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INFLUENCE OF TIO_2 COATING DEPOSITED WITH THE ATOMIC LAYER DEPOSITION ALD TECHNIQUE ON THE PROPERTIES OF Ti13Nb13Zr TITANIUM ALLOY

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The paper presents the geometric structure of the surface, hardness and the results of tribological tests for TiO_2 layers obtained by the ALD technique. The geometrical structure of the surface before and after the tribological tests was assessed using a confocal microscope with interferometry mode. An instrumental indentation was used to measure nanohardness. Model tribo tests were carried out for reciprocating motion under conditions of dry friction and friction lubricated with artificial saliva and saline. The tests showed that the TiO_2 samples showed lower wear and higher hardness.

Keywords: Ti13Nb13Zr, coating, ALD technique, surface texture, properties

INTRODUCTION

The atomic layers deposition technique (ALD) is one of most promising technologies of surface treatment for engineering materials. This method is used for deposition of oxide coatings, e.g. Al_2O_3, TiO_2, or ZrO_2, as well as of metals - Cu, Co, Fe, Ni, and Ag and also of hydroxyapatite [1-3]. Because of its unique properties, i.e. a high mechanical strength, high hardness, thermal and corrosion resistance, and good dielectric and insulating properties, the ALD coatings are applied in numerous branches of industry: chemical, aviation, electronics, and medicine [4-6]. The ALD technique consists in depositing ultra-thin layers, up to a few nanometres thick, in a strictly controlled process. The system utilises usually two gaseous precursor reagents, which are sent to the chamber in an alternating sequence of precisely controlled impulses. Any excessive amount of unreacted precursors in the deposition chamber is blown through with an inert gas - nitrogen [1,7-8]. Solid, liquid or gaseous precursors produce strong chemical bonds, which ensure perfect adhesion to the substrate. The temperature of ALD process is 25 - 500 °C and must be high enough to enable the reaction between precursors, but low enough to prevent the precursor damage. Gases are released very slowly, in a sequential or impulse mode, causing that a coat consisting of atomic monolayers is deposited on the substrate. The advantage of the method consists in a uniform thickness of the coating on all faces and openings of the element subjected to deposition, featuring even very complicated shapes, in the repeatability and high productivity of the process [9].

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MATERIALS AND METHODS

Titanium and its alloys feature high biocompatibility and fatigue strength, the modulus of elasticity close to the modulus of a human bone, and a high resistance to dissolution in the environment of tissues and systemic fluids [10-12]. A titanium alloy Ti13Nb13Zr consisted of: C ≤ 0,08, H ≤ 0,015, O ≤ 0,016, N ≤ 0,05, Fe ≤ 0,25, Nb 12,5 - 14,0, Zr 12,5 - 14,0. The rest was titanium. The values are presented in wt. %. A TiO_2 coating was deposited on it by means of the ALD technique to improve its mechanical, tribological, and practical properties.

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 were alternately introduced to the chamber. The process temperature was 150 °C, 1 000 cycles have been applied. The deposited TiO_2 coating was 150 - 170 nm thick.

A scratch test is the best method to study the adhesion of coat to the substrate. The test was carried out on an Anton Paar instrument. It consisted in making a scratch on the surface of the sample by means of a diamond sphero-conical indenter, at a load increasing linearly from 0,03 to 5 mN, at a loading rate of 20 mN/min, and a scratch 3 mm long.

The method of instrumental indentation is used to determine the hardness and elasticity of coatings. The hardness of the sample was measured using an Anton Paar hardness tester. An indenter with a Berkovich geometry was used during the tests. The load of 0,05 mN and a pause of 1 s was applied.

