

PREPARATION AND STUDY OF THE MECHANICAL AND OPTICAL PROPERTIES OF ANODIZED BIO TITANIUM ALLOYS

Vladimir Petkov^{1✉}, Mihaela Aleksandrova¹, Shaban Uzun¹,
Stancho Yordanov¹, Tatyana Ivanova²

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Abstract

A number of experiments were conducted in an acetic acid electrolyte for anodizing titanium screws made of biocompatible titanium alloy Ti-6Al-4V Eli to obtain a colour range that characterizes different types of implant screws. The parameters of the electrochemical anodizing processes and their influence on the colour of the anodized titanium screws were established. The obtained anodized samples were tested for wear and reflection spectra were measured in the infrared (IR) spectral region. The analysis of the obtained results shows that the best wear resistance is possessed by the anodized samples with blue and violet colours, with the applied voltage in the electrolyte system being of decisive importance. The wear resistance of the obtained anodized screws changes nonlinearly depending on the colour range and the applied voltage in the electrolyte. Optical studies show that the reflectivity is highest in the violet samples, and the main phases are TiO (hongquite) and TiO₂ (anatase).

Key words: electrochemistry, anodizing, bio titanium, wear, reflection

Introduction. Historically, metals have been widely used in orthopaedics [1–3], and more than two-thirds of implants are made of metallic materials [4,5]. Currently, metallic materials used in medicine include 316L stainless steel, Co–Cr,

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Co–Cr–Mo alloys, titanium-based alloys Ti-6Al-4V, and other more specialized alloys, such as Au–Pd [6]. Modulus of elasticity is an extremely important property for medical implants, especially orthopaedic ones. Sometimes alloys show a tendency to loosen over time due to various reasons, such as their high modulus compared to the replaced bone, low wear and corrosion resistance and lack of biocompatibility. Since orthopaedic implants have a lifespan of 12–15 years, a second surgery is usually required at least once after the initial surgery [7].

One of the most commonly used titanium alloys for implants today is the Ti-6Al-4V (Gr 5) alloy. More than 50% of the world's production is of this alloy [8]. The titanium alloy Ti-6Al-4V is widely used in various industries due to its excellent mechanical properties, corrosion resistance and low weight. In the aerospace industry, it is used to manufacture components such as turbine blades, aircraft and missile bodies, and other structural elements. The light weight and high strength of the material make it a preferred choice for reducing the overall weight of aircraft. In the automotive industry, it is used to manufacture parts such as exhaust systems, valves and other high-temperature components. Corrosion resistance and light weight are important factors in improving the efficiency and durability of vehicles. Last but not least, it is used in medicine for the manufacture of orthopaedic implants such as hip joints, knee prostheses and dental implants. This alloy is biocompatible and has good corrosion resistance, which makes it suitable for long-term use in the human body.

Even better and more reliable is the titanium alloy Ti-6Al-4V ELI (extra low interstitial) or (Gr 23), which has improved plasticity, durability in air and salt water. It is purer in terms of the content of chemical elements such as: iron, oxygen and hydrogen, which is a state without ageing with maximum durability over time [9]. New alloys are constantly being developed and researched such as: Ti-6Al-7Nb, Ti-13Nb-13Zr [6], Ti-29Nb-13Ta-4.6Zr [10], etc., which are competitors and possible substitutes for the low modulus Ti-6Al-4V alloy, especially for biomedical applications. Anodizing Ti-6Al-4V ELI further increases its hardness, wear and corrosion resistance [11], as well as its biocompatibility.

The aim of the scientific and applied development is to anodize screws made of bio titanium alloy Ti-6Al-4V ELI in different colours so that orthopaedic surgeons can quickly and accurately distinguish them from those made of bio steel (316 LVM). On the other hand, the colour range allows for the identification of different types of titanium alloy screws such as: cancellous, locking, calendered, etc. Anodizing titanium screws for orthopaedic applications is a process used to improve the biocompatibility and durability of implants. This process involves creating an oxide layer on the surface of the titanium, which can improve bone cell adhesion and reduce the risk of infections.

Experimental. The studied titanium alloy samples subjected to anodization are cylinders with dimensions 10×10 mm and screws with a height of 3.5 mm to 9 mm and a diameter of 2 mm to 8 mm with different threads used as substrates.

The chemical composition of the titanium alloy is as follows: Titanium Grade 23 (Ti-6Al-4V Eli) also known as (ASTM B348 with chemical composition: C – 0.08 max, N – 0.05 max, O – 0.13 max, H – 0.0125, V – 3.50–4.50, Al – 5.50–6.50, Fe – 0.25 max [9,12].

Titanium anodizing is a process in which an oxide layer is created on the surface of the metal through an electrochemical reaction. This process improves the corrosion resistance, wear resistance, as well as the biocompatibility and aesthetic qualities of the titanium alloy. Anodizing of bio titanium is usually carried out in various types of electrolytes, the most commonly used being inorganic and organic xylenes such as: sulphuric acid (H_2SO_4), nitric acid (HNO_3), phosphoric acid (H_3PO_4), oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$), citric acid ($\text{C}_6\text{H}_8\text{O}_7$), acetic acid (CH_3COOH), etc. Electrolytes made from a mixture of acids and also from bases are also used.

