PROPERTIES OF COATINGS USED IN BIOTRIBOLOGICAL SYSTEMS

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Abstract

The properties of diamond-like carbon coatings (DLC) obtained via plasma-assisted chemical vapor deposition (PACVD) on the Ti13Nb13Zr alloy were evaluated. For this purpose, measurements of the thickness, the surface geometric structure, adhesion, as well as tribological tests of the tested coatings were performed. The thickness of the deposited coating was measured using the spherical grinding method. Surface geometry measurements before and after tribological tests were performed with a Leica DCM8 optical profilometer. A scratch test was performed to measure the adhesion of the coating. An indenter with a Rockwell geometry was used during the adhesion tests. The test offered the possibility of real-time recording of the coefficient of friction and acoustic emission. In addition, it was also possible to measure the geometrical parameters of a scratch and to carry out a microscopic analysis of a scratch during the coating damage. The test was carried out on an Anton Paar MCT³ instrument. The model tribological tests were carried out in rotary motion under technically dry friction conditions and friction conditions with lubrication with the Ringer's solution and an artificial saliva solution. The tests were carried out using an Anton Paar TRB³ tribometer. The scratch test proved that the deposited layer was characterized by good adhesion. Based on the results of the tribological tests, it was found that the lower resistance to motion and wear was obtained for the DLC coatings on the Ti13Nb13Zr substrate. The results of the tests performed on the DLC coatings indicate the possibility of their application in biotribological systems.

Keywords: *PACVD technique, titanium alloys, surface texture, hardness, friction, wear*

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Introduction

The increase in demand for modern biomaterials has led to the rapid development of implantology. Implants, in addition to appropriate mechanical properties, must be highly biocompatible and resistant to bacteria and fungi. This poses a huge challenge to modern materials science. In this context, one of the most often studied classes of materials are carbon materials, including diamond-like carbon (DLC) coatings [1-3]. Compared to commonly used anti-wear layers, DLC coatings are characterized by high resistance to wear by friction, high adhesion to the substrate, high hardness, and high thermal and chemical stability [4-7]. DLC coatings are mixtures of amorphous carbon with sp^3 and sp^2 bonds. Hybridisation of sp^3, which is characteristic of the diamond, results in increased resistance to abrasion and hardness, and good thermal conductivity. The sp^2 bonds derived from graphite determine the low resistance to motion values. The carbon hybridisation degree, the mixture composition, and the physicochemical properties of a DLC coating are determined by the selected production method and the production process conditions [8-11]. Carbon coatings are obtained via classical chemical methods which are multi-step and labour-intensive. The surface modification of biomaterials via plasma provides completely new possibilities for tailoring their surface properties to specific applications. In this paper, the authors examined the properties of diamond-like carbon coatings obtained via plasma-assisted chemical vapour deposition (PACVD) in terms of their use in biotribological systems.

Materials and Methods

The subject of the study was the Ti13Nb13Zr titanium alloy with the chemical composition shown in TABLE 1 and the mechanical properties summarised in TABLE 2.

Disks made of the Ti13Nb13Zr titanium alloy with a diameter of 30 mm and a height of 6 mm were processed using a grinding-polishing machine made by Pace Technologies. Silicon carbide abrasive papers with increasing grain size from 120 to 2500 μm were used. The finishing treatment involved polishing on cloth with the addition of a polishing slurry with Al_2O_3, with a grain size of 0.05 μm. After grinding and polishing, the sample surface roughness value of Ra = 0.06 μm was obtained. The other amplitude parameters of the reference surface are shown in TABLE 6. Before coatings were deposited, the samples were degreased in ethanol in an ultrasonic cleaner. A DLC coating was deposited on the prepared material by plasma-assisted chemical vapour deposition (PACVD).

The thickness of the coating was determined using a Calotest device. A steel ball of 20 mm in diameter, rotated on the surface of the coating at the speed of 3000 rpm. The duration of the test was 1240 s. During the test, a diamond paste with a small grain size of < 0.2 μm was used. A diagram of the friction pair in the Calotest device is shown in FIG. 1a. As a result of friction, the material from both the coating and the substrate was removed. The geometric traces of the removed coating and the substrate material had the shape of concentric circles. To determine the thickness of the coating, the diameters of the circles were measured using an optical microscope (FIG. 2). The test was repeated 5 times.

