Acta of Bioengineering and Biomechanics
Vol. 19, No. 4, 2017

Original paper
DOI: 10.5277/ABB-00892-2017-03

Properties of Ti-6Al-7Nb titanium alloy nitrocarburized under glow discharge conditions

ANITA KAJZER[1]*, OLA GRZESZCZUK[1], WOJCIECH KAJZER[1], KATARZYNA NOWIŃSKA[2], MARCIN KACZMAREK[1], MICHAŁ TARNOWSKI[3], TADEUSZ WIERZCHOŃ[3]

[1] Faculty of Biomedical Engineering, Silesian University of Technology, Zabrze, Poland.
[2] Faculty of Mining and Geology, Silesian University of Technology, Gliwice, Poland.
[3] Warsaw University of Technology, Faculty of Materials Science and Engineering, Warsaw, Poland.

Purpose: The paper presents the results of physicochemical and mechanical properties of the Ti-6Al-7Nb alloy with surface modified by formation of a diffusive nitrocarburized layer deposited in a low-temperature plasma process. The main aim of the study was to evaluate the influence of steam sterilization and exposure to Ringer's solution on the utility properties of the alloy. *Methods:* Based on the study of the microstructure, roughness, wettability, resistance to pitting corrosion, ion infiltration and mechanical properties, the usefulness of the proposed method of surface treatment for clinical application was proven. *Results:* Deposition of the nitrocarburized layer increased the surface roughness and surface hardness, but also reduced the contact angle, and corrosion resistance with respect to the polished surfaces. The nitrocarburized layer is a barrier against the infiltration of ions to the solution and sterilization and exposure to Ringer solution have greater effect on the physicochemical properties rather than on the mechanical ones. *Conclusion:* It was found that sterilization, and exposure to Ringer's solution greatly affect the change of physicochemical properties rather than mechanical properties for both nitrocarburized layers and the Ti-6Al-7Nb alloy of mechanically polished surface.

Key words: *Ti-6Al-7Nb alloy, diffusive nitrocarburized layer, electrochemical properties, mechanical properties*

1. Introduction

Ti6Al4V alloy of a two-phase $\alpha + \beta$ structure is used extensively in medicine [3]. Its properties should be adapted to the properties of bone and other biomechanical conditions [16]. However, on the basis of clinical observations disadvantageous interaction of Al and V with a human body was found. Vanadium causes cytotoxic reactions and, consequently, neurogenic disorders while aluminum affects the softening of bones, damages nerve cells and may cause diseases of brain and blood vessels [15]. Hence, Semlitsch et al. [20] studied in detail Ti6Al(3,5-9,5)Nb(1-6)Ta titanium alloys, in which vanadium was eliminated, and replaced with niobium and tantalum. They gained a better corrosion resistance and mechanical properties compared to the Ti6Al4V alloy. Similar research was also conducted by authors of papers [3], [10], [13], [17], [18], who also found a negative influence of these elements and the need to replace them with elements of greater biocompatibility.

Ti-6Al-7Nb alloy does not contain vanadium which was replaced by niobium. This element and its oxides, including Nb_2O_3, belong to the group of compounds inert to a body. Furthermore, due to the greater reactivity, compounds of Nb with O_2 are formed more easily than compounds of Al with O_2. Nb oxides, during the passivation process, form a compact structure of the surface layer that is more resistant to corrosion in the environment of tissues and body fluids, thus reducing the number of post-implantation complications. This issue is associated with greater resistance of these alloys to pitting corrosion [15], [24]. Despite the good corrosion resistance of Ti-6Al-7Nb alloy, it does not have good resistance to abrasive wear, which

* Corresponding author: Anita Kajzer, Silesian University of Technology, Faculty of Biomedical Engineering, ul. Generała Charlesa de Gaulle'a 72, 41-800 Zabrze, Poland. Phone: 48(32)277-74-22, E-mail: Anita.Kajzer@polsl.pl
Received: April 20th, 2017
Accepted for publication: July 12th, 2017

can be enhanced by plastic treatment, but mostly due to different methods of surface engineering, such as electrochemical oxidation, sol-gel method, CVD processes, gas and glow discharge nitriding or innovative processes and oxynitriding and carbonitration in low-temperature plasma [1], [2], [4], [5], [9], [12], [14], [21], [23], [25], [26]. Therefore, the main aim of this work was to compare the mechanical and physicochemical properties of the Ti-6Al-7Nb alloy with nitrocarburized layer in the initial state, after sterilization, and exposure to Ringer's solution, respectively.

2. Materials and methods

Studies were carried out on the Ti-6Al-7Nb alloy (Protasul R100). The samples were in the form of discs 14 mm in diameter and 3 mm thick. This alloy was characterized by properties consistent with the recommendation of ISO 5832-11 standard. In order to obtain a roughness of *Ra* < 0.1 μm, the surface was polished using an abrasive paper of 320 and 1200 grit, and then mechanically polished using a silica suspension. Next, the diffusion surface layer of Ti(CN) + Ti_2N + αTi(N) was deposited in the nitrocarburizing process in a low-temperature plasma. A hybrid process combining glow discharge nitriding at 750 °C under the reactive atmosphere consisting of N_2 + 5% H_2 at the pressure of 180 Pa for 4 hours with the process of carburization in the low-temperature plasma carried out in the same technological cycle by changing the gaseous atmosphere. In the case of glow discharge nitrocarburization the mixture of N_2 + CH_4 (10 vol. %) was used at the pressure of 120 Pa for 1 h. In this way, as demonstrated by our earlier study [6], in a first step, the TiN + Ti_2N + αTi(N) layer is formed, wherein the outer layer zone, titanium nitride (TiN), is non-stoichiometric as it contains approx. 32% of nitrogen, with a developed surface with defects in the crystal structure, which allows, during changing the reactive atmosphere (second process step), the diffusion of carbon in the amount up to 16–18% (atomic). In this manner, the outer zone of titanium carbonitride – Ti(C, N) was obtained.

