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NANOTUBULAR OXIDE FORMATION ON BIOMEDICAL TITANIUM ALLOYS

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ABSTRACT

Titanium and its alloys, particularly commercially pure titanium (cpTi, Grade 2) and Ti-6Al-4V Extra Low Interstitial (ELI), are widely used in biomedical implants due to their excellent biocompatibility and mechanical properties. Surface modifications such as nanotubular oxide formation can further enhance their biological performance by improving osseointegration, corrosion resistance, and antibacterial properties. In this study, cpTi and Ti-6Al-4V ELI were anodized to form nanotubular titanium oxide layers. The anodization process was carried out in an ethylene glycol-based electrolyte containing ammonium fluoride, with an applied potential of 80 V for 30 minutes.

Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) were used to characterize the morphology and chemical composition of the resulting oxide layers. SEM analysis revealed well-organized nanotubular structures on both alloys, with an average inner diameter of approximately 90 nm and nanotube lengths of about 1.1 microns. However, the Ti-6Al-4V ELI alloy exhibited voids in the nanotubular layer, corresponding to regions of the beta phase. EDS analysis confirmed the presence of titanium dioxide (TiO_2) as the primary component of the oxide layer, with the Ti-6Al-4V ELI alloy also showing traces of aluminum, vanadium, and fluorine incorporated during the anodization process.

These results demonstrate that both cpTi and Ti-6Al-4V ELI can form nanotubular oxide layers with distinct morphological and compositional features. The differences in nanotube density and the presence of alloying elements in Ti-6Al-4V ELI suggest potential influences on the mechanical and biological properties of the anodized surfaces, making them suitable for tailored biomedical applications.

1. INTRODUCTION

Titanium and its alloys are widely utilized in biomedical applications due to their excellent biocompatibility, favorable mechanical properties, and remarkable resistance to corrosion. These characteristics make titanium particularly suited for a range of load-bearing applications such as orthopedic implants, dental implants, and cardiovascular stents, where long-term stability and integration with biological tissues are critical. The native oxide layer that spontaneously forms on titanium surfaces contributes to its biocompatibility by promoting osteoconductivity and reducing the release of metal ions into surrounding tissues. Despite these inherent advantages, there has been a significant push in recent years to enhance the surface properties of titanium through engineered surface modifications. This effort is aimed at improving key factors such as osseointegration, corrosion resistance, and antibacterial behavior, which are essential for the longevity and success of implants, especially in more demanding clinical situations such as bone fractures and joint replacements [1–3].

Among the many titanium alloys developed for biomedical applications, commercially pure titanium (cpTi, Grade 2) and Ti-6Al-4V Extra Low Interstitial (ELI) stand out as two of the most commonly employed materials. Commercially pure titanium is highly valued for its superior corrosion resistance and excellent biocompatibility, making it suitable for dental implants and other non-load-bearing applications. On the other hand, Ti-6Al-4V ELI is favored in applications where mechanical strength is critical, such as in load-bearing orthopedic implants, due to its high strength-to-weight ratio and fracture toughness. Despite their extensive use, both alloys exhibit limitations related to their surface properties, which can impact the biological response, particularly in osseointegration, where rapid and strong bone bonding is desired [4]. Therefore, there is a strong demand for surface modification techniques that can enhance these surface characteristics without compromising the bulk mechanical properties of the alloys [5, 6].

One of the most effective techniques for modifying titanium surfaces is anodization, a process that involves the electrochemical treatment of titanium in an electrolyte

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solution to generate an oxide layer. This technique is not only beneficial for thickening the naturally occurring oxide layer but can also be employed to create a variety of controlled surface nanostructures, including nanotubular oxide layers. Nanotubular structures formed through anodization are of particular interest in the field of biomedical implants, as they offer several advantages over conventional oxide layers. These nanostructures significantly increase the surface area, which improves cell adhesion and proliferation, key factors for effective osseointegration [7–9].

