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Tribocorrosion behaviour of plasma nitrided and plasma nitrided + oxidised Ti6Al4V alloy

A.C. Fernandes [a,*], F. Vaz [a], E. Ariza [b], L.A. Rocha [b], A.R.L. Ribeiro [b], A.C. Vieira [b], J.P. Rivière [c], L. Pichon [c]

[a] *Universidade do Minho, Dept. Física, Campus de Azurém, 4800-058 Guimarães, Portugal*
[b] *Universidade do Minho, Dept. Eng. Mecânica, Azurém, 4800-058 Guimarães, Portugal*
[c] *Laboratoire de Métallurgie Physique, Université de Poitiers, 86960 Futuroscope, France*

Abstract

This paper reports the influence of low pressure plasma nitriding treatments, some of them followed by plasma assisted oxidation on the mechanical properties and tribocorrosion resistance of a Ti6Al4V alloy. Nitridation was performed for 640 or 720 min at 600 and 700 °C in a r.f. plasma equipment, using a N_2–H_2 gas mixture at 7.5 Pa. Some of the samples were then post-oxidized at 700 °C for 15 and 60 min, within a O_2 plasma of 9.5 Pa. XRD results revealed the occurrence of the Ti_2N phase for the nitrided samples. The oxidized surface layers are poorly crystallised with rutile and traces of anatase TiO_2 nanocrystallites. Microhardness tests showed a significant improvement of the surface hardness whatever the treatment, with a slight effect of the treatment temperature. The tribocorrosion results clearly showed that plasma treatments have a strong influence on the tribocorrosion behaviour of the material. Both the corrosion and wear performance of the samples are improved by the increase of the processing temperature.

Keywords: Titanium; Pin-on-disc; X-ray diffraction; Plasma treatment

1. Introduction

Ti6Al4V (wt.%) is one of the most used titanium alloys due to its lower density than pure titanium, but with more favourable physical and mechanical properties. Those properties make it of particular interest in biomaterials and aeronautic applications [1–5]. This material has a two-phase structure: a hexagonal α-Ti phase with aluminium in solid solution and a β-Ti phase with vanadium stabilised cubic lattice [6]. This biphase structure contributes to a higher mechanical strength compared to pure Ti [6]. However, the use of this alloy in everyday life applications is still very limited due to its poor wear resistance [2,4,7,8]. In case of oxidant or corrosive atmospheres, the degradation is even worse, leading to the inevitable replacement of the working pieces. Thus, surface treatments such as nitridation or oxidation are being investigated as possible solutions to improve the surface properties of this alloy [4,9–12]. Acting as a diffusion barrier, the nitride layer and the underneath gradient relate a decrease of solubility and also the diffusivity of nitrogen compared to the pure alloy, and thus preventing further oxygen dissolutions deeper into the alloy [10].

Taking this into consideration, the main purpose of this work was to carry out protective oxygen and nitrogen plasma treatments on Ti6Al4V samples, in an original apparatus previously described [13]. The temperature and the duration of the treatments were the studied parameters. These treatments modified the surface structure by the formation of different crystalline phases such as TiO_2, Ti_2N, TiN and α-Ti(N,O) (solid solution of nitrogen and oxygen in titanium) [5,14]. The presence of these crystalline phases results in hardness enhancement of the material [15], and may consequently increase its wear and the corrosion resistance properties in many aggressive environments [7].

2. Experimental

The surface treatment reactor chamber is composed of a quartz tube surrounded by a tubular furnace, allowing the temperature control from room temperature up to 1000 °C [13].

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[*] Corresponding author. Tel.: +351 253 510475; fax: +351 253 510461.
E-mail address: acrist@fisica.uminho.pt (A.C. Fernandes).

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The base pressure in the chamber was about 10^{-5} Pa. Two samples, A and B, were nitrided for 14 h at 600 °C and 12 h at 700 °C, respectively, in a 7.5 Pa atmosphere. A N_2–H_2 (50%–50%) gas mixture was used. The gas reactivity was activated by a radio-frequency (r.f.) electromagnetic excitation (forward power: 700 W), resulting in the creation of a cold plasma (ion density about 10^9 ions/cm^3). In order to study the influence of oxidation, samples B-ox1 and B-ox2 were oxidised at 700 °C with r.f. plasma (700 W) for 15 to 60 min, respectively, in a 9.5 Pa pure oxygen atmosphere, after the 700 °C nitridation process (12 h). The oxidation of sample B-ox1 was carried out after the nitridation without cooling the sample. Sample B-ox2 was cooled after the nitridation to room temperature, and then heated again for the oxidation. For comparison purposes, a solely oxidised sample, ox2, was also prepared at 700 °C for 1 h. The thermal cycle of the nitriding was carried out by heating the samples up to 50 °C below the desired temperature at a rate of 20 °C/min. The last 50 °C was carried out at a rate of 20 °C/min.