The microstructure of the deposited layers was tested using an light microscopy (Nikon microscope LV150N). The samples were cut on the IsoMet 1000 saw (Beuhler), then included in the resin with (OPAL 410, ATA). Grinding was performed using sandpaper of 240–2000 grit with the use of automatic grinding and polishing machine Saphir 530 (ATA). Polishing was carried out using a suspension of SiO_2 with a grain size of 0.2 μm. Next, the samples were etched with the following solution: H_2O + 2 ml HNO_3 + 2 ml HF. The chemical composition (distribution of Ti, C, N, Al from the surface) of the deposited layer was carried out by the WDS method using the CAMEC SU-30 microprobe.

The layers deposited in the glow discharge nitrocarburization process as well as the polished Ti-6Al-7Nb alloy in the initial state were subjected to steam sterilization using the HMT-260F autoclave (HMC EUROPE), with steam at 135 °C at the pressure of 2 atm as the sterilizing agent, for 60 min. To simulate the tissue environment the samples were exposed to the Ringer's solution for 28 days at 37 ± 1 °C in the incubator (Binder).

The samples were subsequently divided into six groups which were designated according to the following scheme:

- Ti67_p – mechanically polished titanium alloy,
- Ti67_p_s – mechanically polished titanium alloy after sterilization,
- Ti67_p_s_e – mechanically polished titanium alloy after sterilization and exposition to Ringer's solution,
- Ti67(C,N) – mechanically polished titanium alloy with Ti(CN) + Ti_2N + αTi(N) layer deposited at the 750 °C,
- Ti67(C,N)_s – mechanically polished titanium alloy with Ti(CN) + Ti_2N + αTi(N) layer deposited at the 750 °C after sterilization,
- Ti67(C,N)_s_e – mechanically polished titanium alloy with Ti(CN) + Ti_2N + αTi(N) layer deposited at the 750 °C after sterilization and exposition to Ringer's solution.

To evaluate the influence of sterilization and exposure to Ringer's solution on the mechanical and physicochemical properties of the Ti-6Al-7Nb alloy before and after the proposed surface modification, electrochemical, morphology, surface wettability and mechanical properties studies have been conducted.

In the first stage of the study the surface roughness was measured using the Surtronic S-100 profilometer (Taylor Hobson). Measurements of the *Ra* and the *Rz* parameters were made for the total measured length equal to *ln* = 4 mm in accordance with the recommendations of the PN-EN ISO 4287: 1999 / A1: 2010.

Surface wettability and surface energy (SEP) were evaluated using the Owens–Wendt method. The wetting angle measurements used two liquids: distilled water (θw) (by Poch S.A.) and diiodomethane (θd) (by Merck). A measurement with a drop of water and diiodomethane, placed on the outer layer of the material, was performed at the temperature T = 23 °C at the test stand incorporating a goniometer Surftens Universal by OEG and a computer with Surftens 4.5 software to analyze the recorded drop image. 5 drops of distilled water and diiodomethane were applied onto the surface of each sample, each with capacity of 1.5 µl. The measurement began 20 seconds after application of the drops. Duration of a single measurement was 60 seconds with the sampling rate of 1 Hz. Next, the determined values of contact angles θ and surface energy γ_s were presented as mean values with standard deviation.

Study of pitting corrosion resistance was performed according to the PN-EN ISO 10993-15 in Ringer solution of the following composition: NaCl = 8.3 g/dm^3, KCl = 0.3 g/dm^3, $CaCl_2$ = 0.33 g/dm^3 at the temperature of $T = 37 \pm 1$ °C and pH = 7 ± 0.2.

The study was carried out by means of the potentiodynamic method using three electrodes: the reference electrode (saturated calomel electrode – SCE), the auxiliary electrode (platinum electrode), and the working electrode – the test sample. The study was realized with the use of the VoltaLab PGP 201 potentiostat. Corrosion tests started from recording the open circuit potential EOCP. Polarization curves were recorded from the initial potential $E_{\text{init}} = E_{\text{OCP}} - 100$ mV. The applied scan rate was equal to 1 mV/s. Once the anode current density had reached the value of 1 mA/cm^2, the direction of polarization was changed. On the basis of the obtained curves the following corrosion parameters were determined: corrosion potential E_{corr} (mV), transpassivation potential E_{tr} (mV) and, using the Stern method, polarization resistance R_p (kΩcm^2).

Measurements of metal ions (Ti, Al, Nb) concentration present in the Ringer's solution resulting from its effect upon the sample surface during 28 days, were made with the use of JY2000 spectrometer and atomic emission method with inductively coupled plasma, ICP-AES (Inductively Coupled Plasma – Atomic Emission Spectrometry). The induction source was a plasma burner linked to 40.68 MHz frequency generator. To draw the reference curve, diluted reference materials by Merck were used.