The geometric structure was examined using confocal microscopy. The measurement involved scanning the surface of the tested materials over an area measuring 1.2 mm x 1.6 mm.

Tribological tests were carried out on a TRB³ tribometer of the ball-on-disc type in rotary motion in technically dry friction conditions and in conditions of friction with lubrication with the Ringer's fluid and with an artificial saliva solution, with constant parameters of the friction pair (TABLE 3). The chemical composition of the lubricants is shown in TABLE 4. The counter samples in the examined friction pairs were Al_2O_3 balls with a diameter of 6 mm. A photograph of a friction pair is shown in FIG. 1b.

The primary method used to determine the coating quality is the evaluation of a mechanical indicator, namely adhesion. The advantage of adhesion testing is that the changes in the coefficient, the friction force, and the acoustic emission can be recorded in real-time. In addition, it is also possible to measure the geometric parameters of a scratch and to perform microscopic analysis of a scratch during coating damage. The technical parameters of the scratch test are shown in TABLE 5.

TABLE 1. Chemical composition of Ti13Nb13Zr titanium alloy, % weight.

Element	% weight							
	C	H	O	N	Fe	Nb	Zr	Ti
Ti13Nb13Zr	≤ 0.08	≤ 0.015	≤ 0.016	≤ 0.05	≤ 0.25	12.5-14.0	12.5-14.0	based

TABLE 2. Mechanical properties of the Ti13Nb13Zr alloy.

Material	Rm [MPa]	Re [MPa]	A [%]	Z [%]	E [GPa]
Ti13Nb13Zr	973-1037	836-908	10-16	27-53	79-84

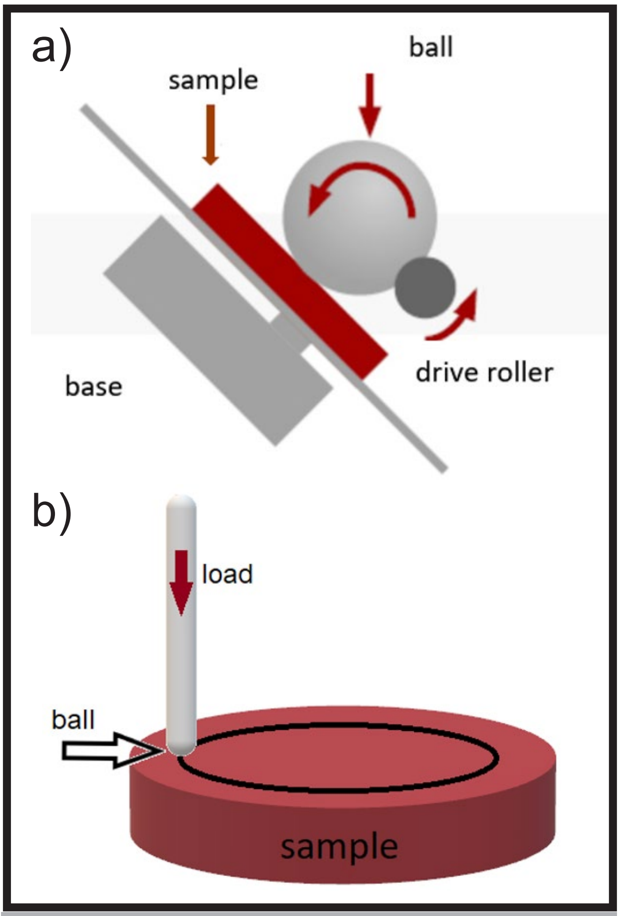

FIG. 1. Friction pair in Calotest (a), friction pair in TRB³ (b).

TABLE 3. Technical and environmental parameters of the tribological test.

Parameter	Unit	Friction pair ball Al_2O_3 – disk Ti13Nb13Zr ball Al_2O_3 – disk Ti13Nb13Zr DLC
Load	N	5
Linear speed	m/s	0.1
Friction path	m	1 000
Radius	mm	11
Cycle	-	14 458
Humidity	%	50 ± 1
Temperature	°C	23 ± 1
Lubricant	-	- Ringer solution Artifical saliva

TABLE 5. Technical parameters of mechanical test.

	Adhesion
Device	MHT³
Indenter	Diamond Rockwell
Load	0.03-30 N
Loading rate	10046.65 mN/min
Unloading rate	-
Scratch length	2 mm

TABLE 4. Chemical composition of the lubricants.

