



Improvements of the surface properties of Ti6Al4V by plasma based ion implantation at high temperatures

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ABSTRACT

Ti6Al4V is a titanium alloy that has many applications in aerospace industry due to its good mechanical and corrosion properties, but its poor tribological characteristics can restrict the use of this material. In order to modify its surface properties, nitrogen PBII treatments were performed. Here, an auxiliary heating system was used to reach the required high temperatures, which can improve the nitrogen diffusion in the titanium alloy. As a consequence, the modified thickness could be increased substantially. After nitrogen PBII experiments, the Ti6Al4V alloy surface properties were evaluated by potentiodynamic polarization, electrochemical impedance spectroscopy, nanoindentation and pin-on-disk tests. The morphology of the surface after corrosion tests was obtained by SEM. The surface properties of the Ti6Al4V alloy were improved after PBII, showing better performance in corrosion, mechanical and tribological tests.

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1. Introduction

Titanium and its alloys have been widely used as biomedical implant materials due to their high strength-to-weight ratio, excellent corrosion resistance and biocompatibility [1,2], besides being largely used in the industries, such as, aeronautic, aerospace, food and chemical. However, the applications of titanium and its alloys are limited because of their poor wear resistance.

The surface modification techniques have been widely used for the improvement of many types of materials, such as titanium and its alloys. Ion implantation offers unique possibilities [3–5] for a large number of actual and potential applications, in widely varying fields of modern technology. Energetic ions are stopped in a near-surface layer after a slowing-down process far from thermal equilibrium, with local cooling rates which are faster by several orders of magnitude compared to any other treatments. Thus, metastable phases and new materials may be generated [6].

The material used in this study was the Ti6Al4V alloy, and the nitrogen plasma-based ion implantation (N-PBII) [7–13] technique was used. In this work, we studied the effects of N-PBII at low energy and high temperatures into Ti6Al4V, looking for improvements in the surface properties of this alloy. N-PBII experiments employing low energy ions (5 keV) were performed mainly, in order to avoid the sputtering of the implanted nitrogen ions of the treated layer. A higher implantation voltage may lead to more extensive sputtering of the

surface, consequently, a lesser amount of incorporated nitrogen in the modified layer. Furthermore, voltages higher than 5 kV led frequently to repetition of arcs which could cause the breakdown of the H.V. pulser and damages to the samples surface. When the temperature exceeds 250 °C, diffusion of implanted species (such as nitrogen ions) plays a significant role in certain metals. As the pieces are fully immersed in the plasma during PBII process, at high temperatures, inward and outward diffusion of nitrogen occurs. Inward diffusion is greater than outward because of high N concentration at the very near surface [10]. This procedure can lead to large retained doses of nitrogen that can result in the improvement of the surface properties of the treated titanium alloy.

The microstructure of the modified surface layers was analysed using SEM. The electrochemical behavior of the treated and untreated specimens was evaluated by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) tests. The mechanical and tribological properties were measured by nanoindentation and pin-on-disk tests, respectively.

2. Materials and methods

Ti6Al4V samples were prepared as received in the commercial form, machined, then they were polished until reaching mirror finish with diamond paste. Prior to loading into the PBII chamber, the specimens were ultrasonically cleaned with acetone.

Nitrogen PBII (N-PBII) experiments were carried out varying treatment time and temperature. In these experiments, the nitrogen glow discharge plasma at pressures of about 6×10^{-3} mbar was used and the high voltage pulses at 5 kV, with 40 μs pulse length, 400 Hz

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repetition rate were applied to the sample-holder. The treatments were carried out for 1, 2 and 4 h. PIII process at high temperatures (close to 800 °C) can promote thick nitrogen-rich layer and enhance the N diffusion in the Ti6Al4V alloy. High temperatures of the specimens were reached by using an auxiliary heating system developed by our research group, according to scheme presented in Refs. [14–16]. The treatment temperatures investigated in the present work were 660 °C and 760 °C.

