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THE PROPERTIES OF DIAMOND - LIKE CARBON (DLC) COATINGS ON TITANIUM ALLOYS FOR BIOMEDICAL APPLICATIONS

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The paper presents the results of DLC coating of produced by the method of physical vapor deposition (PVD) on the titanium alloy for biomedical applications. Surface morphology and elemental composition were determined with the use of Scanning electron microscopy (SEM)/ Energy dispersive spectroscopy (EDS). Hardness was determined by instrumental indentation. Tribological tests were carried out under technically dry friction and friction with lubrication of Ringer's solution. The DLC"s are characterized by high hardness (increased by an 4-fold) and anti-wear properties. In the case of technically dry friction and in the case of Ringer's solution, the coefficient of friction decreased by an 5-fold compared to the results obtained for substrate.

Keywords: diamond-like carbon coatings, titanium alloys, X ray research (SEM, EDS) friction, microstructure, wear

INTRODUCTION

Due to high mechanical strength, low weight and excellent corrosion resistance, titanium and its alloys are widely used in the aerospace, petrol, automotive, energy and biomedical industries. However, due to the relatively high price of titanium and its high reactivity with oxygen, there is a need to develop new production methods [1, 2].

In addition, metal implants implanted in the physiological fluids environment are exposed to corrosion and contribute to the transfer of metal ions and other products to the human organizm [3, 4]. It is known that the vanadium contained in the Ti6Al4V alloy may provoke strong cytotoxic reactions and accumulate in the liver and kidneys. In turn, aluminium softens bones and has negatively effects on nerve cells. Hence the increasing interest in vanadium-free alloys, e.g. Ti6Al7Nb [5, 6]. At the same time, coatings are becoming more and more popular all over the world [5].

Since their invention in 1971 by Aiseberg and Chabot, amorphous diamond-like carbon (DLC) coatings have become more and more popular [7]. This is due to their physical and chemical properties. DLC is an amorphous mixture of C atoms composed mainly of sp^3 bonds, but also sp1 and sp^2. The share of the sp3 phase and the ratio of the sp^2 bonds (typical for graphite) to the sp^3 bonds (typical for diamond) affect the performance of the DLC. Higher sp^3 content causes higher residual stress and lower adhesion of coatings to the substrate [7, 8, 9]. Most often, DLC is obtained in the processes of chemical and physical vapour deposition (CVD, PVD), additionally assisted with plasma (PACVD, PAPVD), magnetron sputtering, pulsed filtered arc discharge,ion beam deposition and laser deposition [7-10].

DLC coatings are characterized by very good mechanical and tribological properties. They are used to coat metal parts exposed to friction wear [8, 9, 10]. Due to their biocompatibility, DLC coatings are also useful in medical applications for coating orthopaedic, dental and vascular implants. This is due to their unique properties: chemical inertness and low surface energy, favouring the adhesion of osteoblasts [10]. They also show the ability to bind albumin molecules, creating a passive layer and reducing the adhesion of platelets to the surface. The coatings constitute an anti-wear layer and a barrier preventing the metal ions release.

MATERIALS AND EXPERIMENTAL METHODS

The study analyses the properties of Ti6Al4V and Ti6Al7Nb alloys with DLC coatings. The most important mechanical properties of the alloys are summarized in Table 1. Deposition of thin DLC coatings was performed using the chemical vapour deposition technique at a lower temperature thanks to the PACVD plasma-assisted process. The DLC coatings were obtained at a temperature of < 250 °C. A benchtop scanning electron microscope Phenom XL was used to evaluate the surface morphology and determine the chemical composition of the DLC coatings specimens.

Mechanical properties of the specimens were tested using a Anton-Paar UNHT3 Ultrananoindentation Tester. The hardness of the DLC coatings was determined based on load-unload curves using the Oliver-Pharr model. Nanoindentation hardness tests were carried out with a Berkovich tip.

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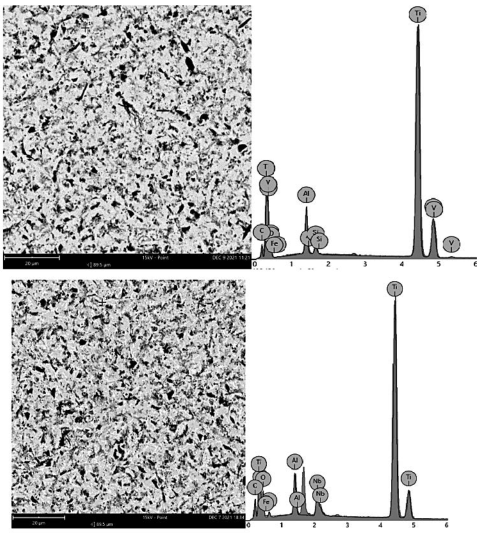
Table 1 **Mechanical properties of titanium alloys**