	Chemical composition [g/dm³]						
	NaCl	KCl	$CaCl_2$	$CaCl_2 \cdot 2H_2O$	$NaH_2PO_4 \cdot 2H_2O$	$Na_2S \cdot 9H_2O$	Urea
Ringer solutions	8.6	0.3	0.243	-	-	-	-
Artificial saliva	0.4	0.4	-	0.906	0.690	0.005	1.0

Results and Discussion

The thickness of the diamond-like carbon coating was measured using optical microscopy. The resulting layer was 1.77 μm thick. FIG. 2 shows an abrasion mark.

FIG. 3 shows the results of the examination of the surface geometric structure. The study presents the axonometric images and the surface profiles of both the reference sample and the DLC coating. The average profiles for each sample were generated based on 100 profiles. The amplitude parameters (acc. to ISO 4287) are shown in TABLE 6.

Examinations of the surface geometric structure revealed that the deposition of a diamond-like carbon coating on the Ti13Nb13Zr alloy did not change the values of the amplitude parameters (there was a slight increase in the *Rp Rv*, *Ra*, and *Rq* indices). Additional information on the surface shape of the studied samples was obtained by determining the coefficient of surface inclination (asymmetry) *Rku* and the clustering coefficient *Rsk*. Both parameters are very sensitive to the presence of local elevations, depressions, and defects on the surface. A negative value of *Rsk* indicates that the surface of the reference sample is flat. If the index for the coating reaches 0.49, the emergence of steep elevations with sharp tops is demonstrated.

FIG. 4 shows the results of the adhesion tests. The critical force was evaluated based on the microscopic observations and the recorded changes in the friction coefficient and the acoustic emission.

Based on the plot of the friction coefficient (μ) and the acoustic emission, it was found that the first cracks in the coating appeared under a load equal to 3.6 N (LC1). Microscopic analysis of the crack at this location showed no changes in the coating structure. When the force of 8.1 N (LC2) was exceeded, a sharp increase in the acoustic emission values was observed. The microscopic image showed the first chipping at the edge of the scratch. The scratch test of the diamond-like carbon coating revealed that the deposited layer became delaminated under the load of 13.3 N (LC3); at the same time, the friction coefficient increased almost threefold from 0.16 (at LC2) to 0.45.

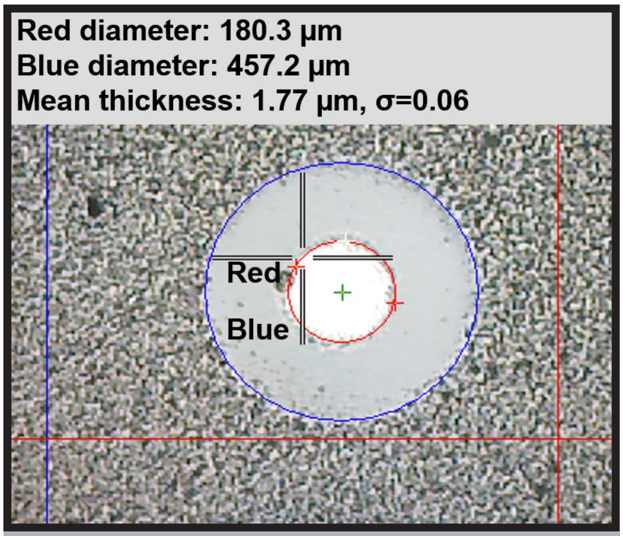

FIG. 2. An image recorded during thickness measurement of the DLC coating.

TABLE 6. The parameters of surface texture.

Parameter	Ti13Nb13Zr reference	Ti13Nb13Zr DLC
	mean	mean
Rp [nm]	268	348
Rv [nm]	243	244
Ra [nm]	65	73
Rq [nm]	80	90
Rsk	-0.03	0.49
Rku	3.41	4.41

