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WEAR RESISTANCE OF NON-ISOTHERMAL NITRIDED TI-6AL-4V ALLOY IN TRIBO-PAIRS WITH UHMWPE AND NITRIDED TITANIUM ALLOY IN PHYSIOLOGICAL ENVIRONMENT

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Abstract. In the process of non-isothermal gas nitriding, the nitride film consisted of tetragonal Ti_2N and face-centered cubic TiN phases was formed on the surface of Ti-6Al-4V alloy. The tribological characteristics of the nitrided Ti-6Al-4V alloy in the tribo-pairs with nitrided titanium alloy and ultra-high molecular weight polyethylene (UHMWPE) were evaluated in a 10% aqueous solution of chondroitin sulfate, which simulates the synovial fluid. It was established that a tribo-pair "nitrided Ti-6Al-4V alloy – UHMWPE" provided significantly lower friction coefficient and wear intensity than a tribo-pair "nitrided Ti-6Al-4V alloy – nitrided titanium alloy". The main mechanisms of wear of the previously mentioned tribo-pairs were established.

Keywords: Ti-6Al-4V alloy, non-isothermal gas nitriding, wear resistance, physiological environment.

1. INTRODUCTION

Many different material combinations as metal–on–metal bearings, metal–on–UHMWPE (ultra-high molecular weight polyethylene), ceramics–on–UHMWPE and ceramic–on–ceramic are used for artificial hip joints [1, 2]. However, they suffer from high wear which may cause aseptic loosening of the implant after various years of function.

Ti-6Al-4V alloy is the most widely used for manufacturing of components of the artificial joints because it has the superior biocompatibility, corrosion resistance, strength enough to withstand the cyclic loads [3–6]. Although, it possesses the low tribological properties: a high friction coefficient and poor behavior under conditions of the abrasive and adhesive wear.

It is well known that the saturation of the near-surface layer of titanium by the interstitial elements (nitrogen, oxygen, carbon, boron) during thermochemical treatment can improve the wear resistance of titanium alloys due to the formation of chemically inert compound layers with a high hardness [7–9]. Gas nitriding of titanium alloys is usually carried out in a static nitrogen atmosphere at high temperatures (850–950 °C), which provides the formation of a thick and hard nitride layer based on titanium nitrides TiN and Ti_2N [10, 11]. The surface layer of titanium nitride of a high hardness and roughness during friction in a physiological environment plows the surface of the counterbody (UHMWPE) like an abrasive, which intensifies the processes of its wear and transfer of the counterbody material to the nitrided titanium surface [12]. In addition, at high temperatures of nitriding, the coarsening of titanium grains has occurred, which leads to a decrease of titanium matrix strength and fatigue resistance and, accordingly, the durability of titanium alloys [10]. Thus, despite the fact that the surface properties of the alloys are improved, the properties of the titanium matrix are deteriorated significantly, which leads to a decrease of the mechanical properties.

Gas nitriding at low temperatures (650–750 °C) does not deteriorate the mechanical characteristics of the titanium matrix but does not ensure the formation of the regulated thickness of the nitride layer,

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which is necessary to increase the wear resistance of titanium alloys in a physiological environment. It is known that by increasing nitriding temperature, he nitriding become more active, enhancing the thickness of the nitride film [11]. However, it does not lead to an increase of the surface roughness and hardness Thus, non-isothermal gas nitriding will improve the wear resistance of Ti-6Al-4V alloy, while preserving the structure of titanium, which will not deteriorate its mechanical characteristics.

Therefore, the aim of the work is to study the effect of non-isothermal nitriding on the wear resistance of Ti-6Al-4V alloy in tribo-pairs with UHMWPE and nitrided titanium alloy in a physiological environment.

2. EXPERIMENTAL

The Ti-6Al-4V alloy was investigated. The cylindrical samples (Ø=10 mm, h=2 mm) were used for microstructural tests, and the samples in the form of a ring with an outer diameter of 27 mm and an inner diameter of 19.5 mm for tribological tests. The samples were polished to achieve a surface roughness of Ra=0.15 μm.