Material	Unit	Ti6Al4V	Ti6Al7Nb
Density	g/cm^3	4.5	4.5
Young's Modulus	GPa	110÷114	105
Tensile Strength	MPa	960÷970	1024
Yield strength	MPa	850÷900	921
Elongation at break	%	14	12

Friction tests were performed using a TRB tester in the ball-disk configuration - reciprocating motion of the disc. Friction coefficient and linear wear values were recorded for specimens made of Ti6Al4V and Ti6Al7Nb alloys coated with DLC. The surface roughness of titanium alloy implants plays an important role in the surgical implantation process. The increased surface of biomechanical contact at the implant-bone interface affects the rate of protein adsorption. Continuous researches on the modification of implant surfaces are aimed at improving osseointegration and enabling immediate or relatively early loading of the prosthesis [3, 4, 11, 12]. The texture and parameters of the surface geometry were determined using a confocal microscope with Leica DCM8 operated in interferometric mode.

RESULTS AND DISCUSSION

Figure 1 shows at 3000 x magnification the morphology and elementary chemical composition of the uncoated surfaces of Ti6Al4V (and) and Ti6Al7Nb titanium alloys (b) and in Figure 2 Ti6Al4V (a) and Ti6Al7Nb (b) titanium alloys coated with DLC.

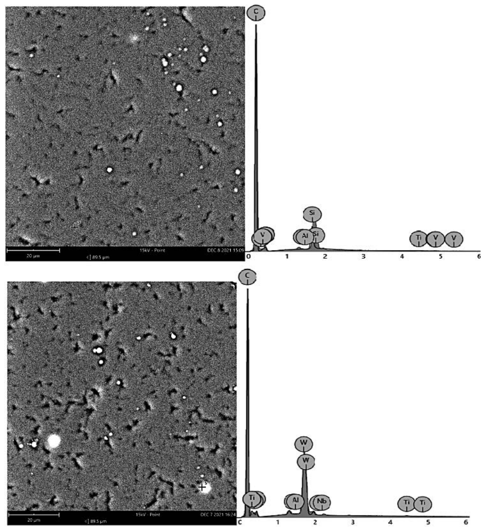


a)

b)

Figure 1 Surface morphology and characteristic X-ray spectrum of the: a) Ti6Al4V and b) Ti6Al7Nb titanium alloys.

The SEM observations proved that the specimens with the DLC coatings had a more uniform morphology than the uncoated ones. Elemental composition analysis of uncoated specimens confirmed that the materials used were titanium alloys. Tests of the specimens with



a)

b)

Figure 2 Surface morphology and characteristic X-ray spectrum of the: a) Ti6Al4V and b) Ti6Al7Nb titanium alloys coated with DLC.

the DLC coatings indicate the presence of carbon in the surface layer and tungsten in the intermediate layer, which are substrates in the process of DLC coatings deposition.

Figure 3 shows the average hardness values of 10 measurements taken.

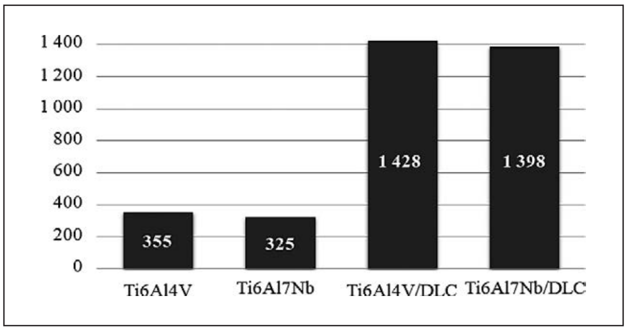


Figure 3 Hardness measurements / HV.

The high hardness of thin DLC layers translates into the durability and reliability of the elements on which they are deposited.

The tribological tests were carried out under the conditions of technically dry friction and lubrication with the Ringer's solution with the following parameters:

- ball material: Al_2O_3,
- disc material: Ti6Al4V and Ti6Al7Nb titanium alloys or Ti6Al4V and Ti6Al7Nb titanium alloys coated with DLC,
- load: P=5 N,
- amplitude A = 5mm,
- frequency T = 1Hz,
- linear speed 0,02 m/s
- 10 000
- relative humidity: 55 ± 5%,
- ambient temperature T_O = 296 ± 1 K.

