Effect of Anodizing Voltage on Surface Properties of Anodic TiO2 Coatings on TC4 Titanium Alloy (Postprint)

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Abstract

TiO2 coatings were prepared on the surface of titanium alloy Ti-6Al-4V (TC4) by anodic oxidation in oxalate, silicate, and phosphate electrolyte systems, and the surface microstructure, chemical composition, and bioactivity of the TiO2 coatings were investigated. Anodic TiO2 coatings on TC4 surfaces were prepared at room temperature using a constant voltage anodic oxidation method, with TC4 as the anode and stainless steel as the cathode. The electrolyte composition was: 20 g/L Na2C2O4, 10 g/L Na2SiO3 • 9H2O, 9.25 g/L NaH2PO4, and 2 g/L NaOH. The anodic oxidation voltage ranged from 10–120 V, the oxidation time was 50 min, and the power supply frequency was 200 Hz. The phase composition, three-dimensional morphology, surface microstructure, and chemical composition of the coatings were measured using XRD, AFM, SEM, and XPS. The results showed that the oxidation voltage had essentially no effect on the phase composition of the TiO2 coatings, and the coatings exhibited amorphous TiO2. When the oxidation voltage was 30 V, the TiO2 coating surface exhibited a rough structure composed of pores with diameters of approximately 1.3 m and protruding particles. As the oxidation voltage increased, the surface protruding particles gradually decreased and the roughness reduced. When the oxidation voltage reached 100 V, the effect of field-induced dissolution made the protruding particles on the TiO2 coating surface less prominent, the surface roughness of the TiO2 coating was lower than that of the TC4 substrate, and the surface pore diameter was 240 nm. The micro/nanostructure and abundant hydroxyl groups (–OH) on the surface of the TC4 anodic TiO2 coating are beneficial for enhancing the bioactivity and bone growth properties of the TiO2 coating.

Full Text

Preamble

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Effect of Applied Voltage on Surface Characteristics of Anodic TiO_2 Films on TC4 Alloy

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Abstract

Anodic TiO_2 films were prepared on Ti-6Al-4V (TC4) titanium alloy surfaces in a hybrid electrolyte system containing oxalate, silicate, and phosphate. The surface microstructure, chemical composition, and bioactivity of these TiO_2 films were systematically investigated. Using a constant voltage method at room temperature, TC4 specimens served as the anode while stainless steel served as the cathode. The electrolyte composition was: 20 g/L $Na_2C_2O_4$, 10 g/L $Na_2SiO_3 \cdot 9H_2O$, 9.25 g/L NaH_2PO_4, and 2 g/L NaOH. Anodic oxidation was performed at voltages ranging from 10–120 V for 50 minutes at a power frequency of 200 Hz. XRD, AFM, SEM, and XPS were employed to characterize the phase composition, three-dimensional topography, surface microstructure, and chemical composition of the films. The results demonstrate that oxidation voltage has minimal influence on the phase composition of TiO_2 films, which remain amorphous. At 30 V, the TiO_2 film surface exhibits a rough structure composed of pores approximately 1.3 m in diameter and protruding particles. As the oxidation voltage increases, these surface protrusions gradually diminish and surface roughness decreases. At 100 V, field-assisted dissolution yields a surface with barely visible protrusions, where the TiO_2 film roughness falls below that of the TC4 substrate and pore diameter reduces to 240 nm. The micro/nano-scale structure and abundant hydroxyl groups (-OH) on the anodized TC4 surface significantly enhance the bioactivity and bone growth characteristics of the TiO_2 films.

Keywords: inorganic non-metallic materials, TC4 titanium alloy, anodic oxidation, surface treatment, TiO_2 film

Introduction

Titanium alloy Ti-6Al-4V (TC4) exhibits excellent biocompatibility, high specific strength, and superior corrosion resistance, making it an ideal material for hard tissue repair applications [1]. However, TC4 implant surfaces lack inherent bioactivity, resulting in passive healing processes and prolonged recovery times. Surface bioactivation is therefore required to accelerate bone tissue regeneration and reduce healing duration. Two primary approaches exist for activating TC4 implants: hydroxyapatite coating deposition and formation of bioactive titanium dioxide layers. The surface morphology and chemical composition of TC4 critically influence biological activity, with studies demonstrating that well-designed micro/nano hierarchical porous structures significantly promote osseointegration [2-4].

