# Electrochemical behavior of the Ti6Al4V alloy implanted by nitrogen PIII

G.S. Savonov [a,b,*], M. Ueda [b], R.M. Oliveira [b], C. Otani [a]

[a] Instituto Tecnológico de Aeronáutica — ITA, Praça Marechal Eduardo Gomes, 50 Vila das Acácias, CEP 12228-900, São José dos Campos, SP, Brazil
[b] Instituto Nacional de Pesquisas Espaciais — INPE, Av. dos Astronautas, 1758, Jardim da Granja, CEP 12227-010 São José dos Campos, SP, Brazil

## ARTICLE INFO

## ABSTRACT

Plasma surface treatments have been used very often to enhance the surface properties of metallic materials. In this work, Ti6Al4V titanium alloy was treated by nitrogen plasma immersion ion implantation (NPIII) in order to obtain improvements in its surface properties, such as corrosion resistance evaluated here. The microstructure and corrosion behavior of the implanted and unimplanted samples were evaluated, using, XRD, GDOES and potentiodynamic polarization and impedance electrochemical spectroscopy tests in 0.6 M NaCl solution. It was verified that the NPIII created resistant layers to corrosive attacks. In corrosion tests by polarization, the implanted samples showed corrosion current density reduction of about 10 times compared to the Ti6Al4V alloy without treatment. Besides that, it was also observed a reduction of the passive current density of one order of the magnitude. In all the studied cases, the polarization curves were shifted to more positive values of potentials, indicating a lower tendency of these PIII treated surfaces to corrosion. The implantation process produced a thin TiN surface layer followed by Ti$_2$N and then a layer with nitrogen in solid solution, all detected by GDOES combined with X-ray diffraction. These layers promoted an excellent polarization resistance of the Ti6Al4V surfaces on impedance spectroscopy tests also. This better performance in these tests can be correlated with the formation of continuous nitride layer, which could retard chloride ions ingress into the substrate.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

Many surface modification methods have been applied to materials aiming at increasing their corrosion resistance by the application of coatings, such as film deposition by PVD, PECVD, sol–gel and electrochemical methods, for instance. Although the deposited films provide good corrosion resistance of the coated surfaces, the adhesion of these films is often a critical problem that limits their use in practical applications. In this context, plasma immersion ion implantation (PIII) [1–10], appears to be a good alternative for adequacy and functionalization of surfaces of various types of materials, improving their surface properties by ion implantation. Through the technique of PIII, a thin modified layer is produced by adding atoms to the subsurface of the material being treated and that results in the chemical and physical modification of the crystaline structure in that region very close to the surface. As the concentration gradient of these new elements is small, a diluted interface is formed without the occurrence of film formation. Thus, delaminations are avoided, as happen in many cases with films deposited by other techniques.

This article deals with the behavior of the Ti6Al4V titanium alloy after surface treatments by nitrogen plasma immersion ion

implantation in high temperature (800 °C), focusing into the corrosion process. Using nitrogen or oxygen PIII, thin modified surface layers between 50 and 500 nm are obtained in the temperature range from 265 to 750 °C, with sufficient nitrogen diffusion into the alloy bulk around 400–500 °C, as our previous results show [11,12]. For low temperature implantations, oxygen and nitrogen depth profiles were found to be in accordance with the calculated ion ranges. This indicates high fluences beyond sputter saturation without any additional diffusion of the implanted atoms. Diffusion of nitrogen in titanium at temperatures above 300 °C leads to the evolution of the profiles ressemble those obtained theoretically. Oxygen in Ti and Ti6Al4V results in a mixture of both processes with titanium diffusing toward the surface and forming a closed titania layer while oxygen diffusing into the bulk leads to interstitial oxygen within the titanium matrix. Correspondingly, closed layer of TiO$_2$ (rutile), respective TiN, followed by a diffusion layer with oxygen or nitrogen in solid solution have been observed [13].

## 2. Materials and methods

Ti6Al4V alloy samples were prepared in disk shape, mechanically polished, followed by ultrasonic cleaning before plasma immersion ion implantation treatments. PIII implantation experiments were performed using a pumped vacuum chamber, a gas injection and plasma systems and a high voltage pulser. The samples heating was carried out by thermionic effect, as described in details by Oliveira et al.

