Corrosion Science 66 (2013) 392–398

Contents lists available at SciVerse ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Corrosion resistance of Ti–6Al–4V alloy with nitride coatings in Ringer's solution

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ARTICLE INFO

Article history:
Received 4 April 2012
Accepted 4 October 2012
Available online 18 October 2012

Keywords:
A. Alloy
A. Ringer's solution
B. Thermodiffusion saturation
C. Nitride coatings
C. Corrosion

ABSTRACT

The corrosion behaviour of Ti–6Al–4V alloy with nitride coatings was investigated in Ringer's solution at 36 and 40 °C. Nitride coatings of different composition, thickness and surface quality were formed because of changing nitrogen partial pressure from 1 to 10^5 Pa and nitriding temperature from 850 to 900 °C. Results shown that nitride coatings improve anticorrosion properties of alloy at both solution temperatures. Corrosion resistance of alloy increases with the content increase of TiN phase in nitride coating. With increase of temperature from 36 to 40 °C the corrosion resistance of alloy is determined significantly by quality of nitride coating.

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1. Introduction

Titanium has been widely used as a biomaterial since the late 1970s. It is caused by its better corrosive and osteointegrating properties compared to the other materials [1–4]. Titanium does not cause an allergy while an allergy on a nickel (required component of stainless steels) is the widespread phenomenon [5]. Application of titanium alloys in medicine is more promising than titanium because of their correlation specific weight is considerably higher compared to the stainless steel [6,7].

The efficiency of application of titanium alloys as implants in the state of delivery is lower significantly than after additional treatment (thermal, thermomechanical, chemical-thermal, etc.) [8–11]. Working in the conditions of the high contact and sign-changing loadings (implants of the orthopedic application), in the streams of bioactive environments (staples, pins, heart valves, etc.), titanium alloys need to improve such characteristics as wear-, corrosion resistance etc.

Nitriding can improve the above mentioned properties of titanium alloys. Titanium nitrides can be formed by various coating techniques: ion implantation [12,13], plasma methods [14–17], laser method [18], thermodiffusion treatment [19,20], etc. Among these methods, thermodiffusion treatment is promising, effective and economically sound method of surface engineering. It is technological, easily reproducible, can treat the workpieces of the arbitrary configuration (including poles), improve physico-chemical characteristics of the treated surfaces. Also it is the finish treatment, provides forming of coatings with high adhesion strength to the matrix by means of forming of the transition diffusion layers.

The corrosion resistance in physiological solutions which model the human body fluid is one of the basic criteria to choose the material as implant [21]. The corrosion behaviour of titanium alloys, in particular Ti–6Al–4V, was investigated in simulated physiological solutions (Ringer's, Hank's) at body temperature of 37 °C [22–24]. The results of investigations showed that above mentioned materials exhibited stable passive polarization behaviour. Alves et al. [25] investigated corrosion resistance of Ti and Ti–6Al–4V through electrochemical impedance spectroscopy and potentiodynamic polarization curves in Hank's solution at 25 and 37 °C. At 25 °C Ti–6Al–4V alloy showed similar corrosion behaviour to that of Ti. Unlike Ti, with increase of immersion time and solution temperature the corrosion resistance of Ti–6Al–4V decreased as a result of dissolution of the TiO_2 passive film. Burstein et al. [26] studied the effect of temperature (20, 37 and 50 °C) on the nucleation of corrosion pits on titanium in Ringer's physiological solution. The frequency of breakdown of the passive film increased significantly with increase of solution temperature.

Tian et al. [27] showed that TiN film deposited by arc ion plating provides effective protection for the Ti–6Al–4V substrate in Hank's solution at 37 °C. In contrast to the bare Ti–6Al–4V, no pitting was observed on the surface of the TiN filn deposited on the bare alloy after potentiodynamic polarization. Manhabosco et al. [17] evaluated the anticorrosive properties of plasma nitrided Ti–6Al–4V in phosphate buffer saline solution, simulating the body environment, at 37 °C. Nitriding increased the alloy resistance to corrosion.

Nowadays, it is a lack of data on the influence of increase of the temperature of physiological solution on the corrosion resistance of untreated titanium alloys and with coatings. Besides, the influence of phase-structural state of surface layers of titanium alloys, which is determined by the parameters of nitriding, on their corrosion behaviour in physiological solutions was not investigated.

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http://dx.doi.org/10.1016/j.corsci.2012.10.005

Purpose of this work is to study the influence of nitriding parameters and temperature of Ringer's solution on corrosion behaviour of Ti–6Al–4V alloy.

2. Material and methods

Ti–6Al–4V alloy, whose chemical composition is presented in Table 1, was used in this study. The samples of 15 × 10 × 1 mm were cut from the sheet, and were mechanically ground by different grades of SiC emery papers, polished by diamond pastes to a surface roughness of R_a = 0.4 μm. After polishing, the samples were ultrasonically cleaned. Then the samples were annealed in a vacuum (T = 800 °C, τ = 2 h, P = 0.05 mPa, I = 0.1 mPa dm^3 s^{-1} (inleakage rate)) to form the original phase-structural state (stress relaxation, dehydrogenization, homogenization and structure stabilization). Before nitriding samples were degreased in benzene, and washed with deionized water.

The thermodiffusion treatment of Ti–6Al–4V alloy in nitrogen was conducted, according to the next regimes (Table 2).