The abrasive wear tests using the "3 rollers – cone" method were carried out in accordance with the PN-83/H-04302 standard. As the counter-sample the cone (120°) made of heat-treated (quenching and tempering) C45 steel was used. As the test specimens three ∅ 8 × 21 mm rollers were used. The linear velocity in contact with the sample was equal to 0.56 m/s, and the loading was equal to 200 MPa. The depth of wear (linear wear) formed on a cylindrical sample is calculated from the formula (1):

$$h = 0{,}5(D - \sqrt{D^2 - a^2}) \tag{1}$$

where: h – the depth of wear (linear wear), D – nominal diameter of the counter-sample, a – the length of the major axis of wear trace [mm].

Scratch tests of the nitrocarburized layers on the Ti-6Al-7Nb alloy substrate were performed with the use of the open platform equipped with the Micro--Combi-Tester (CSM) in accordance with the PN-EN ISO 20502 standard. The study consisted in making the scratch with the use of the penetrator – Rockwell diamond cone – with a gradual increase of the normal force. For the evaluation of scratch resistance a record of the friction force Ft and the penetration depth Pd were used. The tests were performed with the increasing loading force Fc from 0.03 N to 30 N and at the following parameters: loading rate vs = 10 N/min, the speed of the table vt = 1 mm/min, the length of the scratch l = 3 mm. For each sample three measurements were carried out.

In the last stage, hardness and Young's modulus measurements of the deposited layers were conducted with the use of the open platform equipped with a Micro-Combi-Tester (CSM Instruments) using a Vickers indenter. The Oliver & Phar method was applied. The aim of the study was to determine the instrumental hardness versus distance from the surface. Loading and unloading rate was equal to 3000 nm/min, a hold time of the sample at maximum load equal to 5 s. The value of the indenter load was resulting. Microhardness measurements were carried out for the nitrocarburized samples at the following depths of the penetrator: 0.5 µm, 1 µm, 2 µm, 4 µm, 6 µm, 8 µm, 1 µm, 12 µm, 14 µm and 16 µm. Additionally, four hardness measurements at depths of 0.5 µm, 1 µm, 2 µm, 4 µm for samples without the layer at the loading from 25 mN to 1.25 N were carried out.

3. Results

Figure 1 shows the microstructure of the Ti-6Al-7Nb alloy after the hybrid glow discharge nitrocarburizing and the distribution of Ti, N, Al and C in the layer.

The nitrocarburized Ti(CN) + Ti_2N + αTi(N) layer was characterized by a uniform thickness of the zone compounds Ti(CN) + Ti_2N of c.a. 15 µm across the cross-section of the sample. The thickness of the diffusion zone, as the result of nitrogen diffusion into the Ti-6Al-7Nb alloy, was approx. 40 µm.

Based on the analysis of the parameters derived during the evaluation of surface roughness it was

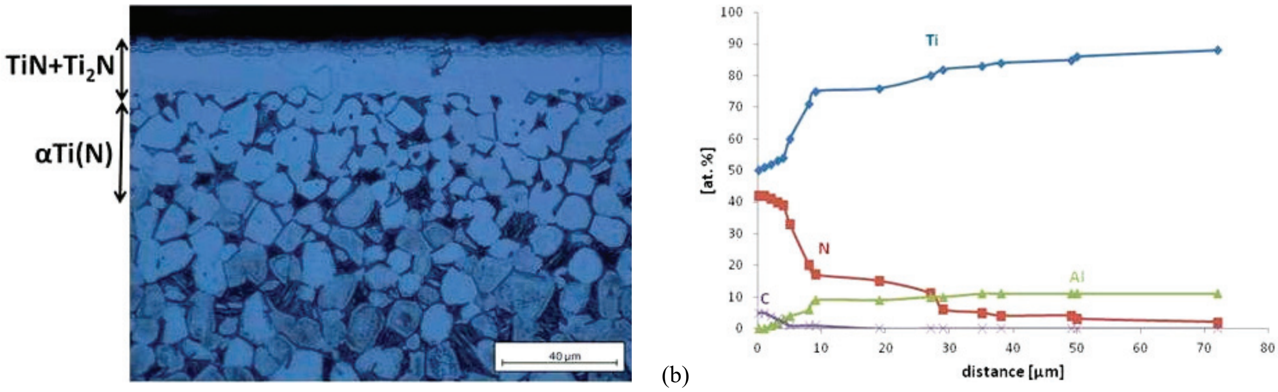

Fig. 1. Microstructure (a) and distribution of elements from the face of the sample (b) after the glow discharge nitrocarburizing in the low-temperature plasma

found that for samples without the layer the *Ra* parameter, for all analyzed samples, was equal to 0.05 µm. For the nitrocarburized layer, the increase in *Ra* and *Rz* in relation to the samples in the initial state was observed (Fig. 2). The results of the contact angle test and sample drops applied on the surface of the samples subjected to mechanical polishing and samples with the nitrocarburized layer are shown in Figs. 3 and 4.

