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EVALUATION OF PLASMA NITRIDING EFFICIENCY OF TITANIUM ALLOYS FOR MEDICAL APPLICATIONS

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The surface layers obtained on selected titanium alloys, used in medicine, by the nitriding under glow discharge condition were investigated. The results concern of: α- titanium alloy Grade 2 and $\alpha + \beta$ alloys Grade 5 and Grade 5 ELI nitrided in temperature below 873 K. The nitriding experiments were performed in a current glow-discharge furnace JON-600 with assisting of unconventional methods. After nitriding surface layers were characterised by surface microhardness measurements, chemical depth profiles, microhardness depth profiles and wear resistance tests.

Key words: titanium alloys, glow discharge nitriding, surface layer structure

Procjena učinka nitriranja plazmom titanovih legura za primjenu u medicini. Istraživan je površinski sloj dobiven nitriranjem pri toplinskim postupcima odabranih titanovih legura, a koje se rabe u medicini. Rezultati se odnose na α-titanovu leguru 2. stupnja i $\alpha+\beta$ legure 5. stupnja i 5. stupnja ELI nitriranim na temperaturama ispod 873 K. Pokusi nitriranja su provedeni u prolaznoj toplinskoj peći JON-600 primjenom nekonvencijalnih metoda. Poslije nitriranja površinski slojevi su karakterizirani mjerenjem površinske tvrdoće, te po presjecima dubinski kemijski i mikrotvrdoće te otpor na trošenje.

Ključne riječi: titanove legure; nitriranje toplinskim postupkom; struktura površinskog sloja

INTRODUCTION

Wide use of titanium alloys results from their unique physical and chemical properties [1]. Combination of low density and improved corrosion resistance with good plasticity and mechanical properties determines application of titanium alloys in such industries as aviation, automotive, power and shipbuilding industries or architecture as well as medicine and sports equipment. Despite numerous advantages, a fundamental drawbacks which limits wider use of titanium alloys include their tribological properties. This causes a more intensive wear as a result of creation of adhesion couplings and mechanical instability of passive layer of oxides, particularly with presence of third bodies. Analysis of application of titanium and its alloys also reveals unfavourable impact of reactive nature of titanium and its susceptibility to oxidation. Layer of oxides created in ambient temperature is thin and has low strength, which favours its removal during friction. Negative impact on wear in surfaces made of titanium alloys is produced by low friction resistance resulting from hexagonal crystal structure of α-Ti [2, 3]. Electron configuration causing high titanium reactivity, crystal structure and inefficiency of used conventional lubrication limit application of titanium an its alloys for conditions which require resistance to tribological wear [4].

The first titanium alloy used for medicine was Grade 5 [5]. This alloy, due to its contents of aluminium and vanadium in particular, turned out to be an alloy with low biotolerance, thus its composition was modified by means of exchanging these two components with elements better tolerated by the body, such as: Nb, Zr, Ta or Fe. Currently preferred titanium alloys with additions of niobium and zirconium are characterized with very good biotolerance [5, 6].

An alternative solution is modification of surface layers in relatively cheap alloys, such as e.g. titanium alloy Grade 5 ELI, causing change in chemical properties of the surface and in tribological properties, and, in consequence, change in biotolerance [5÷7]. One of the methods of surface treatment of titanium alloys is nitriding using glow discharge methods. Glow discharge processes enable constitution of surface layers with particular structure, phase and chemical composition, which enables considerable improvement in tribological properties of titanium alloys [8]. Factor which limits thickness of layers obtained by means of nitriding is low nitrogen diffusion index in titanium [8]. Thus, such nitriding is performed in most of cases within the range of temperatures of 973 ÷1423 K. Considerable improvement in wear and corrosion resistance in titanium alloys

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can also be observed after glow discharge nitriding in temperature ranges lower than the abovementioned [9÷12]. The results of investigations of glow discharge nitriding at the temperature lower than 873 K seem to be particularly interesting. Despite obtaining of surface layer with considerably smaller thicknesses, this method of treatment is used for improvement in quality of titanium alloy surfaces. The authors of this paper became particularly concerned with the question if it is possible to modify low-temperature glow discharge nitriding process so that surface layers with increased thicknesses and properties comparable with cathode nitriding are obtained in titanium alloys. This paper concerns investigations of surface layers obtained on selected titanium alloys which were subject to glow discharge nitriding at the temperature lower than 873 K using screens for nitriding process supporting.

INVESTIGATION MATERIAL AND SCOPE OF THE INVESTIGATIONS

The following types of titanium alloys have been selected for investigations:

- one-phase alloy α: commercially pure titanium – Grade 2
- two-phase alloys $\alpha + \beta$: Grade 5 and Grade 5 ELI.