The samples of Ti-6Al-4V alloy were nitrided in a static nitrogen atmosphere (10^5 Pa) according to non-isothermal regime. They were heated at 650 °C for 10 h, then heated to 800 °C and cooled. By the additional heating to a temperature of 800 ºC, the thickness of the nitride film is enhanced, while preserving the structure of titanium formed at 650 ºC, which does not deteriorate its mechanical characteristics.

The phase composition of the nitrided Ti-6Al-4V alloy was determined by X-ray phase analysis in CuKα radiation. The phase content in the surface layer was determined from X-ray diffraction patterns by the Rietveld method, using the FullProf software.

The cross section of nitrided alloy sample for microstructural studies was prepared according to standard methods. The cross section was etched by using Kroll's reagent. The surface microhardness was measured using PMT-3M microhardness tester under a load of 0.49 N. The surface roughness was evaluated using a portable roughness tester RT-10.

The microstructural studies were carried out using an Epiquant microscope and an EVO 40XVP scanning electron microscope with an INCA Energy 350 X-Ray microanalysis system. SEM worn surface micrographs were linked to EDS elemental maps to determine the elemental composition of surface layers.

The tribological tests were carried out using the end friction machine according to «ring–on–disk» friction scheme where disk made of ultra-high molecular weight polyethylene (UHMWPE) or Ti-6Al-4V alloy nitrided according to stage regime. The test parameters were chosen in accordance with the ASTM F732-82 standard. The tests were performed at sliding speed of V=0.057 m/s and contact pressure of P=3.54 MPa. The medical drug "Artiflex chondro" (pharmaceutical company "Zdorovye", Kharkiv, Ukraine) was used as a working fluid. The drug is a 10% aqueous solution of chondroitin sulfate, which simulates the synovial fluid. The tribological properties were evaluated by the friction coefficient (f) of tribo-pairs and the wear intensity (I) of the counterbody (UHMWPE or nitrided Ti-6Al-4V alloy), which was determined as the ratio of volumetric wear of a counterbody to the friction path.

3. RESULTS AND DISCUSSION

3.1. Nitrided layer characterizations

In the process of non-isothermal gas nitriding, according to the results of XRD analysis, a nitride film is formed on the surface of the Ti-6Al-4V alloy, since the reflections of TiN nitride with a face-centered cubic structure and Ti_2N nitride with a tetragonal structure were recorded (Figure 1). The nitride phase Ti_2N is predominant, which is confirmed by the higher intensity of its reflections. The content of the Ti_2N phase is 31.95%, and the TiN phase is 9.34%. The analysis of the intensities of the reflections of Ti_2N and TiN phases indicates the predominant orientation of the crystallites of these phases in the (002) direction. The nitride film is not thick, as evidenced by the presence of α-Ti and β-Ti reflections with increased interplanar distances in the diffraction spectrum. This is because in the process of gas nitriding, nitrogen atoms penetrate the near-surface layer of titanium by diffusion, which causes tensile stress in its crystal lattice. In this way, a diffusion zone is formed based on a solid solutions of nitrogen in titanium.

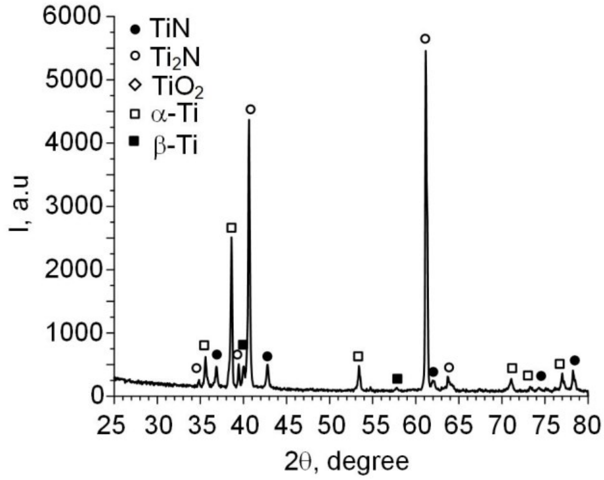

Figure 1. XRD pattern of Ti-6Al-4V alloy after non-isothermal nitriding.