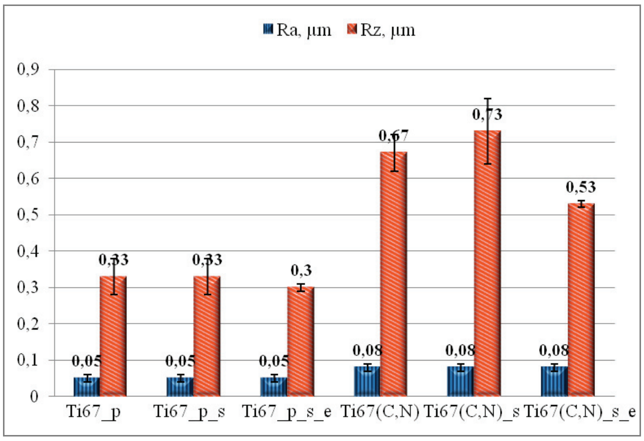

Fig. 2. Results of surface roughness measurement, parameters

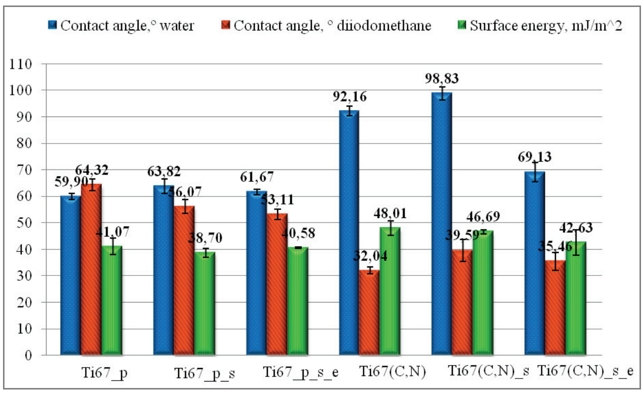

Fig. 3. The surface energy calculated based on the contact angle measurements – OW method

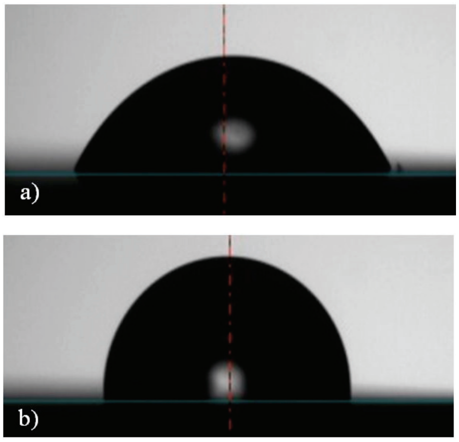

Fig. 4. Measurement of wetting angle, for the group: a) Ti67_p (θ_{av} = 59.90°), b) Ti67 (C, N) (θ_{av} = 92.16°)

It was found that for all the samples before the glow discharge nitrocarburizing (sample: Ti67_p, Ti67_p_s and Ti67_p_s_e) no difference in the values of contact angle and surface energy was observed (ie., Ti67_p_s_e). But for the samples with the Ti(C, N) + Ti_2N + αTi(N) layer (sample: Ti67 (C, N) and Ti67 (C, N)_s_e of larger surface roughness) decreased wettability of the surface was observed. Respectively, the average value of the contact angle was equal to θ_{av} was 92.16° and 98.83°.

Based on the recorded corrosion parameters, for all the analyzed groups (Fig. 5) a decrease of corrosion resistance of the alloy Ti-6Al-7Nb with the nitrocarburized layer was observed (Table 1), what was mainly caused by development of the surface after the nitrocarburizing (Fig. 5).

The Ti-6Al-7Nb alloy with the polished surface is resistant to pitting corrosion in the entire measuring range. On the other hand, sterilization (Ti67 (C, N)_s)
and exposure to Ringer's solution (Ti67_p_s_e, Ti67 (C, N)_s_e) has increased the value of the corrosion

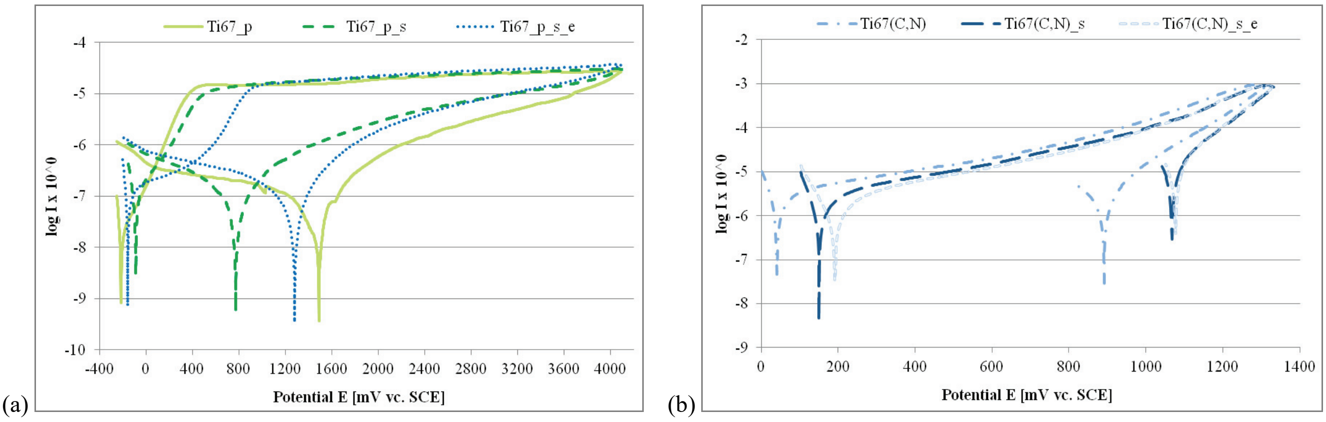

Fig. 5. Examples of polarization curves for: (a) Ti67_p, Ti67_p_s, Ti67_p_s_e, (b) Ti67(C, N), Ti67(C, N)_s, Ti67(C, N)_s_e