Nitriding was carried out at the temperature of T = 803 K, pressure of p = 150 Pa and time of t = 39,6 ks. The ambient obtained from nitrogen was used for execution of glow discharge process.

Process of nitriding was performed in equipment for glow-discharge treatment with JON-600 cooled anode, employing four variants of nitriding:

1. Variant I – samples nitrified on cathode
2. Variant II – samples nitrified on the surface both isolated from cathode and anode, i.e. in 'plasma potential'
3. Variant III – samples nitrified on cathode covered with supporting screen
4. Variant IV – samples nitrified in plasma potential covered with supporting screen.

Supporting screen was made of perforated titanium sheet.

Measurements of surface hardness and microhardness in surface layer were taken by means of Knopp method with FM-7 hardness tester.

Chemical composition tests were performed by means of GDOES with JY GD-PROFILER 2 device. RF generator was used with frequency of changes in cathode potential being 13,56 MHz.

X-ray analysis of quality in surface layer was performed by means of DRON-2 diffractometer with CoK_α radiation ($\lambda CoK_{\alpha\ av.}$ = 0,17902 nm).

Observations of the structures obtained after the process of nitriding was carried out using Axiovert 25 optical microscope.

Tribological tests in conditions of dry friction were performed using T-05 tester with friction couple of roll-block type. The assumed measure of wear was loss in sample weight.

RESULTS OF INVESTIGATIONS AND DESCRIPTION

Highest surface hardness was obtained in case of cathode nitriding in samples placed under supporting screen; the highest, 8-times increase in hardness (in relation to hardness before nitriding) was observed in case of Grade 2 titanium nitriding, nearly 4-times rise in hardness in case of Grade 5 and titanium alloy Grade 5 ELI. Nitriding of samples on cathode caused 4-times increase in case of titanium Grade 2 while over 2-times in case of nitriding in the two other titanium alloys. In case of nitriding in plasma potential, use of supporting screens caused 4-times increase in surface hardness in case of Grade 2 titanium nitriding and lower (2-times) in case of Grade 5 and Grade 5 ELI nitriding. The results of surface hardness in the investigated titanium alloys are graphically presented in Figure 1.

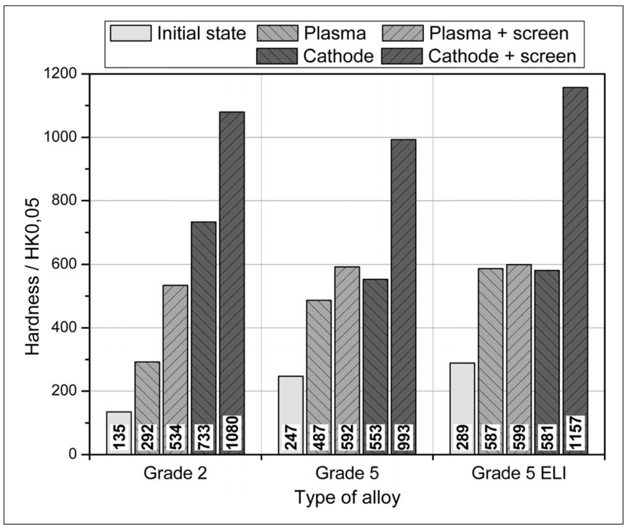

Figure 1. Surface hardness of investigated Ti alloys after glow discharge nitriding

Chemical composition tests revealed that use of screens for supporting glow discharge nitriding process caused intensification of surface processes, which was manifested in several-times rise in concentration of nitrogen in surface layers in the nitrified titanium alloys.

Depending on process variant, zones rich in nitrogen and oxygen in surface layers with thickness of from more than ten to a few tens of millimetres are mainly obtained. Examples of profiles for distribution of the elements in surface layer of titanium Grade 2 after glow discharge nitriding on cathode and cathode with supporting screen are graphically illustrated in Figure 2. Results of investigations are presented in the form of distribution of concentration in analysed elements as a function of time of spraying in the investigated sample.