The tribological tests were carried out using an Anton Paar nanotribometer. Tests were carried out in a re-

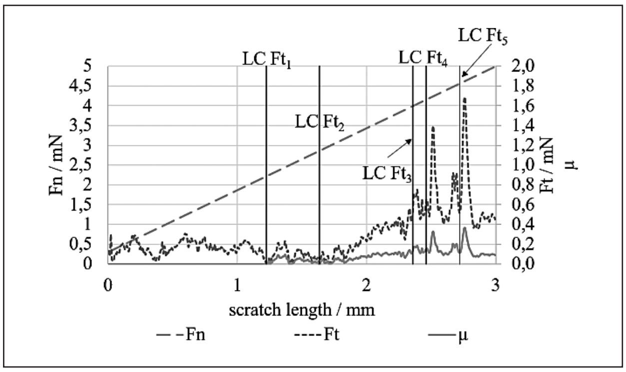

Figure 1 Scratch test results - graph of variation of loading force (Fn), coefficient of friction (μ), friction force (Ft)

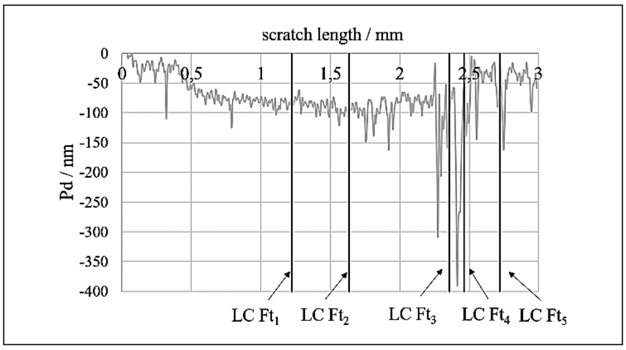

Figure 2 Scratch test results - penetration depth of the indenter (Pd)

Table 1 **The adhesion tests of Ti13Nb13Zr TiO_2**

Lp.	LC_1	LC_2	LC_3	LC_4	LC_5
1	2,2	2,84	3,97	4,14	4,54
2	2,82	3,68	4,15	4,58	4,74
3	2,68	2,96	3,47	3,91	4,69
mean	2,57	3,16	3,86	4,21	4,66
std dev	0,32	0,45	0,35	0,34	0,1

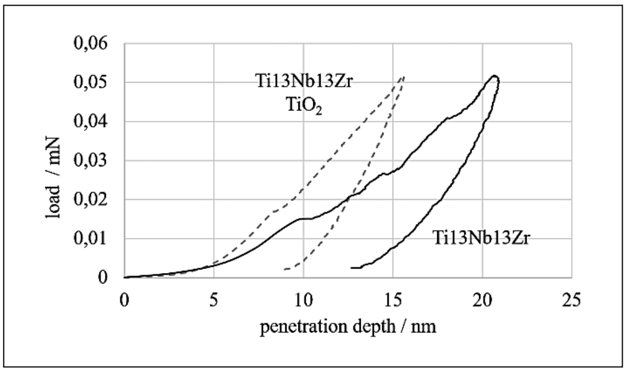

Figure 3 Load – penetration depth curves from indentation tests

Table 2 **Mechanical parameters**

Para-meter	Unit	Sample			
		Ti13Nb13Zr		Ti13Nb13Zr TiO_2	
		mean	std dev	mean	std dev
H_{IT}	GPa	2,75	0,08	4,46	0,45
E_{IT}	GPa	89,06	5,93	95,02	5,45
W_{plast}	pJ	0,2	0,21	0,14	0,02
W_{elast}	pJ	0,16	0,01	0,14	0,01
W_{tot}	pJ	0,36	0,01	0,28	0,02
h_m	nm	20,56	0,47	16,19	0,63

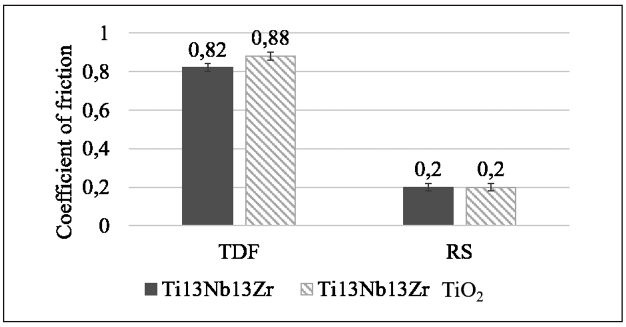

Figure 4 Average friction coefficient obtained under dry friction (TDF) and with the use of Ringer's solution (RS) as a lubricant.

ciprocating motion under conditions of technically dry friction and friction in a Ringer solution environment. The applied loading force was 5 mN and the frequency was 1 Hz.