Additionally, the unique nanotubular topography enhances the mechanical interlocking between the implant and surrounding tissue, further promoting stable integration. Beyond cellular responses, these nanostructures also have the potential to act as reservoirs for drug or ion delivery, which could further reduce inflammation or infection around the implant site [10]. The nanotubular oxide layers produced by anodization have demonstrated superior biological performance in several studies, showing enhanced cell adhesion, proliferation, and osteogenic differentiation. These improvements make anodized titanium surfaces highly promising for use in orthopedic and dental implants. Moreover, the increased corrosion resistance provided by the nanotubular oxide layers is an important advantage, as corrosion products from titanium alloys in the body can negatively impact surrounding tissues and compromise implant longevity. Another critical aspect is the ability of these nanostructured surfaces to inhibit bacterial adhesion, which helps to reduce the risk of postoperative infections, which is a common complication associated with implant surgeries [11, 12].

Given these multifaceted benefits, anodization has become a widely studied technique for the enhancement of biomedical titanium alloys.

In this study, we aim to explore the formation of nanotubular oxide layers on two of the most widely used biomedical titanium alloys, cpTi (Grade 2) and Ti-6Al-4V ELI, via anodization. The primary objective of this research is to characterize the resulting oxide layers in terms of morphology and chemical composition using Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). Through this analysis, we seek to evaluate the potential of these nanotubular oxide layers in improving the surface properties of titanium implants, with a particular focus on enhancing their biological and corrosion performance in biomedical applications.

2. EXPOSITION

Materials

Two commonly used titanium alloys in biomedical applications were employed in this study: commercially pure titanium (cpTi, Grade 2) and Ti-6Al-4V ELI. Both alloys were supplied in the form of rods with a diameter of 12 mm. Cylindrical samples with a diameter of 12 mm and a thickness of 4 mm were prepared by cutting from the rod bars using a low-speed cutting machine to ensure precision and minimize thermal effects during sectioning.

Prior to anodization, the samples underwent a thorough cleaning process to eliminate any contaminants or debris from the surface. The samples were first ultrasonically cleaned in acetone and isopropanol to remove organic residues. Following this, they were rinsed with deionized water to eliminate any remaining solvents and impurities. Finally, the samples were dried at room temperature before being used in the anodization process.

Anodization Procedure

The anodization process was performed using a two-electrode setup consisting of the titanium alloy sample as an anode and a titanium mesh (cpTi, Grade 2) as a cathode. The electrolyte used for the anodization contained 0.3 wt% ammonium fluoride (NH_4F), 3 wt% deionized water, and ethylene glycol as the solvent. Analytical grade reagents were employed to ensure the purity of the electrolyte solution.

Anodization was conducted at a constant potential of 80 V for a duration of 15 minutes at room temperature. A DC power supply was used to provide the required voltage, while the cathode consisted of the titanium mesh. Throughout the process, continuous stirring of the electrolyte was applied to remove bubbles formed on the surface of the anode. This ensured consistent exposure of the titanium surface to the electrolyte, promoting current flow, ion migration and consequently the uniform formation of the nanotubular oxide structures on the titanium alloys.

Characterization

The resulting anodized surfaces were characterized using a Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS) to examine the morphology and chemical composition of the nanotubular oxide layers. A HIROX SH-5500P SEM equipped with a QUANTAX 100 Advanced – Bruker EDS module was employed for the analysis. SEM was used to observe the surface topography and dimensions of the nanotubes, while EDS provided elemental composition data of the oxide layers.

Results

The formation of nanotubular oxide layers on the surfaces of cpTi (Grade 2) and Ti-6Al-4V ELI alloys was successfully achieved through anodization, and the resulting structures were characterized using SEM and EDS. Figure 1 presents the SEM images and EDS analysis zones of the anodized surfaces, revealing key details about the morphology and chemical composition of the nanotubular oxide layers.

Nanotubular Oxide Morphology

SEM analysis of the anodized surfaces shows the formation of highly ordered nanotubular oxide structures on both cpTi and Ti-6Al-4V ELI (Figure 1A and 1B).