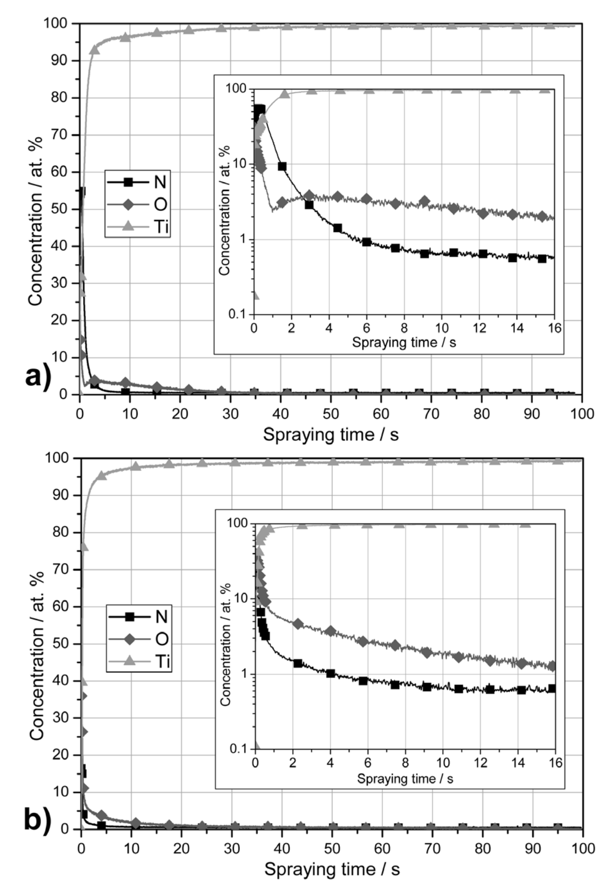

Figure 2. Profile of distribution of elements in surface layer after glow discharge nitriding: a) on cathode, b) on cathode with supporting screen

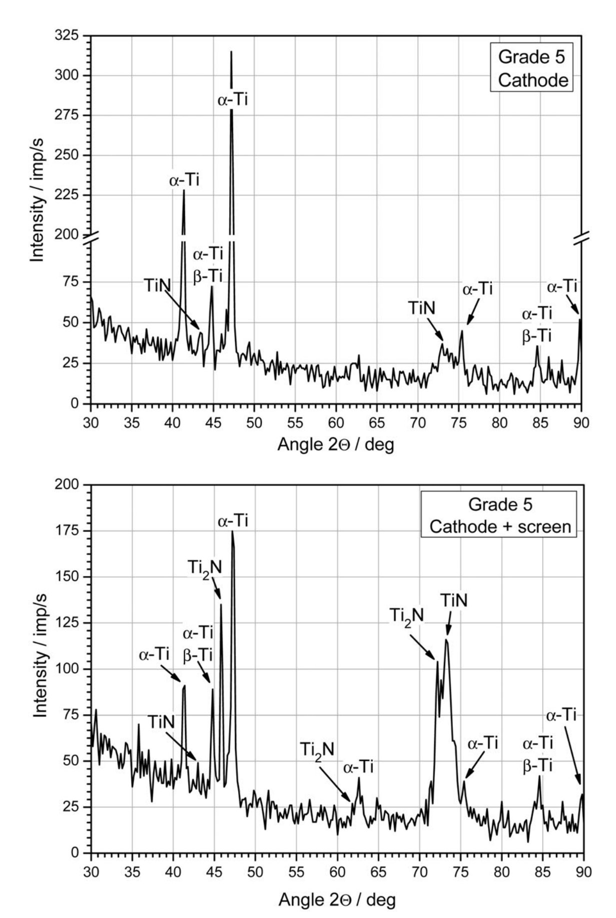

Figure 3. X-ray diffractograms of Grade 2 alloy after nitriding

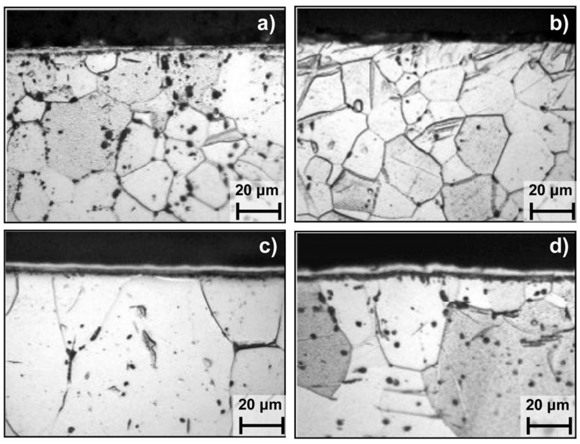

Figure 4. Structures of surface layers for commercially pure titanium Grade 2 after different variants of glow discharge nitriding: a) cathode, b) plasma potential, c) cathode + screen, d) plasma + screen

Investigations of two-phase composition revealed that during nitriding mainly TiN nitrides are created on cathode, while employing supporting screens causes also appearance of Ti_2N nitrides. Characteristic fact is, however, that nitriding with supporting screen caused creation of nitride layer also on the surface of the sample adhering to cathode (bottom of the sample). In case of nitriding on cathode without supporting screen no nitrides were found on the bottom of samples. Diffractograms obtained from samples nitrified in plasma potential did not prove appearance of titanium nitrides on the investigated surfaces, while use of supporting screens is conducive to appearance of TiN. Examples of Grade 2 titanium diffractograms after glow discharge nitriding are presented in Figure 3.