The results of the tribological tests are presented graphically in Fig. 4 for technically dry frictrion and in Fig. 5 for lubricated Ringer's solution.

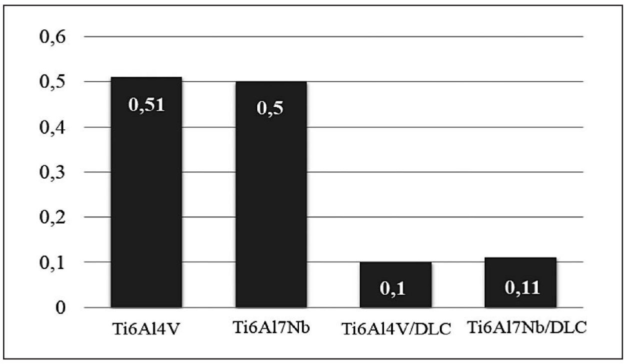


Figure 4 Tribological tests for technically dry friction.

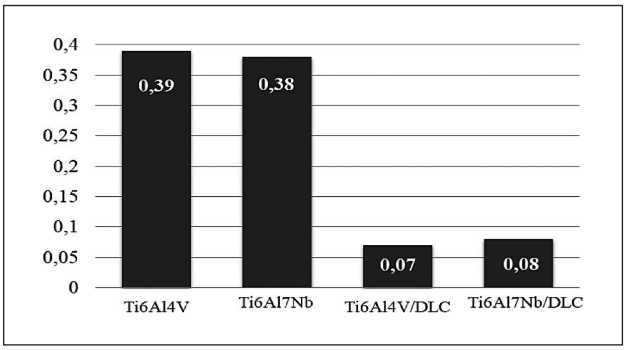


Figure 5 Tribological tests for lubricated in Ringer's solution.

The friction coefficient obtained indicates that the best parameters were obtained for the surfaces coated with DLC under the conditions of the Ringer's solution lubrication. In that case, the friction coefficient for Ti6Al4V coated DLC was 0,07, and the wear marks on the disc surface were almost invisible. Under technically dry friction conditions, the friction coefficient for titanium alloys coated with the DLC were respectively 0,07 and 0,08 for DLC coated Ti6Al4V and Ti6Al7Nb titatium alloys. The values of the friction coefficient obtained for the titanium alloys not coated with DLC were higher than for the material coated with the DLC by an order of magnitude.

After tribological tests analysis of the geometric structure of the surface were conducted (Figure 6 and 7). The most important parameters of the surface geometrical structure, as well as the wear depth and area were determined. Measurements made by optical profilometry after tribological tests showed that the diamond-like coatings have a high resistance to abrasion under technically dry friction and lubrication with Ringer's solution.

The analysis of the wear profiles of the specimens that were lubricated with the Ringer's solution showed increased wear of the specimens for titanium alloys. The characteristic grooves were also found on the titanium alloys specimens not coated with DLC. Also tests carried out with the use of the Ringer's solution showed that the specimens with coatings were more resistant to abrasion compared to the specimen without the coating. In the test of DLC coated samples with the use of the Ringer's solution lubrication, the wear depths was too small to be measured.

a) Ti6Al4V

b) Ti6Al7Nb

c) Ti6Al4V/DLC

d) Ti6Al7Nb/DLC

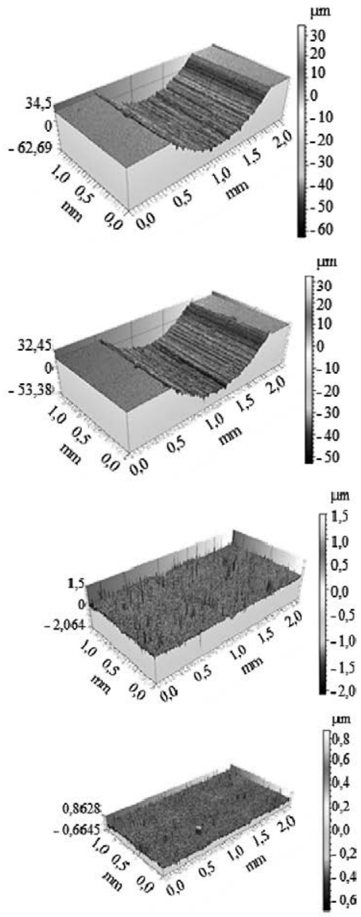


Figure 6 The isometric image of the trace of wear after technically dry friction.