TiO_2 has recently emerged as a stable bioceramic material suitable for bone growth [5]. Nevertheless, the native TiO_2 oxide film on TC4 remains passivated and cannot effectively induce calcium phosphate formation, rendering it bioinactive. Appropriate activation treatments are necessary to modify the oxide film' s structure, morphology, and composition to promote hydroxyapatite nucleation and growth on the titanium alloy surface. Treatments involving hydrogen peroxide and heating can generate abundant terminal titanium hydroxyl groups (Ti-OH) on TC4 surfaces, which play a crucial role in inducing hydroxyapatite formation and promoting bone growth [6-10]. These Ti-OH groups substantially enhance the bioactivity of TC4 surfaces.

Anodic oxidation represents one of the primary techniques for fabricating porous coatings on titanium alloy implants for bone regeneration [11, 12]. By adjusting anodic oxidation parameters, TiO_2 films with varying surface structures and chemical compositions can be prepared to enhance bone growth [13]. Li et al. controlled oxidation voltage, time, and HF concentration to produce micron-scale porous TiO_2 films with pore diameters of 1.5–2.2 m by ensuring the dissolution rate of the passive film exceeded its formation rate [14]. Yang et al. [15] fabricated bioceramic porous coatings on titanium alloys via anodic oxidation in H_2SO_4 solution, demonstrating that oxidation voltage modulates the surface structure of titania films, with increasing voltage enlarging pore size and porosity. Kuromoto et al. [16] similarly reported that higher oxidation voltages increase pore size, porosity, and film thickness. Consequently, tailoring electrolyte composition and power parameters, particularly oxidation voltage, enables fabrication of TC4 surface oxide films with desired architectures.

Oxidation voltage is widely recognized as a key factor governing the surface structure of anodic films on titanium alloys. To achieve effective bioactivation of TC4 surfaces, oxide films with specific surface structures and chemical compositions are required. Therefore, investigating how different voltages affect the surface structure of anodized titanium alloy oxide films under given electrolyte conditions is essential. This study employs anodic oxidation in a NaOH-containing electrolyte system to hydroxylate and bioactivate TC4 surfaces, examining the influence of asymmetric bipolar pulse oxidation voltage on the surface structure and chemical composition of anodic films.

1.1 Film Sample Preparation

Cylindrical TC4 titanium alloy specimens (20 mm diameter, 5 mm thickness) served as the anode, while square stainless steel plates (100 mm × 100 mm × 2 mm) functioned as the cathode in a 3.5 L glass electrolytic cell. The electrolyte contained 20 g/L sodium oxalate ($Na_2C_2O_4$), 10 g/L sodium silicate nonahydrate ($Na_2SiO_3 \cdot 9H_2O$), 9.25 g/L sodium dihydrogen phosphate (NaH_2PO_4), and 2 g/L sodium hydroxide (NaOH). Prior to anodization, TC4 substrates underwent pretreatment: chemical degreasing, water rinsing, sequential polishing with 120#, 400#, 600#, 800#, 1000#, and 1200# abrasive papers, acid pickling, activation, and final water rinsing. Anodic oxidation was performed using a WHD-30 micro-arc oxidation power supply providing asymmetric bipolar pulses with forward voltages of 10–120 V, reverse voltage of 0 V, pulse number of 1, frequency of 200 Hz, and duty cycles of 50% for both positive and negative pulses. The oxidation duration was 50 minutes at room temperature. Post-treatment involved sealing the anodic films in boiling deionized water at 100°C for 30 minutes, followed by cleaning and drying.

