Properties of TiO_2 Coatings Obtained by Atomic Layer Deposition (ALD) on the Ti13Nb13Zr Titanium Alloy

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Keywords: Ti13Nb13Zr, Coating, ALD and PVD Technique, Surface Technique, Properties

Abstract. The paper presents the results of research on the surface texture, adhesion, and the results of tribological tests of TiO_2 coatings obtained with the ALD technique. The geometric structure of the surface before and after the tribological tests was assessed using a confocal microscope with an interferometric mode. Model tribological tests were carried out for a reciprocating motion under the conditions of technically dry friction and friction lubricated with Ringer's solution. The tests showed that the TiO_2 coating has better tribological characteristics compared to Ti13Nb13Zr. The study of the geometric structure of the surface after tribological tests showed that the use of the lubricant resulted in a 3-times reduction in wear.

Introduction

Biomaterials consist of a number of materials with different compositions, structures, and properties. Regardless of whether they are made of a metal alloy, ceramic, or polymer, high biocompatibility, i.e. biological compatibility with a living organism, is required from them. After implantation, all biomaterials shouldn't cause allergic reactions and inflammation of the tissues surrounding the implant. They shouldn't also lead to implant rejection. Metallic materials account for the largest share of the global biomedical market. They are characterized by very good strength parameters, corrosion resistance, and well-mastered manufacturing techniques. Despite the continuous improvement of metallic materials, there is still the problem of their stabilization in the human body environment. Harmful products of their wear, including metal ions, entering the bloodstream may cause inflammatory processes and accumulate in tissues and organs [1].
Therefore, for many years, research has been conducted on surface modification of biomaterials to protect metal ions from entering the patient's body. The most commonly considered are various types of surface layers and coatings produced by physical and chemical methods [2-6].

The atomic thin film deposition (ALD) technique is used to produce nanoscale coatings. The system was invented by V. Aleskovsky and his associates in the 1960s. At the turn of the century, the technique was modified and applied mainly in electronics. The first publication using the ALD technique in corrosion protection was published in 1999 [7-9]. Then, there were further publications and patents on the application of the above technique in biomedical materials [10-12]. Previous research on thin coatings has focused on ceramic materials including Al_2O_3 aluminum oxide [13,14]. Although the coatings have very good properties, such as high hardness, and mechanical and thermal strength, they have some disadvantages which should be subject to extensive analysis. Aluminum oxide, Al_2O_3, has very excellent barrier properties, but can be chemically unstable and even dissolve in body fluid environments [15,16]. Therefore, the authors

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of this paper proposed the use of TiO_2 coating as a barrier/antiwear layer deposited on Ti13Nb13Zr titanium alloy.

Materials and Methods

The test substrate was titanium alloy Ti13Nb13Zr with the elemental composition shown in Table 1. The choice of material was dictated by its biocompatibility, mechanical properties, and high resistance to dissolution in body fluids [2]. In order to improve the functional and operational properties, a TiO_2 coating was applied to the Ti13Nb13Zr alloy using the atomic thin film chemical deposition (ALD) technique.

Table 1. *Chemical composition of the Ti13Nb13Zr, [wag. %]*

C	*H*	*O*	*N*	*Fe*	*Nb*	*Zr*	*Ti*
≤ 0.08	≤ 0.015	≤ 0.016	≤ 0.05	≤ 0.25	12.5–14.0	12.5–14.0	rest

The TiO_2 coating was deposited by means of the method of atomic layers deposition from a gaseous phase - ALD, using the Beneq system. Two precursors, Titanium Tetrachloride ($TiCl_4$) and water (H_2O) were used during the process, which was alternately introduced to the chamber. The process temperature was 130 °C, and 700 cycles have been applied. The assumed thickness of the deposited TiO_2 layer was 110 nm.

The surface texture before and after tribological tests was analyzed using a confocal microscope with Leica DCM8 interferometric mode. Axonometric images along with surface profiles on the cross-section are shown in Figure 1.

The tribological tests were carried out using an Anton Paar NTR^3 nanotribometer. Tests were carried out in a reciprocating motion under conditions of technically dry friction and friction in a Ringer solution environment. The applied loading force was 5 mN, the frequency was 1 Hz, cycle number was 10000. The counter-sample in the tested friction pairs was a ball 2 mm in diameter made of Al_2O_3. The lubricant with pH 5.5 and a volume of 1000 ml consisted of NaCl - 8.6 g, KCl 0.3 g, and $CaCl_2$ 0.48 g. The tests were repeated five times for each friction pair with the given parameters.