After PBII processing, the samples were tested to evaluate their new properties. The corrosion resistance was estimated by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). In these tests, a conventional cell of three electrodes (work electrode, reference electrode (Ag/AgCl|KCl_{3M}) and a platinum wire as auxiliary electrode) was employed. As the electrolytic solution, NaCl 3.5 wt.% at room temperature was used. All EIS measurements were carried out after seven days of immersion in salt solution, for the open circuit potential (OCP) stabilization. In these tests, AC signal of 5 mV (rms) were applied to the work electrode, starting from 10⁵ Hz to 10^{−2} Hz and 10 measurements per frequency decade. The polarization curves were recorded from −1.0 V to 1.5 V vs. Ag/AgCl at 1 mV/s scan rate. These corrosion tests were performed using an Autolab potentiostat/galvanostat, PGSTAT-302 model, and the data were obtained by FRA and GPES softwares.

After corrosion tests, the samples were also investigated using scanning electron microscopy (SEM) to disclose the appearance and structures of the corroded surfaces. The SEM measurements were carried out using a microscope JEOL, JSM-5310 model.

The nanomechanical properties were measured by nanoindentation technique using the MTS, Nano Indenter XP model, varying the load from 0.4 to 100 mN. The tribological properties were measured using a CSM-Instruments Pin-on-disk Tribometer. All wear experiments were conducted with 3 mm diameter alumina (Al₂O₃) balls in sliding contact and carried out with a load of 1 N at a sliding velocity of 5 cm/s, 3 mm of wear track radius, stopping at 1000 revolutions at room temperature in air. After these pin-on-disk tests, the wear track profiles were measured employing a profilometer TENCOR, Alfa-Step 500 model.

After the treatments, AES was applied to find out the nitrogen concentration inside the samples. Nitrogen and other elements depth profiling were obtained using a FISON Instruments Surface Science, model MICROLAB 310-F spectrometer with Ar ion sputtering.

3. Results and discussion

The electrochemical behavior of the Ti6Al4V titanium alloy, before and after N-PBII processing, was investigated by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization. The first method is a powerful tool to evaluate corrosion process in detail. The impedance data will be compared before and after the nitrogen PBII process, in order to verify the influence of the treatment time and temperature.

The Nyquist and Bode plots for all samples are shown in Fig. 1 (a) and (b), respectively. The Nyquist plot for unimplanted sample shows a tendency to a capacitive semicircle. In Fig. 1(a), it was observed that, after the N-PBII treatments, the samples presented an increase in the capacitive arcs diameter, with the exception of the implanted sample during 1 h at 660 °C. It was verified that these samples had a tendency to two semicircle formation, e.g., two time constants. These behaviors can be attributed to the formation of two different protective layers on the surface of the treated alloy during corrosion tests, i.e., two electrochemical processes occurs on two different time scales: an outer porous layer and an inner compact layer, which act as protective barriers. This performance, shown for the samples treated at different temperatures and processing time, is an evidence of the increase in the corrosion resistance of the N-PBII treated Ti6Al4V.

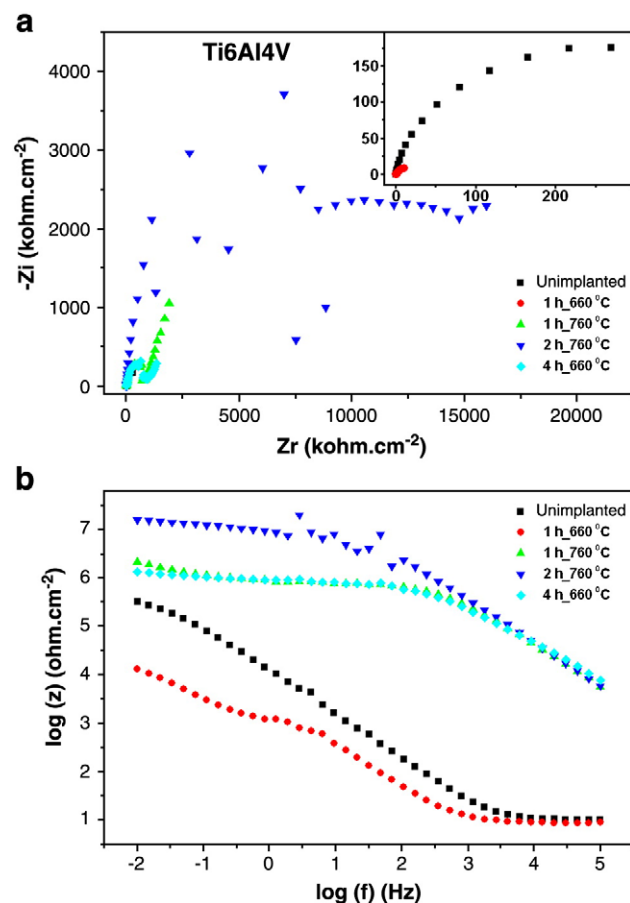


Fig. 1. EIS spectra for unimplanted and implanted samples by PBII.