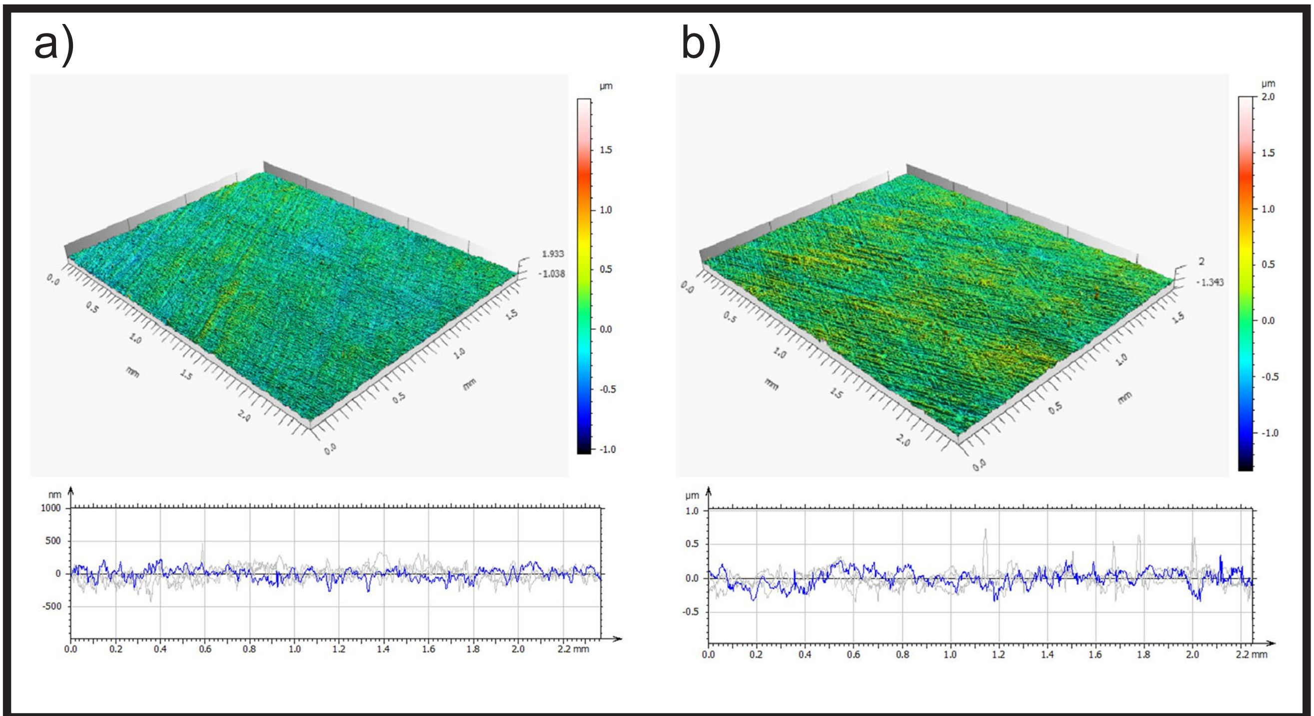

FIG. 3. The isometric image of surface and the sample profile of the surface: a) Ti13Nb13Zr, b) Ti13Nb13Zr DLC.