potential E_{corr} while reducing the polarization resistance R_p. Deposition of the nitrocarburized layer caused an increase of the corrosion potential but concurrent reduction of the polarization resistance R_p. In this case an occurrence of transpassivation potential was observed.

Table 1. Results of potentiodynamic tests – mean values

No. of group	E_{corr}, mV	R_p, kΩcm^2	E_{tr}, mV
	Ti-6Al-7Nb mechanically polished		
Ti67_p	–213 ± 7	1230 ± 155	–
Ti67_p_s	–83 ± 32	293 ± 51	–
Ti67_p_s_e	–154 ± 52	222 ± 55	–
	Ti-6Al-7Nb with the layer		
Ti67(C,N)	+53 ± 5	13 ± 2	+1061 ± 6
Ti67(C,N)_s	+155 ± 11	15 ± 5	+1183 ± 3
Ti67(C,N)_s_e	+196 ± 13	22 ± 1	+1124 ± 2

Table 2. Results of metal ions infiltration

Metal ions infiltration tests, $\frac{\mu g}{cm^2}$ (mean value)			
Group	Ti	Al	Nb
Ti67_p	97.8 ± 0.01	85.8 ± 0.02	65.9 ± 0.01
Ti67_p_s	88.5 ± 0.01	72.3 ± 0.01	64.6 ± 0.02
Ti67(C, N)	65.1 ± 0.02	64.5 ± 0.01	58.6 ± 0.01
Ti67(C, N)_s	57.9 ± 0.01	56.8 ± 0.03	58.4 ± 0.05

Despite the reduced corrosion resistance in relation to the polished alloy, the deposited nitrocarburized layer beneficially reduces the concentration of ions of metal elements infiltrating to Ringer's solution (Table 2). Ions infiltration studies allowed to determine the presence of ions of the main alloying elements – Ti, Al, Nb. The greatest concentration of elements which penetrated to the solution was observed for Ti ions (97.8 μg/cm^2) for the samples from the Ti67_p group, while the smalles Ti (57.9 μg/cm^2) was recorded for the samples from the Ti67 (C, N)_s group, i.e., the surface coated with the nitrocarburized layer subjected to sterilization process. The sterilization combined with the exposure to Ringer's solution for 28 days caused the reduction of concentration of metal ions infiltrating to the solution as compared to other variants.

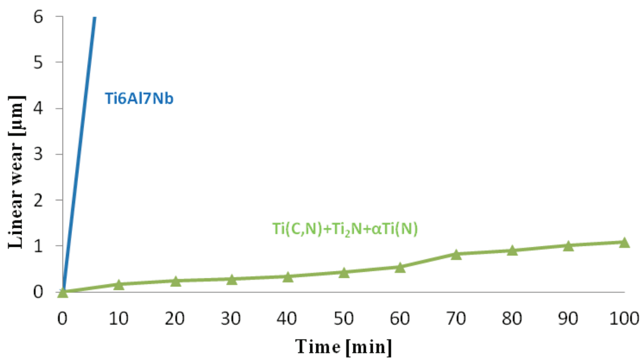

Fig. 6. Resistance to abrasive wear of the Ti-6Al-7Nb alloy in the initial state and after the glow discharged nitrocarburizing

The results of resistance to abrasive wear using the "3 rollers + cone" method are shown in Fig. 6. The process of nitrocarburizing significantly improved resistance to abrasive wear of the Ti-6Al-7Nb alloy. The Ti-6Al-7Nb alloy in the initial state has been damaged after the first stage of the test (10 min), whereas in the case of the alloy with the deposited Ti(CN) + Ti_2N + αTi(N) layer formed Ti (CN) + Ti_2N + αTi (N), the linear wear was only approx. 1.2 μm after 100 minutes.

The results of the scratch resistance of the nitrocarburized layer, including the sterilization, and the exposure to Ringer's solution, are presented in Fig. 7. The highest scratch resistance was recorded for the nitrocarburized layer after the exposure to Ringer's solution (Ti67 (C, N) _p_s_e) for which, the value of friction force was the lowest *Ft* – Fig. 7. While the sterilization process ((Ti67 (C,N)_s) caused the decrease in the scratch resistance, compared to the initial state (Ti67 (C, N)). For this case, the friction force *Ft* reached the highest value – Fig. 7.

