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Optical methods applied in thickness and topography testing of passive layers on implantable titanium alloys

JANUSZ SZEWCZENKO[1*], JANUSZ JAGLARZ[2], MARCIN BASIAGA[1], JAN KURZYK[2], ZBIGNIEW PASZENDA[1]

[1] Department of Biomaterials and Medical Devices Engineering, Faculty of Biomedical Engineering, Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland

[2] Institute of Physics, Cracow University of Technology, ul. Podchorążych 1, 30-084 Cracow, Poland

[*] Corresponding author: janusz.szewczenko@polsl.pl

The work presents the results of the applied surface pretreatment on topography and thickness of a passive layer of the anodically oxidized Ti6Al7Nb alloy. In our study were used: integrating sphere spectral measurements, bidirectional reflection distribution function (BRDF) method and optical profilometry. On the basis of the study, the passive layer thickness, roughness, waviness and the autocorrelation length were determined. The influence of voltage of anodization on topographical parameters of TiO_2 has been discussed.

Keywords: biomaterials, Ti6Al7Nb, passive layer, light scattering, bidirectional reflection distribution function (BRDF), thin films optics.

1. Introduction

The basic criterion for demonstrating the usefulness of the material for implantation purposes is its good biocompatibility in the environment of tissues and body fluids. It is most commonly identified with high corrosion resistance of the biomaterial. Titanium and its alloys are currently the most widely used biomaterials to produce long-term metal implants. Their usefulness is determined by lower density, as compared to stainless steel and cobalt alloys, and good biocompatibility in the environment of tissues and body fluids [1]. Basically, it is associated with good corrosion resistance and physicochemical properties of implant's surface, which are determined by the structure, roughness and thickness of the produced surface layer [2–5]. Structure, roughness and composition of the surface layer of implants made of titanium and its alloys can be modified using various methods, among which mechanical methods, chemical, electrochemical and thermal are dominating. As a result, the surface consists of titanium oxides and other oxides which presence is correlated with the chemical composition of the substrate [1, 2].

The primary purpose of surface modification of titanium and its alloys is to produce a passive layer consisting mainly of TiO_2. The most common final surface treatment methods of titanium alloys are electropolishing and anodic oxidation. Depending on the applied pretreatment as well as parameters of the final surface treatment, the obtained surface is characterized by diverse roughness and thickness of a passive layer [6]. Implant surface should be uniform with reference to the mentioned roughness and thickness, what should ensure homogeneity, low electron transmission, thermodynamic stability and the ability to repassivation in the presence of oxygen or water. This passive layer reduces the penetration of the alloying elements ions into the body [7].

Optical techniques of rough layer characterization are excellent tools for determination of thickness, roughness, autocorrelation length, and other statistical moments of film surface. The important advantages of optical methods are as follow: these methods are non-destructive and contactless.

The fundamental optical technique in layers study is spectroscopic ellipsometry [8]. Although, due to large depolarization induced by roughness, we had to limit ellipsometric study only to the determination of optical parameters, *i.e.*, refractive index and extinction coefficient of Ti6Al7Nb extra-polished substrate.

Due to large depolarization of beams reflected from TiO_2 layers it was impossible to determine thickness, refractive index and extinction coefficient from the ellipsometric study only. Ellipsometry is basically used for flat films with $\sigma \ll \lambda$ (σ – roughness, λ – wavelength) [9]. Rougher surface or films strongly depolarize reflected light and determination of ellipsometric angles is impossible. Thus also thickness cannot be determined from ellipsometric study.

If roughness is comparable to light wavelength, the specular reflection from the sample disappears and all reflected light spreads in wide solid angle, in which case it seems reasonable to use an integrating sphere. Then, interference fringes would be observed in total reflectance spectra measured by sphere. In our case TiO_2 layers exhibit rough behavior so specular reflection does not occur. Therefore we had to determine the thickness of film from integrating sphere measurements.