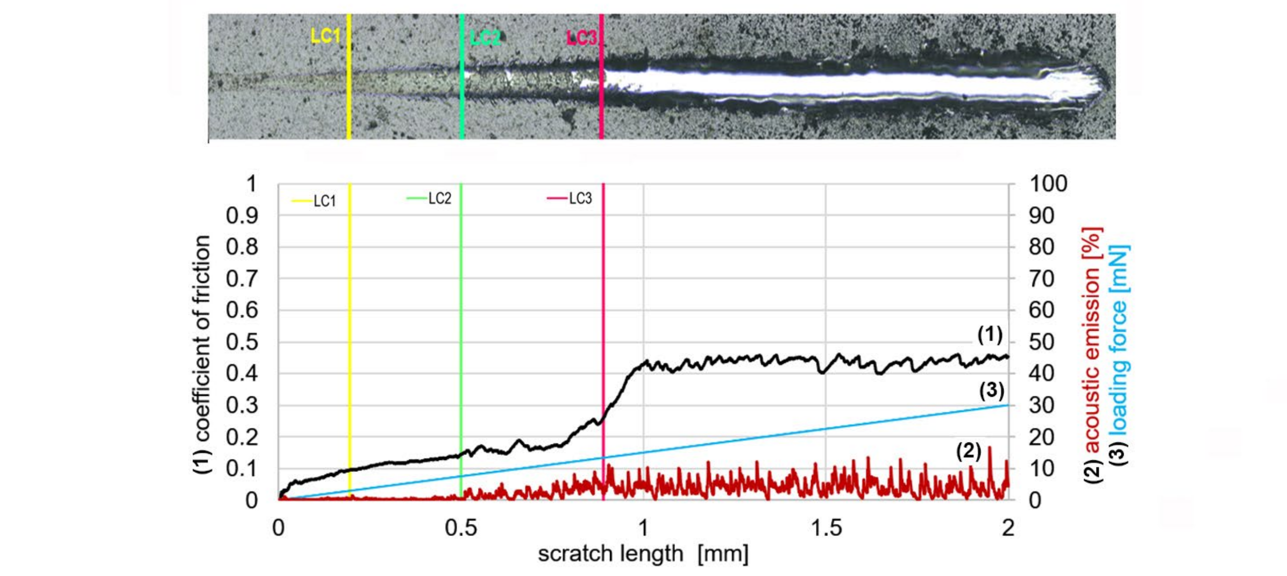

FIG. 4. Scratch test results - graph of variation of loading force (Fn), coefficient of friction (μ), acoustic emission.

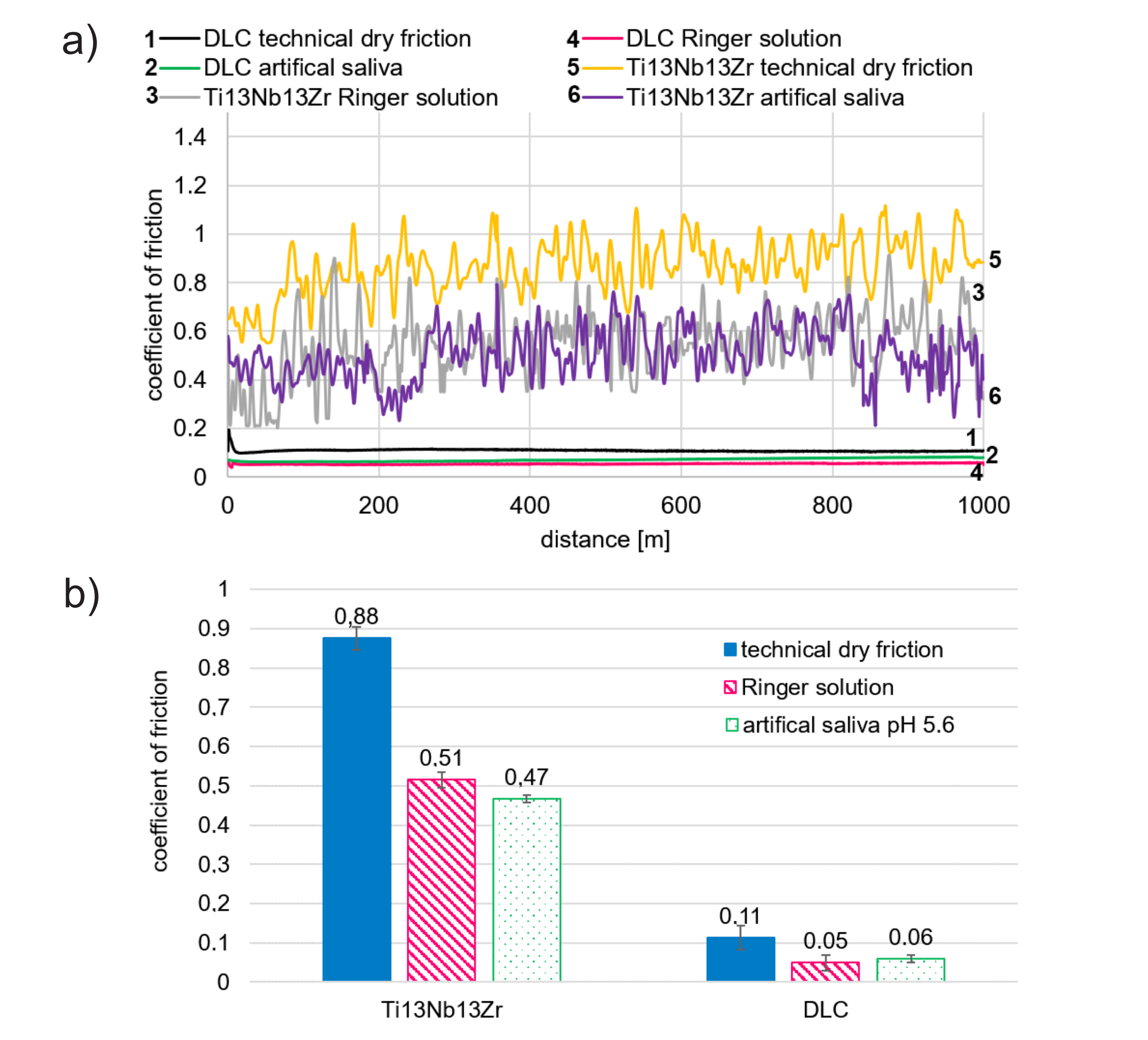

FIG. 5. a) Sample plots of the coefficient of friction, b) mean coefficient of friction.

