Surface modification of Ti6Al4V alloy by duplex plasma processing

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Abstract. *Based on the fact that the Ti6Al4V alloy has good mechanical properties, excellent resistance to corrosion and also excellent biocompatibility, however, low wear, this work aims to test plasma processes or combination of plasma and ion implantation processes to improve these characteristics, besides moving aluminium and vanadium from the surface, because both of then are not desirable in this place, for biomedical applications. Two types of treatments have been made: a) PIII (Plasma Immersion Ion Implantation) combined with PN (Plasma Nitriding); b) treatment with PIII alone.*
The best result of retained dose obtained by Auger Electron Spectroscopy (AES) is for PIII of 100 minutes, achieving ~90 nm of nitrogen implanted layer, while the sample treated with PIII (75 min) and PN (75 min) reached ~35 nm implanted layer. The improvement of surface properties could also be confirmed by the nanoindentation technique, with values of hardness increasing around 30 %, for both processes. The results of characterizations, showed that the simple process of PIII demonstrated greater efficiency than the duplex process (PIII + PN), probably because the sputtering during PN removed a thick implanted layer. Other variations of surface treatments are being tested with the objective of getting more improved surface results.

Keywords*: Ti6Al4V, Plasma Nitriding, Plasma Immersion Ion Implantation, surface modification, tribological properties.*

1. Introduction

The Ti-6Al-4V alloy, [also called Ti-64 (Seagle and Giangiordano, 1999), T-A6V (Apert, 1976)], is one of the mostly used titanium alloys in aeronautical industries and in biomedical applications because of its excellent combination of mechanical, toughness, corrosion resistance, and chemical stability properties (Khan, Williams and Williams, 1999) and (Cai et al, 1999). Its excellent corrosion resistance is attributed to the formation of a passive titanium oxide film. This protection layer, formed during the contact of metal surface with air avoids further oxidation of the bulk, thus providing alloy passivity and biocompatibility (Muster et al, 2000) and (Silva, 2001). The major application for this material is in the area of aeronautic and space industries, in particular, constructing parts like pressure vessels, aircraft turbines and compressor blades. Moreover, it has been also related important applications of this material to medical implantations (Nishiguchi et al, 1999) and (Rinner, Gerlach and Ensinger, 2000), due to its good characteristic of biocompatibility (Nishiguchi et al, 1999a). Plasma Nitriding and Plasma Immersion Ion Implantation are processes where the surfaces modifications are produced inside of a reactor having mainly: electrons, atoms, molecules, positive ions, negative and radicals. This treatment allows changing the physical and chemical characteristics of the alloy and produces significant increase in the hardness, also increasing the wear resistence (Barbieri et al, 2002). Modified layer exhibiting more superior wear resistance could be obtained by combined plasma nitriding and nitrogen PIII process sometimes called “hybrid” or “duplex” technique (Kostov et al, 2004).

The present work aims to improve the tribological properties of the Ti6Al4V alloy through the combination of two plasma assisted processes: Plasma Nitriding and Plasma Immersion Ion Implantation, with the objective to increase the layer thickness as observed in another preliminary work (Silva, 2001a), comparing it with PIII only treatment, in two different conditions.

2. Experimental Procedure

The experiments were carried out at LAP (Laboratório Associado de Plasma) of INPE (Instituto Nacional de Pesquisas Espaciais). The samples have been prepared as disk of 10 mm in diameter by 1 mm in thickness, and then polished to mirror like surface. They were mounted in a sample holder and taken to the reactor chamber for the treatment. The plasma chamber is initially pumped down to ~2,1 X 10^{-3} Pa , then argon gas is introduced and a sputter cleaning process is applied for approximately 10 min. After this cleaning stage, the argon gas is replaced by nitrogen and the treatments are carried out. The experimental conditions are presented in table 1. The ionic bombardment heats the sample up to around 400ºC.

Table 1. Experimental conditions used

Sample #	1	2		3	4	
Treatment	PIII	PIII	PN	PIII	PIII	PN
Voltage (V)	11k	15k	-700	17k	17k	-750
Pressure (Pa)	$2,1x10^{-1}$	$8x10^{-2}$	$8x10^{-2}$	$7.2x10^{-2}$	$8x10^{-2}$	$8x10^{-2}$
Time (min)	100	75	75	150	75	240
Frequency (Hz)	2000	400		400	400	
Pulse (µs)	60	20		20	20	

The surface hardness was analyzed by nanoindentation technique, conducted with a Triboscope nanomechanical indentation tester from Hysitron (UFPR). And the composition profile by Auger Electron Spectroscopy (AES) to find out the nitrogen concentration inside the samples (IIBPMR).