Figure 2 shows the surface morphology of the nitrided Ti-6Al-4V alloy, the roughness of which is 0.27 μm, so the surface quality corresponds to N4 of roughness N grade ISO numbers. The surface microhardness of the nitrided alloy is 8.4 GPa.

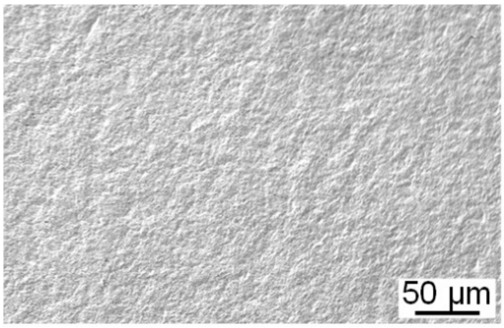

Figure 2. Surface morphology of Ti-6Al-4V alloy after non-isothermal nitriding.

The morphology and thickness of the nitrided layer formed on the Ti-6Al-4V alloy is shown in Figure 3a, b. It should be noted that two clear layers were formed on the nitrided sample: the first one (outer) – compound (nitride) layer with a thickness of 4 μm, and the second one – an alpha-case layer with a thickness of 13 μm.

The microstructure of the matrix is shown in Figure 3c, where the globular α-Ti phase and the short stick β-Ti phase can be observed. The β-phase is distributed between the globules of the α-phase.

3.2. Tribological characterization

Figure 4 shows the dependences of the friction coefficient of tribo-pair "nitrided Ti-6Al-4V alloy – UHMWPE" (a) and the wear intensity of the UHMWPE counterbody (b) on the friction path. By increasing friction path to ~ 8 km, the friction coefficient is decreased (Figure 4a) and the wear intensity of the UHMWPE is increased (Figure 4b). This can be explained by the fact that in the friction process, the running-in of the surfaces of the tribo-pair components is observed, as evidenced by the fact that the surface roughness of the titanium component is decreased most intensively on the friction path up to ~ 8 km (Figure 4c). By further increasing friction path to 21 km, the values of the friction coefficient and the wear intensity almost aren't changed.

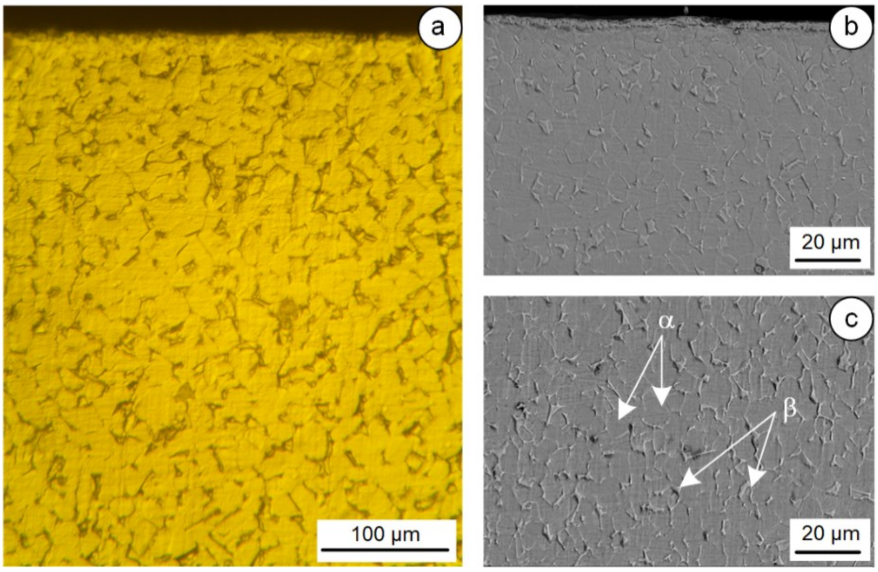

Figure 3. Longitudinal optical (a) and SEM (b) micrographs of non-isothermal nitrided Ti-6Al-4V specimen: 1 – compound layer, 2 – alpha-case layer; SEM micrograph of titanium matrix (c)