FIG. 5a shows the sample plots of friction coefficient μ as a function of the number of recorded friction pair cycles. The values in FIG. 5b are averaged values of the friction coefficient measured during three measurement series. The diagram shows the average values of the friction coefficient calculated from three measurement series. The results of the tribological tests showed that the diamond-like carbon coating is characterized by low resistance to motion. In the case of technically dry friction, the average friction coefficient was 0.11 which was eight times lower than the Ti13Nb13Zr alloy. Moreover, it was observed that for both the reference sample and the coated sample, the application of lubricants resulted in a reduction in the resistance to motion.

After the tribological tests, microscopic observations were performed on the samples. FIG. 6-8 shows examples of the axonometric images of abrasion marks and the abrasion profiles on a cross-section. TABLE 7 shows the average wear area for the samples on the cross-sectional area determined after five measurement series.

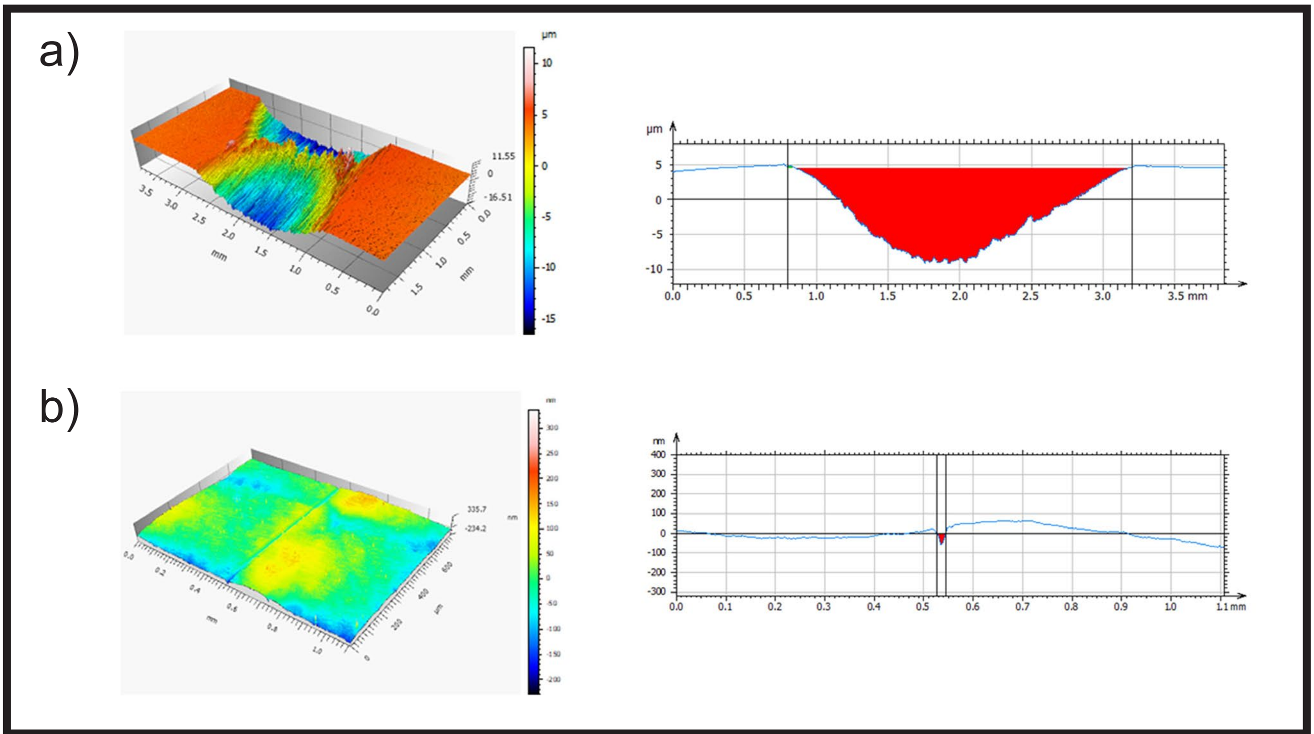

FIG. 6. The axonometric image of the trace of wear and the wear profile in a cross-section during technical dry friction: a) Ti13Nb13Zr, b) Ti13Nb13Zr DLC.

