

**EXPLORING THE IMPACT OF POTENTIAL, AMMONIUM
FLUORIDE CONCENTRATION, AND ANODIZATION TIME
ON THE STRUCTURE, SURFACE CHARACTERISTICS,
AND CORROSION RESISTANCE OF NANOTUBULAR
TITANIUM OXIDE COATINGS ON BIOMEDICAL ALLOY
TI-6AL-4V ELI**

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Abstract

The current research delves into assessing the impact of applied potential, ammonium fluoride concentration, and anodization duration on the structural, phase compositional, microhardness, and surface roughness attributes of nanotubular titanium oxide coatings on anodized Ti-6Al-4V ELI. A meticulous experimental design was executed to systematically investigate the varied effects of these factors. Scanning electron microscopy (SEM) unveiled the presence of well-defined titania nanotubes on the surfaces of the anodized specimens. X-ray diffraction (XRD) analysis discerned the composition of the nanotubular oxide layer, revealing the presence of both anatase and a mixture of anatase and rutile phases contingent upon the anodization parameters. Notably, surface microhardness, surface roughness, and corrosion resistance manifested noticeable variations in response to alterations in applied voltage, NH_4F concentration, and anodization duration within the designated experimental ranges.

Key words: titania nanotubes, nanotubular growth, titanium anodizing, surface treatment, biomedical alloy

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Introduction. The use of titania nanotubes (NTs) in implant design has the potential to improve the long-term success and stability of implant devices through enhanced osseointegration [1]. Titanium oxide NTs have been shown to impact significantly the process of bone formation around an implanted material, which is crucial for the long-term success and stability of implant devices [2]. The unique nanotubular structure of titanium oxide provides a larger surface area for cell attachment, proliferation, and differentiation, ultimately leading to increased osteoblast adhesion and spreading [3]. Furthermore, the size and surface properties of the NTs can be tailored to meet specific requirements, enabling a more effective interaction between the implant and surrounding bone tissue [4]. Another key advantage of titanium oxide NTs is the ability to use them for the controlled release of therapeutic agents, which can stimulate bone growth and angiogenesis, further enhancing osseointegration [5].

The use of titania NTs in implant design offers significant potential for improving the clinical outcomes of implant devices. However, the design and implementation of nanotubular layers require careful consideration of several critical factors, including stability, corrosion resistance, and mechanical properties [6]. Ensuring the stability of the titania NTs over time is vital to ensure the long-term performance of the implant device [7]. Additionally, the corrosion resistance of the NTs is a key consideration, as it can affect the longevity and effectiveness of the nanotubular layer [8]. Furthermore, the mechanical properties of the nanotube layer must be optimized to ensure adequate durability and resistance to wear and tear [9]. By addressing these factors, the use of nanotubes in implant design can provide significant benefits, including enhanced biocompatibility and osseointegration, leading to improved clinical outcomes.

During the growth of titanium oxide nanotubular layers, several factors can influence their overall properties, including fluoride content and electrolyte composition, electrical parameters, anodization time, etc. The electrolyte composition has a determining impact on the morphology and surface chemistry of the nanotubes [10]. The voltage and the current applied during the anodization process can impact the size, density, and shape of the produced NTs. The growth time can significantly impact the thickness and length of the nanotubes [11]. By carefully controlling these factors, it is possible to tailor the properties of titanium oxide nanotubular layers.

The present study aims to investigate the influence of the ammonium fluoride content in the electrolyte, potential, and anodization time on the formation of nanotubular oxide layers on one of the most versatile titanium alloys used for the production of biomedical implants – Ti-6Al-4V ELI.

Experimental. For this study, one of the most commonly used titanium implant materials Ti-6Al-4V ELI (Grade 5) was anodized. The chemical composition of the used alloy is available in [12]. Cylindrical test samples with dimensions of ϕ 12 mm and thickness of 4 mm were cut from rod bar using a low-speed cutting ma-

chine DTQ-5. Initially, the flat surfaces of the cut samples underwent mechanical grinding using SiC papers with grit sizes P220, P400, P800, P1000, and P3000, followed by polishing with diamond suspensions of 1 μm and 0.25 μm . Before anodizing the samples were ultrasonically cleaned with acetone and isopropanol, rinsed with de-ionized water, and dried.