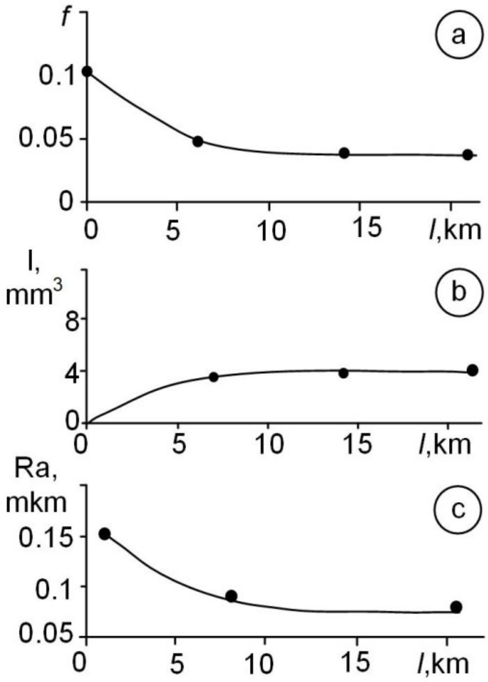

Figure 4. Dependence of friction coefficient of tribo-pair of non-isothermal nitrided Ti-6Al-4V alloy – UHMWPE (a), wear intensity of UHMWPE counterbody (b) and surface roughness of nitrided Ti-6Al-4V alloy.

To determine the wear mechanisms of the tribo-pair "nitrided Ti-6Al-4V alloy – UHMWPE", the topographic features of the worn surfaces were evaluated. According to the SEM analysis of the worn surfaces of the nitrided alloy, it was established that the relief has changed slightly, and a little wear debris was fixed on the surface (Figure 5). Obviously, the wear debris indicates the transfer of softer material of the counterbody (UHMWPE) to the surface of the nitrided Ti-6Al-4V alloy. This is confirmed by EDX analysis, which recorded the increased content of carbon (the main component of UHMWPE) on the nitrided surface. It can be assumed that the wear debris are formed because of both abrasive and adhesive wear of the UHMWPE counterbody (Figure 6), since the abrasive grooves and adhesive craters which characterize these wear mechanisms were observed on the surface.

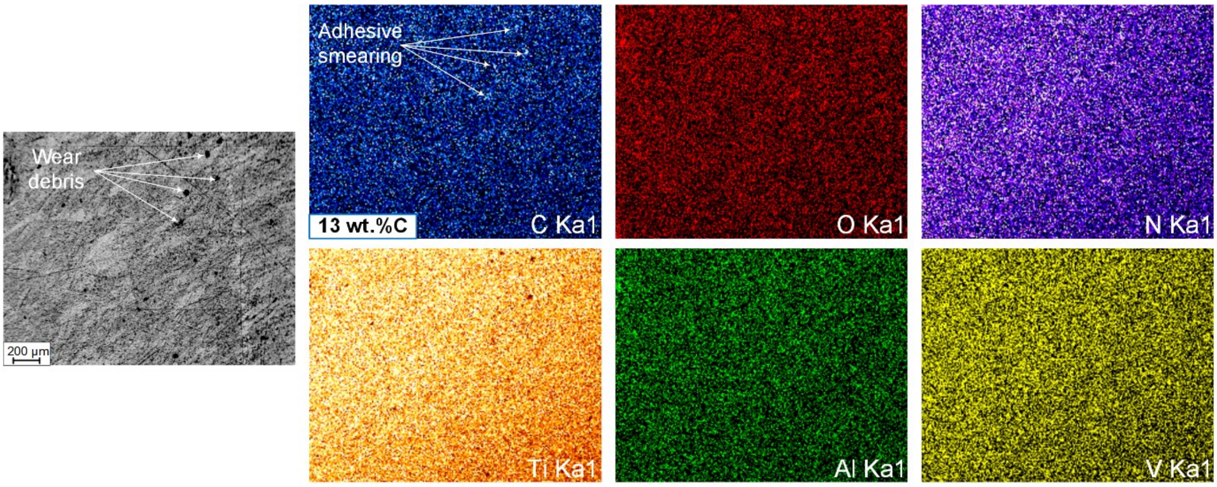

Figure 5. SEM–EDX elemental mapping of worn surface of non-isothermal nitrided Ti-6Al-4V alloy.