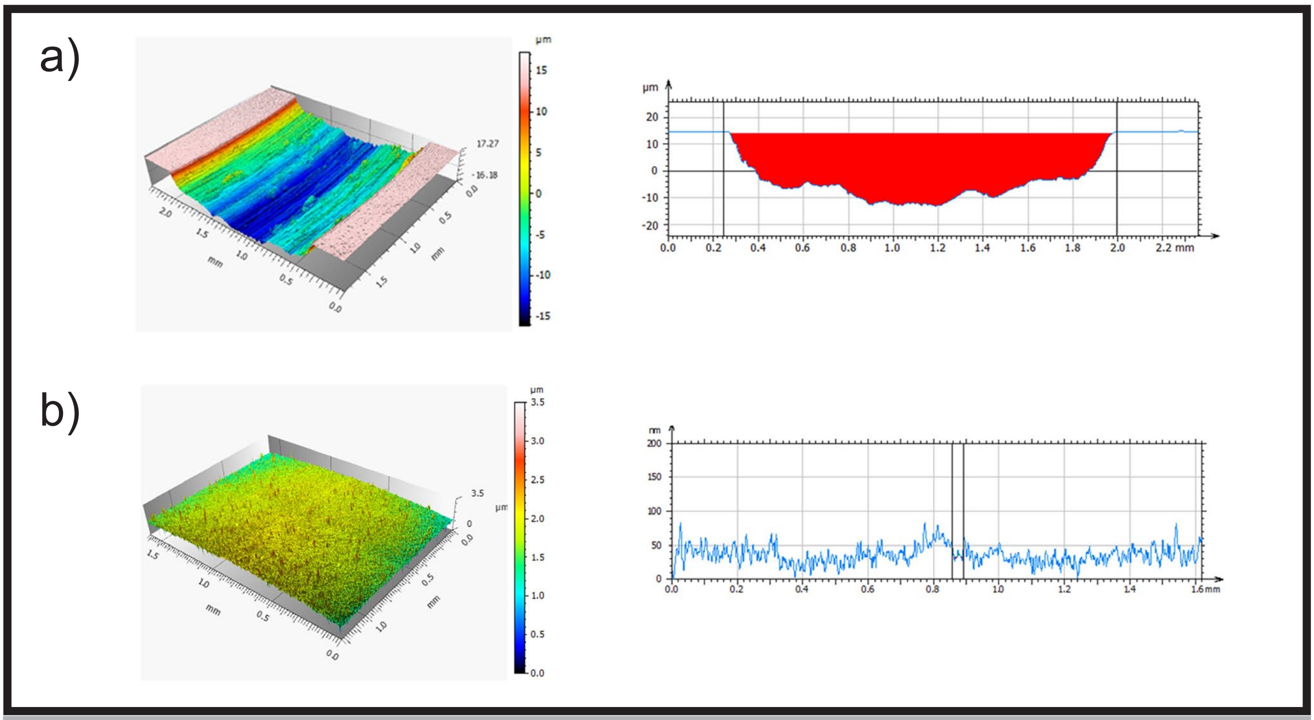

FIG. 7. The axonometric image of the trace of wear and the wear profile in a cross-section during friction in the Ringer's solution environment: a) Ti13Nb13Zr, b) Ti13Nb13Zr DLC.