3. Results and discussions

3.1 Surface characterization

Figure 1 presents the AES result that shows the composition profiles of the standard sample. It shows the composition profile of untreated Ti6Al4V alloy used as a reference, showing thin layers of carbon and oxygen compounds, probably, TiC and TiO_2.

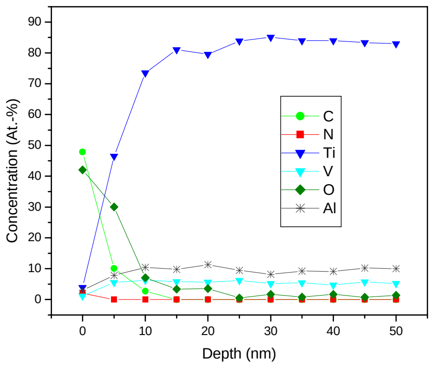

Figure 1a. AES analysis results - Reference sample

Figure 1b shows the composition profile of the sample #1, that presents the thickest nitrogen enriched layer with thickness of approximately 90nm, with atomic concentration between 20 and 32% of nitrogen.

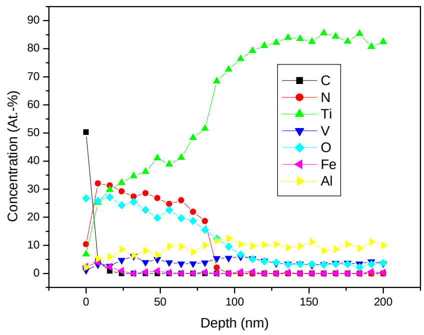

Figure 1b. AES analysis results – # 1 (PIII 100min)

Figure 1c shows the composition profile of the sample #2 with nitrogen layer thickness of approximately 35nm, with atomic concentration between 20 and 30 at.% of nitrogen.

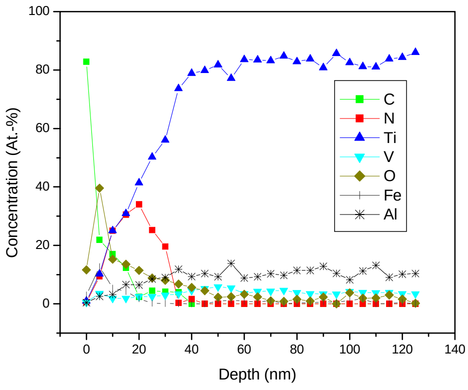

Figure 1c. AES analysis results – # 2 (PIII 75 min + PN 75 min)

The sample #3, figure 1c, presented nitrogen enriched layer thickness of 65nm, with atomic concentration between 20 and 35 at. % of nitrogen.

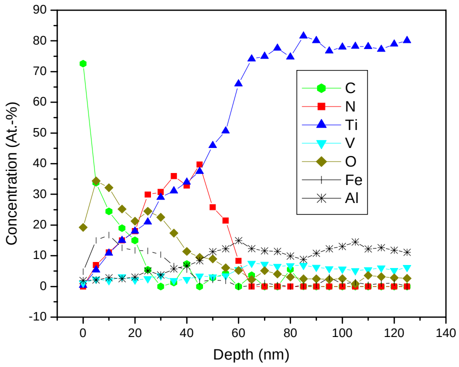

Figure 1c. AES analysis results – # 3 (PIII 150 min)

The lowest nitrogen enriched layer thickness was presented by sample #4, figure 1d, with 15 nm of depth, and only 5 at%.

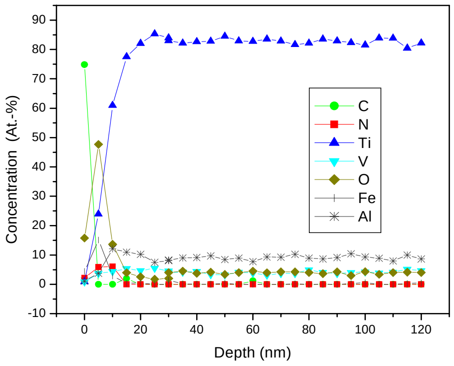

Figure 1d. AES analysis results – # 4 (PIII 75 min + PN 240 min)

Figure 2 presents the hardness profile obtained through nanoindentation technique for some of the samples subjected to the treatments above. The untreated sample (reference), presents values of hardness varying from 3.8 to 4.7 GPa. The highest hardness value is obtained by the sample # 1 treated by PIII during 100 minutes, with hardness values around 4 and 8 GPa, with an increase of about 47% compared to the untreated sample. The sample # 2 treated according to duplex process, PIII (75 min) + PN (75 min), presents an increase of about 38%, with values ranging from 4.2 to 7.5 GPa. For the sample #3 treated by PIII during 150 min, an increase of approximately 22% in the hardness values is noted, its values being around 4.3 to 6.1 GPa. For the sample #4 treated by PIII (75 min) + PN (240 min), the increase in hardness is around 25%, the values being situated between 4.0 to 6.6 GPa.