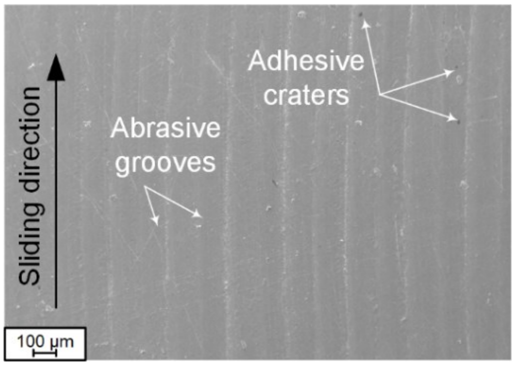

Figure 6. SEM image of worn surface of UHMWPE after friction with non-isothermal nitrided Ti-6Al-4V alloy.

Accordingly, it can be stated that the main wear mechanisms of the tribo-pair "nitrided Ti-6Al-4V alloy – UHMWPE" are abrasive with minor traces of adhesive wear. It is obviously that during friction in a 10% aqueous solution of chondroitin sulfate, the harder and rougher surface of the nitrided alloy, like an abrasive, will cut or plow the surface of the counterbody (UHMWPE) and intensify the processes of its wear and material transfer (Figure 7).

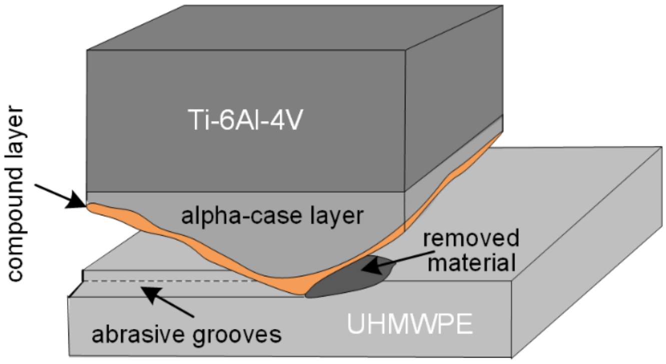

Figure 7. Wear mechanism of tribo-pair "nitrided Ti-6Al-4V alloy – UHMWPE".

For comparison, a friction pair "non-isothermal nitrided Ti-6Al-4V alloy – stage nitrided Ti-6Al-4V alloy" was tested. Figure 8 shows the surface morphology of the latter, where the grain boundaries of the nitride clearly repeat the grain boundaries of the titanium matrix. The surface roughness of the stage nitrided alloy is 0.08 µm, and that is, the surface quality of the counterbody is higher than the quality of the body. However, the surface microhardness is close to the hardness of the body and is 7.5 GPa.

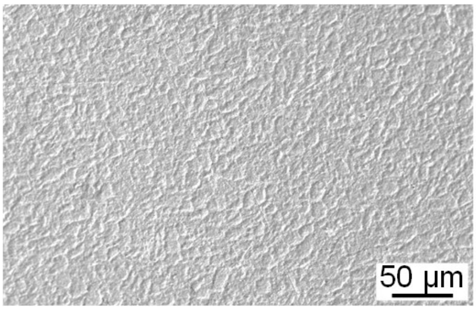

Figure 8. Surface morphology of Ti-6Al-4V alloy (counterbody) after stage nitriding.

