

Effects of Plasma Immersion Ion Implantation (PIII) of Nitrogen on Hardness, Composition and Corrosion Resistance of Ti-6Al-4V Alloy

Leide Lili G. da Silva¹, Mario Ueda¹, Maria M. da Silva², and Eduardo N. Codaro³

¹Laboratório Associado de Plasma, Instituto Nacional de Pesquisas Espaciais,
Caixa Postal 515, 12245-970 São José dos Campos-SP, Brazil

²Departamento de Engenharia Mecânica, Instituto Tecnológico de Aeronáutica, São José dos Campos-SP, Brazil

³Departamento de Física e Química, Universidade do Estado de São Paulo, Guaratinguetá-SP, Brazil

Received on 8 December, 2005

Ti-6Al-4V samples have been treated by PIII processing at different temperatures (400-800 °C), treatment time (30-150 min) and plasma potential (100 and 420 V). Hardness measurements results showed an enhancement of the hardness for all implanted samples. XRD results detected the Ti₂N phase and the best corrosion resistance was found for the samples processed at higher temperature and lower PIII time.

Keywords: Corrosion; Hardness; Plasma immersion ion implantation; Ti-6Al-4V; X-ray diffraction

I. INTRODUCTION

PIII was developed for the beneficial modification of surface-sensitive properties [1]. In analogy to conventional beam-line ion implantation, it uses energetic ions, mostly nitrogen, that are implanted into near-surface region of material. A sample is immersed in plasma and subjected to negative high-voltage pulses. In the electrical field, the ions are accelerated to high energies and incorporated into the sample [2]. This technique circumvents the line-of-sight and retained dose limitation inherent to conventional beam-line ion implantation, and is thus particularly suitable for large components possessing non-planar and complex geometries [3]. Most of the PIII processing was performed at low and moderate temperatures (< 400 °C) [4] and few works investigated the effects of the high temperature plasma immersion ion implantation (PIII) in Ti alloys [5-6]. Pichon et al. [6] carried out PIII treatment of Ti-6Al-4V alloys using R.F. plasma in the range of 200-800 °C. At the highest temperature (800 °C), a 2 μm nitride layer, composed of a mixture of TiN and Ti₂N phases, has been attained and nitrogen has diffused to 20-30 μm in the alloy. In another work, Berberich et al. [5] performed PIII implantation of Ti-6Al-4V samples using Electron Cyclotron Resonance Plasma source with temperatures below 200 °C. After that, annealing procedures were accomplished on the samples. Annealing at temperatures above 500 °C, leads to the reduction of TiN phase and the formation of Ti₂N deeper in the material. The hardness increases after annealing by a factor of 2.5 compared to the unimplanted state. Consequently, enhancing of the hardness and wear process of the materials due to the N-enriched layer caused by diffusion of N in the sample at high temperature PIII process can be expected. However, in previous studies, the corrosion behaviour of PIII treated Ti-6Al-4V samples at high temperature has not been investigated. So, the objective of this work is to study the effects of N-PIII on surface properties of Ti-6Al-4V alloys.

II. EXPERIMENTAL

The basic components of the PIII processing and their functions were already described elsewhere [7]. The novel parts

of this system are the locally heated sample support (SS), and the electrical system to drive the coiled tungsten filament inserted inside the SS, including the high voltage pulse isolator transformer. As described in the previous paper, we used the commercial RUP-4 device to pulse the SS at the high negative voltages (nominal of 30 kV, 100 μs and 1.1 kHz maximum). The filament potential floats with the high voltage pulse while ~110V, ~5 A is used to heat the SS up to 800 °C which remains constant during the PIII treatment. Nitrogen gas was used as plasma source. For all experiments the following parameters were kept constant: pressure= 6x10⁻⁴ mbar, repetition frequency= 400 Hz, pulse length = 40 μs, plasma potential=400 V and pulse voltage = 5 kV. Three different sets of Ti-6Al-4V samples were PIII processed. The experimental conditions are shown in the table 1 and 2.