Anodization was carried out using a two-electrode setup including a counter electrode made of titanium mesh (cpTi – Grade 2). The chemical composition of the anodization electrolyte consists of ammonium fluoride (NH_4F) 0.5–1 wt%, 20 %wt. glycerol, and deionized water. The employed anodization potentials range from 20 V to 60 V for 1800–5400 seconds. Table 1 presents the utilized design of experiments (DOE), outlining the variations in potential (V), NH_4F concentration (%wt.), and reaction time (s) across different samples, denoted as Sample 1 through Sample 8, to investigate their effects on the studied parameters.

T a b l e 1
Design of experiment

Sample No	Potential, V	NH_4F , %wt.	Time, sec.
Sample 1	20	1	5400
Sample 2	60	0.5	5400
Sample 3	60	1	5400
Sample 4	20	0.5	5400
Sample 5	20	1	1800
Sample 6	60	1	1800
Sample 7	20	0.5	1800
Sample 8	60	0.5	1800

The microstructure of the anodized surfaces was observed using a scanning electron microscope (SEM) model SH-5500P produced by HIROX. Phase analysis was conducted on an X-ray diffractometer (XRD) Tongda TDM-10 employing CuK α radiation. The XRD patterns were acquired using continuous scan mode, covering the 2theta (2θ) angle range from 20 to 90 degrees at a scan speed of 1.5 degrees/minute. The X'pert HighScore software by Malvern Panalytical was employed for peak identification, matching, and comprehensive analysis of the acquired XRD data. The surface microhardness (HV) of the anodized samples was evaluated using a DVK 1-AT semi-automatic Vickers microhardness tester manufactured by EBPu Electromechanical Equipment Co., Ltd. The surface roughness of the anodized samples was quantified using the DGT-SRT200A profilometer, manufactured by Baxit.

The corrosion resistance of the anodized samples was assessed using the Corrtest CS350 single-channel potentiostat/galvanostat. This evaluation employed a three-electrode configuration, consisting of a platinum (Pt) counter electrode, a silver/silver chloride (Ag/AgCl) reference electrode, and the anodized sample

serving as the working electrode. Before testing, the anodized samples underwent a thorough cleaning regimen involving isopropanol, followed by rinsing with deionized (DI) water and subsequent air drying. Following cleaning, the anodized samples were immersed in a 3.5% wt. sodium chloride (NaCl) solution until a stable open circuit potential (OCP) was established. Subsequently, potentiodynamic polarization measurements were conducted. To ensure consistency, the surface area exposed to the salt solution was confined to 1 cm². All experiments were carried out using freshly prepared solutions and maintained at room temperature. Analytical grade reactants were utilized in all experimental procedures. All operations were carried out at room temperature.

Results and discussion. *Microstructure and chemical composition.*

The microstructure of the titanium alloy Ti-6Al-4V ELI, after electrochemical anodization, reveals a fascinating array of nanotubular structures upon examination using scanning electron microscopy. These nanotubular arrays, as depicted in Fig. 1A, illustrate the intricate surface morphology achieved through the anodization process. The diameter of the nanotubes formed within the limits of this study varies in the range of approximately 40 nm to 110 nm. Such structures are of significant interest due to their potential applications in various fields, including biomedical implants, catalysis, and sensor technologies.

In addition to the microstructural observations, phase analysis conducted via X-ray diffraction (XRD) offers interesting insights into the crystalline composition of the anodized titanium alloy (Fig. 1B). Complementing the XRD diffraction patterns of the anodized samples, a diffraction pattern of the substrate titanium alloy Ti-6Al-4V ELI is also provided, highlighting the formation of a titanium