The results of the tribological tests showed that the friction pair "non-isothermal nitrided Ti-6Al-4V alloy – stage nitrided Ti-6Al-4V alloy" worked a friction path of only 290 m. The linear size of the body increased by 0.02 mm. This is caused by the mutual transfer of the same material of the body and counterbody, which is confirmed by the results of the SEM analysis of the worn surfaces (Figure 9). The surface roughness of the counterbody increased to 6 µm, which confirms its significant wear. The roughness of the surface increased to 1.8 µm, but it should be noted that the deterioration probably occurred due to mutual transfer (cold micro-welding) of the material. The main wear mechanism of tribo-pair "non-isothermal nitrided Ti-6Al-4V alloy – stage nitrided Ti-6Al-4V alloy" is abrasive, which is transitioned into adhesive. It should also be noted that an increased content of the oxygen (27...36 wt. %) was recorded on the wear surfaces. This is explained by the fact that in the process of friction in a 10% aqueous solution of chondroitin sulfate the oxidation of the nitride layers is occurred. Thus, the mechanism of the oxidative wear is also implemented.

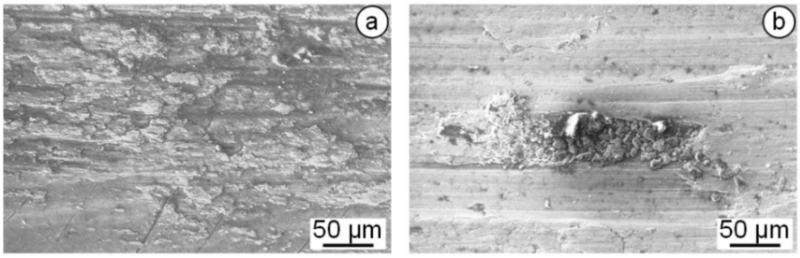

Figure 9. SEM images of worn surface of non-isothermal nitrided Ti-6Al-4V alloy (body) – stage nitrided Ti-6Al-4V alloy (counterbody) after friction.

Figure 10 presents the values of the friction coefficient of the tribo-pairs and the wear intensity of the counterbodies (UHMWPE and stage nitrided Ti-6Al-4V alloy). Comparing the results of the tribological studies, it can be confirmed that the tribo-pair "non-isothermal nitrided Ti-6Al-4V alloy – UHMWPE" provides significantly lower values of the friction coefficient (by one order) and the wear intensity (by two orders) than the tribo-pair "non-isothermal nitrided Ti-6Al-4V alloy – stage nitrided Ti-6Al-4V alloy".

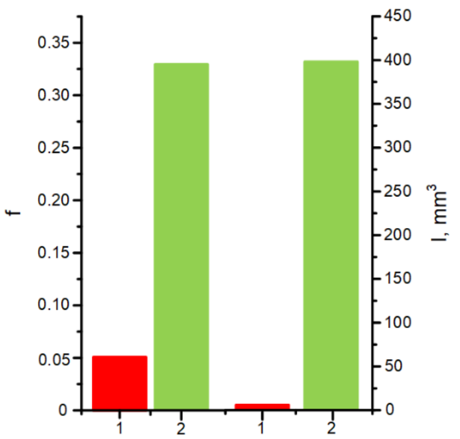

Figure 9. Friction coefficient of tribo-pairs and wear intensity of counterbodies: 1 – non-isothermal nitrided Ti-6Al-4V alloy – UHMWPE; 2 – non-isothermal nitrided Ti-6Al-4V alloy – stage nitrided Ti-6Al-4V alloy.

Thus, the tribo-pair "non-isothermal nitrided Ti-6Al-4V alloy – UHMWPE" has a significant prospect for the use as a tribo-pair of joint endoprostheses.

4. CONCLUSIONS

It was established that in the process of non-isothermal gas nitriding, an outer (compound + alpha-case) 3 μm-thick and inner (diffusion) 10 μm-thick layers are formed on the surface of Ti-6Al-4V titanium alloy. The nitride layer contains the tetragonal Ti_2N and the face-centered cubic TiN phases.

The tribological characteristics of the non-isothermal nitrided Ti-6Al-4V alloy in tribo-pairs with stage nitrided titanium alloy and UHMWPE in a 10% aqueous solution of chondroitin sulfate, which simulates the synovial fluid, were evaluated. It was shown that the tribo-pair "non-isothermal nitrided Ti-6Al-4V alloy – UHMWPE" provides significantly lower values of the friction coefficient (by one order) and wear intensity (by two orders) than the tribo-pair "non-isothermal nitrided Ti-6Al-4V alloy – stage nitrided Ti-6Al-4V alloy". It was determined that the wear mechanisms of such a tribo-pair are the abrasive and adhesive ones, and the mechanism of oxidative wear is absent. Therefore, the tribo-pair "non-isothermal nitrided Ti-6Al-4V alloy – UHMWPE" has a significant prospect for use as a tribo-pair of joint endoprostheses.