The major impedance values presented in the respective Bode plots (Fig. 1b) indicate the enhancement of the corrosion resistance of the alloy after N-PBII at higher temperatures (760 °C). These samples showed impedance values which are one and two orders of magnitude higher than the reference and, consequently, more polarization resistant. The impedance value for unimplanted Ti6Al4V was 300 $\text{k}\Omega \cdot \text{cm}^2$ at low frequencies. After N-PBII, the impedance value of about 1600 $\text{k}\Omega \cdot \text{cm}^2$ was observed for the case of the sample treated during 1 h. For sample treated during 2 h, this value was of about 16,000 $\text{k}\Omega \cdot \text{cm}^2$. In both cases, the achieved temperature was 760 °C. The sample implanted at 660 °C during 4 h, showed similar behavior to the sample implanted at 760 °C, during 1 h. An overlap of Bode plots was verified for these implanted samples. Only in the case of sample treated during 1 h at 660 °C, this higher performance was not observed.

In the diagrams presented in Fig. 1, it was possible to verify that the treatment performed during 2 h at 760 °C, promoted the best performance against corrosion.

The large data dispersions on Nyquist diagrams are evidences of metastable layer formation. This can be confirmed by the shape of the polarization curves presented in Fig. 2. In this figure, a shift of the anodic branches (superior part of the curves) of all implanted samples to lower current densities was observed. Before N-PBII, the passive current density was of about 10^{-5} Acm^{-2} and, after the treatments, the measured values were of about 10^{-6} Acm^{-2} . This reduction, of about ten times on passive current densities, indicated a large increase of corrosion resistance for this alloy after nitrogen implantation at high temperatures. In the nitrogen PBII treatments at 800 °C [Refs. 17,18] and in the treatments of this work, the polarization curves analysis indicated that the corrosion rate is very similar for all the treated samples at high temperature, i.e., the corrosion current density values are very similar. For all treatments at temperatures between 660 °C and 800 °C, the

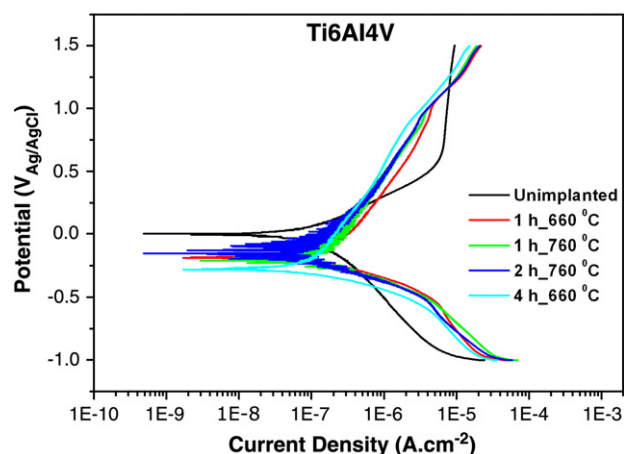


Fig. 2. Polarization curves of the unimplanted and implanted samples by PBII.

corrosion potential was below the corrosion potential of the untreated sample. A very resistant passive layer was formed in the surface of the treated samples of this work, much more resistant than that formed in the treated samples at 800 °C. This is evidenced by the reduction of one order of magnitude of the passive current densities.

The Ti6Al4V samples morphology after corrosion tests was evaluated by the analysis of the scanning electron microscopy (SEM) images, as can be seen in Fig. 3. It was verified that the unimplanted sample displays some deep attacks. Pitting formation was mainly observed in the α phase regions. For the implanted samples, it was verified that, after N-PBII, the microstructure was revealed in all cases. As sputtering also occurs during N-PBII process, the samples showed a clear distinction between α (light) and β (dark) phases, after the treatment. Besides, it was possible to observe the grain boundary on the surface alloy. Same observations were seen by L.L.G. da Silva et al. in Ref. [18]. The Ti6Al4V surfaces submitted to corrosion tests exhibited less intense attacks after nitrogen implantation at high temperatures than before these treatments.