Table I. Experimental conditions for N-PIII treatment of Ti-6Al-4V samples.

Samples	TEMPERATURE (°C)	Time (min)	Plasma Potential (V)	Hardness (GPa)
SET1				
11a	800	30	420	12
3a	800	60	420	14
12a	800	90	420	14
7a	800	120	420	19
15a	800	150	420	24
SET2				
10	400	60	420	8.5
8	550	60	420	11.5
16a	700	60	420	10.5
3a	800	60	420	14

The reduction of the plasma potential was obtained through the electron shower which allowed the decrease of the plasma potential from 420 V to around 100 V. By actuating this electron shower at different powers, the potential of the plasma can be controlled and it was measured with a Langmuir probe. To characterize the Ti-6Al-4V samples subjected to high temperature PIII we used X-ray diffraction (Philips 3410 diffrac-

tometer in the Seeman-Bohlin 2 θ mode); nanoindentation (tri-boindenter from Hysitron Inc.) and Auger electron Spectroscopy (FISONS Instruments surface Science, model MICROLAB 310-F). The temperature of SS was measured by infrared pyrometer from MIKRON, model M90-Q. The corrosion behavior of the samples was investigated by potentiodynamic polarization curves. They were obtained by means of an EG&G PAR potentiostat/galvanostat model 283 using a conventional three-electrode glass cell containing 3.5 % NaCl solution, pH=6. Ti-6Al-4V slices, untreated and treated by PIII processing, were employed as the working electrode (cross-section $\sim 0.07 \text{ cm}^2$). The counter electrode was a graphite rod and an Ag/AgCl, KCl saturated electrode served as a reference electrode.

III. RESULTS AND DISCUSSION

Nanohardness measurements were performed on the Ti-6Al-4V samples treated at different experimental conditions as presented in table 1. Enhancement of the hardness for all PIII treated samples was observed. The hardness values were higher for the PIII-treated samples at higher temperatures (700-800 °C) than those treated at lower temperatures (400-550 °C) as shown in the table I. The hardness values showed in the table I are associated to the maximum values of the obtained hardness profile. This mechanical behaviour is due to the higher nitrogen diffusion in the PIII treated samples at higher temperatures. There was an enhancement of the hardness from approximately 8.5 GPa up to 14 GPa for the set 2 samples as the PIII process temperatures rises from 400 to 800 °C in 60 minutes of treatment. Therefore, we obtained a hardness improvement of about 2.5 times compared to the untreated specimen. This behaviour is in agreement with Berberich et al. [5] results since they obtained for N-PIII at 200 °C in Ti-6Al-4V alloy an enhancement factor of 2.5 compared to the unimplanted state, after annealing of the samples at 650 °C. At 800 °C, an increase of the hardness (12-24 GPa) was also observed as the PIII process time varied in the range of 30-150 minutes (set 1), respectively. There was an improvement of the hardness of nearly 4 times in comparison with the untreated standard sample, for the case of 150 minutes treatment at 800 °C. The obtained hardness value of 24 GPa is in accordance with the one reported by G.B. Souza et al. [8] in their work about hardness and elastic modulus of ion-nitrided titanium measured by nanoindentation. They used different N₂/H₂ mixtures and temperatures (600-900 °C) during nitriding process. Microindentation results also indicated improvement of the surface hardness for set 3 (table II). This measurement presents only the trends of hardness behaviour for set 3 due to the thin nitrided layer after PIII treatment. Further nanohardness measurement will be carried out in these samples. For both analyzed temperatures (550 ° and 800 °C), the highest hardness value was obtained for the samples treated at lower plasma floating potential (100 V) as shown in table 2. This effect is due to the lower surface sputtering in these conditions which probably led to thicker nitride layer.