The electrochemical process of anodizing titanium samples was carried out in an acetic acid electrolyte. In our case, we used 0.3–1.0 M acetic acid. Titanium samples are first cleaned physico-mechanically from chips and irregularities, then degreased, etched and then immersed in the anodizing electrolyte. The anodizing process is usually carried out at temperatures between 20–30 °C and a voltage of 15 V to 100 V, which together with the duration depends on what colour and thickness of the layer we want to obtain. Stainless steel (316L, 304L) is used as the cathode. Figure 1 shows an original bio titanium rod (Ti-6Al-4V Eli) with a diameter of $\phi - 10$ mm, from which all the anodizing screws and the cylindrical test samples with dimensions $\phi - 10$ mm, $h - 10$ –15 mm are made.

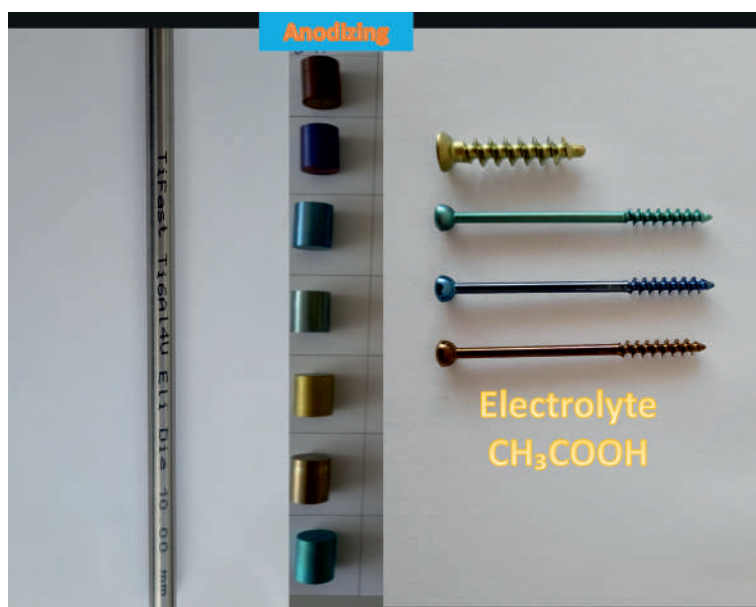


Fig. 1. Titanium rod Ti-6Al-4V Eli, from which screws and test cylindrical specimens are made and electrochemically anodized

Results and discussion. The wear resistance of seven types of anodized titanium cylindrical specimens prepared in an electrolyte of CH_3COOH at different voltages giving characteristic colouration of the specimens was investigated. Table 1 shows the results of the mass wear of the test specimens. The studies were carried out with “TABER ABRASER” tribotester. The “Taber” abrasion tester is used to determine the wear resistance of materials and evaluate the degree of wear resistance, such as measuring mass loss, thickness loss and permeability, etc.

T a b l e 1. Mass wear of differently coloured anodized titanium samples

Sample No.	Applied voltage, V	Colour	Mass before friction, g	Mass after friction, g	Mass wear, g
1	20	Violet	5.3302	5.3299	0.0003
2	30	Blue	5.4610	5.4608	0.0002
3	50	Yellow (ochre)	5.0543	5.0534	0.0009
4	15	Brownish	5.1343	5.1337	0.0006
5	40	Light blue	5.2155	5.2154	0.0001
6	60	Coppery golden	5.2762	5.2758	0.0004
7	95	Green	5.0710	5.0708	0.0002
0, Ti64 Eli	–	Silver gray	3.9803	3.9802	0.0001

Table 1 shows seven different colours with applied voltage that they are obtained. It is evident that the mass wear of the anodized titanium samples shown in Table 1 has a nonlinear character. When using voltages from 15 to 40 V for anodizing the samples, a decrease in wear (0.0006 to 0.0002 g) is observed, while when an applied voltage of 50 V is applied to anodize the samples, an increase in wear is observed max up to 0.0009 g. When using an operating voltage of 60 to 95 V (0.0004 to 0.0002 g), again we have a reduction in mass wear. It is known that with increasing applied voltage, the roughness of the anodized titanium layer increases [13], from which statement it follows that wear will also increase with equal adhesion of the titanium oxide layer deposited on the titanium alloy.

Fourier Transform Infrared (FTIR) spectrophotometer IR Prestige – 21, Shimadzu and a specular reflection attachment were used to measure the samples. Measurements of the samples against sample No. 0, Ti64 Eli (primary non anodized sample used to determine the background and baseline) are shown in Fig. 2A. In Fig. 2B, the reflectance of the samples was measured against an Al mirror (Al mirror used to determine the background and baseline). The highest reflectance in the range of $400\text{--}1200\text{ cm}^{-1}$ is possessed by sample 3 followed by sample two and one. The ratio between them is about 5%.