Parameters of layers such as thickness, roughness, autocorrelation length are strongly dependent on surface topography of substrate and anodization voltages. Therefore the main goal of this work is determination of macroscopic parameters characterizing films topography. For this purpose we applied BRDF technique for film description.

Long spatial wavelength irregularities were detected by means of an optical profilometer. The waviness occurring on layers substantially enlarges the total roughness. Thus optical profilometry measurements complete the topography description in long spatial wavelengths.

2. Material and methods

The research was carried out on Ti6Al7Nb alloy of the chemical composition according to the standard ISO5832-11 [10]. Samples were taken from rods with a diameter of 14 mm and subjected to a combination of different surface treatments. The individual treatments are as-signed with the following designations: 1 – mechanical grinding, 3 – mechanical polishing, 4 – sandblasting, 5 – electrolytic polishing, XV – anodization (*X* is the value of the potential at which the process was carried out). In addition, samples were sterilized in steam – S.

The mechanical grinding (1) was carried out successively on abrasive papers of grit 120, 320 and 600. The mechanical polishing (3) was performed using a hand-held grinder, a sisal brush and polishing paste. The sandblasting (4) was performed in the injection blasting chamber using glass beads as the working medium. The electrolytic polishing (5) was performed in a bath of chromic acid-based (E-395 Services POLIGRAT GmbH), at a current density $j = 10$ A/dm^2–30 A/dm^2. The anodizing process (XV) was carried out using an electrolyte based on phosphoric and sulfuric acids (Titan Color Company POLIGRAT GmbH), at potentials 57, 77, 87 and 97 V. As a result of differentiation of the applied potential values, different colors of the samples were obtained. The steam sterilization (S) was carried out at 134 °C at a pressure of 2.1 bar for 12 minutes.

For special extra-polished Ti6Al7Nb, the ellipsometric measurements were performed by means of the M2000 ellipsometer (Woollam Co.) to obtain its dispersion relation for refractive and extinction coefficients. For total reflectance spectra measurements we applied integrating sphere [11] ISP-REF of a diameter of 50 mm with a build-in tungsten-halogen lamp as a light source connected by a fiber cable with a spectrophotometer PC2000 (Ocean Optics Co.). These investigations allowed to determine the thickness of studied layers.

BRDF measurements were performed be means of an automatic home-made scatterometer. It consists of a 650 nm laser diode as a light source with the beam diameter of 2 mm mounted on a goniometric table with 0.1 deg resolution. The light scattered at the sample surface is measured with a silicon photodiode detector. The rotations are obtained by computer controlled stepper motors. For a fixed angle of incidence, the scattered intensity in the plane of incidence has been measured by varying the detector orientation. All measurements have been carried out with the *s*-polarized incident beam. In any case, the sample surface size was much larger than the beam diameter. From BRDF measurements were determined roughness and autocorrelation length of films.

For waviness detection we used an optical profilometer (OP) equipped with a reflection probe R200-7. That solution allowed to determine reflectance over smaller areas [12]. The probe consisted of a bundle of 7 optical fibers, *i.e.*, 6 illumination fibers around one “read fiber” (which read reflected light), each with a diameter of

200 μm. The investigated surface was illuminated by a laser diode ($\lambda = 635$ nm). The *XY* positioning stage is actuated by a lead screw stepper motor. It allows to scan 20 mm×20 mm surface area with steep of 50 μm.

3. Results and discussion

The large roughness of TiO_2 layers did not let to determine the layer thickness by the use of a spectroscopic ellipsometer. However, the refractive indices were determined and the absorption for an extra-polished surface Ti6Al7Nb. Additionally, for smooth TiO_2 film ($\sigma = 3.1$ nm), the dispersion relation depending *n* and *k* have been determined. Figure 1 shows the spectral dependence of refractive and extinction indices for Ti6Al7Nb substrate and for TiO_2 film.

Obtained values *n* and *k* for the substrate and for the TiO_2 were used to determine the thickness of layers.