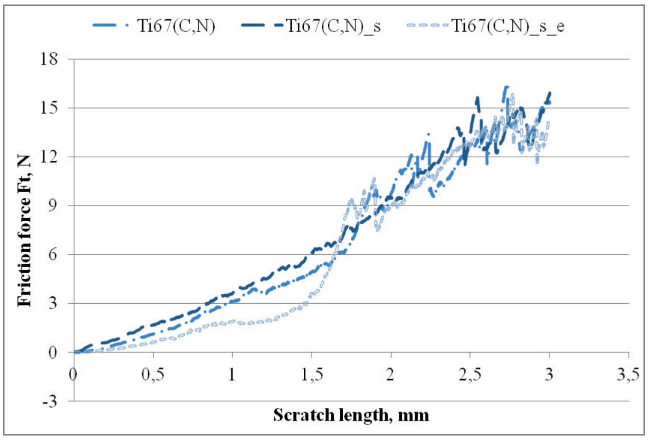

Fig. 7. Example relation of the friction force as a function of the scratch length

The results of micro-hardness also confirmed the beneficial influence of the deposited layer on the mechanical properties of the surface. The results for all the analyzed samples are shown in Tables 3 and 4 and in Fig. 8.

Based on the performed measurements a slight difference in the values of hardness and Young's modulus, depending on the method of surface preparation, was observed. It was found that sterilization (Ti67_p_s) and exposure to Ringer's solution (Ti67_p_s_e) resulted in a slight decrease in hardness compared to the initial state (Ti67_p). Deposition of the nitrocarburized layer increased the hardness, compared to the Ti-6Al-7Nb substrate (Table 4). The highest hardness was measured for the samples exposed to Ringer's solution (Ti67 (C, N)_p_s_e) (Table 4, Fig. 8). On the other hand, the sterilization process (Ti67 (C, N)_s) caused a slight decrease in hardness of the nitrocarburized layer compared to the initial state (Ti67 (C, N)).

Table 3. Hardness of Ti-6Al-7Nb surface

	Number of measurment			
	1	2	3	4
	0.5 μm	1 μm	2 μm	4 μm
	Ti67_p			
Nanohardness H_{IT}, MPa	4178 ± 169	4505 ± 142	4296 ± 196	3973 ± 158
Young's modulus *E*, GPa	124 ± 18	136 ± 17	143 ± 20	127 ± 19
	Ti67_p_s			
Nanohardness H_{IT}, MPa	3579 ± 132	4094 ± 187	3954 ± 201	3921 ± 140
Young's modulus *E*, GPa	127 ± 20	137 ± 15	140 ± 21	130 ± 18
	Ti67_p_s_e			
Nanohardness H_{IT}, MPa	3042 ± 155	4046 ± 173	4026 ± 210	4275 ± 191
Young's modulus E, GPa	128 ± 16	142 ± 17	149 ± 16	133 ± 14

Table 4. Hardness and Young's modulus of the nitrocarburized layers on Ti-6Al-7Nb

	Number of measurement									
	1	2	3	4	5	6	7	8	9	10
	0.5 μm	1 μm	2 μm	4 μm	6 μm	8 μm	10 μm	12 μm	14 μm	16 μm
	Ti67(C, N)									
Nanohardness H_{IT}, MPa	6549 ± 214	6687 ± 193	6448 ± 199	5384 ± 176	5015 ± 185	4700 ± 169	4525 ± 154	4420 ± 149	4200 ± 183	4207 ± 205
Young's modulus *E*, GPa	152 ± 16	160 ± 18	135 ± 15	130 ± 20	121 ± 21	117 ± 19	114 ± 22	112 ± 17	110 ±18	107 ± 16
	Ti67(C, N)_s									
Nanohardness H_{IT}, MPa	6466 ± 208	6339 ± 191	6259 ± 178	5375 ± 206	4650 ± 170	4626 ± 185	4619 ± 172	4490 ± 188	4227 ± 176	4271 ± 206
Young's Modulus *E*, GPa	155 ± 17	139 ± 16	141 ± 19	125 ± 21	115 ± 18	118 ± 20	113 ± 17	111 ± 18	104 ± 21	103 ± 19
	Ti67(C, N)_p_s_e									
Nanohardness H_{IT}, MPa	6272 ± 169	6511 ± 175	6494 ± 172	6004 ± 198	5218 ± 206	5231 ± 192	4802 ± 196	4727 ± 173	4749 ± 181	4518 ± 176
Young's Modulus *E*, GPa	138 ± 19	146 ± 22	150 ± 20	135 ± 17	121 ± 18	118 ± 20	113 ± 19	108 ± 21	106 ± 17	100 ± 18

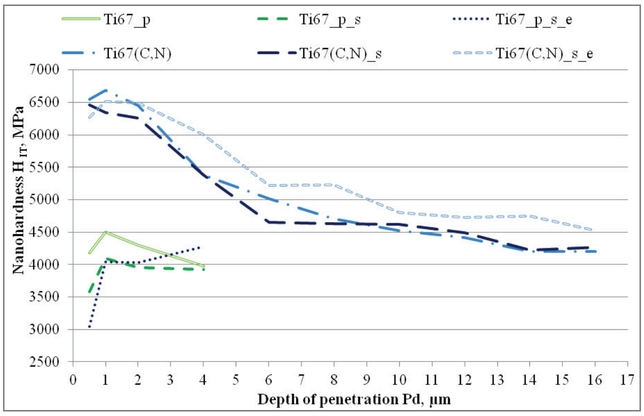

Fig. 8. Hardness as a function of the penetration depth

4. Discussion

Based on the results obtained it may be stated that the sterilization and exposure to Ringer solution have a greater effect on the physicochemical properties rather than on the mechanical ones.