The adhesion of the coating to the Ti13Nb13Zr substrate was investigated using a scratch test. The test was carried out using an Anton Paar NHT^3 The test consisted in scratching the surface of the specimen with a Sphero-conical diamond indenter with a rounded radius of 2 μm at a load linearly increasing from 0.03 to 5 mN, a loading rate of 20 mN/min and a scratch length of 3 mm.

Results

The functional properties of a material determine the surface roughness. The geometric structure of the surface, especially of the mating elements, should be analyzed in 3D. Fig. 1 and Table 2 show axonometric (3D) images with surface profiles and amplitude parameters of the tested elements. The pink color indicates the average profile.

The analysis of the results of the geometric structure of the surface revealed that the values of all the analyzed amplitude parameters – Sp, Sv, Sz, Sa, Sq were lower for the TiO_2 coating. The positive value of the Ssk parameter for the reference sample informs about the presence of steep hills with sharp tops. The negative value of Ssk of the Ti13Nb13Zr TiO_2 sample proves its plateau surface formation – gentle slopes and rounded peaks.

The results of friction tests were summarized on a graph of the friction coefficient – μ (Fig. 2) of test elements depending on the types of materials, friction pairs and lubricants used.

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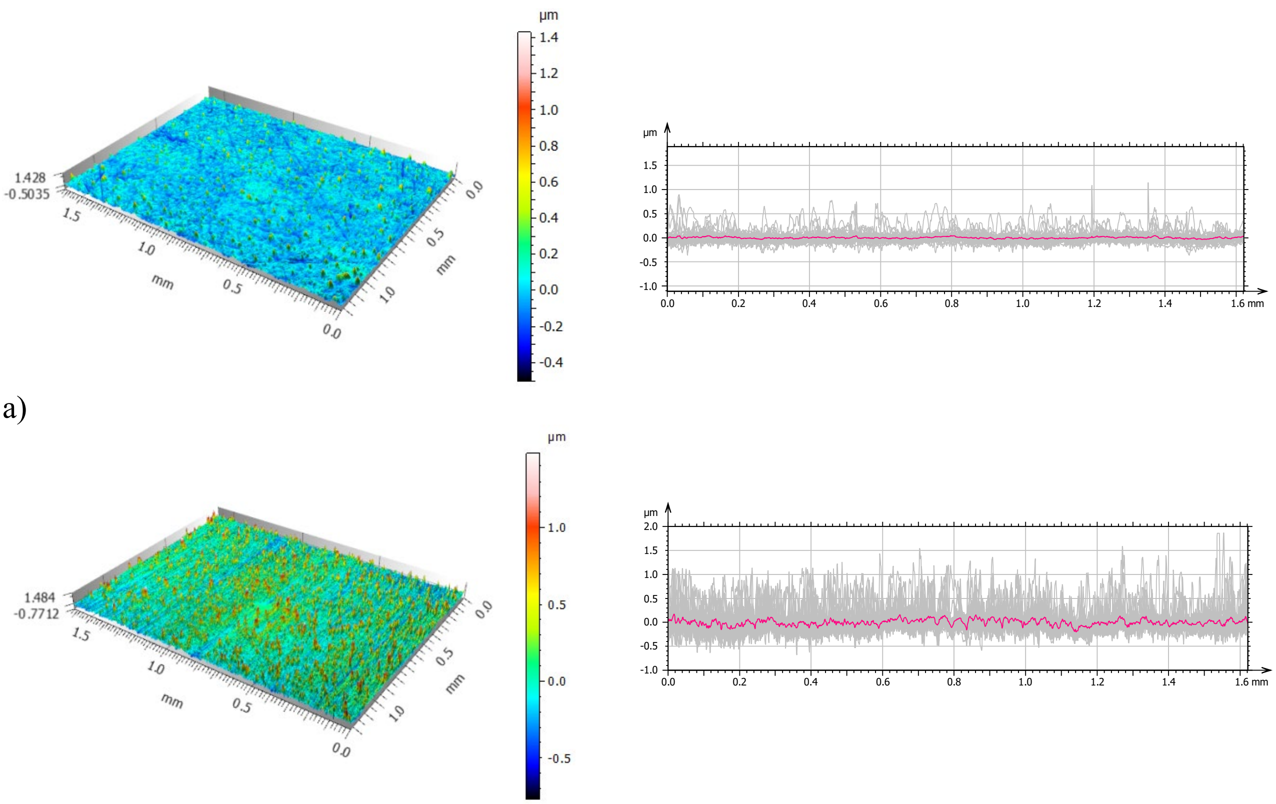
https://doi.org/10.21741/9781644902059-9