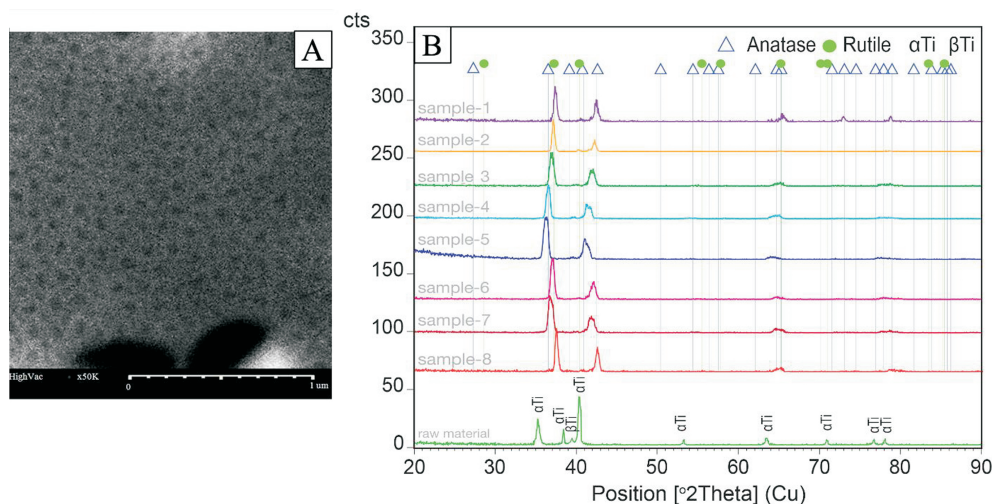


Fig. 1. SEM image depicting the microstructure of an anodized sample (sample 3) – A, and phase analysis of the anodized samples – B

oxide layer on the surface after electrochemical anodization. The phase analysis further establishes a clear correlation between the experimental parameters (voltage, concentration of ammonium fluoride in the electrolyte, and anodization time) and the resultant phase composition. Notably, lower values of these parameters predominantly yield the anatase phase, indicating the significant influence of electrochemical conditions on phase selection during anodization. Conversely, higher experimental values result in the coexistence of rutile alongside anatase, suggesting a potential phase transformation or concurrent crystallization under more intense anodization conditions. This nuanced understanding of phase evolution elucidates the intricate interplay between electrochemical parameters and phase composition, offering avenues for tailoring material properties to suit specific application requirements. Collectively, the combination of microstructural observations and phase analysis provides a comprehensive understanding of the electrochemically anodized titanium alloy, paving the path for further advancements in surface engineering and materials science.

Microhardness. Microhardness examination is a pivotal method offering invaluable insights into the mechanical properties of materials. By providing localized information on surface hardness variations and the material's response to external forces, microhardness testing plays a crucial role in material characterization. In the specific context of electrochemically anodized titanium alloy Ti-6Al-4V ELI, microhardness testing serves as a fundamental tool to assess the impact of surface modification on the material's mechanical behaviour, particularly on the formed surface oxide.

This examination allows for the identification of potential enhancements or alterations in hardness resulting from the anodization process, providing crucial insights into the structural integrity and wear resistance of the modified surface. In essence, microhardness testing offers a quantitative measure of the material's resistance to plastic deformation under applied loads, thereby offering a comprehensive understanding of its mechanical performance.

To evaluate the microhardness of the anodized samples, five measurements were taken from different areas of the anodized surfaces. The acquired data on the measured values, including average values and extrema, is presented in Fig. 2A, while linear regression analysis with confidence intervals is exhibited in Fig. 2B. These visual representations offer a clear overview of the microhardness characteristics and trends observed in the anodized samples.

Analysis of the microhardness data reveals interesting insights. In general, with an increase in potential from 20 V to 60 V, an increase in the concentration of ammonium fluoride from 0.5%wt. to 1%wt., and an extension of anodization time from 1800 s to 5400 s, there is a notable increase in the surface microhardness. The recorded values span a range from a minimum of 350.2 HV to a maximum of 569.1 HV, indicating significant variations in hardness across the anodized samples.

Moreover, to thoroughly dissect the collective impact of voltage, ammonium

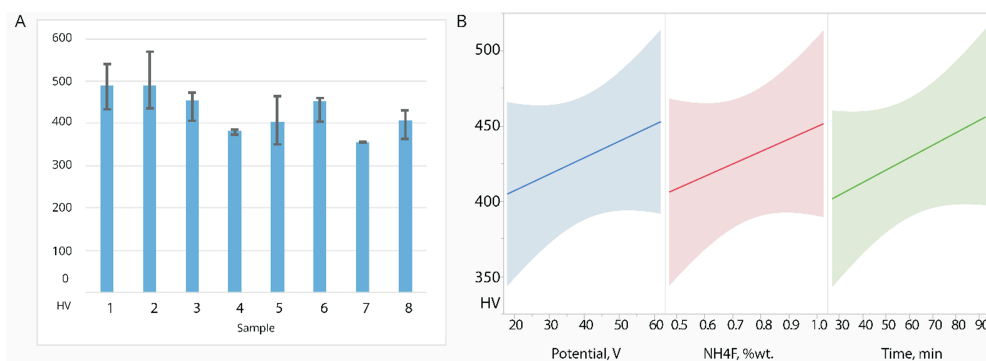


Fig. 2. Surface microhardness of anodized Ti-6Al-4V ELI samples. Measured values (A) and linear regression with confidence intervals (B)

fluoride concentration, and anodization time on the microhardness of the anodized surfaces, a comprehensive analysis of the acquired dataset is imperative. When scrutinizing the influence of potential in isolation, a discernible trend emerges, revealing that elevated voltages generally yield heightened microhardness values. This inference is substantiated by the consistent augmentation of both maximum and average HV values with escalating voltage levels across several experimental instances.