Nanoindentation testing was used to characterize the mechanical properties on a very small scale. The hardness profiles, presented in Fig. 4, shows that, after all treatments, the surfaces became more mechanically resistant, due to the high hardness. The best result of hardness was obtained for Ti6Al4V alloy implanted during 4 h at 660 °C. Its hardness values increased about 100% in relation to the unimplanted alloy. Before N-PBII, the surface presented a surface hardness of 6.1 GPa, and after the treatment, this value increased to 12.9 GPa. In the other cases with N-PBII treatments, the surface hardness values were very much similar, of about 9 GPa, representing an increase of about 50%.

The improvement of the mechanical strength was probably caused by the formation of new compounds in the implanted surfaces. Moreover, the nitrogen atoms introduced in the alloy surface by PBII can generate propagation of defects in the crystal lattice. These changes on the crystalline lattice, that can make the movement of the dislocations more difficult, combined with the formation of the new nitrogen compounds, promoted the increase in the hardness values of the implanted surfaces [16]. This increase of the surface hardness resulted in a reduction of the wear of implanted alloy. Pin-on-disks tests showed that the implanted samples had smaller wear tracks volume. The sample treated by N-PBII during 4 h at 660 °C presented the largest reduction of the wear. For this case, a reduction of about 40% was observed, when compared to the unimplanted Ti6Al4V. The other implanted samples also presented reduction of the wear, but in a smaller scale.

Besides wear evaluation by pin-on-disks tests of the treated samples, the friction coefficient was also measured. In Fig. 5, it can be seen that, after nitrogen implantation at high temperatures, a

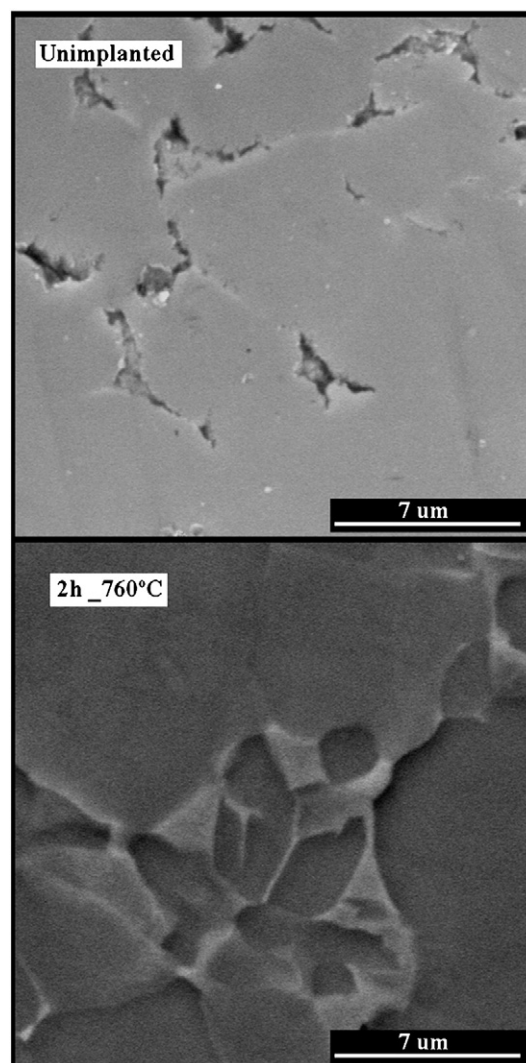


Fig. 3. SEM image of the Ti6Al4V alloy: untreated sample and PBII-treated sample at 760 °C (2 h) after corrosion.

reduction of the friction coefficient the Ti6Al4V titanium alloy occurred. Before N-PBII, this value was 0.35, changing to about 0.15 after the treatments, generally, in the beginning of the test. The delayed increase of the friction coefficient of the treated samples within the first 100–200 revolutions is due to the modified layer

