CORROSION PROPERTIES OF Ti-6Al-4V ALLOY WITH NITRIDE AND OXYNITRIDE COATINGS IN PHYSIOLOGICAL SOLUTIONS

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Abstract: In this work, the corrosion resistance of Ti-6Al-4V alloy with nitride and oxynitride coatings was investigated in isotonic 0.9 % NaCl solution and Ringer's solution at temperatures of 36 °C and 40 °C, which simulates the transition from normal to inflammatory condition of the human body. It was determined that the change of temperature of both physiological solutions does not decrease the protective function of nitride coating on Ti-6Al-4V alloy. It was shown that the corrosion properties of oxynitride coating are deteriorated by increasing the temperature up to 40 °C, especially in 0.9 % NaCl solution.

Keywords: TI-6AL-4V ALLOY, NITRIDE AND OXYNITRIDE COATINGS, CORROSION, 0.9 % NACL, RINGER'S SOLUTION

1. Introduction

Titanium alloys are widely used for orthopaedic and dental implants under load-bearing conditions because of their excellent characteristics such as chemical inertia, low density, mechanical resistance, absence of toxicity, resistance to corrosion and biocompatibility [1–4]. Among all titanium alloys, Ti-6Al-4V alloy is the most frequently used as hard tissue replacement in artificial bones, joints and dental implants [5–7].

The relatively poor tribological properties and possible corrosion problems using titanium implants require the surface engineering to increase near-surface strength, improving the hardness and abrasive wear resistance thereby reducing the coefficient of friction as well as avoiding or reducing the transference of ions from the surface or bulk material to the surrounding tissue [4, 7–10]. Titanium nitrides can effectively improve the corrosion and wear resistance of titanium alloys, so they are widely used in implants as coating material [8, 9, 11]. The addition of oxygen to titanium nitride (TiN) to form titanium oxynitride (TiN_xO_y) has recently attracted attention [8, 9, 12, 13]. This is due to the fact that titanium oxynitrides benefit from many remarkable properties of both insulating titanium oxides (chemical stability, optical properties) and metallic titanium nitrides (hardness, wear resistance). In comparison with TiN, titanium oxynitride has shown new interesting properties that can be used as biomaterials.

All the surgically implantable metallic materials, including the most corrosion-resistant materials, undergo chemical or electrochemical dissolution due to the influence of corrosive environment of human body [14, 15]. Therefore, the investigations of the corrosion behaviour of Ti-6Al-4V alloy with protective coatings in physiological solutions simulating the human body fluid are sufficiently urgent.

The purpose of this work is to study the corrosion resistance of Ti-6Al-4V alloy with nitride and oxynitride coatings at the change of temperature of the physiological solutions (0.9 % NaCl solution and Ringer's solution) from 36 °C to 40 °C.

2. Experimental procedure

The samples of ($\alpha+\beta$) Ti-6Al-4V alloy (Al – 6.0, V – 4.0, Fe – 0.25, C – 0.1, O – 0.15, N – 0.04, H – 0.015 wt. %, Ti – balance) of dimensions 15×10×1 mm were investigated. The samples were mechanically ground using different grades of SiC papers, followed by diamond polishing to a surface roughness of R_a=0.06 μm. Then they were ultrasonically cleaned with alcohol and dried.

Nitriding of Ti-6Al-4V alloy was conducted by the thermodiffusion treatment in nitrogen at 850 °C for 12 h. The partial pressure of nitrogen was 1 Pa.

Titanium oxynitrides were formed by the subsequent oxidation of preformed titanium nitrides in oxygen-containing gas medium on the cooling stage from 650 °C to 500 °C.

The phase of surface layers of Ti-6Al-4V alloy after thermodiffusion treatment was determined using X-ray diffractometer (XRD) with CuK_α radiation operated at 30 кV and 20 mA. The diffraction pattern profiles were refined by the Rietveld method with two different pseudo-Voigt functions using Powder Cell 2.4 [16] and Sietronix programs. 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.

Elemental analysis of the alloy surface after potentiodynamic polarization was evaluated using energy dispersive X-ray spectrometer INCA Energy 350.

The electrochemical tests of Ti-6Al-4V alloy with nitride and oxynitride coatings were carried out in isotonic 0.9 % NaCl solution and Ringer's solution ((in g/l): NaCl – 9.0; KCl – 0.43; $CaCl_2$ – 0.24; $NaHCO_3$ – 0.20) at temperatures of 36 °C and 40 °C. The transition from normal to inflammatory condition of the human body was simulated by the change of temperature of the solution. The potentiodynamic polarization curves were recorded using IPC-pro potentiostat in the potential range of -1.0...2.5 V at a scan rate of 2 mV/s. All potentials were measured against the Ag/AgCl reference electrode. Three-electrode glass cell with a platinum counter electrode and a saturated Ag/AgCl reference electrode was used. Surface of the working electrode of Ti-6Al-4V alloy was coated with epoxy resin, leaving area for exposure to the electrolyte of 1 cm^2.