The samples were heated to the nitriding temperature in a vacuum of 10^{-3} Pa [20]. Heating rate was 0.040 °C/s. After the isothermal exposure, the samples were cooled in nitrogen at an average cooling rate of 0.028 °C/s. After cooling to 500 °C system was vacuumized.

Phase composition of surface layers after nitriding was determined by means of X-ray analysis (CuK_α radiation). The tube focusing system was made using Bragg–Brentano method. Voltage on the anode of X-ray tube was of 40 κV and current was of 30 mA. The scan step was 0.02° and rate was 10°/min. The diffraction pattern profiles were refined by the Rietveld method with two different pseudo-Voigt function using Powder Cell 2.4 and Sietronix programs [28], by means of which conducted Fourier analysis of diffractograms, determined the places of diffraction maximums of reflections, lattice parameters and phases content identified from data of card index of JCPDS-ASTM phases [29].

The profilograms of samples surface were received in the untreated state and after nitriding. The quantitative characteristics of surface microgeometry (height parameters of R_a, R_z, R_{max} and foot-pace parameters of S and S_m) were determined by special programs [30].

The microstructure and microhardness of surface layers were evaluated with mounted cross-sections of the samples after etching with Kroll's reagent. The microstructure of the treated samples was examined by optical metallographic techniques, scanning electron microscope EVO-40XVP with the system of microanalysis INCA Energy. Depth profile and surface microhardness measurements were obtained by means of Vickers indenter with a load of 50 g for 15 s.

The electrochemical tests of untreated Ti–6Al–4V alloy and with nitride coatings were carried out using IPC-pro potentiostat. The electrolyte used for simulating human body fluid condition was Ringer's solution, prepared using laboratory grade chemicals and double distilled water. The composition of Ringer's solution was (in g/l): NaCl – 9.0; KCl – 0.43; $CaCl_2$ – 0.24; $NaHCO_3$ – 0.20 [31,32]. Experiments were performed at (36 ± 0.5) and (40 ± 0.5) °C, using three-electrode glass cell (50 ml) with a platinum counter electrode and a saturated Ag/AgCl with 3 M KCl (+0.207 V vs. SHE) reference electrode. 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. Ringer's solution was maintained at 36 and 40 °C throughout the tests. Upon immersion of the samples into Ringer's solution, the open-circuit potential was measured as a function of time for 1 h at 0.5 s intervals. The polarization curves for Ti–6Al–4V alloy were recorded in the potential range −1.0...2.5 V vs. Ag/AgCl at a scan rate of 2 mV/s. The corrosion potential and corrosion current density were determined from the polarization curves by Tafel extrapolation method. The tests were repeated at least three times for each sample.

Table 1
Chemical composition (wt.%) of Ti–6Al–4V alloy.

Alloy	C	H	N	O	Fe	Al	V	Ti
Ti–6Al–4V	0.1	0.015	0.04	0.15	0.25	6.0	4.0	Bal.

Table 2
Nitriding regimes of Ti–6Al–4V alloy.

Coating	Nitriding parameters			
	T, °C	t, h	p_{N2}, Pa	I, Pa/s
I	850	12	1	7 × 10^{-3}
II	850	12	10^5	Static conditions
III	900	12	10^5	Static conditions

3. Results and discussion

3.1. Nitriding

The nitride coating is formed as the result of nitriding of Ti–6Al–4V alloy. It contains the nitride zone and diffusion zone (solid solution of nitrogen in α-titanium), according to the results of X-ray analysis (Fig. 1, Fig. 2). The nitride zone consists of cubic δ-TiN phase and ε-Ti_2N phase. The portion of each nitride depends on the nitriding regime (Fig. 3). Investigations showed that after nitriding in the rarefied nitrogen (coating I) the portion of TiN in nitride zone is 4%, while in nitrogen of atmospheric pressure (coating II) – 67%. After nitriding in nitrogen of the atmospheric pressure at higher temperature (coating III) the portion of TiN in the nitride zone is lower (58%). That's why, the nitride zone of coating I is mainly composed of Ti_2N. It's confirmed also by the results of energy-dispersive X-ray spectroscopy (Fig. 4): the content of nitrogen in surface layer is 9.66 mas.% (26.77 at.%). TiN prevails in nitride zone of coatings II and III.

The presence of α-titanium lines on the diffractograms with increased interplanar spacings indicates on the formation of diffusion layer which separates the nitride zone from matrix. The lattice parameter of titanium increases durinh forming of the interstitial solid solutions (Table 3). Data from the table demonstrate that the pressure during nitriding is the most significant factor affecting saturation of nitrogen in titanium.

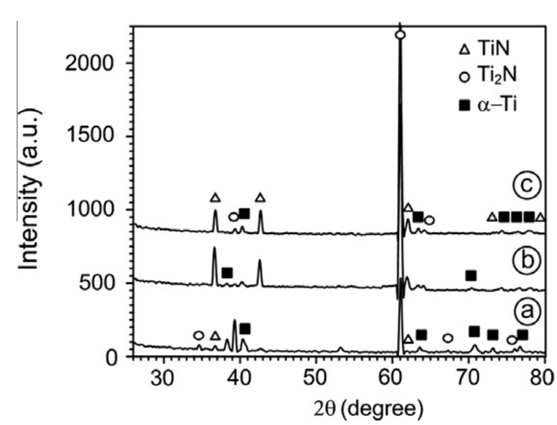

Fig. 1. X-ray diffraction patterns of Ti–6Al–4V alloy after different regimes of nitriding: a – I; b – II; c – III.

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