In both titanium alloys, the self-assembled nanotubular oxide layers appeared tightly packed and aligned perpendicular to the surface, which is typical for anodized titanium. However, slight variations in surface morphology between cpTi and Ti-6Al-4V ELI were observed. This is potentially due to differences in alloy composition. Specifically, in the Ti-6Al-4V ELI alpha+beta titanium alloy, voids were observed in the nanotubular oxide layer in regions where the beta phase is located. The presence of the beta phase, influenced by the alloying element vanadium, appears to disrupt the uniform formation of the nanotubes, resulting in localized voids within the oxide structure.

The analysis of the nanotubular structures formed on cpTi (Grade 2) and Ti-6Al-4V ELI reveals notable differences in nanotube density and dimensions between the two alloys. The nanotube density on cpTi was found to be

higher, with approximately 36 nanotubes per square micron, compared to 25 nanotubes per square micron on Ti-6Al-4V ELI. However, this difference is primarily due to the presence of void spaces in the alpha+beta titanium alloy. Despite this variation in density, the average inner diameters of the nanotubes were very similar, with cpTi having an average diameter of 91.13 nm and Ti-6Al-4V ELI slightly lower at 90.13 nm. The minimum average inner diameters were also comparable, with cpTi at 70.11 nm and Ti-6Al-4V ELI at 71.05 nm. Maximum inner diameters, however, showed a slight difference, with cpTi reaching 109.33 nm and Ti-6Al-4V ELI having a slightly lower maximum of 104.56 nm. The nanotube lengths were slightly greater for cpTi, measuring approximately 1.15 microns, while the nanotubes on Ti-6Al-4V ELI had an average length of 1.09 microns. These results suggest that while the two alloys exhibit similar nanotubular dimensions, cpTi supports a denser arrangement of nanotubes compared to Ti-6Al-4V ELI, potentially due to differences in their surface compositions and anodization behaviors.

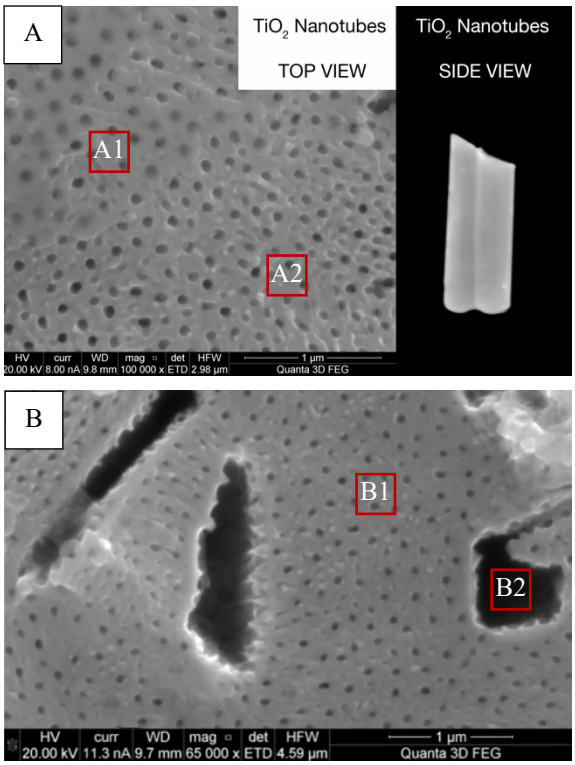

Fig. 1. SEM images nanotubular titanium oxide formed on the surface of A: cpTi, B:Ti-6Al-4V ELI

Chemical Composition Analysis

Energy Dispersive Spectroscopy (EDS) was performed to analyze the elemental composition of the anodized surfaces. EDS data were collected from four distinct zones across the two materials: A1 and A2 for cpTi (Grade 2) and B1 and B2 for Ti-6Al-4V ELI (Figure 1). The results are summarized in Table 1.