RESULTS AND DISCUSSION

Figures 1-2 presents results of the scratch test. The critical force was assessed based on microscopic observations and recorded changes in the friction force. Table

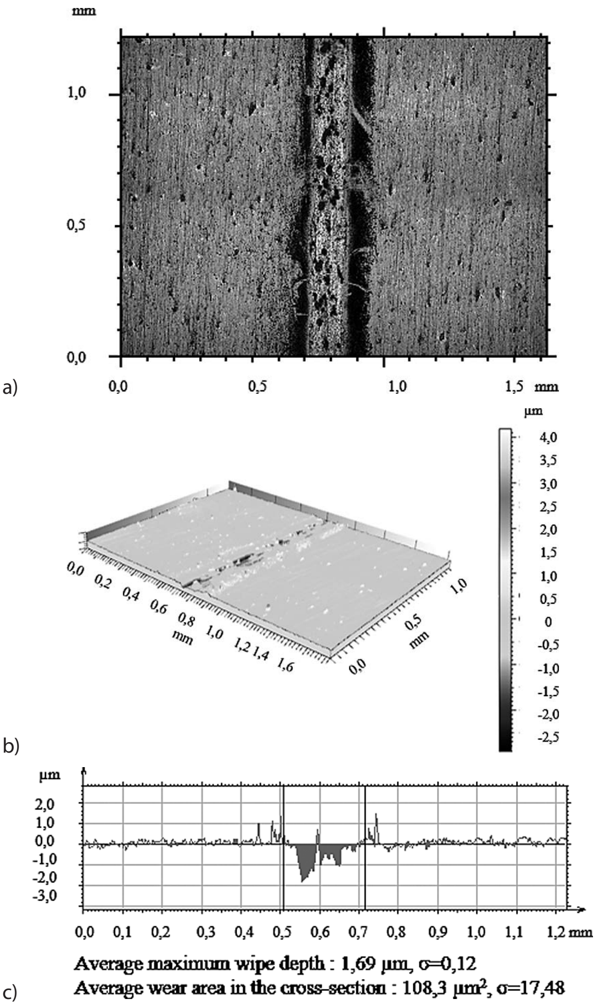

Figure 5 Optical and axonometric views of sample wear track (a, b) and the wear profile on transverse cross-section (c) after the dry sliding of Ti13Nb13Zr—Al_2O_3 friction pair.

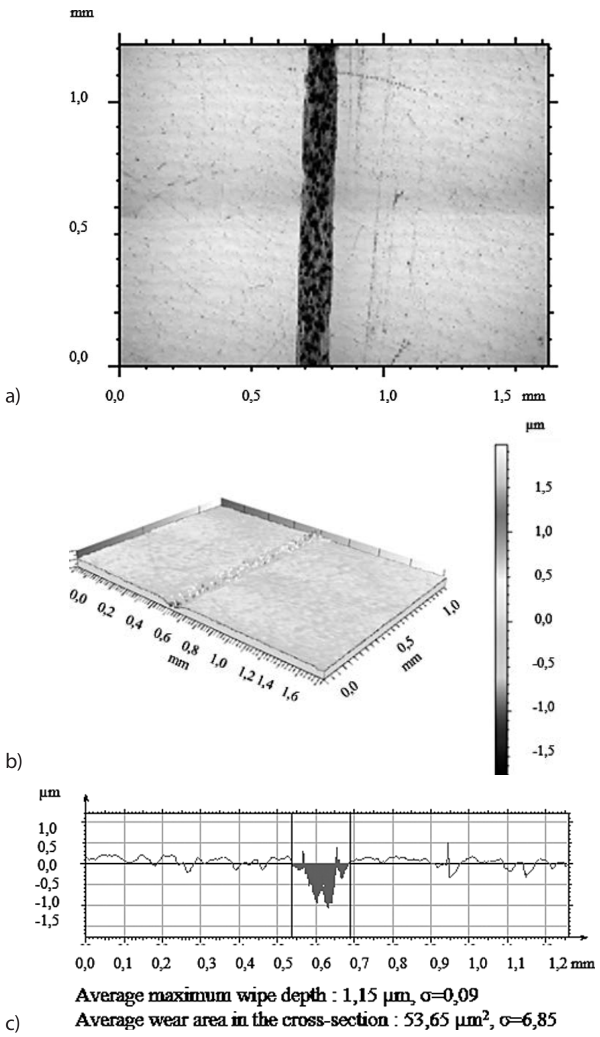

Figure 6 Optical and axonometric views of sample wear track (a, b) and the wear profile on transverse cross-section (c) after the RS-lubricated of Ti13Nb13Zr — Al_2O_3 friction pair.

