was utilized as the working electrode for the 2nd step anodization at 0.2 mA·cm^{-2} for 0.5 h at room temperature in an electrolyte of 1 M H_3PO_4 + 85% v/v C_2H_5OH + 4 wt% NaF. Water was used to clean the TiO_2 anodized films for a few minutes. TiO_2 Anodized films were annealed at 800°C to 1000°C for 2 h in air to improve crystallinity. FESEM (Carl Zeiss Auria, Germany) was used to examine the morphology of the TiO_2 anodized films. AFM (XE-120 Park System, Korea) was used to examine the topographies of treated and untreated Ti-6Al-4V substrates. To explore the structural characteristics of the TiO_2 anodized films, XRD (Bruker D2 advance) experiments were performed. Deionized water with a drop size of 5 µL was used to measure the water contact angle to investigate the hydrophilic properties of the TiO_2 anodized films. XPS (AXIS ULTRADLD, Kratos analytical, Manchester, UK) with a JEOL JPS-9010 instrument with a monochromatic Mg Kα X-ray source was used to analyze the chemical species.

3. Results and discussion

3.1 Hydrophilicity of the TiO_2 anodized films

From previous work, the contact angles of the Ti-6Al-4V and the TiO_2 anodized film before annealed is 75° and 30.77°, respectively [12]. As shown in Figure 1, the contact angles of the TiO_2 anodized films annealed at 800°C, 850°C, 900°C, 950°C and 1000°C, are 22.90° ± 5.81°, 21.25° ± 5.00°, 17.39° ± 4.29°, 20.51° ± 3.73° and 16.52° ± 3.48°, respectively, indicating the five films are highly hydrophilic. The TiO_2 anodized films annealed at 1000°C shows the highest hydrophilicity. Therefore, the annealing temperature increase, the contact angle of water decreased. Moreover, the contact angle of the TiO_2 anodized films annealed at 900°C decreased because the surface roughness increased [20].

3.2 Structure of the TiO_2 anodized films

Figure 2 shows the XRD pattern of TiO_2 anodized films annealed at different temperatures. Ti-6Al-4V and the TiO_2 anodized films before annealing only exhibit a relatively weak and broad peak at 2θ = 25.4° and 2θ = 27.5°, indicating that the TiO_2 anodized films are amorphous or incompletely crystallized. At 800°C, 850°C, 900°C, 950°C, and 1000°C, an obvious diffraction peak appears at 2θ = 25.4°, corresponding to the (101) plane of anatase TiO_2. Furthermore, at 800°C, 850°C, 900°C, 950°C, and 1000°C, a rutile peak appears at 2θ = 27.5°, 36.18°, 41.35°, 54.45°, and 56.8°, indicating the presence of the rutile crystal planes (110), (101), (111), (211), and (220) (JCPDS 21-1276). As the temperature increases to 850°C, the percentage peak area of anatase TiO_2 increases, as shown in Table 1, implying an improvement in anatase crystallinity. However, when the annealing temperature is further increased to 900°C, 950°C, and 1000°C, the percentage peak area of anatase decreases, and the percentage peak area of rutile increases, as shown in Table 1. This indicates an anatase-to-rutile phase transformation occurring at 900°C,950°C, and 1000°C.

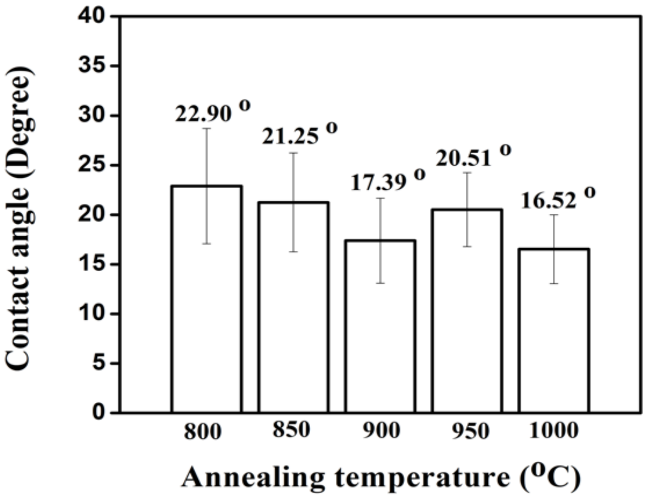

Figure 1. Water contact angles of the TiO_2 anodized films annealed at 800°C, 850°C, 900°C, 950°C, and 1000°C.