The variations in ammonium fluoride concentrations also exert discernible effects on microhardness values. While certain scenarios demonstrate a positive correlation between increased NH_4F concentration and elevated microhardness, others manifest less definitive relationships. Overall, a discernable tendency emerges, indicating a marginal inclination towards heightened microhardness values with augmented NH_4F concentrations.

Anodization time emerges as a pivotal determinant in microhardness outcomes, with lengthier durations generally correlating with heightened microhardness values. However, this trend is not universal, as evidenced by instances where prolonged anodization periods yield diminished microhardness values. This disparity suggests plausible interactions with additional parameters, potentially inducing escalated stresses and dissolution of the oxide layer.

Upon consideration of the combined influence of all three parameters, the intricate interplay among them becomes palpable, giving rise to variegated microhardness outcomes. Certain amalgamations of voltage, NH_4F concentration, and anodization time may instigate synergistic effects, yielding elevated microhardness values, while others may cause antagonistic repercussions, resulting in diminished microhardness values.

Surface roughness. Surface roughness plays a pivotal role in determining the functional performance and characteristics of materials in various applications, ranging from mechanical components to biomedical implants. The topography of

a surface influences crucial factors such as friction, wear resistance, adhesion, and contact mechanics. In the context of the particular study on electrochemically anodized titanium alloy, understanding surface roughness parameters like Ra (average roughness) and Rz (maximum peak-to-valley height) is essential for several reasons. Ra provides insights into the overall roughness of the surface, reflecting the average deviation of surface heights from the mean line within a sampling length. On the other hand, Rz represents the maximum height difference between the highest peak and the lowest valley within a sampling length, offering information on the surface's macroscopic irregularities. Studying these parameters allows assessment of the effectiveness of the anodization process in modifying surface topography, which in turn influences various material properties such as adhesion, biocompatibility, and tribological behaviour. Therefore, analyzing Ra and Rz is crucial for evaluating the suitability of the anodized titanium alloy for specific applications and optimizing the surface engineering process to achieve desired functional characteristics. For the evaluation of the surface roughness of the anodized samples, five profile measurements were taken from different areas of the anodized surfaces. The acquired data on the measured values, including average values and extrema, is presented in Fig. 3A, while linear regression analysis with confidence intervals is exhibited in Fig. 3B. These visual representations offer a clear overview of the surface roughness characteristics, particularly Ra and Rz and trends observed in the anodized samples.

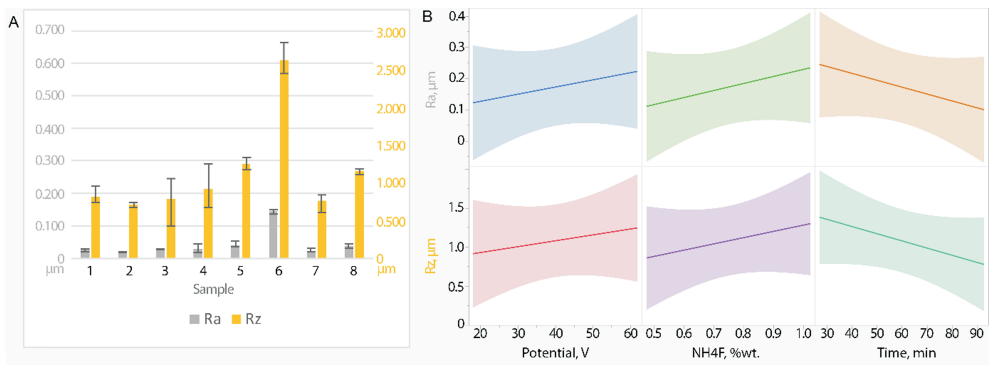


Fig. 3. Surface roughness Ra and Rz of anodized Ti-6Al-4V ELI samples. Measured values (A) and linear regression with confidence intervals (B)

Analysis of the acquired data shows that when considering the effect of potential on surface roughness parameters Ra and Rz, we observe variations in these parameters with different voltage levels. For instance, for a constant NH_4F concentration and anodization time, increasing voltage from 20 V to 60 V generally leads to slight changes in both Ra and Rz values. This suggests that higher voltages may contribute to slightly higher surface roughness.