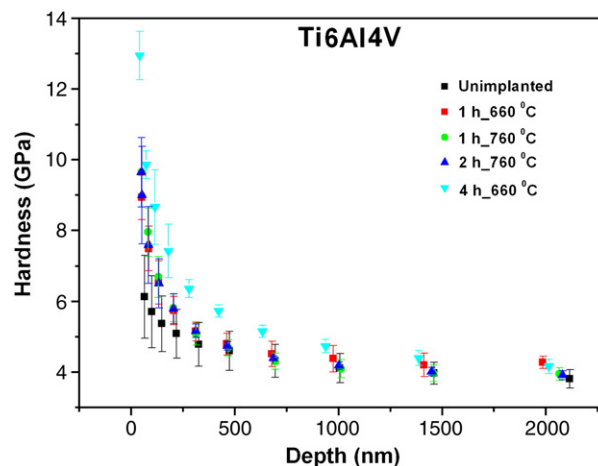


Fig. 4. Hardness profiles for Ti6Al4V samples before and after treatments.

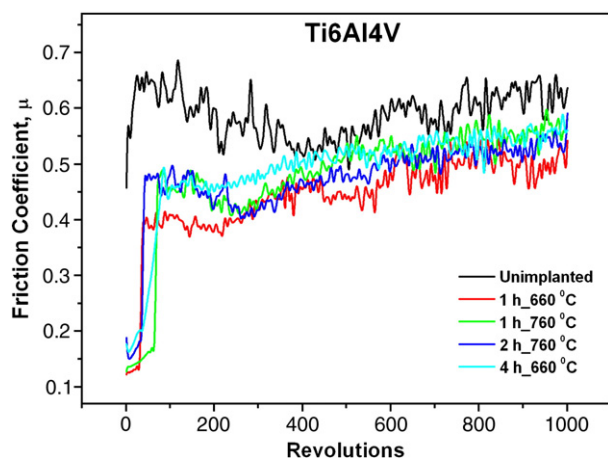


Fig. 5. Friction coefficients measurements for Ti6Al4V samples before and after treatments.

caused by the PBII process and, probably, the compound formation on the surface. It was observed that the treated samples presented very similar behavior until 400 revolutions approximately, i.e., all the samples presented the same average value of the friction coefficient, but a lower value than the unimplanted sample. After that, all implanted samples showed friction coefficient with a tendency to reach the same level of the unimplanted sample. This fact can be due the removal of the implanted layer after 400 revolutions, when the pin reaches the material bulk.

In the spectra of the AES analysis (not shown here), it was possible to verify that implanted samples treated during long times presented thicker layers. The sample treated during 2 h at 760 °C and 4 h at 660 °C showed a N-rich layer with thickness of about 90 nm and 140 nm, respectively. Meanwhile, the samples treated during 1 h showed implanted layers with 25 nm of thickness. Compared to the previous results of PBII at high temperature (up to 800 °C) in the same alloy [18], the depth profiles obtained for samples treated at 760 °C and 800 °C were very similar. The small difference in the treatment temperature (40 °C) did not have a great influence in the thickness of the N-rich layer.

These changes in the composition of the Ti6Al4V alloy surface resulted in the improvement of its properties. The final modified layer is a result of the implantation in the first nanometers, diffusion caused by the high temperature and treatment time and sputtering process. However, the enhancement of the properties against corrosion did not necessarily imply improvements in its tribological and mechanical properties.

4. Conclusions

Nitrogen PBII in high temperatures were carried out to improve the surface properties of the Ti6Al4V titanium alloy. After N-PBII,

better performances of the alloy were observed with respect to corrosion, mechanical and wear resistances. The best behavior against corrosion attack was reached in the treatment performed during 2 h at 760 °C.

The best result of mechanical resistance was obtained for sample implanted during 4 h at 660 °C. This new feature of the N-PBII treated Ti6Al4V alloy promoted a reduction on its wear. The friction coefficients of the treated samples were reduced by about 130% when compared with non treated sample.

Based on these results, it was possible to infer that the increase of the treatment time does not lead to a major corrosion resistance, but the increase of the temperature was very effective. However, in the case of mechanical and tribological properties, the increase of the processing time was more important, as it could be seen by the higher hardness and lower wear obtained after the nitrogen implantation during 4 h at 660 °C. The high temperatures employed in this work promoted the improvement of the surface properties of the Ti6Al4V alloy, even using nitrogen ions at low energy (~5 keV).

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