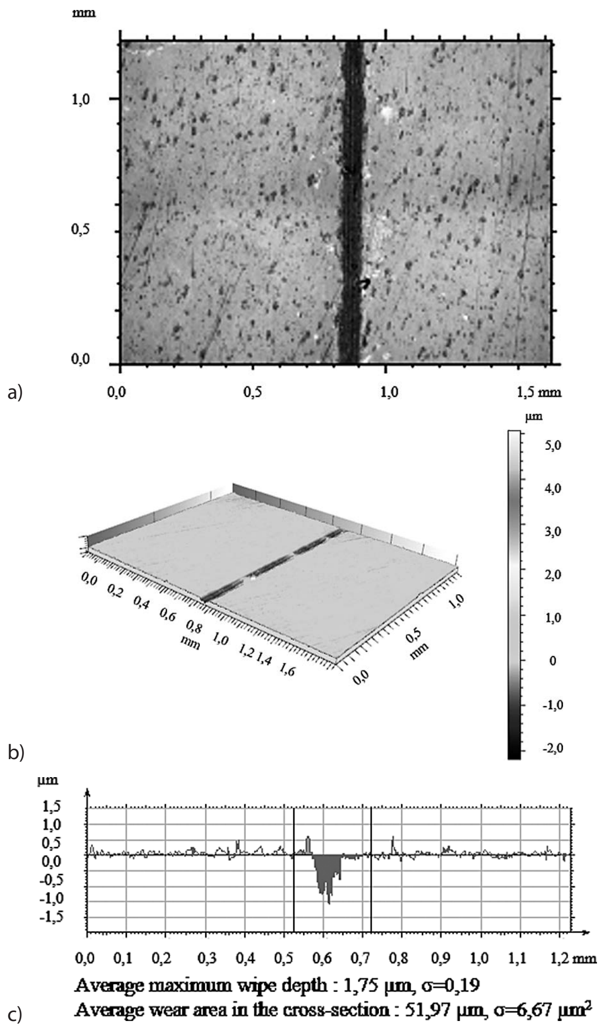

Figure 7 Optical and axonometric views of sample wear track (a ,b) and the wear profile on transverse cross-section (c) after the dry sliding of Ti13Nb13Zr TiO_2— Al_2O_3 friction pair.

1 presents values of forces causing chipping of the deposited coat.

The scratch test of the TiO_2 coating has shown that as a result of the applied loading the deposited layer was not entirely delaminated. Based on the graph of the friction force (Ft), coefficient of friction (µ), indenter penetration (Pd) and microscopic analysis it was found that the coating was chipping only in places marked as LC Ft_1—LC Ft_5 / mN. At the moment of coating peeling characteristic increases in the value of acoustic force were appearing on the graphs, proving the coating damage. The damage to TiO_2 layer had a nature of adhesion cracks, featuring local delamination on sides of the scratch trace.

Figure 3 presents an example of indenter penetration curve for Ti13Nb13Zr and Ti13Nb13Zr TiO_2 at a nominal loading force of 0,05 mN.

The maximum value of the loading force is marked on the y axis, for which the value of maximum indent h_{max} is determined (x axis). The most important mechanical parameters were determined based on the measurement of indenter penetration depth. Table 2 presents their averaged values obtained from 5 measurements.

The results of hardness tests presented in Table 2 confirmed the expected increase in mechanical parameters as a result of coating deposition. In the case of instrumental hardness an increase of approx. 40 % was recorded, and in the case of Young's modulus of about 10 %. This is also reflected in the maximum depth of indenter penetration. It was 16,19 nm and was by approx. 20 % smaller as compared with the value obtained for Ti13Nb13Zr titanium alloy.

Figure 4 presents results of examples of coefficient of friction µ curves versus the number of cycles registered during the interaction of tested rubbing pairs. Average values of coefficient of friction calculated based on three series of measurements are marked on the graph.

