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КОРОЗІЙНА ПОВЕДІНКА ТИТАНУ З ОКСИНІТРИДНИМИ ПОКРИТТЯМИ У ФІЗІОЛОГІЧНОМУ РОЗЧИНІ

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CORROSION BEHAVIOUR OF TITANIUM WITH OXYNITRIDE COATINGS IN PHYSIOLOGICAL SOLUTION

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ABSTRACT. In present work the corrosion-electrochemical behavior of titanium alloy Grade 2 with combined coatings – presaturated with nitrogen and oxygen diffusion layer by thermal-chemical treatment and oxynitride coating TiN_xO_y with nearly equiatomic compositions deposited by magnetron sputtering – in physiological saline (isotonic solution of 0,9% NaCl) was studied. It was found that oxynitride coatings increase the corrosion resistance in 1,2 times as compared to nontreated alloy. When titanium alloy was presaturated with oxygen or nitrogen the combination of oxynitride coating and diffusion layer of thickness 50 μm assists in additional enhancement of corrosion properties in 1,5-3 times.

KEY WORDS: *titanium alloy Grade 2, magnetron sputtering, diffusion saturation, oxynitride coatings, corrosion, physiological saline.*

INTRODUCTION

It is well-known that the effectiveness of titanium implants is lower than those after additional treatment (thermal, thermo-mechanical, chemical-heat, etc.) [1-4], because at high contact and alternating working loads (for example, orthopedic implants destination) as well as in the flows of bioactive media (such as, paper clips, pins, valves, etc.) titanium alloys need to additionally improve its wear and corrosion resistance.

The oxynitrides give the promising opportunities to improve the corrosion resistance of titanium alloys. They inherit most of characteristics of binary compounds (oxide and nitride) and even exceed, including biomedical properties (adhesion of platelets, blood coagulation reactions) as well as surface hardness and corrosion resistance [5-7].

The purpose of article was to study the corrosion-electrochemical behavior of titanium alloy Grade 2 with oxynitride coatings deposited on untreated surface and presaturated with oxygen and nitrogen diffusion layer in isotonic solution of 0.9% NaCl.

EXPERIMENTAL

The samples of commercially pure titanium Grade 2 (Fe – 0,3; O – 0,25; H – 0,015; N – 0,03; C – 0,1 max.%, Ti – balance; USA, ASTM) of dimensions 20×20×2 mm were studied. Before processing the samples have been polished, washed in alcohol and dried.

Oxynitride coatings TiN_xO_y with nearly equiatomic compositions were deposited on the titanium surface by magnetron sputtering [8]. Coatings were applied on: 1) unsaturated surface and 2) presaturated with oxygen and nitrogen diffusion layer at following treatment modes: Oxidizing – 800 °C, $P_{O2}=5\times10^{-2}$ Pa, 3 h; Nitriding – 800 °C, 4 h, P_{N2} = 1 Pa . This processing allows to form a diffusion gradient sub-layer (α-solid solution of oxygen or nitrogen in α-titanium) of thickness up to 50 μm.

The X-ray analysis was carried out using a diffractometer with CuKα-radiation at a voltage of