Phase composition was analyzed using a Bruker D8-Advance X-ray diffractometer (XRD). Surface and cross-sectional microstructure and chemical composition were examined with a Philips ESEM X30 scanning electron microscope equipped with an EDAX EDS system. Chemical states and contents were determined using a PHI 600 X-ray photoelectron spectrometer (XPS), with binding energies calibrated against the C-C bond at 284.80 eV. For bioactivity testing, TC4 cylinders (3 mm diameter, 5 mm length) were anodized at different voltages, sterilized at high temperature, implanted into the femurs of Japanese white rabbits, and evaluated via X-ray imaging after 24 weeks. The implants were then retrieved for morphological and compositional analysis.

2.1 Phase Analysis

Figure 1 [Figure 1: see original paper] presents XRD patterns of TC4 surface films prepared at constant voltages of 20–80 V for 50 minutes at room temperature, followed by deionized water rinsing and drying. The patterns reveal that the primary crystalline phases in anodized TC4 samples are the α-phase (PDF 44-1294) and β-phase (PDF 44-1288) of the titanium alloy substrate, with α-phase dominating. The XRD signals from the TC4 surface oxide film are extremely weak, showing no detectable anatase or rutile TiO_2 peaks. Only a broad amorphous peak appears near 2 40°, indicating that the titania film formed by anodic oxidation is amorphous. Oxidation voltage has essentially no effect on the phase composition of the surface film. The anodic oxidation of TC4 at room temperature, under the combined action of electrolyte and electric field, generates a series of amorphous titanium oxides TiO (x = 1-2). The process initially forms an amorphous titania passivation layer, which gradually transforms into anatase or rutile TiO_2 under continued electrolyte and voltage action. Previous studies show that higher DC or pulse voltages, concentrated acidic electrolytes, and extended oxidation times facilitate conversion of intermediate oxides to stable TiO_2, yielding anatase- or rutile-dominated surface films [17-21]. Conversely, low electrolyte concentrations and low voltages produce only amorphous TiO_2.

Figure 2 [Figure 2: see original paper] shows the full XPS survey spectrum of a TC4 anodic film prepared at 80 V, revealing major elements C, O, Ti, and trace amounts of Al, Si, Na, V, and P. High-resolution XPS analysis of C, O, and Ti was performed to investigate chemical states, with C 1s used for binding energy calibration. The high-resolution O 1s and Ti 2p spectra are presented in Figure 3 [Figure 3: see original paper]. In crystalline TiO_2, oxygen exists as uniform Ti-O octahedral lattice oxygen, yielding a normal O 1s XPS peak distribution. However, the complex composition and structure of the anodic film alter the chemical environment around oxygen atoms, causing binding energy shifts. The O 1s spectrum in Figure 3a can be deconvoluted into three sub-peaks: OH_2O at 533.70 eV (adsorbed water), OOH at 531.53 eV (hydroxyl oxygen), and OL at 529.57 eV (TiO_2 lattice oxygen) [22]. As shown in Figure 3a and Table 1 , the TC4 oxide film contains substantial Ti-OH functional hydroxyl groups. Formation of Ti-OH likely occurs through hydrolysis of surface-adsorbed water: $Ti\text{-}O\text{-}Ti + H_2O \rightarrow 2Ti\text{-}OH$ [23]. The porous anodic film on TC4 possesses large surface area and high surface atom ratio, increasing the number of surface -OH groups and enhancing hydrophilicity and wettability [24]. Additionally, oxygen-deficient regions within the oxide film create oxygen vacancies that serve as active centers for water molecule adsorption, generating highly oxidative active hydroxyl groups and reducing water contact angle to produce superhydrophilic surfaces [25]. Superhydrophilicity facilitates transport and growth of human tissue cells within porous structures, promotes hydroxyapatite nucleation and growth, and significantly improves bioactivity and bone bonding [26-28].