Observation of the obtained structures revealed that using screens for support of glow discharge nitriding process causes creation of a compact and thick titanium nitrides zone, both in the case of nitriding on cathode and in 'plasma potential'. Nitride zone in case of nitriding only in 'plasma potential' were not observed. Samples of surface layer structures obtained after the process of glow discharge nitriding were illustrated in Figure 4.

The assumed parameters of glow discharge nitriding process caused creation of diffusion layers with thickness of up to 150 μm. The thickness of diffusion layers obtained as a result of nitriding are presented in Figure 5.

The process of titanium nitriding, with the applied parameters of the process, causes reduction in value of friction coefficient and rise in friction wear resistance in the case of each variant of nitriding process selected for titanium alloy tests. Highest rise in friction wear resistance appeared in the case of nitriding on cathode with use of supporting screen. This is proved by nearly 4-times lower loss in sample weight in the nitrified tita-

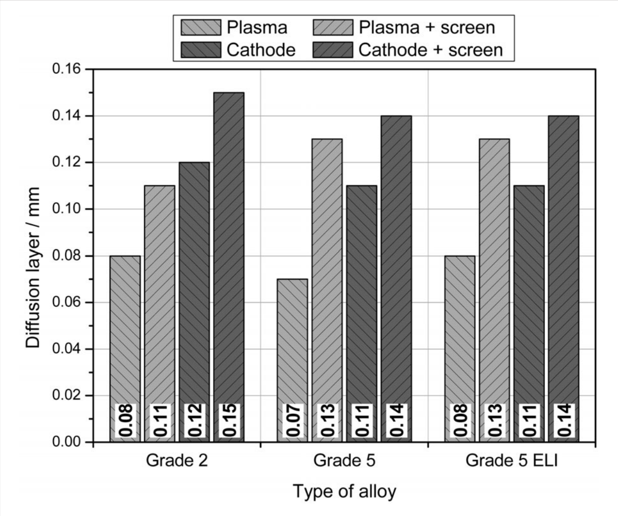

Figure 5. Thickness of diffusion layers in the investigated titanium alloys after glow discharge nitriding

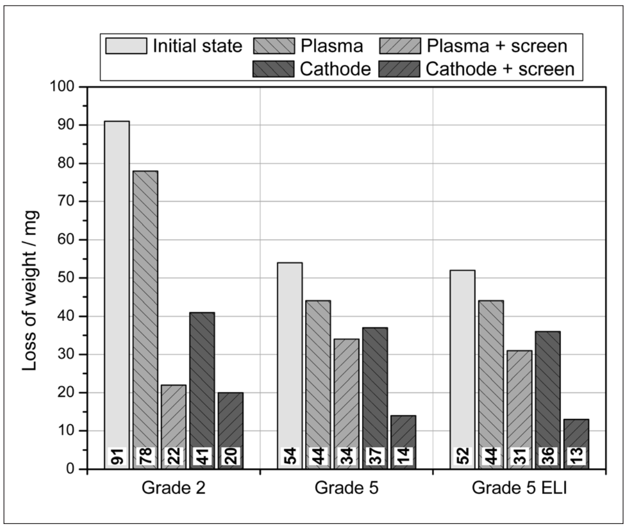

Figure 6. Friction wear in the investigated titanium alloys

nium alloy samples in comparison to initial state. Value of loss in sample weight in the investigated samples of titanium alloys are presented in Figure 6.

CONCLUSIONS

1. Glow discharge nitriding causes increase in surface hardness in the investigated titanium alloys. The highest, several-times rise in surface hardness takes place in the case of use of screens for supporting of nitriding process.
2. Application of the screen for supporting of glow discharge nitriding process causes intensification of surface processes, which is manifested by several-times rise in nitrogen concentration in surface layer in nitrified titanium alloys.
3. Use of supporting screens in the case of cathode nitriding intensifies creation of nitrides of TiN and Ti_2N type, while in the case of nitriding in plasma potential it favours creation of nitrides of TiN type.
4. Screens for support of nitriding process cause creation of nitrides layer also on the surface of samples adhering cathode (on the bottom of a sample).
5. Application of supporting screens causes creation of a compact and tight layer of titanium nitrides on nitrified surfaces.
6. The accepted parameters of nitriding process cause rise in resistance to friction wear, in case of each variant of nitriding process in the investigated titanium alloys.

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Note: The responsible translator for English language is A. Tokarz.