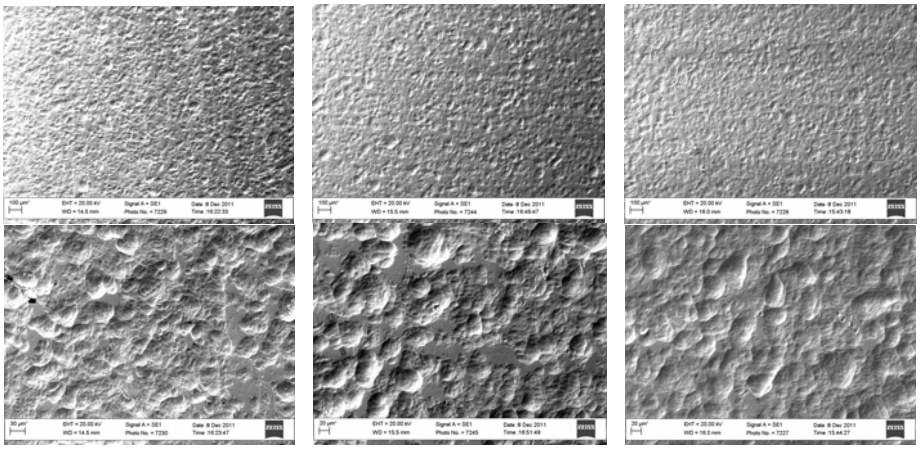
35 kV and a current of 20 mA. The tube focusing system was made using Bragg–Brentano method. The scan step was 0.02°. The step counting time was 5 s. The diffraction pattern profiles were refined by the Rietveld method with two different pseudo-Voigt function using Powder Cell 2.4 program [16]. R_p (R-pattern) and R_{wp} (R-weighted pattern) were used as numerical criteria of fit. Titanium oxynitride was identified using the standard diffraction pattern obtained in accordance with the model by Levi et al. [17]. This model assumed that the non-metal sub-lattice was disordered (the N and O atoms randomly occupied the (½ ½ ½) positions, whereas the Ti atoms occupied the (0 0 0) positions). The accuracy of lattice parameter measurement was ±0,00002 Å. No preferred orientations were observed on the non-treated titanium specimens.

The surface structure and chemical composition of layers were studied using scanning electron microscope EVO 40XVP with microanalysis system INCA Energy.

Corrosion-electrochemical behavior was studied in isotonic 0.9% NaCl solution at room temperature. Polarization curves were obtained on potentiostat PI-50.1.1 at speeds 2 mV/sec. Potential related to chlorine-silver electrode was measured. Samples previously cleaned with alcohol and covered by lacquer to isolate the surface, leaving uncovered a working surface.

RESULTS AND DISCUSSIONS

The titanium surface after oxynitride coating formation is gray-violet-pink colored which does not depend on preliminary processing. The light reflection is typical for surface. However, it weakens when the titanium was pre-saturated with alloying elements (oxygen and nitrogen) (Fig. 1).



a *b* *c*

Fig. 1. Surface of alloy Grade 2 after oxynitride coating deposition: *a* – without presaturation; *b* – after diffusion presaturation with oxygen; *c* – after diffusion presaturation with nitrogen.

Oxynitride compound was identified by the reference line (200) on diffraction pattern (Fig. 2). The metallographic analysis of surface shows that formed oxynitride coating follows the surface topography of titanium matrix (Fig. 3 a).

A composition of oxynitride, according to EPMA slightly depends on the surface pre-treatment. The content of oxygen and nitrogen in oxynitride formed after the presaturation with oxygen or nitrogen is slightly higher (Table).

Table. Composition of titanium oxynitride deposited on alloy Grade 2

Element	TiN_xO_y					
	Without diffusion presaturation		After diffusion presaturation with oxygen		After diffusion presaturation with nitrogen	
	Mass. %	At. %	Mass. %	At. %	Mass. %	At. %
N K	10,31	21,25	10,70	21,80	10,93	22,19
O K	20,57	37,11	21,06	37,55	21,02	37,39
Ti K	69,11	41,64	68,24	40,65	68,05	40,42

The adhesion of oxynitride coating depends on pre-treatment of titanium. This assumption is confirmed by the oxynitride detachment after 5-7 min of treatment in alcohol by the ultrasonic washing (Fig. 3 b-d). Thermodiffusion saturation with oxygen and nitrogen before oxynitride deposition influences positively on adhesion of coating to surface. At that after pre-saturation with oxygen the effect is maximal (Fig. 3 *c*).

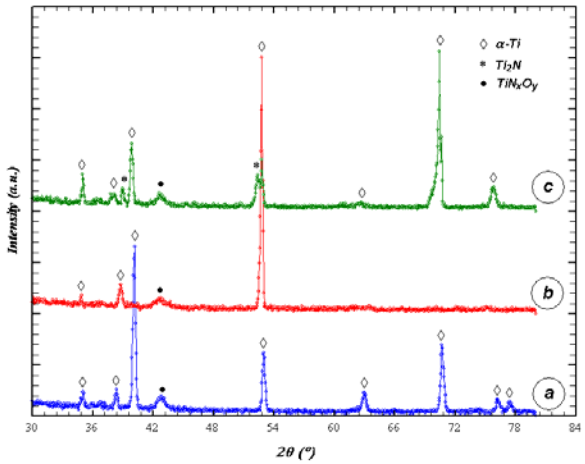


Fig. 2. Diffraction patterns from Grade 2 after oxynitride coating deposition : *a* – without presaturation; *b* – after diffusion presaturation with oxygen; *c* – after diffusion presaturation with nitrogen.