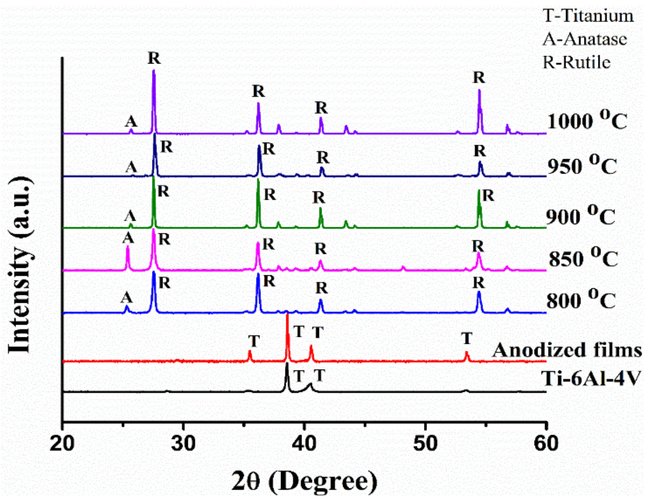

Figure 2. XRD patterns of Ti-6Al-4V, the TiO_2 anodized films before and after annealed at 800°C, 850°C, 900°C, 950°C, and 1000°C, respectively.

Table 1. The peak area of Anatase and Rutile TiO_2.

Sample	Peak area			
	Anatase phase	Rutile phase	% Anatase	% Rutile
800°C	61.48	397.51	15.5	84.5
850°C	152.74	404.93	37.7	62.3
900°C	23.64	263.24	9.0	91.0
950°C	6.11	299.57	2.0	98.0
1000°C	30.66	404.68	7.6	92.4

During the annealing of TiO_2, the crystal structure can undergo a transformation from the less thermodynamically stable anatase phase to the more stable rutile phase. However, this phase transition is temperature-dependent, and higher annealing temperatures generally promote the conversion of anatase to rutile. However, at 1000°C, the decrease in the rutile phase occurs as the annealing temperature exceeds a certain threshold, and subsequent temperature increases have minimal effect on the percentage peak area of rutile TiO_2. This phenomenon can be attributed to factors such as the completion of the phase transformation or limitations in grain growth. F. Nasirpouri *et al.* reported that after annealing, the TiO_2 anatase phase transforms into the rutile phase. However, the amorphous phase cannot directly transform into the rutile phase [18].

Therefore, the annealing temperature significantly affects the structure of the TiO_2 anodized films. As the annealing temperature increases, several structural changes occur. Higher temperatures promote atomic diffusion within the TiO_2 anodized films. This increased atomic mobility allows atoms to rearrange themselves, leading to the growth of crystalline domains. Moreover, the annealing temperature can induce phase transformations, as shown in Figure 2. Moreover, after annealing, the reaction of oxygen with TiO_2 anodized films has significant effects on their properties. This reaction, known as oxidation, results in the formation of a thin oxide layer on the TiO_2 anodized films. The presence of the oxide layer influences the surface morphology, roughness, and phase transformation of the annealed film, inducing changes in surface topography, roughness, and phase transformation.