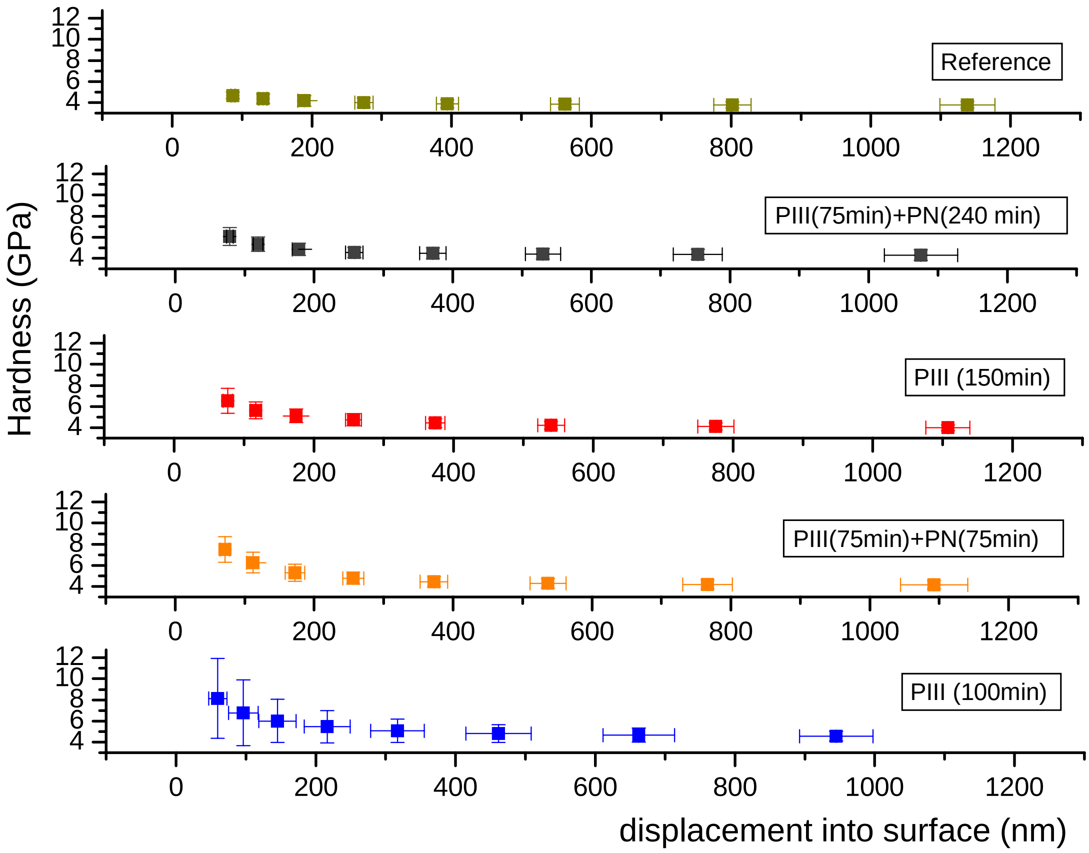

Figure 2: Surface hardness (nanoindentation) of the samples treated under conditions shown in table 1 including reference sample.

4. Discussion and Conclusions

Nitrogen implantation effect in Ti6Al4V sample is confirmed by an increase of surface hardness, due to an enrichment of nitrogen in the structure as verified by the nitrogen profile measured through AES technique. The sample treated only by PIII method, during 100 min, with different conditions from the others like higher pressure, frequency and pulse length, presents the thickest nitrogen enriched layer of around 90 nm. The thinnest layer was obtained for the material treated by duplex process of PIII (75 min) + PN (240 min) of around 15 nm, and this result is attributed to a strong sputtering by nitrogen during the second step (PN processing). The best results for sample #1, its values of hardness obtained by nanoindentation technique is also the highest one, was obtained amongst all the treatments shown in table 1. The nanoindentation tests confirm the surface hardness increase in Ti6Al4V samples for both the duplex process as well as for the simple step process PIII, the results being about 22% for the first and 47 % for the last, when compared to the untreated sample. The superior results of the PIII treatment for sample #1 was expected because it was performed at much higher frequency (2000Hz) and longer pulse length (60µs). Therefore, implantation was faster than sputtering, in contrast with the other treatments of table 1.

New combinations of processing parameters and conditions are being carried out aiming thicker layer of implanted nitrogen.

5. Acknowledgments

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