The results of the friction tests carried out indicate that the TiO_2 coating has the best tribological characteristics. The observed friction coefficients were comparable for both materials studied. Tests conducted with a lubricant indicate that resistance to the motion was 4-fold lower compared to values obtained from technically dry friction.

Table. 2. *Parameters of the surface texture*

Parameter	*Sp*	*Sv*	*Sz*	*Sa*	*Sq*	*Ssk*	*Sku*
Unit	*[µm]*	*[µm]*	*[µm]*	*[µm]*	*[µm]*		
Ti13Nb13Zr	1.42	0.5	1.93	0.06	0.09	1.97	12.27
Ti13Nb13Zr TiO_2	1.24	0.4	1.65	0.05	0.06	-0.02	3.45



a)

b)

Fig. 1. *Axonometric images and surface profiles of the reference sample Ti13Nb13Zr (a) and TiO_2 coating (b).*

The measure of adhesion of the coating to the substrate is the critical force. This force first causes cracking of the coating L Ft 1 - L Ft 4, and then its destruction - L Ft 5. Fig. 3 shows the results of the scratch test. The critical force was assessed on the basis of the registered changes in the coefficient of friction and frictional force and the indenter penetration depth.

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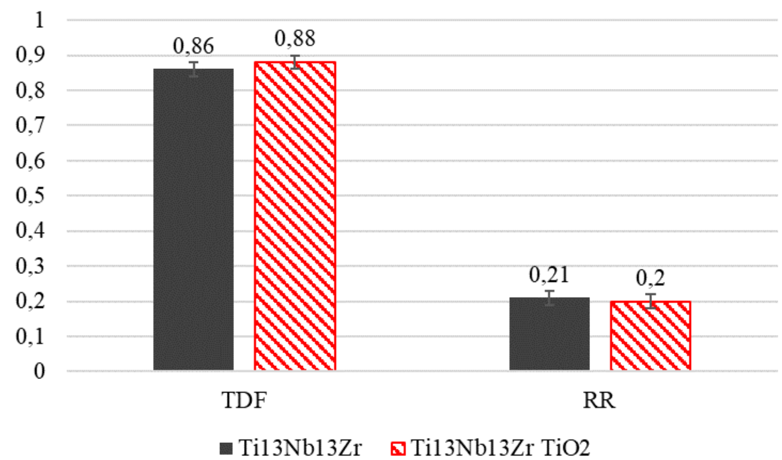

Fig. 2. *Average friction coefficient obtained under dry friction (TDF) and with the use of Ringer's solution (RS) as a lubricant.*

Tests of adhesion of the TiO_2 coating to the substrate showed that the coating was completely delaminated as a result of the applied load. On the friction force and friction coefficient diagrams, characteristic changes proving that the deposited layer was breaking off were registered. These points are marked as L Ft 1 - L Ft 5. At the point L Ft 5, the coating has completely failed. The maximum indenter depth was approximately 160 nm.