a *b* *c* *d*

Fig.3. Detachment of oxynitride coating: *a, b* – deposited without diffusion presaturation, *c* – after diffusion presaturation with oxygen, *d* – after diffusion presaturation with nitgoren

Corrosion of oxynitride coatings were evaluated by the time change of electrode potential (Fig. 4).

For the non-treated sample the slight instability in the electrode potential change with time accompanied with a weak tendency to positive shifting is observed: on 3600 s exposure the electrode potential increases to 0,04 V. The change of electrode potential of the oxynitride coating deposited on non-treated titanium is the same, but its absolute values are higher and degree of instability is lower. It makes possible to expect the higher corrosion resistance of oxynitrided surface.

Oxynitride coating deposited on pre-oxidized surface provides a much higher value of electrode potential (-0,22 V). Within 620 s potential shifted into positive values and within next 360 s decreases slightly, but not below the initial value. Then the potential grows rapidly to -0,1 V. After 1200 s of exposure the rate of electrode potential change reduced insignificantly. Further it continues to grow monotonically and after 2500 s it enters to the positive area. Such kinetics of electrode potential indicates the tendency for surface passivation.

At the initial period of exposure the surface of oxynitride coating deposited on pre-nitrided sample is characterized by the highest electrode potential: - 0,21 V. During the first 110 s of exposure the potential increases to -0,15 V and for the further 360 s returns to its original value. Then the monotonous shifting of electrode potential to positive values is observed. At the exposure within 2220 ... 2670 s the potential stabilizes at -0,013 ... 0,016 V, then decreases slightly (to -0,022 V) and starts to increase monotonically going in the positive interval of values after 3500 s.

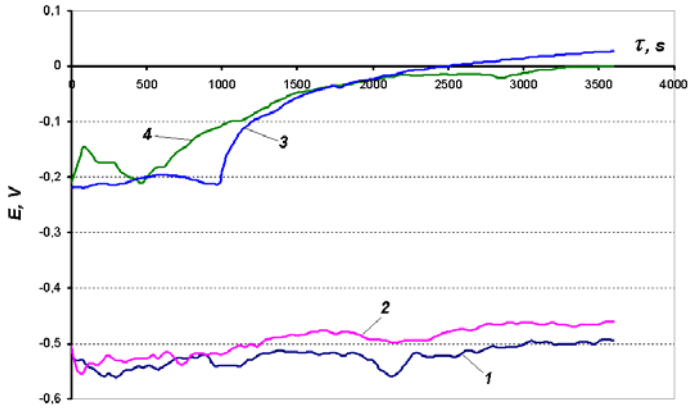


Fig. 4. Kinetics of electrode potential of alloy Grade 2 in as-received condition (*1*) and with oxynitride coatings (*2-4*) in 0,9% NaCl: *2* – without diffusion presaturation; *3* – after diffusion presaturation with oxygen; *4* – after diffusion presaturation with nitrogen

All these features of oxynitride coating deposited on pre-oxidized and pre-nitrided surface, i.e. a higher values of electrode potential, its shifting to positive values with time indicates that the preliminary formation of a diffusion sub-layer influences positively on the corrosion characteristics of the oxynitride surface.

Potentiodynamic tests revealed that the formation of oxynitride coating on alloy Grade 2 provides the corrosion potential shifting of 230 ... 290 mV to the positive values and the corrosion current decreasing of 1,1 ... 5,1 mA/m^2 (Fig. 5). Other words, it increases the corrosion characteristics of titanium surface.

The shape of potential curves of the alloy without treatment and after oxynitriding shows that the processes occurred in both cathode and anode areas of potentials are identical (Fig. 6).

During cathode polarization in 0.9% NaCl a release of hydrogen takes places.