3.3 Spectroscopic investigation of the TiO_2 anodized films surface

In the XPS spectra shown in Figure 3 performed for the TiO_2 anodized films annealed at 800°C and 1000°C, the Ti2p signal consists of two peaks, Ti2p1/2 with binding energy of 464.1 eV and 464.3 eV, respectively and Ti2p3/2 with binding energy of 458.4 eV and 458.6 eV, respectively. From a chemical point of view, titanium was present in form of TiO_2 (Ti^{4+}) at 458.4 eV to 458.6 eV and 464.1 eV to 464.3 eV [21-27]. Main peaks of O1s at 529.7 eV to 529.9 eV [24, 25,28] refer to oxygen in TiO_2 (yellow component). The peaks located at 530.8 eV and 530.9 eV are ascribed to oxygen vacancy, which generates in oxygen-deficient regions within the TiO_2 anodized films (purple component) [29]. Other components were present, attributions to hydroxyl groups (OH^-) on the titanium oxide at 531.5 eV to 531.9 eV (green component) [21,30], and H_2O at 533.0 eV to 533.8 eV (blue component) were detected as well. The peak areas of TiO_2, oxygen vacancy, hydroxyl groups (OH^-) and H_2O is shown in Table 2.

For the TiO_2 anodized films annealed at 800°C, and 1000°C, when a droplet of water is deposited on the surface of TiO_2 thin films, the water molecules occupy oxygen vacancies and the hydrophilic OH groups are adsorbed on the surface, resulting in a highly hydrophilic surface [30-33]. Furthermore, rutile has a higher bioactivity than anatase [34]. Therefore, the annealing process causes phase transformation and the formation of oxygen vacancies in the structure of the TiO_2 anodized films.

When compared to our earlier studies, the amount of F decreases with increasing annealing temperature [12]. This finding implies that fluorine may be doped into the TiO_2 lattice [35]. As for the TiO_2 anodized films produced by two-step anodization with 1 M H_3PO_4 + 80 v/v C_2H_5OH + 4 wt% NaF. F 1s XPS spectra at 684.24 eV might be attributed to F anions physically absorbed on the surface of TiO_2 [12]. However, nearly no F 1s XPS spectra were found on TiO_2 anodized films annealed at 800°C and 1000°C (see supplementary).

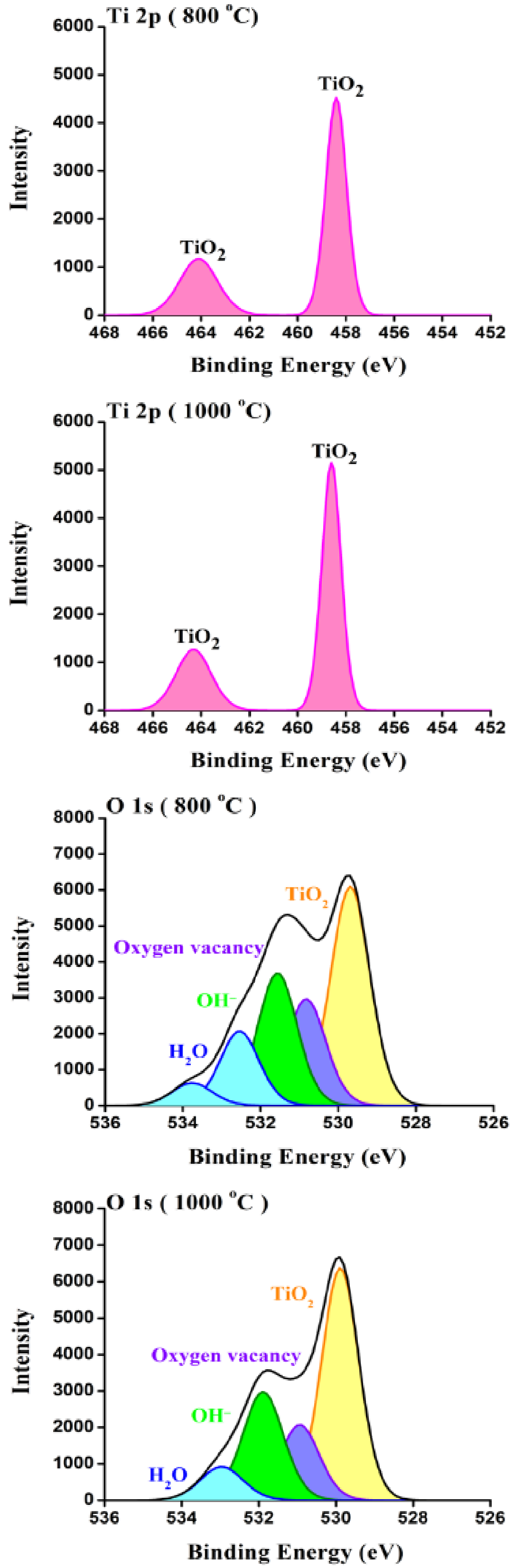

Figure 3. XPS spectra of the TiO_2 anodized films annealed at 800°C and 1000°C.