The EDS analysis provided insights into the elemental composition of the anodized surfaces of both cpTi (Grade 2) and Ti-6Al-4V ELI alloys. For cpTi, EDS spectra from zones A1 and A2 show that the oxide layer is primarily composed of oxygen (O) and titanium (Ti), confirming the formation of titanium dioxide (TiO_2). In zone A1, oxygen was detected at 29.78 wt% (55.92 at%), while titanium made up 70.22 wt% (44.08 at%), indicating a relatively thick oxide layer. In contrast, zone A2 had a lower oxygen content of 16.90 wt% (37.83 at%) and a correspondingly higher titanium concentration of 83.10 wt% (55.92 at%), suggesting a thinner or less fully oxidized region of the surface.

Table 1 *Elemental composition of nanotubular oxide layers on titanium alloys cpTi and Ti-6Al-4V ELI, determined by EDS analysis*

	A1		A2	
Elt.	Wt. %	At. %	Wt. %	At %
O	29.78	55.92	16.90	37.83
Ti	70.22	44.08	83.10	55.92
	B1		B2	
O	31.56	54.25	13.60	31.33
Al	4.36	4.44	3.84	5.24
Ti	57.13	32.80	80.66	62.06
V	1.71	0.93	1.90	1.38
F	5.24	7.59	-	-

For the Ti-6Al-4V ELI alloy, the EDS results from zones B1 and B2 reveal a more complex composition due to the presence of alloying elements. In zone B1, oxygen accounted for 31.56 wt% (54.25 at%), while titanium made up 57.13 wt% (32.80 at%). Notably, aluminum (Al) and vanadium (V), present as alloying elements, were detected at 4.36 wt% (4.44 at%) and 1.71 wt% (0.93 at%), respectively, alongside fluorine (F) at 5.24 wt% (7.59 at%). This suggests that fluorine from the anodization electrolyte may have been incorporated into the oxide layer. In contrast, zone B2, which corresponds to a scan of a void in the nanotubular oxide layer, exhibited a lower oxygen content of 13.60 wt% (31.33 at%) and a significantly higher titanium concentration at 80.66 wt% (62.06 at%). The presence of aluminum (3.84 wt%, 5.24 at%) and vanadium (1.90 wt%, 1.38 at%) was also noted, but there was an absence of fluorine. The lack of fluorine in zone B2 indicates possible variations in fluoride incorporation across the sample surface. These differences in elemental composition between zones suggest heterogeneity in the oxide layer, particularly in the Ti-6Al-4V ELI sample, likely influenced by the distribution of alloying elements and the anodization process, as well as the presence of voids corresponding to the beta phase in the material.

3. CONCLUSION

This study successfully demonstrated the formation of nanotubular oxide layers on the surfaces of commercially pure titanium (cpTi, Grade 2) and Ti-6Al-4V Extra Low Interstitial (ELI) alloys via anodization. The resulting nanotubes exhibited uniform dimensions, with inner diameters around 90 nm and lengths of approximately 1.1 microns. However, the nanotube density was higher on cpTi compared to Ti-6Al-4V ELI, which also exhibited voids in the nanotubular layer corresponding to regions of the beta phase. The presence of these holes suggests that alloy composition significantly influences the uniformity of the oxide layer.

EDS analysis confirmed the formation of titanium dioxide (TiO_2) on both alloys, with additional elements such as aluminum, vanadium, and fluorine detected in Ti-6Al-4V ELI. The incorporation of fluorine and alloying

elements into the oxide layer may offer additional benefits such as enhanced corrosion resistance or changes in surface chemistry, which could be advantageous for biomedical applications.

Overall, these findings highlight the potential of both cpTi and Ti-6Al-4V ELI alloys for biomedical implant applications, where tailored surface modifications such as nanotubular oxide formation can improve the biological response and functionality of the materials. Future studies may further explore the effects of these surface modifications on the mechanical properties and long-term performance in biological environments.

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