* Corresponding author at: Instituto Nacional de Pesquisas Espaciais — INPE, Av. dos Astronautas, 1758, Jardim da Granja, CEP 12227-010 São José dos Campos, SP, Brazil. Tel.: +55 1232086881; fax: +55 1232086890.
E-mail addresses: grazielads@ig.com.br, graziela.savonov@inpe.br (G.S. Savonov).

[14]. The implantation experimental conditions are presented in Table 1.

The corrosion resistance of titanium alloy was evaluated by potentiodynamic polarization and the electrochemical impendance spectroscopy (EIS) measurements. They were carried out using an Autolab Potentiostat/Galvanostat system, PGSTAT 302N model. A three electrode electrochemical cell was used with a platinum wire as counter electrode, Ag/AgCl electrode as the reference electrode and the Ti6Al4V samples were the work electrodes. All the electrochemical tests were performed in 0.6 M NaCl solution at room temperature. The lower and upper potential limits of linear sweep voltammetry were set at $-1$ V and 1.5 V and the sweep rate used was 1 mV/s. The Tafel plots, i.e., polarization curves were obtained after these electrochemical measurements.

For impedance tests, the samples were kept in the solution for 7 days prior to the connections, in order to establish the open circuit potential (OCP) or the steady state potential. These measurements were conducted using a frequency response analyzer. The spectrum was recorded in the frequency range of 10 mHz–100 kHz with a data density of 10 points per decade. The applied alternating potential had a root-mean square amplitude of 5 mV on the open circuit potential. After each experiment, the impedance data were recorded as Nyquist and Bode plots.

The phase composition of the surface alloy before and after PIII treatments was investigated by XRD diffraction with CuKα radiation, using a Philips/Panalytical diffractometer, X'Pert PRO MPD model. The nitrogen profile depths were obtained by Radio-Frequency Glow Discharge Optical Emission Spectrometry (GDOES) on a Horiba-Jobin-Yvon GD profiler.

## 3. Results and discussion

The analysis of the corrosion resistance of implanted samples treated during 1 h, applying high voltage pulses of 7, 10 and 12 kV, was based on the polarization curves presented in Fig. 1. In this figure, it was observed that after these three treatments, the surfaces showed better resistance against corrosion. The polarization curves of the treated samples were shifted to the left, indicating a remarkable reduction in corrosion current densities and also in the passive current densities. The untreated standard sample, presented corrosion current density of $1.2 \times 10^{-6}$ A cm$^2$. After treatments, the current densities values presented by the implanted samples were approximately ten times smaller, as it can be seen by values presented in Table 2. Another factor that reveals the best behavior of the treated alloy in the corrosion tests was the increase of the values of corrosion potentials provided by these samples. Because more positive values of corrosion potentials indicate a lower tendency to the corrosion process.

It was verified that the increasing of the high voltage pulses applied to the treatment of Ti6Al4V alloy by nitrogen PIII at high temperatures did not result in a greater increase in the corrosion resistance of that surface. Because when the alloy was implanted with nitrogen ions at 7 and 10 keV the polarization curves were overlapping, and when the alloy was treated at 12 keV showed a smaller shift in the anodic branch, providing the corrosion current density and passive current density that were slightly lower than for the two previous samples.
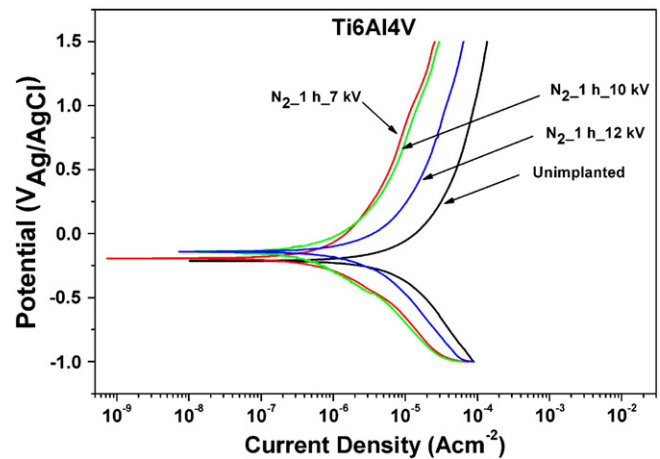