Table 2. The peak area of TiO_2, oxygen vacancy, hydroxyl groups (OH^-) and H_2O.

Sample	Peak area (%)			
	Oxide species (O^{2-})	Oxygen vacancy	Hydroxyl groups (OH^-)	Adsorbed molecular water (H_2O)
800°C	39.3	19.2	23.9	17.6
1000°C	49.6	16.9	25.3	8.2

3.4 Surface morphology and roughness

FESEM was used to examine the surface morphologies of TiO_2 anodized films before and after the annealing process, as illustrated in Figure 4. It was found that the TiO_2 anodized films after annealing had superior hydrophilicity than the TiO_2 anodized films before annealing due to increased roughness. The average roughness of the TiO_2 anodized films and the Ti-6Al-4V substrate was determined by AFM scanning regions of 25 mm × 25 mm, as shown in Figure 5. The roughness of the TiO_2 anodized films annealed at 800°C (R_a=203 nm), 850°C (R_a=150 nm), 900°C (R_a=341 nm), 950°C (R_a=267 nm) and 1000°C (R_a=732 nm) is greater than that of both the Ti-6Al-4V substrate (R_a=30 nm) and the TiO_2 anodized films before annealing (R_a=148 nm). These results are in good agreement with the results of FESEM. In general, the Wenzel model links surface roughness to hydrophilicity [31]. It is generally known that increasing the roughness increases the hydrophilicity [30]. Therefore, surface roughness are the most important variables influencing surface hydrophilicity.

Significant differences in surface roughness were observed between the TiO_2 anodized films before and after annealing at 800°C and 1000°C. However, the contact angle remained relatively unchanged across all conditions. This lack of variation in the contact angle could be due to the formation of a mixed composition of anatase and rutile TiO_2 during annealing, which potentially masked the influence of surface roughness.

It is indicated that annealing, a high-temperature process, generally improves a material's hydrophilic properties by eliminating organic impurities and increasing surface roughness. The removal of impurities enhances hydrophilic behavior, while increased roughness promotes better wetting and greater interactions with water. The altered morphology resulting from annealing, including phase transformations and structural changes, contributes to the enhanced hydrophilicity of the TiO_2 anodized films.