We found strong interference fringes in total reflectance spectra determined from integrating sphere measurements. This evidences that the upper and bottom film interfaces are strongly correlated, *i.e.*, the upper surface of TiO_2 is a replica of the bottom one and the positions of minima and maxima are independent of surface roughness.

Film thicknesses were determined from the maxima and minima positions of total spectral reflectance. Such methodology is reasonable because the roughness of the sample does not affect the position of minima and maxima on the wavelength axis. It only changes the values of total reflection from the layer [13]. Thickness values of TiO_2 films were in a range 120 to 200 nm. The greater voltage used in forming TiO_2 films by anodization process, the larger thicknesses of TiO_2 layer were obtained.

In Figure 2 the total reflectance spectra of investigated layers are presented.

The BRDF studies for substrate Ti6Al7Nb obtained in 1/3/4/XV/S and 1/3/4/5/XV/S processes and for TiO_2 films on Ti6Al7Nb were performed. Figure 3 shows BRDF vs. spatial frequency for samples related to both processes of polishing.

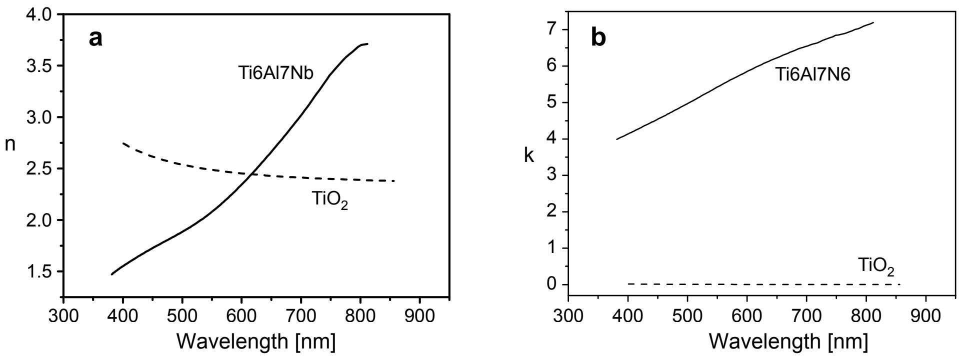

Fig. 1. Dispersion relations for *n* and *k* for the substrate Ti6Al7Nb and for the TiO_2 film.

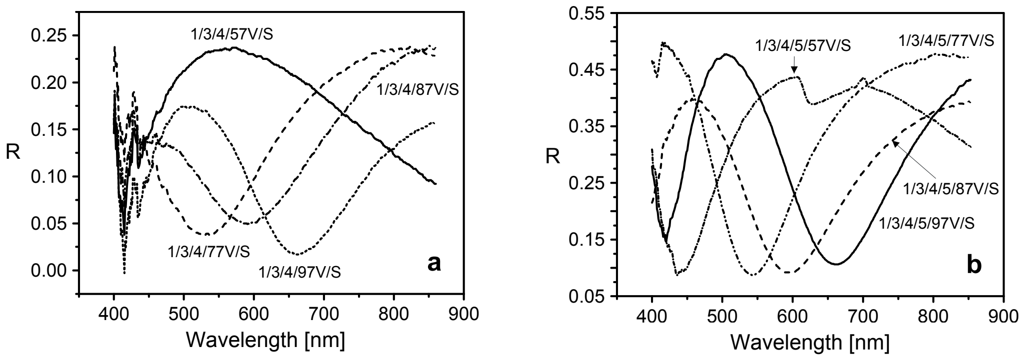

Fig. 2. Total reflectance from samples anodized and sterilized after sandblasting (**a**) and samples anodized and sterilized after electropolishing (**b**).