Table II. Microindentation for samples treated at two different plasma potential (PP) – SET 3

Samples	Temperature (°C)	Time (min)	PP (V)	Hardness (HV)
untreated				350.0
treated	550	60	100	356.6
treated	550	60	420	351.0
treated	800	120	100	677.3
treated	800	120	420	580.0

Typical X-ray diffraction patterns from 2 θ =30 ° to 50 ° are shown in Fig. 1 of samples treated at 800 °C with different plasma floating potentials of 420V(Fig. 1a) and 100V (Fig. 1b). These spectra depict the Ti substrate peaks (Ti α and Ti β phases) as well as the phase formed after the PIII processing -Ti₂N phase. Comparing figure 1 with figure 2, the preferred orientation of Ti₂N (111) at lowest plasma potential (100V) was noted. This fact could be attributed to the reduced surface sputtering of the sample during the PIII processing which led to higher nitrogen content and consequently enhanced hardness as shown in table II. Ti₂N phase was observed only for the PIII samples treated at highest temperature (800 °C) during 2 h whereas for the others the Ti₂N phase was not identified. This phase was also noted by other authors [5-6].

Corrosion behaviour of PIII-treated Ti-6Al-4V samples at low and high temperatures was analyzed using potentiodynamic polarization curves. Fig. 2 shows the polarization curves for untreated and treated samples obtained at highest temperature (800 °C) with different PIII treatment time, 30-150minutes (set 1) in 3.5% NaCl solution. A potential range from -0.8 V up to 3.5 V was applied with the sweep rate of 0.33 mV s⁻¹. For all samples analyzed, the cathodic branches of the polarization curves exhibit current densities that decrease as the applied potential increases. Cathodic reaction is assumed to be proton and/or oxygen reduction. The anodic branches of the polarization curves of all Ti-6Al-4V samples showed a large passive region ($\sim 1.5 \text{ V}$) where the current density was kept constant. This region is associated with the formation of a protective film [9]. Small oscillations of the current density are related to the consecutive formation and repassivation of microsize pits, usually called metastable pits [9].

Figure 2 also shows that, the current density of the passive regions of the set 1 samples increase from 3×10^{-7} up to $3 \times 10^{-6} \text{ A cm}^{-2}$ with the N-PIII treatment time increasing from 30 to 150 minutes. The passive current density for PIII-treatment of 30 minutes is approximately the same as for the untreated sample, being about 4 times higher than the one of the untreated specimen ($8.5 \times 10^{-8} \text{ A cm}^{-2}$). The corrosion resistance decreases with the PIII-treatment time but the current densities are rather low and a good corrosion resistance is still maintained. This behavior can be explained as increase of the PIII treatment time (30-150 min), resulting in the increase of N penetration (30-150 nm), not sufficient to form a protective nitrided layer on the surface.