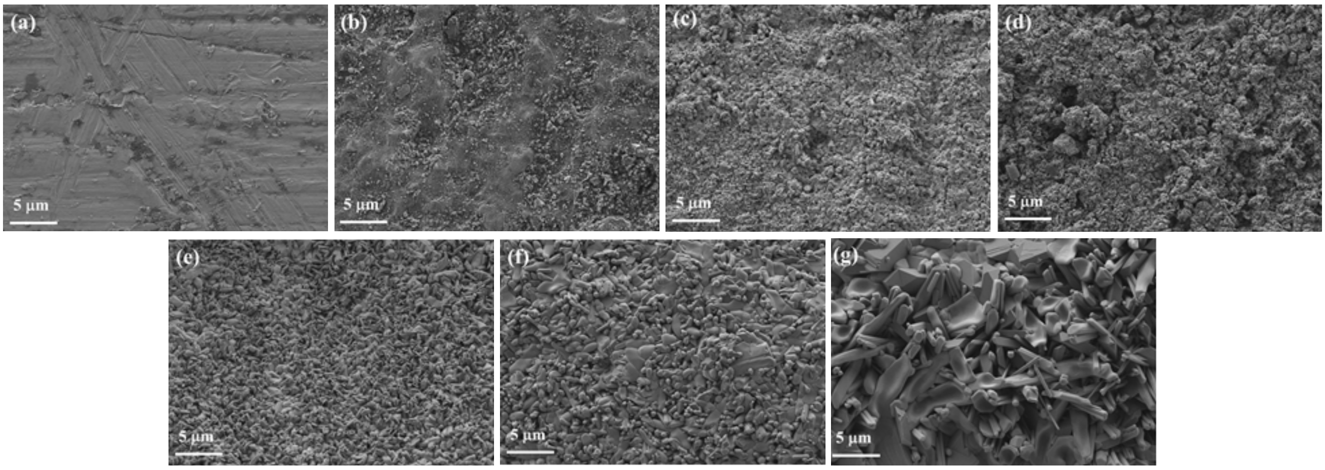

Figure 4. FESEM of (a) Ti-6Al-4V, the TiO_2 anodized films before (b) and after annealed at (c-g) 800°C, 850°C, 900°C, 950°C and 1000°C, respectively.

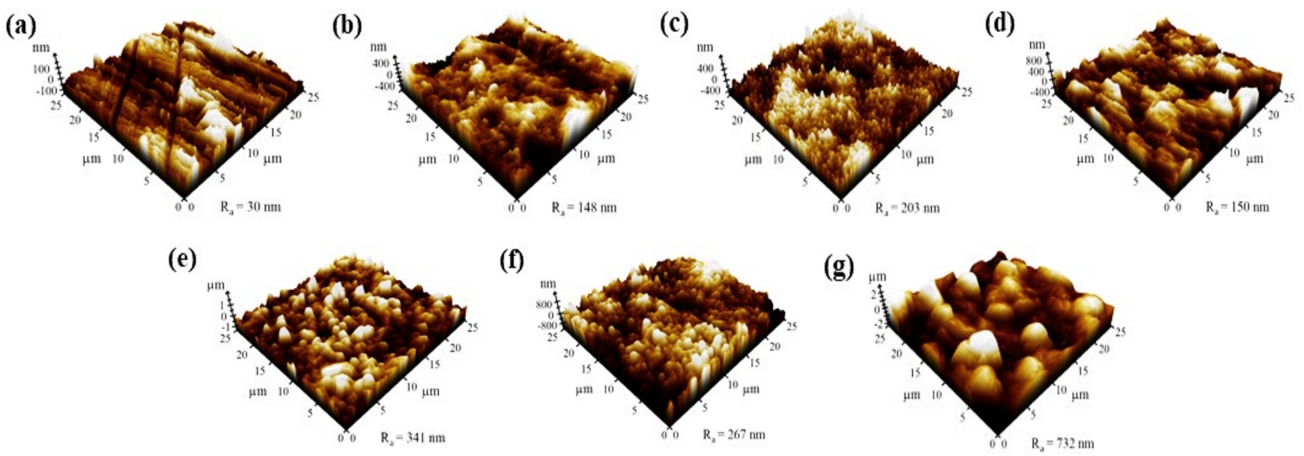

Figure 5. AFM images of (a) Ti-6Al-4V, the TiO_2 anodized films before (b) and after annealed at (c-g) 800°C, 850°C, 900°C, 950°C and 1000°C, respectively.

4. Conclusions

The TiO_2 anodized films were produced by two step anodization at low current density and annealing at various temperatures. These samples were annealed at temperature between 800°C to 1000°C to convert the TiO_2 anodized amorphous phase to rutile phase. The roughness of the films increased as the annealing temperature rose from 800°C to 1000°C. Because the hydrophilicity of TiO_2 anodized films with rough surfaces is linked to oxygen vacancies and hydroxyl groups, increasing the annealing temperature can enhance the hydrophilicity of TiO_2 anodized films. The results show that annealing temperatures ranging from 800°C to 1000°C are optimal for TiO_2 anodized films produced by two-step anodization. These discoveries will help to improve the characteristics of TiO_2 anodized films and their future applications, especially in dental implant application.

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