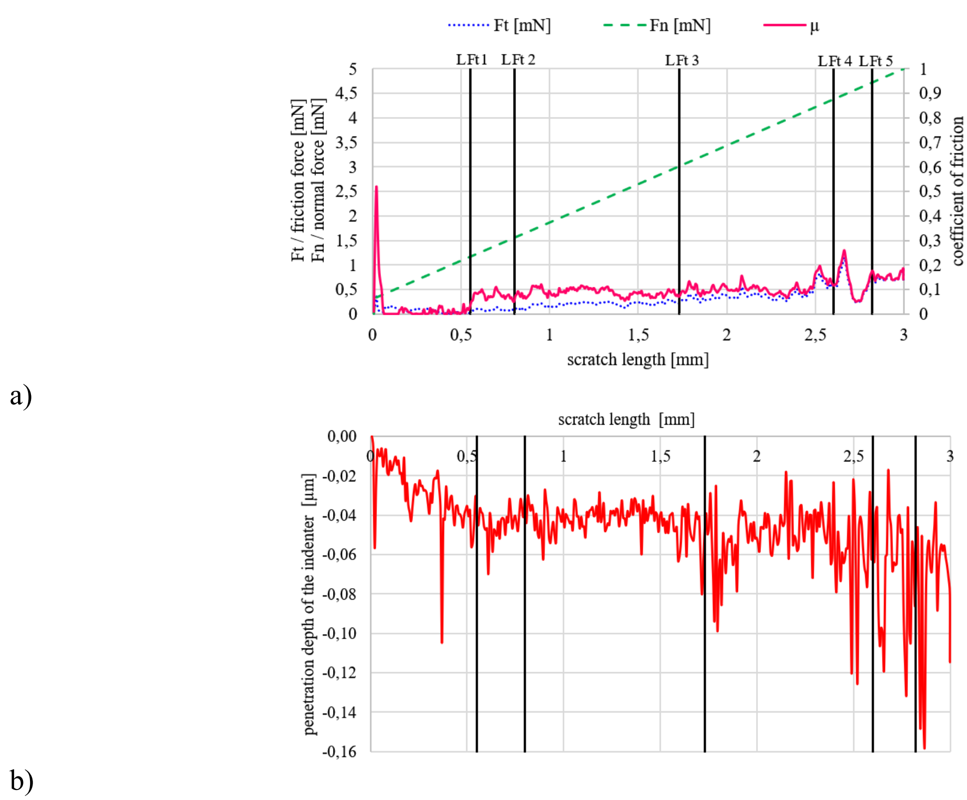

Fig. 3. *Scratch test results of the TiO_2 coating a) graph of variation of friction force, normal force and coefficient of friction, b) graph of penetration depth of the indenter.*

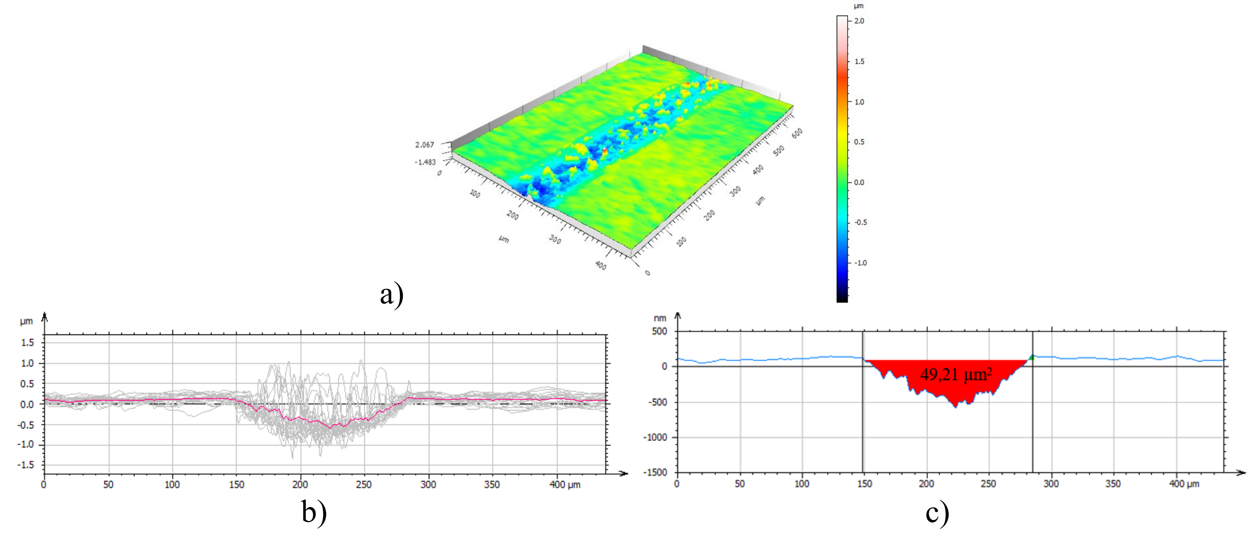

Fig. 4. *Axonometric views of sample wear track (a), mean the wear profile on transverse cross-section (b) volume of the wear track after the RS–lubricated sliding of Ti13Nb13Zr–Al_2O_3 friction pair.*

After tribological tests, the samples were subjected to wear trace measurements. The average depth and average area of wear of the samples after friction in Ringer's solution environment are shown in Fig. 4 and Fig. 5.