The Ti 2p level splits into Ti $2p_3/_2$ and Ti $2p_1/_2$ doublets due to spin-orbit coupling. In Figure 3b, both peaks are fitted with two sub-peaks each. The Ti $2p_3/_2$Ti-O-Ti sub-peak at 458.58 eV and Ti $2p_1/_2$Ti-O-Ti sub-peak at 464.63 eV correspond to TiO_2 binding energies according to Perkin-Elmer' s XPS Handbook, confirming the film composition as TiO_2. The energy separation of 6.05 eV exceeds the handbook value of 5.7 eV. The Ti $2p_3/_2$Ti-OH sub-peak at 459.91 eV and Ti $2p_1/_2$Ti-OH sub-peak at 466.49 eV show a separation of 6.58 eV. The presence of two sub-peaks for each spin-orbit component indicates that titanium exists not only in Ti-O bonding but also in Ti-OH bonding. Most Ti forms Ti-O bonds as TiO_2 constituting the main film structure, while a minor portion bonds with hydroxyl groups. The Ti $2p_3/_2$ peak full-width at half-maximum (1.8 eV) substantially exceeds that of single-crystal TiO_2 (1.1 eV), confirming the amorphous nature of the TiO_2 film [29] with titanium present as Ti^{4+}. XPS analysis thus explains the absence of TiO_2 crystalline peaks in XRD patterns due to the amorphous state of the oxide film.

2.2 Surface Structure and Chemical Composition of Oxide Films

Figure 4 [Figure 4: see original paper] shows secondary electron images of anodized TC4 surfaces at various oxidation voltages. At 30 V, the oxide film exhibits numerous irregular microstructures, including micropores and protruding particles formed during anodization. As voltage increases to 70 V, both the size and density of micropores and protrusions decrease. At 100 V, these features become barely visible, indicating that oxidation voltage significantly influences surface microstructure. At low voltages, electrochemical corrosion dominates, dissolving titanium and forming titania films. With increasing voltage, enhanced electrolyte dissolution of the titania film continuously removes surface material, yielding smoother surface morphologies.

Figure 5 [Figure 5: see original paper] presents higher-magnification SEM images of pore structures. At 30 V, micropores measure approximately 1.3 m in diameter with protruding oxide particles around 1.8 m. At 70 V, pore diameter remains ~1.3 m while particle size decreases to ~1.5 m. At 100 V, pore diameter shrinks to ~240 nm and protruding particles become indistinct, creating a micro/nano hierarchical structure.

Figure 6 [Figure 6: see original paper] displays AFM three-dimensional surface morphologies. At 30 V, the maximum surface roughness (Ra) reaches 0.622 m, decreasing to 0.283 m at 70 V and 0.247 m at 100 V. The reduction in surface protrusions with increasing voltage correlates with the oscillation waveform characteristics of the anodic process [30]. Higher voltages reduce roughness through two mechanisms: first, increased migration of anionic species to the anode facilitates formation of compounds that deposit on the film surface, smoothing the morphology; second, enhanced field-assisted dissolution at elevated voltages dissolves compounds formed at lower voltages, particularly at protruding regions.

TC4 is a dual-phase alloy containing α and β phases with differing corrosion resistance, which contributes to the uneven surface morphology of the oxide film. Oxide film growth involves a dynamic equilibrium between formation and dissolution. Initially, formation exceeds dissolution, increasing film thickness. Film dissolution represents an electric field-supported chemical process (field-assisted dissolution). Higher voltages intensify this dissolution, significantly affecting pore size and protruding particles. However, as voltage increases, the corrosion capability of the anodic system strengthens, enabling oxidation of the more corrosion-resistant β-phase. Consequently, at 100 V the TC4 surface appears relatively flat with no obvious protrusions [31].

To further analyze the chemical composition of protruding particles formed at low voltage, secondary electron imaging, backscattered electron imaging, and EDS analysis were performed on a sample anodized at 30 V (Figure 7 [Figure 7: see original paper]). The secondary electron image (Figure 7a) shows a gray-contrast oxide film with low-contrast micropores and high-contrast protruding particles. The backscattered electron image (Figure 7b) reveals a high-contrast oxide film matrix with low-contrast pores and gray-contrast particles. EDS analysis of the film matrix (position 1, Figure 7c) shows high Al content, indicating an α-phase region, while analysis of a protruding particle (position 2, Figure 7d) shows high V content plus Si and Na, identifying it as a β-phase region. The anodic film consists primarily of high-atomic-number amorphous titania, while protruding particles are amorphous oxides containing Si and Na that form preferentially on β-phase regions. The amorphous oxide XRD peak corresponds to the broad feature near 2 40° in Figure 1.