3. Results and discussion

The nitride film delimited from the alloy matrix by diffusion zone was formed in the process of nitriding of Ti-6Al-4V alloy. According to the results of X-ray analysis (Fig 1 a), the film contains mainly Ti_2N phase (~ 65 %), represented by the (101), (111), (002), (320) and (321) reflections. At the same time the (111), (200) and (220) reflections of the weak relative intensity indicate on the presence of TiN phase (~ 4 %).

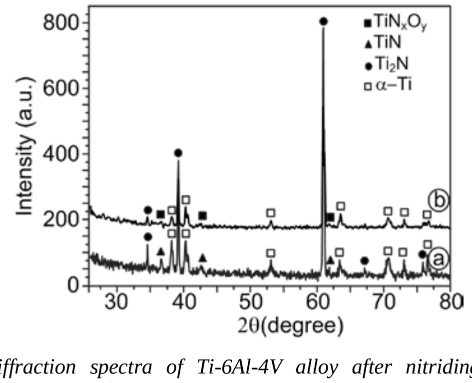

Fig. 1 *Diffraction spectra of Ti-6Al-4V alloy after nitriding (a) and subsequent oxidation of nitride coating (b).*

During oxidation of Ti-6Al-4V alloy with nitride coating the oxynitride film was formed on its surface. It is represented by the (111), (200) and (220) reflections (Fig 1 b). In addition, the reflections of Ti_2N phase and α-Ti phase are presented in the diffraction spectrum of the alloy.

The potentiodynamic polarization curves obtained for Ti-6Al-4V alloy with nitride and oxynitride coatings in isotonic 0.9 % NaCl solution and Ringer's solution at 36 °C and 40 °C are shown in Fig. 2–Fig. 5. Table 1 and Table 2 represent the corresponding corrosion parameters.

On the anodic branch of the potentiodynamic curve of Ti-6Al-4V alloy with nitride coating in 0.9 % NaCl solution at 36 °C (Fig. 2, curve 1) there are two peaks of the anodic dissolution at potentials of 0.07 and 0.3 V after the region of the active dissolution of the film. They are associated with the dissolution of the nitride film with the formation of corrosion products on the surface.

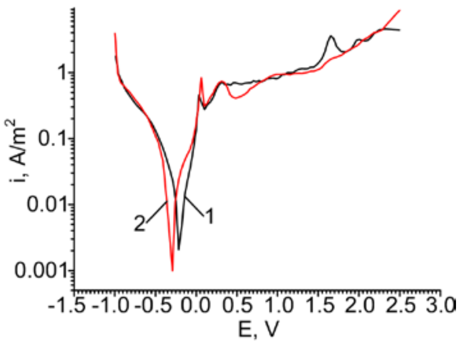

Fig. 2 *Potentiodynamic curves of Ti-6Al-4V alloy with nitride coatings in 0.9 % NaCl solution at 36 °C (curve 1) and 40 °C (curve 2).*

By increasing the temperature of the solution to 40 °C two peaks of the anodic dissolution are observed on the anodic branch of potentiodynamic curve also (Fig. 2, curve 2). The passive region is observed in the range of potentials 0.75…1.5 V. The passive current density is 0.9 A/m^2. This is due to the formation of more protective passive films on the surface which slow the anodic dissolution of surface. The decrease of chlorine content on the surface from 0.23 to 0.11 wt. % also indicates on the less dissolution of nitride film at 40 °C. The corrosion current density decreases in 1.5 times (Table 1).

Table 1: *Corrosion parameters of Ti-6Al-4V alloy with nitride coatings in physiological solutions.*

Physiological solution	36 °C		40 °C	
	i_k [A/m^2]	E_k [V]	i_k [A/m^2]	E_k [V]
0.9 % NaCl solution	0.006	-0.20	0.004	-0.30
Ringer's solution	0.020	-0.23	0.023	-0.41

On the anodic branch of the potentiodynamic curve of Ti-6Al-4V alloy with nitride coating in Ringer's solution at 36 °C (Fig. 3, curve 1) the anodic dissolution of surface film is occured to potential of 0.45 V. Further decrease of the anodic current density is obviously caused by the formation of unstable films on the surface, which then dissolve.

By increasing the temperature of the solution to 40 °C the corrosion current density of Ti-6Al-4V alloy with nitride coating isn't changed practically (Table 1). The first passive region is occurred in the range of potentials -0.1…0.4 V (Fig. 3, curve 2). The passive current density is 0.08 A/m^2. The second passive region is observed at the potentials of 1.10…1.34 V. It is due to the formation of more protective passive films on the surface. The passive current density is 0.3 A/m^2.