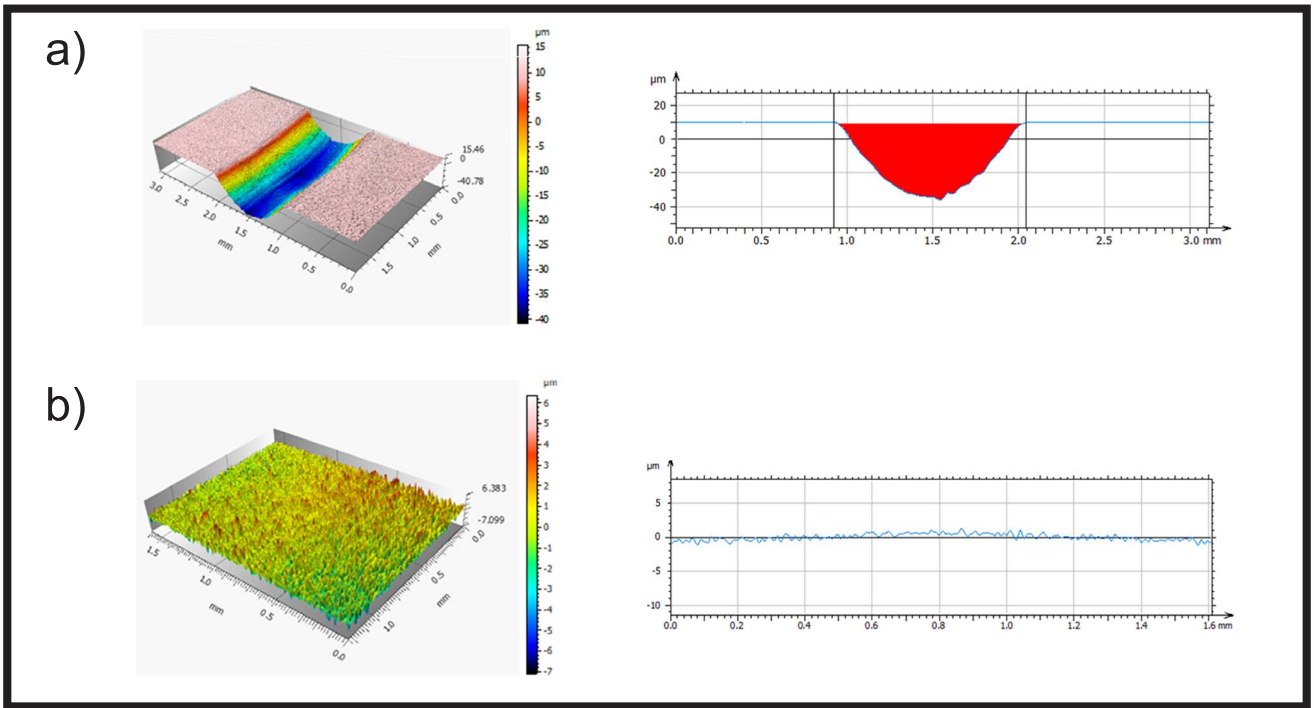

FIG. 8. The axonometric image of the trace of wear and the wear profile in a cross-section during friction in an artificial saliva environment: a) Ti13Nb13Zr, b) Ti13Nb13Zr DLC.

TABLE 7. Average wear area on the cross-section.

	Ti13Nb13Zr	Ti13Nb13Zr DLC
Technical dry friction	17 000 000 μm^2	0.54 μm^2
Ringer solution	34 000 000 μm^2	0.08 μm^2
Artificial saliva	31 000 000 μm^2	0.05 μm^2

The analysis of the surface geometric structure examinations after the tribological tests showed that the Ti13Nb13Zr titanium alloy had lower wear resistance compared to the DLC coating. It was observed that the use of lubricants in the case of the Ti13Nb13Zr resulted in an almost twofold increase in wear. Most likely, the reason for the increased wear of the titanium alloy was the presence of chloride ions (Cl^-) contained in the lubricants, both the Ringer's solution and the artificial saliva. In the case of the DLC coating, there was a reduction in wear after the application of the lubricants, which was probably associated with the passive nature of the coating. The analysis of axonometric images of the reference sample indicated the presence of numerous free wear products on the tested surfaces, which intensified the wear processes.

Conclusions

The tested DLC coating deposited on the Ti13Nb13Zr titanium alloy, using the PACVD technique, was 1.77 µm thick. The examination of the surface geometric structure showed that the amplitude indices did not change significantly as a result of the coating deposition. The scratch test revealed that the deposited layer was characterized by the high adhesion. The tribological tests proved that the DLC coating was characterized by the low resistance to motion and that the use of lubricants reduced this index almost twofold. The highest friction coefficient was obtained during the technically dry friction of the Ti13Nb13Zr - Al_2O_3 friction pair. It was eight times higher than the values recorded for the coating. The results of the friction-wear tests indicated that the Ti13Nb13Zr titanium alloy was characterized by the lower resistance to wear by friction than the DLC coating, and the lubricants application increased its wear almost twofold.

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