Chemical depth profiles were obtained by Glow Discharge Optical Emission Spectroscopy (GDOES), on a Jobyn-Yvon RF-GD Profiler. Structure was investigated by X-ray diffraction (XRD), using a Siemens D5005 diffractometer (Cu Kα monochromatic radiation). Microhardness was measured on a SHIMADZU HMV 2000 apparatus, equipped with a Vickers indenter. The measurements were performed on the sample surface and cross-sections (using a “sandwich” of two samples with treated faces glowed together), using 100 and 25 g during 15 s, respectively.

Wear-corrosion experiments were carried out in a pin-on-plate tribometer (Plint TE67/R) with an alumina pin. The contact was immersed in a 0.9 wt.% NaCl electrolyte and all open-circuit potentials (OCP) were measured and expressed with reference to a saturated calomel electrode (SCE), and a platinum wire with an area of 1 cm^2 was used as counter electrode. The displacement amplitude was 3 mm and the normal load was fixed at 3 N. Electrochemical Impedance Spectroscopy (EIS) measurements were performed before and after the sliding at open-circuit potential in the frequency range of 100 kHz to 10 mHz, applying an ac current with an amplitude of 10 mV. The area of the working electrode was set at 0.64 cm^2. A PGP201 Potentiostat/Galvanostat (Radiometer Analytical, Denmark), controlled by the VoltaMaster software, was used to carry out the polarization measurements, while a Voltalab PGZ100 Potentiostat (Radiometer Analytical, Denmark), controlled by the VoltaMaster-4 software, was used for the EIS measurements.

3. Results

3.1. Surface composition

Results of chemical profiles obtained by GDOES are shown in Fig. 1, illustrating 4 of the analyzed samples. On the top surface of all samples, a pollution and native oxide layer of few nanometers was found. Below this layer, the nitrided samples revealed a nitride layer of about 0.25 μm at 600 °C and 0.7 μm at 700 °C, and close to an average Ti_2N stoichiometry. These results are in agreement with the literature data and the N diffusion coefficient in Ti, Ti_2N and TiN [16].

Regarding the Ti6Al4V sample oxidized for 1 h (Ox2), an oxide layer of about 0.5 μm can be observed. The oxygen composition of the whole oxide layer (~55 at.%) is slightly

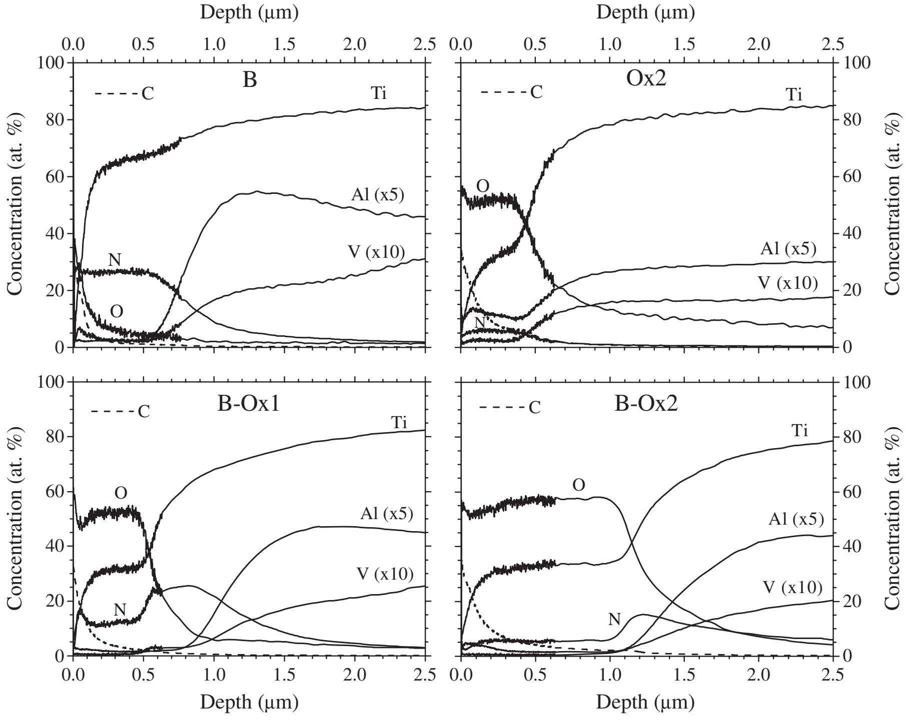

Fig. 1. Element profiles obtained by GDOES for B, Ox2, B-Ox1 and B-Ox2 samples. The results obtained for Al and V are multiplied by 5 and 10, respectively.