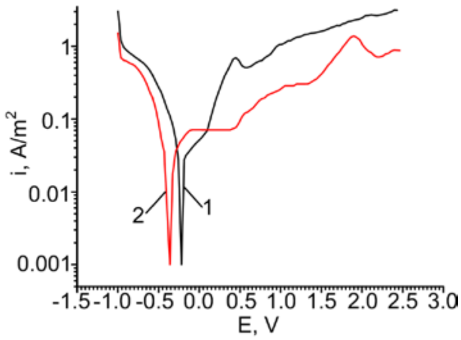

Fig. 3 *Potentiodynamic curves of Ti-6Al-4V alloy with nitride coatings in Ringer's solution at 36 °C (curve 1) and 40 °C (curve 2).*

Thus, increasing the temperature of both 0.9 % NaCl solution and Ringer's solution from 36 °C to 40 °C does not deteriorate the corrosion properties of Ti-6Al-4V alloy with nitride coating.

On the anodic branch of the potentiodynamic curve of Ti-6Al-4V alloy with oxynitride coating in 0.9 % NaCl solution at 36 °C (Fig 4, curve 1) the wide passive region at the potentials of 0.1….1 V is observed. The passive current density is 0.013 A/m^2. The existence of this passive region is caused by the resistance of oxynitride film formed in the process of oxidation of preformed titanium nitride. In addition, according to the results of the energy dispersive X-ray spectroscopy, the corrosion products on the base of titanium, oxygen and chlorine are formed on the surface in the process of polarization. It obviously provides the additional protection of the surface.

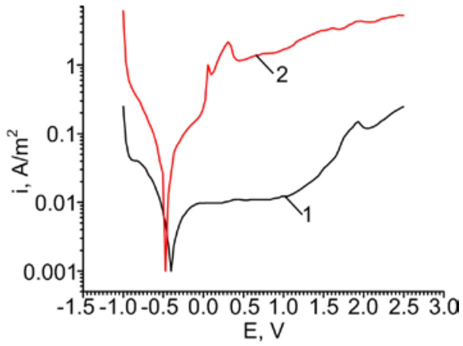

Fig. 4 *Potentiodynamic curves of Ti-6Al-4V alloy with oxynitride coatings in 0.9 % NaCl solution at 36 °C (curve 1) and 40 °C (curve 2).*

By increasing the temperature of the solution to 40 °C the corrosion current density increases in 6.5 times (Table 2) and corrosion potential shifts to more negative potential range (Fig. 4, curve 2). It indicates on the decrease of the corrosion resistance of oxynitride film.

Table 2: *Corrosion parameters of Ti-6Al-4V alloy with oxynitride coatings in physiological solutions.*

Physiological solution	36 °C		40 °C	
	i_k [A/m^2]	E_k [V]	i_k [A/m^2]	E_k [V]
0.9 % NaCl solution	0.002	-0.41	0.013	-0.43
Ringer's solution	0.017	-0.33	0.022	-0.40

On the anodic branch of the potentiodynamic curve of Ti-6Al-4V alloy with oxynitride coating in Ringer's solution at 36 °C (Fig. 5, curve 1) there is a wide passive region at the potentials of -0.1….0.7 V. It is due to the resistance of oxynitride film formed in the process of the oxidation of preformed titanium nitride. The passive current density is 0.06 A/m^2.

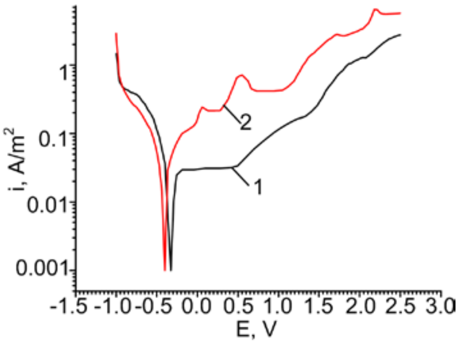

Fig. 5 *Potentiodynamic curves of Ti-6Al-4V alloy with oxynitride coatings in Ringer's solution at 36 °C (curve 1) and 40 °C (curve 2).*

By increasing the temperature of the solution to 40 °C the interaction of chloride ions with the surface intensifies: the content of chlorine increases to 1.14 wt.%. The corrosion potential shifts to more negative potential range and corrosion current density increases (Table 2). The short passive region is observed in the potential range of 0.10…0.25 V (Fig. 5, curve 2). The passive current density is 0.2 A/m^2. Further increase of the current density is caused by the dissolution of surface film. The passivation of surface is observed at the potentials of 0.65…1.0 V. The passive current density is 0.4 A/m^2.

Thus, increasing the temperature of both physiological solutions from 36 °C to 40 °C leads to decrease of the corrosion protection of Ti-6Al-4V with oxynitride coating, especially in 0.9 % NaCl solution.

4. Conclusions

Increasing the temperature of both 0.9 % NaCl solution and Ringer's solution from 36 °C to 40 °C, which simulates the environment of human body in normal and inflammatory conditions, does not deteriorate the protective function of nitride coating on Ti-6Al-4V alloy.

By increasing the temperature of the physiological solutions from 36 °C to 40 °C the corrosion protection of Ti-6Al-4V alloy by oxynitride coating is deteriorated due to an activation of the interaction of the surface with chlorine ions.

5. References

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