Figure 3 shows the characteristic absorption peaks in the infrared region of the studied samples. In the anodized samples in violet colour, the peaks at $414, 424\text{ cm}^{-1}$ indicate the presence of a titanium suboxide (TiO) phase. The IR bands

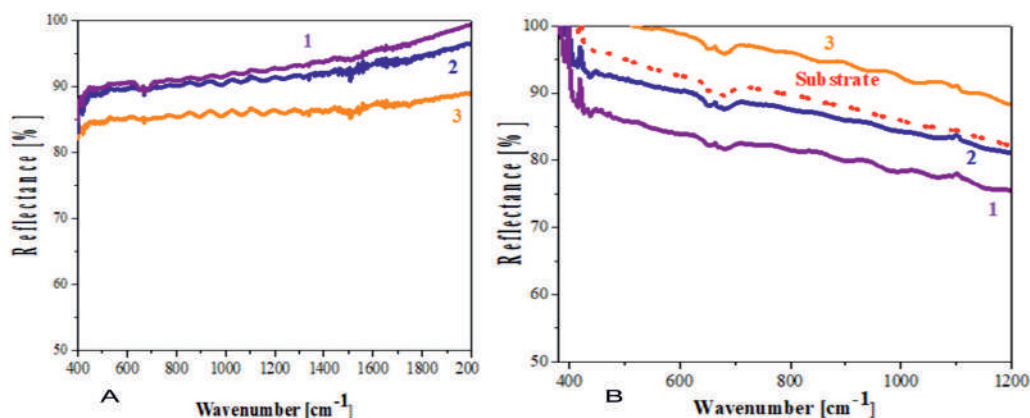


Fig. 2. Testing the durability of anodized titanium samples

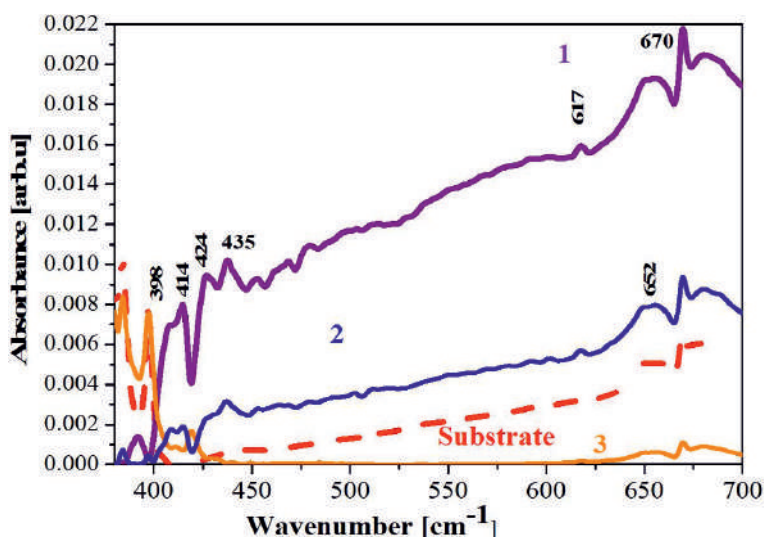


Fig. 3. Infrared absorption spectrum study of anodized titanium samples

at 435 cm^{-1} correspond to the characteristic absorption bands of anatase (TiO_2). The line at 652 cm^{-1} is due to TiO_6 octahedra vibrations of O–Ti–O and Ti–O–Ti bonds. The absorption bands at 670 cm^{-1} are attributed to Ti–O–Ti bonds in anatase (TiO_2).

Conclusions. Based on the experiments carried out, the following main conclusions can be drawn:

1. The parameters of electrochemical anodizing in an electrolyte of CH_3COOH have been established.
2. A total of seven colours of anodized bio titanium screws with applied voltage from 15 to 95 V were obtained.

3. A colour scale has been established to characterize certain types of bio titanium screws.
4. Two main phases, TiO (hongquite) and TiO₂ (anatase) the second being predominant, by infrared spectroscopy have been established.
5. It has been proven that the highest reflectivity is possessed by the violet (1) and blue (2) anodized samples shown in Fig. 2A at wavelengths from 400 nm to 4000 nm.
6. The nonlinear nature of mass wear depending on the applied stress has been determined.
7. It has been found that the acetic acid electrolyte for electrochemical anodizing Ti-6Al-4V Eli is reliable, safe and cost-effective for the acetalization of titanium screws used in implantology.

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¹*Institute of Metal Science, Equipment and Technologies with Hydro- and Aerodynamics Centre “Acad. A. Balevski”, Bulgarian Academy of Sciences, 67 Shipchenski prohod Blvd, 1574 Sofia, Bulgaria*
e-mails: vladimir2pe@yahoo.com, mihaelaaleksandrova204@gmail.com, shaban_uzun@abv.bg, stanchov14@abv.bg

²*Central Laboratory of Solar Energy and New Energy Sources, Bulgarian Academy of Sciences, 72 Tsarigradsko Shosse Blvd, 1784 Sofia, Bulgaria*
e-mail: tativan@phys.bas.bg