**Fig. 1.** Polarization curves of the treated and untreated samples by N$_2$ PIII, with different high voltage pulses.

When the treatment time was increased from 1 h to 1 h and 40 min, we obtained the polarization curves of Fig. 2 that showed that the samples treated under these conditions had very similar behavior. However, the sample treated for a longer time, 1 h 40 min, showed a 43% reduction in the value of corrosion current density compared to the sample treated for 1 h. The value of corrosion current density presented by the sample implanted during 1 h was $4.3 \times 10^{-7}$ A cm$^2$, and for the sample implanted during 1 h and 40 min was $3.0 \times 10^{-7}$ A cm$^2$. With respect to the sample without treatment (reference), it was verified a 25% reduction in the value of corrosion current density. That means a greater increasing in the corrosion resistance of treated Ti6Al4V with increasing treatment time at high temperatures.

The effects of PIII treatment employing mixture of nitrogen and hydrogen in the corrosion resistance of Ti6Al4V are shown in Fig. 3. It is observed that the surface treated with plasma from this mixture has superior resistance to the alloy surface implanted with nitrogen only. When the titanium alloy was treated with pure nitrogen PIII, it was verified that it presented a corrosion potential slightly more positive ($-141$ mV) than the standard sample ($-211$ mV). While the corrosion potential presented by the surface treated with mixture plasma was practically the same presented by untreated sample ($-211$ mV). The sample treated with a mixture N$_2$:H$_2$, showed corrosion current density value of approximately a half of the value of the sample treated with nitrogen only. In the first case, the value of the corrosion current density was about $2.2 \times 10^{-7}$ A cm$^2$ and in the second, $4.3 \times 10^{-7}$ A cm$^2$. The PIII treatment with a mixture N$_2$:H$_2$ promoted also a reduction by a half of the value of passive current density when compared to the value presented by implanted sample only nitrogen plasma. The values of the passive current densities verified were from approximately $2.6 \times 10^{-5}$ A cm$^2$ to $1.4 \times 10^{-5}$ A cm$^2$ for these respective treatment conditions.

For a more systematic analysis of the corrosion resistance of titanium alloy, before and after ion implantation treatment at high temperature, electrochemical impedance spectroscopy tests were carried out. The Fig. 4 shows the Nyquist (a) and Bode (b) diagrams of all

**Table 1**
Experimental Parameters.

| Conditions | Gases | t (h) | T (°C) |
|---|---|---|---|
| 7 kV, 40 μs, 400 Hz | N$_2$ | 1 | 800 |
| 10 kV, 40 μs, 400 Hz | N$_2$ | 1 | 800 |
| 12 kV, 30 μs, 300 Hz | N$_2$ | 1 | 800 |
| 12 kV, 30 μs, 300 Hz | N$_2$ | 1:40 | 800 |
| 12 kV, 40 μs, 300 Hz | N$_2$:H$_2$ (1:1) | 1 | 800 |

**Table 2**
Electrochemical parameters of the treated and untreated samples by nitrogen PIII, with different high voltage pulses.

| Sample | t (h) | Ecorr (mV) | Jcorr (A cm$^{-2}$) | Jpass at 750 mV (A cm$^{-2}$) |
|---|---|---|---|---|
| Unimplanted | – | $-211$ | $1.2 \times 10^{-6}$ | $7.0 \times 10^{-5}$ |
| 7 kV | 1 | $-191$ | $1.5 \times 10^{-7}$ | $8.4 \times 10^{-6}$ |
| 10 kV | 1 | $-140$ | $1.2 \times 10^{-7}$ | $9.9 \times 10^{-6}$ |
| 12 kV | 1 | $-141$ | $4.3 \times 10^{-7}$ | $2.6 \times 10^{-5}$ |