REFERENCES

[1] Österle W., Klaffke D., Griepentrog M., Gross U., Kranz I., Knabe Ch. Potential of wear resistant coatings on Ti–6Al–4V for artificial hip joint bearing surfaces. Wear. 264 (2008) 505–517. https://doi.org/10.1016/j.wear.2007.04.001
[2] Sullivan S.J.L., Topoleski L.D.T. Surface modifications for improved wear performance in artificial joints: a review. JOM. 67 (2015) 2502–2517. https://doi.org/10.1007/s11837-015-1543-0
[3] Pratap T., Patra K. Tribological performances of symmetrically micro-textured Ti-6Al-4V alloy for hip joint. International Journal of Mechanical Sciences. 182 (2020) 105736. https://doi.org/10.1016/j.ijmecsci.2020.105736
[4] Cremer L., Nortje B.D., van der Merwe J., Becker T.H. Wear of conventional UHMWPE articulating against additively manufactured Ti-6Al-4V and Co-Cr-Mo. Biotribology. 33–34 (2023) 100231. https://doi.org/10.1016/j.biotri.2022.100231
[5] Nagentrau M., Mohd Tobi A.L., Jamian S., Otsuka Y., Hussin R. Delamination-fretting wear failure evaluation at HAp-Ti-6Al–4V interface of uncemented artificial hip implant. Journal of the Mechanical Behavior of Biomedical Materials. 122 (2021) 104657. https://doi.org/10.1016/j.jmbbm.2021.104657
[6] Liu G., Leng K., He X., Tang L., Gao W., Fu Y. Microstructure evolution of Ti–6Al–4V under cold rolling + low temperature nitriding process. Progress in Natural Science: Materials International 32 (2022) 424–432. https://doi.org/10.1016/j.pnsc.2022.06.004
[7] Zhao X., Zhang H., Liu H., Li Sh., Li W., Wang X. In vitro bio-tribological behaviour of textured nitride coating on selective laser melted Ti-6Al-4V alloy. Surface and Coatings Technology. 409 (2021) 126904. https://doi.org/10.1016/j.surfcoat.2021.126904
[8] Pohrelyuk I.M., Tkachuk O.V., Sambors'kyi O.V. Influence of oxynitriding on the wear resistance of VT14 titanium alloy. Materials Science 46 (2011) 834–840. https://doi.org/10.1007/s11003-011-9359-8
[9] Pohrelyuk I.N., Skvortsova S.V., Fedirko V.N., Lukyanenko A.G., Spector V.S., Tkachuk O.V. Effect of hydrogen heat treatment on antifriction properties of nitrided VT6 titanium-based alloy. Journal of Friction and Wear. 37 (2016) 274–281. https://doi.org/10.3103/S1068366616030144
[10] Kikuchi Sh., Yoshida Sh., Ueno A. Improvement of fatigue properties of Ti-6Al-4V alloy under four-point bending by low temperature nitriding. International Journal of Fatigue. 120 (2019) 134–140. https://doi.org/10.1016/j.ijfatigue.2018.11.005
[11] Pohrelyuk I. and Fedirko V. Titanium alloys – towards achieving enhanced properties for diversified applications. Chapter 7. Chemico-thermal treatment of titanium alloys – nitriding. InTech, Rijeka, 2012. 240.
[12] Pohrelyuk I.M., Sheykin S.E., Dub S.M., Mamalis A.G., Rostotskii I.Yu., Tkachuk O.V., Lavrys S.M. Increasing of functionality of c.p. titanium/UHMWPE tribo-pairs by thermodiffusion nitriding of titanium component. Biotribology 7 (2016) 38–45. https://doi.org/10.1016/j.biotri.2016.08.002