Comparing data acquired from anodized samples using the same voltage and

anodization time but varying NH_4F concentrations, we also observe changes in surface roughness parameters Ra and Rz. Generally, increasing NH_4F concentration from 0.5 %wt. to 1%wt. tends to result in slightly higher Ra and Rz values, indicating a potential correlation between NH_4F concentration and surface roughness.

Anodization time also influences the surface roughness parameters Ra and Rz but in a manner opposite to voltage and ammonium fluoride concentration. Longer anodization times are found to slightly lower the surface roughness values for Ra and Rz.

Corrosion resistance. The corrosion resistance of the anodized samples in a 3.5% NaCl environment was investigated through a comprehensive study comprising Open Circuit Potential (OCP) measurements followed by potentiodynamic testing. These sequential methodologies provided a robust framework for evaluating the samples' susceptibility to corrosion under aggressive saline conditions. The OCP measurements offered valuable insights into the samples' initial electrochemical state, shedding light on their inherent tendency towards corrosion initiation. Subsequently, potentiodynamic tests facilitated a detailed characterization of the samples' corrosion behaviour, enabling the determination of critical parameters such as breakdown potential and corrosion rate. This dual approach not only allowed for the identification of vulnerable regions within the electrochemical potential spectrum but also provided a nuanced understanding of the samples' corrosion kinetics and stability under dynamic conditions. The integration of OCP and potentiodynamic testing thus facilitated a comprehensive assessment of the anodized samples' corrosion resistance, offering valuable insights for the optimization of protective surface treatments in saline environments.

Analysis of the results obtained from the OCP and the potentiodynamic studies highlighted that the increase in voltage generally correlates with more negative OCP values and higher corrosion rates, indicating reduced corrosion resistance. On the other hand, the increase in the concentration of NH_4F and anodization time within the studied range showed a slight improvement in the corrosion resistance of the anodized layers.

In the realm of corrosion science, the corrosion rate stands as a fundamental metric, offering a quantitative measure of a material's resistance to degradation within a corrosive environment. Across the spectrum of measured corrosion rates, ranging from 0.00026538 mm/year to 0.001093 mm/year, each value serves as a testament to the material's interaction with its surroundings. Lower corrosion rates, such as those observed at 0.00026538 mm/year obtained from measurements of sample 4 and 0.00029954 mm/year from sample 1, indicate a heightened resistance to corrosive attack, reflective of robust protective mechanisms at play. Conversely, higher corrosion rates, exemplified by 0.001093 mm/year (sample 8), signify a diminished ability to withstand corrosion-induced deterioration.

In general, the corrosion resistance analysis reveals that higher voltages, lower

NH₄F concentrations, and shorter anodization times generally lead to reduced corrosion resistance, as evidenced by more negative OCP values and higher corrosion rates. However, the influence of each parameter on corrosion resistance may be complex and dependent on various factors, necessitating further investigation for a comprehensive understanding.

Conclusion. Nanotubular arrays were successfully formed on the surface of the anodized biomedical titanium alloy Ti-6Al-4V ELI. XRD analysis showed that the surface oxide layers consist of either anatase or a mixture of anatase and rutile, depending on the employed anodizing parameters. It was found that lower voltage, ammonium fluoride concentration, and anodizing duration lead to the formation of anatase.

The multifaceted influence of voltage, NH₄F concentration, and anodization time on microhardness underscore the complexity of their interrelations, with each parameter contributing to the overall outcome in a nuanced and intricate manner. The highest value of surface microhardness measured was 569.1 HV and the lowest was 350.2 HV.

Considering the combined influence of investigated parameters it becomes evident that their interactions are complex and can lead to varied surface roughness outcomes. The test results suggest that voltage, NH₄F concentration, and anodization time all play roles in influencing surface roughness parameters Ra and Rz of the anodized biomedical titanium alloy. However, the relationships are not straightforward and may depend on various factors, including interactions between parameters.

The analysis of corrosion resistance elucidated that elevated potentials, diminished NH₄F concentrations, and abbreviated anodization durations typically correlate with diminished resilience against corrosion. This inference is drawn from the manifestation of more negative Open Circuit Potential (OCP) values and elevated corrosion rates under such conditions. However, it is imperative to acknowledge the nuanced interplay of each parameter in influencing corrosion resistance, which may be intricately intertwined with a multitude of factors.

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