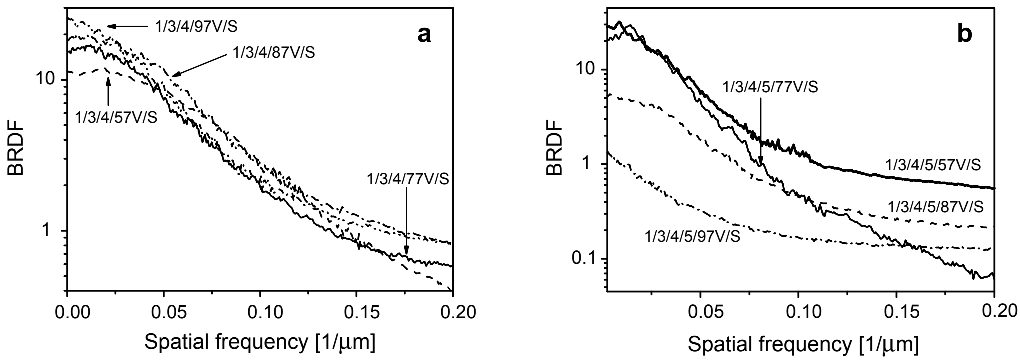

Fig. 3. BRDF as a function of spatial frequency for samples anodized and sterilized after sandblasting (**a**) and samples anodized and sterilized after electropolishing (**b**).

To determine the roughness σ and autocorrelation length T we fitted Davies model of light scattering from rough surfaces [14] to experimental BRDF data. Fitted values of σ and T for TiO_2 layers on 1/3/4/XV/S and 1/3/4/5/XV/S substrate are presented in Table 1.

As can be seen in Tab. 1, the values of voltage used in TiO_2 layers influence the film roughness. The higher the applied voltage, the rougher the surface is. Anodized samples have 2 or 3 fold autocorrelation lengths T of that of the substrate, and are bigger for substrate with greater values of T. Autocorrelation length weakly depends on used anodization voltage. Autocorrelation length increases with increasing voltage.

To characterize samples waviness, we determined optical profiles from optical profilometry (OP) measurements. The scattered radiation measured by OP is a function of heights of irregularities and slopes of microfacets, but sensitivity of this method derives mainly from detection of the slope change [12].

Figure 4 shows optical map obtained for samples anodized and sterilized after the sandblasting (1/3/4/57V/S) (Fig. 4**a**) and (1/3/4/87V/S) (Fig. 4**b**) and samples

T a b l e 1. Values of thickness, roughness and autocorrelation length determined from optical study.

	Substrate	1/3/4/57V/S	1/3/4/77V/S	1/3/4/87V/S	1/3/4/97V/S
Thickness [nm]	–	124	152	161	174
Roughness [nm]	231	259	297	343	397
Correlation length [μm]	0.885	2.11	2.17	2.26	2.61
	Substrate	1/3/4/5/57V/S	1/3/4/5/77V/S	1/3/4/5/87V/S	1/3/4/5/97V/S
Thickness [nm]	–	133	170	172	201
Roughness [nm]	176	286	302	339	407
Correlation length [μm]	1.01	3.02	2.98	2.92	3.13