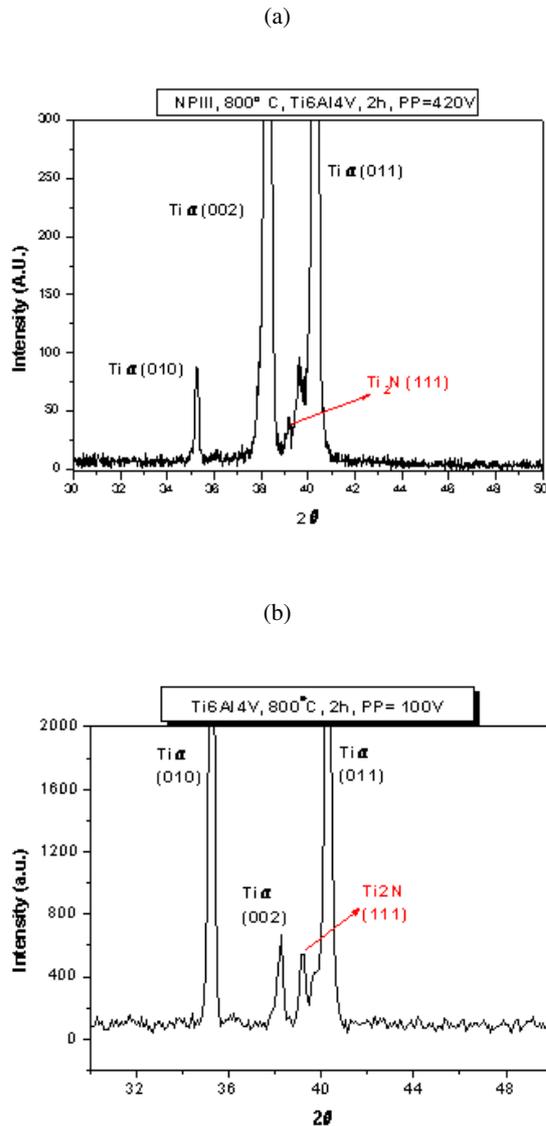


FIG. 1: X-ray diffraction of Ti-6Al-4V treated by PIII at 800 ° C, 120 min.: a) with plasma potential of 420V; b) with plasma potential of 100V.

Figure 3 shows the polarization curves for untreated and treated samples (90 min) obtained at different PIII treatment temperatures (set 2) in 3.5% NaCl. The polarization curves exhibited the same characteristics as detailed in the Fig. 2. As the temperature increases from 400 up to 800 ° C, the passive current density decreases from $3 \times 10^{-6} \text{ A cm}^{-2}$ to $1.5 \times 10^{-6} \text{ A cm}^{-2}$. This behaviour is coherent because there is more heterogeneity on the sample surface treated in low temperature than the one treated in high temperature. So the corrosion process begins at the surface defects that provoke the discontinuity of the passive film. Besides the passive current density ($1.5 \times 10^{-6} \text{ A cm}^{-2}$) is about 17 times higher than untreated sample the corrosion resistance is still good.

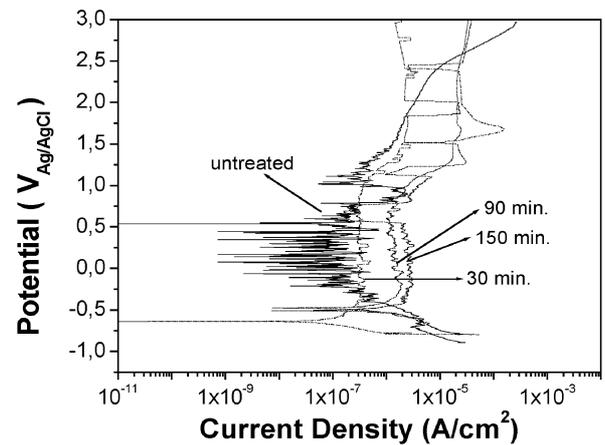


FIG. 2: Potentiodynamic polarization curves of the Ti-6Al-4V samples: (–) Untreated sample, (...) PIII treated samples with different processing time (30-150 minutes).

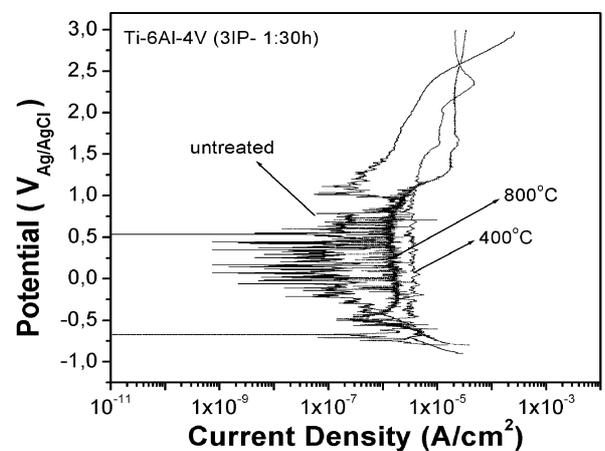


FIG. 3: Polarization curves of the Ti-6Al-4V samples: (–) Untreated sample, (...) PIII treated samples with different processing temperatures (400 e 800 ° C).

Some preliminary results from PIII treatment at different plasma potential of 420 V and 100 V are shown in Fig. 4. The same characteristics pointed for the others analyzed polarization curves (Fig. 2 and 3) were observed.