The results of tribological tests have shown that the obtained mean values of coefficients of friction were comparable for both studied materials, during the technically dry friction and friction in a lubricating environment as well.

After tribological tests the samples were subjected to microscopic observations. An average maximum depth and an average surface area of sample wear on the

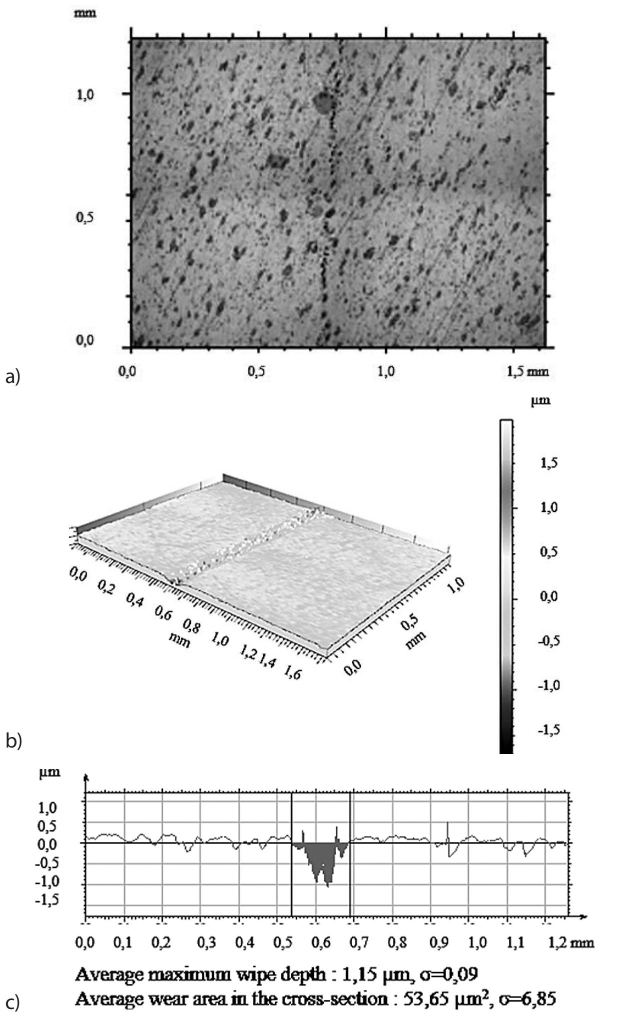

Figure 8 Optical and axonometric views of sample wear track (a, b) and the wear profile on transverse cross-section (c) after the RS-lubricated sliding of Ti13Nb13Zr TiO_2—Al_2O_3 friction pair.

cross-section were determined based on five series of measurements. Figures 5-8 present the test results.

The analysis of studies on the geometrical structure of the surface after tribological tests has shown that the Ti13Nb13Zr titanium alloy featured heavier wear as compared with Ti13Nb13Zr with a TiO_2 coating. The rubbed out area of Ti13Nb13Zr on the cross-section was nearly twice larger under conditions of technically dry friction and 15 times larger under conditions of lubrication with the Ringer solution as compared with Ti13Nb13Zr TiO_2. It was also noticed that in both cases the application of a lubricant resulted in reduction of wear.

CONCLUSION

The results of frictional and wear tests have shown that both tested materials featured similar coefficients of friction. For the technically dry friction they amounted to approx. 0,86, and for the friction in the Ringer solution environment – 0,2. In addition, the application of a lubricant resulted in decreasing the resistance to motion by approx. 75 %. The mechanical tests have shown that the suggested process of TiO_2 coating formation as a result of atomic layers deposition had a favourable effect both for the hardness and Young's modulus. The curves of load - indenter penetration depth have shown that the deposited layer features smaller elasticity as compared with the reference sample. The analysis of geometrical structure of samples surfaces after tribological tests have shown that the reference sample was the most wearing out material in the frictional connection with a counter-sample of aluminium (III) oxide. This effect was noticeable both during technically dry friction and friction in the Ringer solution environment. The obtained results of studies have shown that the application of a TiO_2 coating results in the improvement in both mechanical and tribological properties.

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Note: The responsible for English language is: Małgorzata Dembińska Lingua Lab.