On the anode branches of potential curves the slower growth of corrosion current density with growth potential followed after areas of active dissolution. The process of anodic dissolution of titanium with oxynitride coating deposited on the presaturated surface in the interval of potentials -0,2 ... 0,4 V slows down. At that on the surface the titanium oxychloride is possibly formed [9]:

$$TiNO + 2Cl^- = TiOCl_2 + 0{,}5N_2 + 2e^-$$

Due to oxychloride's instability it can be oxidized to titanium dioxide:

$$TiOCl_2 + H_2O = TiO_2 + 2HCl_{hydr.},$$

that causes the existence of a second area of slower growth of corrosion current density in the interval of potentials above 0,5 ... 0,6 V. At that, the defects of oxide formed on the surface are less when the titanium was presaturated with nitrogen. It is confirmed by the lower currents of anodic dissolution.

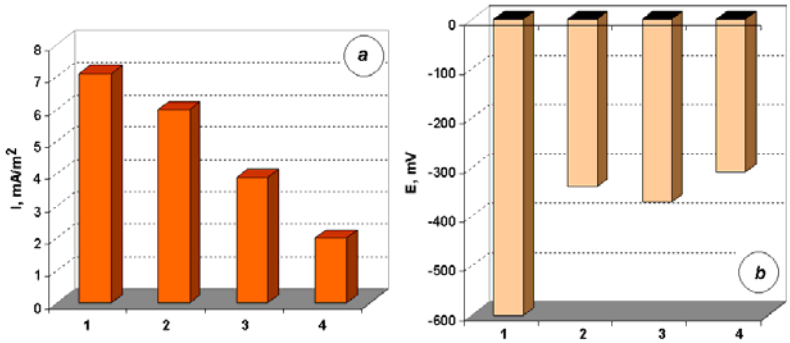


Fig. 5. Corrosion current (*a*) and potential (*b*) of alloy Grade 2 in as-received condition (*1*) and with oxynitride coatings (*2-4*) in 0,9% NaCl: *2* – without diffusion presaturation; *3* – after diffusion presaturation with oxygen; *4* – after diffusion presaturation with nitrogen

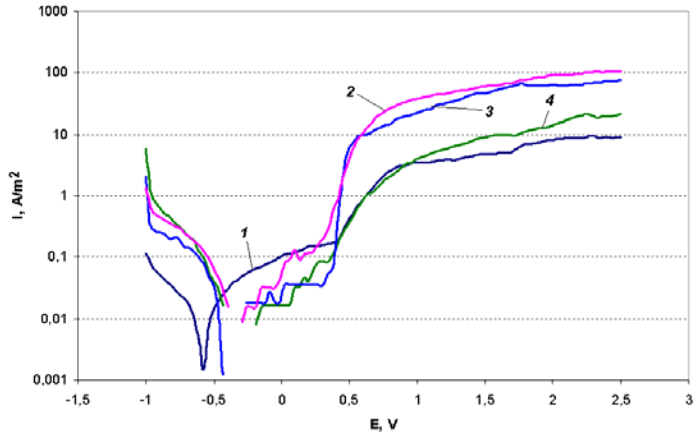


Fig. 6. Polarization curves of alloy Grade 2 in as-received condition (1) and with oxynitride coatings (*2-4*) in 0,9% NaCl: *2* – without diffusion presaturation; *3* – after diffusion presaturation with oxygen; *4* – after diffusion presaturation with nitrogen

The lowest current density and the more positive corrosion potential were demonstrated by oxynitride coating formed on presaturated with nitrogen sub-layer (Fig. 5). The corrosion current density decreased in three times as compared with oxynitride coating deposited on untreated titanium surface. Presaturation of titanium with oxygen before oxynitride deposition provides less shifting of potential to positive values and increasing in two times of the current corrosion. This may be explained by the fact that nitrogen provides the formation of modified layers with stronger covalent bonds [10].

CONCLUSIONS

Magnetron sputtering deposition of oxynitride coating increases the corrosion resistance of titanium alloy Grade 2 in isotonic 0,9% NaCl solution.

Thermodiffusion presaturation of the surface layers of titanium with oxygen and nitrogen with the formation of diffusion sub-layer of thickness up to 50 μm intensifies this effect in 1,5-3 times.

Presaturation of the surface layers of titanium with oxygen and nitrogen increases the adhesion of oxynitride coating.

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