For both curves the first passive region is around $2.3 \times 10^{-7} \text{ A cm}^{-2}$. A second passive region above 1.6 V was evidenced, however the passive current density for the sample treated at 100 V is about one order of magnitude lower than the one for the sample treated at potential plasma of 420 V. So, this behaviour suggests that the PIII-treated samples at lower plasma potential (100 V) are more corrosion resistant in strong oxidizing media. For all analyzed samples (Fig. 2-4), the polarization curves showed an apparent active/passive region. Ramires et al. [10] inferred that this process is associated with the increase of the oxide layer thickness on the surface, while Marino et al. [11] related it to the formation of the secondary

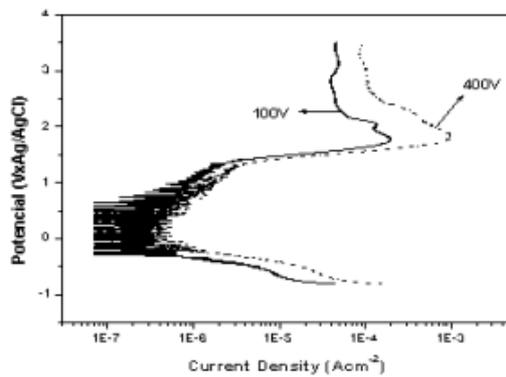


FIG. 4: Polarization curves at 550 °C, 600 min: (–) with plasma potential of 100 V, (---) with plasma potential of 420 V.

oxide or a phase transformation induced during the potentiodynamic scan. Anyway, a second passive region above 1.6

V was only evidenced for the PIII-treated samples while for the untreated specimen the corrosion current density increased rapidly above 2.5V.

IV. CONCLUSIONS

Nitrogen PIII in Ti-6Al-4V alloy at high temperature (800 °C) and 150 min treatment time increases the surface hardness by forming crystalline Ti_2N phase. However, the best corrosion resistance was found for the samples processed at higher temperature and lower PIII time (30min). PIII treatment with variation of the plasma potential produces more intensive effect on the surface hardness than on the corrosion resistance of the Ti-6Al-4V alloys.

Acknowledgement

Leide Lili Gonçalves da Silva was supported by CNPq (process: 382838/2004-1).

-
- [1] A. Anders, *Handbook of Plasma Immersion Ion Implantation and Deposition*, John Wiley & Sons New York, p. 3, (2000).
- [2] W. Ensinger, *Surface and Coatings Technology* **100-101**, 341 (1998).
- [3] X. Tian and P. K. Chu, *Scripta Mater*, **43(5)**, 417 (2000).
- [4] A. Tóth, M. Mohai, T. Ujvári, T. Bell, H. Dong, and I. Bertti, *Surface & Coatings Technology* **186(1-2)**, 248 (2004).
- [5] F. Berberich, W. Matz, U. Kreissig, E. Richter, N. Schell, and W. Möller, *Applied Surface Science* **179(1-4)**, 13 (2001).
- [6] V. Fouquet, L. Pichon, A. Straboni, and M. Drouet, *Surface & Coatings Technology* **186(1-2)**, 34 (2004).
- [7] M. Ueda, L. A. Berni, G. F. Gomes, A. F. Beloto, E. Abramof, and H. Reutheer, *J. Appl. Phys.* **86**, 4821 (1999).
- [8] G. B. de Souza, C. E. Foester, S. L. R. da Silva, F. C. Serbena, C. M. Lepienski, and C. A. dos Santos, *Surface & Coatings Technology* **191(1)**, 76 (2005).
- [9] A. P. R. Alves, F. A. Santana, L. A. A. Rosa, S. A. Cursino, and E. N. Codaro, *Materials Science and Engineering C*, **24(5)**, 693 (2004).
- [10] I. Ramires and A. C. Guastaldi, *Química Nova*, **25(1)**, 10 (2002).
- [11] C. E. B. Marino, S. R. Biaggio, and R. C. Rocha Filho *Corrosion Science*, **43(8)**, 1465 (2001).