It has been observed that surface development has a significant influence on wettability, i.e., for the larger values of the *Ra* parameter the wettability of the surface is smaller. The process of the glow discharge nitrocarburizing influenced the hydrophobicity of the surface. In contrast, the exposure to Ringer's solution caused that the wettability was similar to the polished surfaces.

Whereas decrease of corrosion resistance of the alloy Ti-6Al-7Nb with the nitrocarburized layer was mainly caused by development of the surface after the nitrocarburizing (Fig. 2), it is also connected with the change in surface energy (Fig. 3), especially after the sterilization, during which on the surface of the Ti(C, N) + Ti2N + αTi(N) layer, a nanometer-thick layer of titanium oxides may be formed [6], as observed during the sterilization of the polished Ti-6Al-7Nb alloy [3], [22]. Deposition of the nitrocarburized layer caused the favorable increase of the corrosion potential but concurrent reduction of the polarization resistance R_p. For these surfaces the occurrence of transpassivation potential was also observed, indicating the reduction of corrosion resistance in relation to the polished Ti-6Al-7Nb alloy. Simultaneously, for the sterilized and exposed to Ringer's solution samples, a slight increase in the E_{tr} was recorded. The influence of the deposited layer on electrochemical properties was also observed by authors of [11], who found a positive increase of the corrosion potential E_{corr} for the Ti-6Al-7Nb alloy with the diffusion nitrided layer compared to the biomaterial substrate.

On the other hand, assuming the amount of degradation products infiltrating into the body as an important criterion for demonstrating the biocompatibility of the studied material, it must be concluded that the deposited nitrocarburized layer affects the barrier properties. The greatest concentration of elements which penetrated to the solution was observed for Ti. This is, most likely, caused by the presence of stoichiometric interlayer of titanium nitride Ti2N underneath the carbonitride Ti(C, N) layer [9].

The obtained results of the scratch resistance of the nitrocarburized layer, including the sterilization, and the exposure to Ringer's solution indicated slight differences in the friction force Ft depending on the surface preparation. Similar research conducted by Farokhzadeh K. et al. [8] who produced nitrided layer on the Ti-6Al-4V alloy. They also found the reduction of friction force when using the nitrided samples, compared to the samples in the initial state. The values of hardness obtained in the present work are higher in comparison to studies conducted by Fare [7]. In turn, the nitrided layer obtained by Rahman [19] on the Ti-6Al-4V substrate was characterized by significantly higher values of hardness.

5. Conclusions

Based on the obtained results the following can be stated:

– deposition of the nitrocarburized layer increased the surface roughness and surface hardness but also reduced the contact angle, and corrosion resistance with respect to the polished surfaces,
– the nitrocarburized layer is a barrier against the infiltration of ions to the solution, as a consequence of the presence of the transition zone – stoichiometric Ti_2N between the outer layer of titanium carbonitride (Ti (CN)) with a developed topography and the αTi(N) diffusion zone [6], [27],
– deposition of the Ti(CN) + Ti_2N + αTi(N) layer on the Ti-6Al-7Nb alloy significantly increases its resistance to abrasive wear,
– sterilization and exposure to Ringer solution have a greater effect on the physicochemical properties rather than on the mechanical ones.

Summarizing, instead of increase in pitting corrosion resistance, it can be concluded that the proposed method of surface modification contributed to the improvement of utility properties. This involves the possibility of a wider use of Ti-6Al-7Nb alloy for implants in bone surgery.

References

[1] BASIAGA M., KAJZER W., WALKE W., KAJZER A., KACZMAREK M., *Evaluation of physicochemical properties of surface modified Ti6Al4V and Ti6Al7Nb alloys used for orthopeadic implants*, Mat. Sci. Eng. C-Mater., 2016, 68, 851–860.

[2] BASIAGA M., WALKE W., PASZENDA Z., KAJZER A., *The effect of EO and steam sterilization on mechanical and electrochemical properties of titanium grade 4*, Mater. Technol., 2016, 50(1), 153–158.

[3] BRUNETTE D.M., TENGVALL P., TEXTOR M., THOMSEN P., *Titanium in Medicine*, Springer-Verlag, Berlin, Heidelberg, 2001.

[4] CHRZANOWSKI W., *Corrosion behavior of Ti-6Al-7Nb alloy after different surface treatments*, JAMME, 2006, 18, 67–70.

[5] CZARNOWSKA E., MORGIEL J., OSSOWSKI M., MAJOR R., WIERZCHOŃ T., *Microstructure and biocompatibility of titanium oxide produced on nitrided surface layer under glow discharge conditions*, J. Nanosci. Nanotechnol., 2011, 11(10), 8917–8923.

[6] CZARNOWSKA E., WIERZCHOŃ T., MARANDA A., KACZMAREWICZ E., *Improvement of titanium alloy for biomedical applications by nitriding and carbonitriding process under glow discharge conditions*, J. Mater. Sci.: Med. Mat., 2000, 11(2), 73–81.

[7] FARÈ S., LECIS N., VEDANI M., SILIPIGNI A., FAVOINO P., *Properties of nitrided layers formed during plasma nitriding of commercially pure Ti and Ti-6Vl-4V alloy*, Surf. Coat. Tech., 2012, 206, 2287–2292.