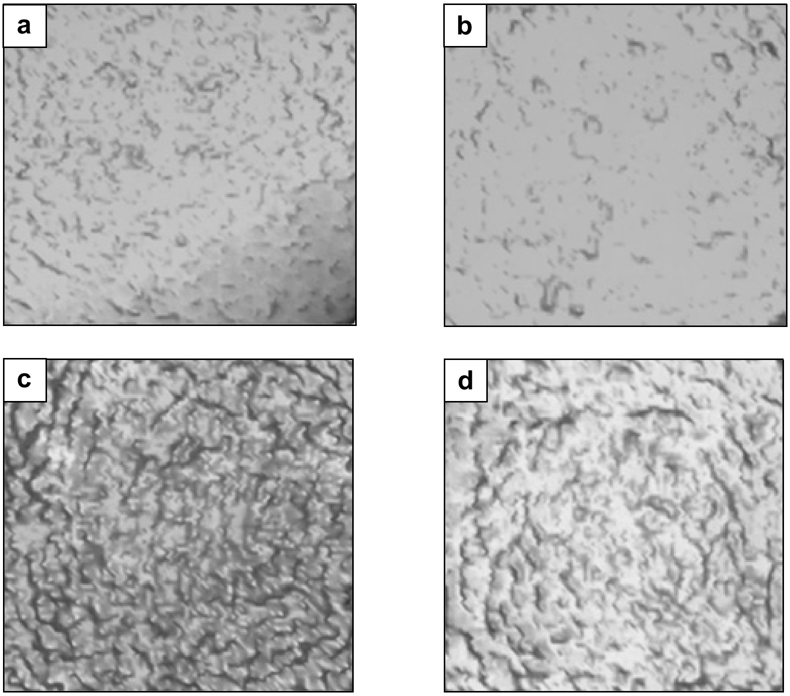

Fig. 4. Optical profile of samples: 1/3/4/57V/S (**a**), 1/3/4/87V/S (**b**), 1/3/4/5/57V/S (**b**), 1/3/4/5/87V/S (**d**).

anodized and sterilized after the electropolishing (1/3/4/5/57V/S) (Fig. 4**c**) and (1/3/4/5/87V/S) (Fig. 4**d**).

Some topographical features in optical profiles from Fig. 4 can easily be noticed. In fact, the optical map obtained from OP shows the intensity of reflected radiation which is a function of local surface slope in the illuminated sample area. The waviness was measured in a range 0.1 to 1 mm. As may be noticed, distribution of waviness shifts toward longer spatial wavelengths with growing anodization voltage. When voltage increases, the TiO_2 layer deposition process is more turbulent and film surface

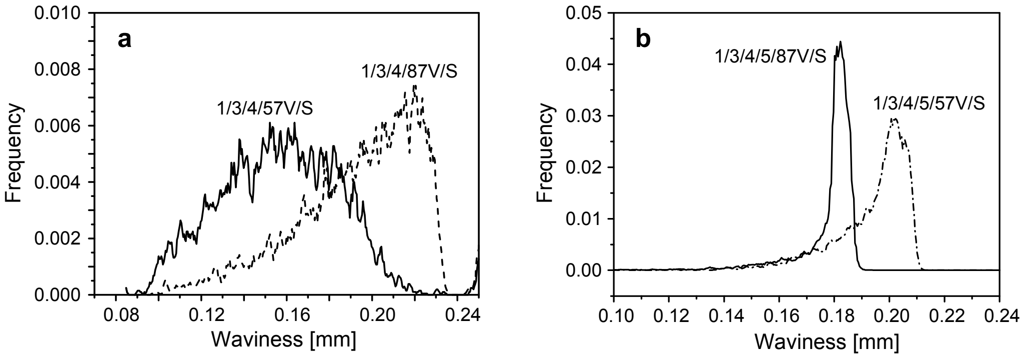

Fig. 5. Histogram of waviness distributions for samples anodized and sterilized after sandblasting (**a**) and samples anodized and sterilized after electropolishing (**b**).

is more inhomogeneous causing the growth of roughness for longer spatial wavelengths (waviness).

In Figure 5 the histogram is shown of measured slopes determined from optical profiles presented in Fig. 4.

As it may be noticed from Fig. 5, the higher voltage used in anodization results in larger dispersion of slopes, increasing the surface inhomogeneity.

4. Conclusions

The combined optical investigations (ellipsometry, reflectometry and BRDF measurements) of TiO_2 films created on the surfaces of Ti6Al7Nb alloy due to the anodizing process allowed to determine the thickness of layers and topographical parameters, such roughness and autocorrelation lengths. Also the study performed by the use of an optical profilometer allowed to obtain additional information on topography in a long spatial wavelengths (waviness) range. The obtained results enabled us to conclude that the increase in the anodization voltage caused enlarging thickness, roughness and autocorrelation length of the created TiO_2 layer.

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