a) Ti6Al4V

b) Ti6Al7Nb

c) Ti6Al4V/DLC

d) Ti6Al7Nb/DLC

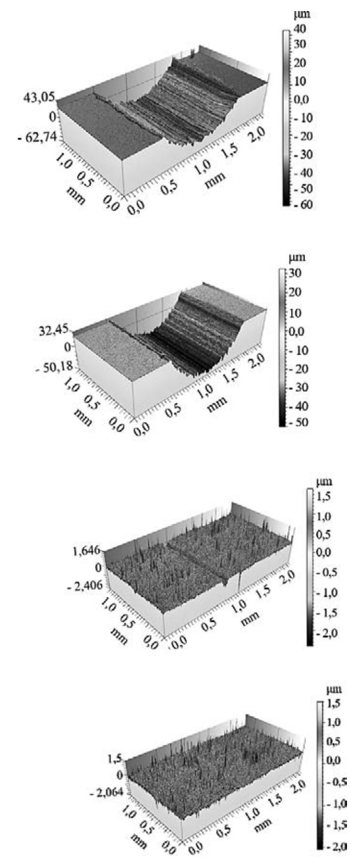


Figure 7 The isometric image of the trace of wear after Ringer's solution lubricated.

CONCLUSION

The results clearly show that the DLC deposited on the substrate of titanium alloys improves the tribological properties of the mating friction pairs of the contacting surfaces. It can be concluded that the obtained values of the coefficient of friction and depth of surface wear on the DLC-coated titanium alloys were lower both under dry friction conditions and the Ringer's solution lubrication condition compared to the uncoated specimens. Analysis of uncoated titanium alloys shows that the friction coefficient was approximately 25-30% lower when Ringer's solution lubrication was used, which is also corrosive. In the tribocorrosion environment, the value of the friction coefficient of DLC-coated titanium alloys was doubled. The experimental results show that the titanium alloys with DLC coatings had a much higher hardness - over 4 times move and higher tribological wear resistance - approximately 5 times move. The use of the DLC coatings improves the tribological properties and ensures a more stable frictional connection. It can be concluded that the obtained values of the friction coefficient and the depth of wear for the DLC-coated titanium alloys were lower both in dry friction conditions and when the Ringer's solution lubrication was used.

REFERENCES

[1] L. Zhang, L. Chen, L. Wang. Surface Modification of Titanium and Titanium Alloys: Technologies, Developments, and Future Interests. Adv. Eng. Mater. 22 (2020), 1901258 (1-37).

[2] G. Gałuszka, M. Madej, D. Ozimina, J. Kasińska, R. Gałuszka. The characterisation of pure titanium for biomedical applications, Metalurgija 56 (2017) 1-2, 191-194

[3] W. Liu, S. Liu S., L. Wang. Surface modification of biomedical titanium micromorphology, microstructure evolution biomedical applications. Coatings 9 (2019), 249

[4] R. Pokrowiecki, B. Szaraniec, J. Chłopek, M. Zaleska. Recent trends in surface modification of the titanium biomaterials used for endoosseus dental implants. Eng. Biomater. 124 (2014), 2–10.

[5] K. Piotrowska, A. Granek, M. Madej. Assessment of Mechanical and Tribological Properties of Diamond-Like Carbon Coatings on the Ti13Nb13Zr Alloy, Open Engineering 10 (2020), 536-545.

[6] M. Merola, S. Affatato. Materials for Hip Prostheses: A Review of Wear and Loading Considerations. Materials 12 (2019), 495

[7] S. Aisenberg. Properties and applications of diamondlike carbon films. Journal of Vacuum Science & Technology A2 (1984), 369.

[8] M. Vicen, J. Brontek, O. Bokůvka, R. Nikolić, N. Radek. Tribological Behaviour of the Sucaslide Diamond-like Carbon Coating. Transactions of Famena 45 (2021) 2, 31-40

[9] M. Madej. Tribological Properties of Diamond-Like Carbon Coatings. 8th Int. Conf. Terotechnology 874 (2014), 9-15.

[10] G. Capotea, D. Lugo, J. Gutiérrez, G. Mastrapa, V. Trava-Airoldi. Effect of amorphous silicon interlayer on the adherence of amorphous hydrogenated carbon coatings deposited on several metallic surfaces. Surf. Coat. Technol. 344 (2018), 644-655.

[11] M. Niemczewska-Wójcik. Multi-sensor measurements of titanium alloy surface texture formed AT subsequentoperations of precision machining process. Measurement 96 (2017), 8–17.

[12] D. Gogolewski, T. Bartkowiak, T. Kozior, P. Zmarzły. Multiscale Analysis of Surface Texture Quality of Models Manufactured by Laser Powder-BedFusion Technology and Machining from 316L Steel, Materials 14 (2021), 2794.

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