[8] FAROKHZADEH K., EDRISY A., PIGOTT G., LIDSTER P., *Scratch resistance analysis of plasma-nitrided Ti-6Al-4V alloy*, Wear, 2013, 302, 845–853.

[9] FLESZAR A., WIERZCHOŃ T., SUN K.K., SOBIECKI J.R., *Properties of surface layers produced on the Ti6Al2Cr2Mo titanium alloy inder glow discharge conditions*, Surf. Coat. Tech., 2001, 31, 73–81.

[10] GEETHA M., SING A.K., ASOKAMANI R., GOGIA A.K., *Ti based biomaterials, the ultimate choice for othopaedic implants – a review*, Prog. Mater. Sci., 2009, 54, 397–425.

[11] GOKUL LAKSHMI S., RAMAN V., RAJENDRAN N., BABI M.A.K., ARIVUOLI D., *In vitro behavior of plasma nitrided Ti-6Al-7Nb orthopaedic alloy in Hanks solution*, Sci. Technol. Adv. Mat., 2003, 4, 415–418.

[12] KIEL M., SZEWCZENKO J., BASIAGA M., NOWIŃSKA K., *Technological capabilities of surface layers formation on implants made of Ti-6Al-4V alloy*, Acta Bioeng. Biomech., 2015, 17(1), 31–37.

[13] LUKINA E., LAKA A., KOLLEROV M., SAMPIEV M., MASON P., WAGSTAFF P., NOORDEEN H., YOON W.W., BLUNN G., *Metal concectrations in the blood and tissues after implantation of titanium growth guidance sliding instrumentation*, Spine J., 2016, 16(3), 380–388.

[14] MARCINIAK J., SZEWCZENKO J., KAJZER W., *Surface modification of implants for bone surgery*, Arch. Metal. Mater., 2015, 60(3B), 2123–2129.

[15] MARCINIAK J., *Biomateriały*, Wydawnictwo Politechniki Śląskiej, Gliwice, 2013, (in Polish).

[16] MARCINIAK J., CHRZANOWSKI W., KAJZER A., *Gwoździowanie śródszpikowe w osteosyntezie*, Wydawnictwo Politechniki Śląskiej, Giwice, 2008, (in Polish).

[17] OKAZAKI Y., GOTOH E., *Comparison of metal release from various metallic biomaterials in vitro*, Biomaterials, 2005, 26, 11–20.

[18] OKAZAKI Y., ITO Y., *New Ti alloy without Al and V for medical implants*, Adv. Eng. Mater., 2000, 2(5), 278–281.

[19] RAHMAN M., REID I., DUGGAN P., DOWLING D.P., HUGHES G., HASHMI M.S.J., *Structural and tribological properties of the plasma nitrided Ti-alloy biomaterials: Influence of the treatment temperature*, Surf. Coat. Tech., 2007, 201, 4865–4872.

[20] SEMLISCH M., STAUB F., WEBER H., *Develompent of vital highstrength Ti-Al-Nb alloy for surgical implants*, [in:] P. Christer, A. Meunier, A.J.C. Lee (eds.), *Perfomance of Biomaterials*, Elsevier Science Publishers, Amsterdam, 1986, 69–74.

[21] THAIR L., KAMACHI MUDALI U., BHUVANESWARAN N., NAIR K.G.M., ASOKAMANI R., RAJ B., *Nitrogen ion implantation and in vitro behavior of as-cast Ti-6Al-7Nb alloy*, Corros. Sci., 2002, 44(11), 2439–2457.

[22] THIERRY B., TABRIZIAN M., SAVADOGO O., YAHIA L., *Effects of sterilization processes on NiTi alloy, surface characterization*, J. Biomed. Mater. Res., 2000, 49(1), 88–98.

[23] WALKE W., BASIAGA M., PASZENDA Z., MARCINIAK J., *Physicochemical properties of Ti67 alloy after EO and stem sterilization*, Mater. Technol., 2016, 50(3), 323–329.

[24] WALKE W., PASZENDA Z., KARASIŃSKI P., MARCINIAK J., BASIAGA M., *Investigations of mechanical properties of SiO_2/TiO_2 coatings deposited by sol-gel method on cpTi and Ti-6Al-7Nb*, Proceedings of the Institution of Mechanical Engineers, Part L: Journal of Materials: Design and Applications, 2016, 230, 3, 799–804

[25] WIERZCHOŃ T., CZARNOWSKA E., GRZONKA J., SOWIŃSKA A., TARNOWSKI M., KAMIŃSKI J., BOROWSKI T., KURZYDŁOWSKI K.J., *Glow discharge assisted oxynitriding process of tinanium for medical application*, Appl. Surf. Sci., 2015, 334, 74–79.

[26] WIERZCHOŃ T., SOBIECKI J.R., KRUPA D., *The formation of Ti(OCN) layers produced from metal-organic compounds using plasma assisted chemical vapor deposition*, Surf. Coat. Tech., 1993, 59(1–3), 217–220.

[27] WIERZCHOŃ T., CZARNOWSKA E., MORGIEL J., SOWIŃSKA A., TARNOWSKI M., ROGUSKA A., *The importance of surface topography for the biological properties of nitrided diffusion layer produced on Ti6Al4V titanium alloy*, Arch. Metalland. Mater., 2015, 60, 2153–2159.