Fig. 4 and Fig. 5 show axonometric images of wear traces (a) wear profiles on a cross-section with the average profile marked (b), and the volume of the abrasion trace on the average profile (c) after friction with the use of Ringer's solution as a lubricant. It can be seen from the figure that the TiO_2 coating shows less wear compared to Ti13Nb13Zr. In the case of technically dry friction, the wear trace volume was 90.9 µm^2 for the titanium alloy and 49.5 µm^2 for the TiO_2 coating. The results of the geometric structure of the surface after tribological tests clearly indicate that the application of the coating favorably affects the functional properties of the Ti13Nb13Zr titanium alloy.

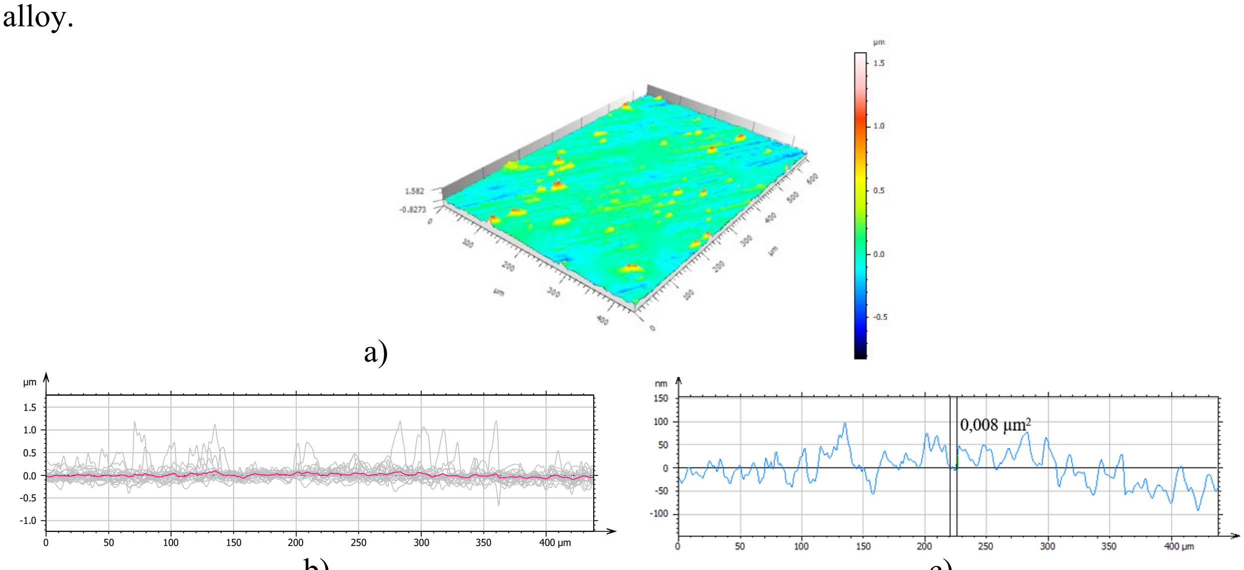

Fig. 5. *Axonometric views of sample wear track (a), mean the wear profile on transverse cross-section (b) volume of the wear track after the RS–lubricated sliding of Ti13Nb13Zr TiO_2–Al_2O_3 friction pair.*

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Conclusions

The results of tribological tests indicated that both materials tested had similar coefficients of friction. In the case of technically dry friction, it amounted on average to 0.84, and in the case of friction in the environment of Ringer's solution to 0.2. Microscopic analysis of abrasion traces showed that the TiO_2 coating wore less, regardless of the environmental conditions of the tests conducted. Adhesion tests of the coating revealed that the deposited layer delaminated after reaching a critical force of about 4.4 mN. This is indicated by both the friction coefficient and force diagram as well as the indenter penetration change diagram. When the critical force of 4.5 mN was reached, the indenter was at a depth of about 120 nm and the coating thickness was 110 nm.

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