Table 2 summarizes the chemical composition at different voltages. At 30 V, significant compositional differences exist between the titania film and protruding particles: the film contains 29.88 at% O and 60.66 at% Ti, while particles contain 47.68 at% O and 41.8 at% Ti. The Al/V ratio is 4.3 in the film versus 2.2 in particles, indicating higher V content in protrusions. Particles also contain 1.94 at% Si and 1.23 at% Na, confirming that Na^+ and SiO_3^{2-} from the electrolyte participate in formation of these oxide particles under thermodynamic driving forces. The average chemical composition of anodic films is similar across voltages, but at low voltages Si and Na segregate into protruding particles, whereas at high voltages they incorporate uniformly into the oxide film due to enhanced field-assisted dissolution.

2.3 Bioactivity

Figure 8 [Figure 8: see original paper] shows X-ray images of anodized TC4 implants in rabbit femurs after 24 weeks. No radiolucent zones are observed around any implants, and no linear shadows or bone density reductions appear at the implant-femur interfaces. All anodized implants show clear, tight integration with bone without infection or bone resorption, demonstrating excellent biocompatibility. With increasing oxidation voltage, obvious bone tissue growth occurs at the implant-femur interface. At 100 V, high-density bone bridges form between the femur and implant.

The anodized TC4 porous films exhibit micro/nano dual-scale structures that generate capillary forces, reducing contact angle and increasing surface energy compared to pure Ti, thereby promoting early protein adsorption and cell attachment [32]. The X-ray results indicate that higher voltage anodized surfaces with micro/nano hierarchical structures and high concentrations of active Ti-OH groups effectively promote hydroxyapatite deposition and growth, thereby stimulating bone formation.

Figure 9 [Figure 9: see original paper] presents SEM images and EDS analyses of implant surfaces after 24 weeks. At 30 V, small deposition particles with low Ca and P content are observed. At 70 V, larger deposition particles appear with increased Ca and P content, accompanied by numerous chondrocytes and fibroblasts. At 100 V, the surface shows deposited particles with high Ca and P content along with bone and fibrous tissue growth. As oxidation voltage increases, contact angle decreases and surface hydrophilicity improves, enhancing adsorption of water and ions to better induce hydroxyapatite formation, promote cell adhesion and proliferation, and facilitate phosphate particle deposition and bone tissue formation [10, 33]. Higher voltage anodization thus yields superior phosphate deposition, bone growth characteristics, and overall bioactivity.

Conclusions

1. Anodized TC4 samples retain the α and β phases of the titanium alloy substrate, with α-phase predominating. The surface TiO_2 film shows extremely weak XRD signals without detectable anatase or rutile peaks, exhibiting only a broad amorphous feature near 2   40°. This amorphous TiO_2 formation results from the low electrolyte concentration and low applied voltage.

2. The films contain substantial active Ti-OH hydroxyl groups with titanium present as Ti^{4+}. Two primary mechanisms generate these hydroxyls: hydrolysis of surface-adsorbed water reacting with TiO_2 (Ti-O-Ti + $H_2O \rightarrow$ 2Ti-OH), and formation of oxygen vacancies in the oxygen-deficient film that serve as active centers for water adsorption. The resulting active hydroxyl groups impart strong hydrophilicity, while the high surface area and porosity of the film further enhance superhydrophilicity.

3. Anodic oxidation voltage significantly affects TiO_2 film surface structure. With increasing voltage, protruding particles dissolve via field-assisted dissolution, reducing surface roughness and increasing flatness. Higher voltages thus produce smoother oxide films.

4. Micro/nano surface structures and high -OH group concentrations formed at elevated anodic oxidation voltages exhibit excellent bioactivity and bone tissue growth. Increased voltage enhances surface hydrophilicity, promoting adsorption of water and ions to induce hydroxyapatite formation, stimulate cell adhesion and proliferation, and facilitate phosphate deposition and bone tissue formation. High-voltage anodized titanium alloy surfaces thus demonstrate superior phosphate deposition, bone growth, and bioactive properties.

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Note: Figure translations are in progress. See original paper for figures.