ISSN: 2230-9926

Available online at http://www.journalijdr.com

IJDR

International Journal of Development Research
Vol. 11, Issue, 09, pp. 50054-50058, September, 2021
https://doi.org/10.37118/ijdr.22874.09.2021

RESEARCH ARTICLE OPEN ACCESS

CHARACTERIZATION OF THE SURFACE LAYER MODIFIED IN TI6-AL7-NB ALLOYS BY PLASMA NITRIDING USING CATHODIC CAGE

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ARTICLE INFO

Article History:

Received 14th June, 2021
Received in revised form
26th July, 2021
Accepted 09th August, 2021
Published online 27th September, 2021

Key Words:

Ti6-Al7-Nb, Plasma Nitriding, Cathodic cage.

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ABSTRACT

Using titanium as the base metal of biomaterials has gained attention due to its excellent mechanical properties, biocompatibility, and resistance to corrosion and wear. In this research, Ti6-Al7-Nb (wt%) alloy has been superficially modified by cationic cathode plasma nitration (CCN) in order to improve the pre-existing biocompatible characteristics in the alloy. Four treatment conditions and a standard sample, for comparative purposes, were chosen. Nitriding was implemented using a cathodic cage technique at a different time and temperature conditions, and at constant pressure. Samples 1 and 2 were treated at a temperature of 300°C for 1h and 2h, while samples 3 and 4 were treated at 400°C for 1h and 2h, respectively. The characterization techniques used were: SEM, EDS, XRD, microhardness, and roughness. The results regarding SEM and EDS techniques revealed the formation of a TiO_2 film for three samples. The XRD analysis showed the existence of a peak related to the formation of titanium nitride (TiN), in various proportions, for all analyzed samples. The formation of the film also confirms a hardness increase for conditions 1, 2 and 3. The analysis of the roughness demonstrated results for rounded peaks for samples 1, 2 and 4, where sample 4 revealed the lowest roughness value. In light of the results, it was possible to verify that the nitrided samples had their properties, partially or integrally, improved in relation to the standard one.

Citation: **Jessika Kalline Lopes Moura, Marina de Oliveira Cardoso Macêdo, Haroldo Reis Alves de Macêdo and Ayrton de Sá Brandim, *2021.*** "Characterization of the surface layer modified in ti6-al7-nb alloys by plasma nitriding using cathodic cage", *International Journal of Development Research*, 11, (09), 50054-50058.

INTRODUCTION

Currently, technological advances have contributed to an increase in the quality of life. However, with an ageing population, it is necessary to build new devices, modified superficially through thermochemical treatments, which more efficiently supply the physical, chemical, biological and mechanical properties for human activity [1]. Plasma nitriding is a thermochemical procedure generated by the application of a voltage between two electrodes in a hermetic system, where the electrons are accelerated by an electric field and collide with other particles. This type of surface treatment has been gaining strength by allowing the formation of a uniform and high-quality texture in addition to an ease of control of the roughness in the film formed by the procedure [2]. The plasma treatment efficiency is achieved by the deposition of a surface film formed mainly of titanium nitride (TiN), as well as other titanate compounds, such as titanium oxides (TiO_x). TiN compound has unique physicochemical, optical and mechanical properties if compared to other film deposition techniques. TiN presents fine resistance to oxidation, increased hardness and sensible thermal and electrical conductivity. Such advantages are instigating, considering the wide variety of fields of application for this film. The TiN structure typically exhibits high values of hardness and wear resistance, as well as high melting points and a high degree of stability. Its superior resistance to severe oxidative processes is leading researchers to consider it a viable solution for the development of biocompatible materials that incorporate TiN as the major compound of films formed on the surface of these materials [2]. Considering the aforementioned aspects, the plasma nitriding treatment becomes an important object of research in the field of materials engineering. This technique promotes the formation of a surface film basically composed of titanium nitrides, a relevant subsidy for future studies with titanate materials.

MATERIALS AND METHODS

Sample Preparation: Ten discs of 10 mm in diameter per 1 mm in thickness were used and prepared. The preparation involved the use of metallographic sanding (220, 360, 400, 600, 1200 and 2000 mash) and polishing procedures (with a diamond paste of 0.5 µm and 1µm), in order to eliminate defects derived from the cutting process. After polishing, the ultrasonic cleaning of the samples was performed, employing enzymatic detergent, distilled water and acetone. Finally, the discs were stored in a sterilized plastic bag and sealed for further of the treatment.

Cathodic Cage Plasma Nitriding (CCN): Prior to performing the Nitriding, a surface cleaning process was executed through a procedure called argon gas sputtering, with a pressure of 1.5 mbar, a gas flow of 12 sccm, a cleaning time of 20 min, and at a temperature of 300°C. After the cleaning was accomplished, the Nitration treatment was carried out. The NGC treatment conditions are set forth in Table 1. Furthermore, at the end of the Nitration process, the samples were cooled inside the nitriding chamber for further characterization analysis.

and Rz were considered. The Rp/Rz ratio was then calculated in order to obtain a better conclusion about the shape of the peaks on the surface. Five different measurements were adopted for each sample analysis, and with a scanning range of 40 µm.

RESULTS AND DISCUSSION

Sem: Figure 1 shows the SEM micrographs of CCN-treated Ti6-Al7-Nb alloy and the results of EDS analysis, respectively. The superficial modification is evidenced by the formation of oxides on the surface of the four samples (A1, A2, A3 and A4), and confirmed by the formation of visible clusters. It was also verified that the topography of the obtained surfaces presented degrees of organization of the varied grains. The conditions applied to Nitriding influenced the degree of uniformity of the film, reflecting in the surface hardness and roughness values.

Table 1. Parameters used in the NGC method

Technique	Temperature/	Time	Name	Pressure	Atmosphere	Gas Flow
CC	300 ºC	1h	A1	1,5 mbar	80 % H_2 e 20 % N_2	15 sccm
	300 ºC	2h	A2			
	400 ºC	1h	A3			
	400 ºC	2h	A4			
No treatment			Standard			

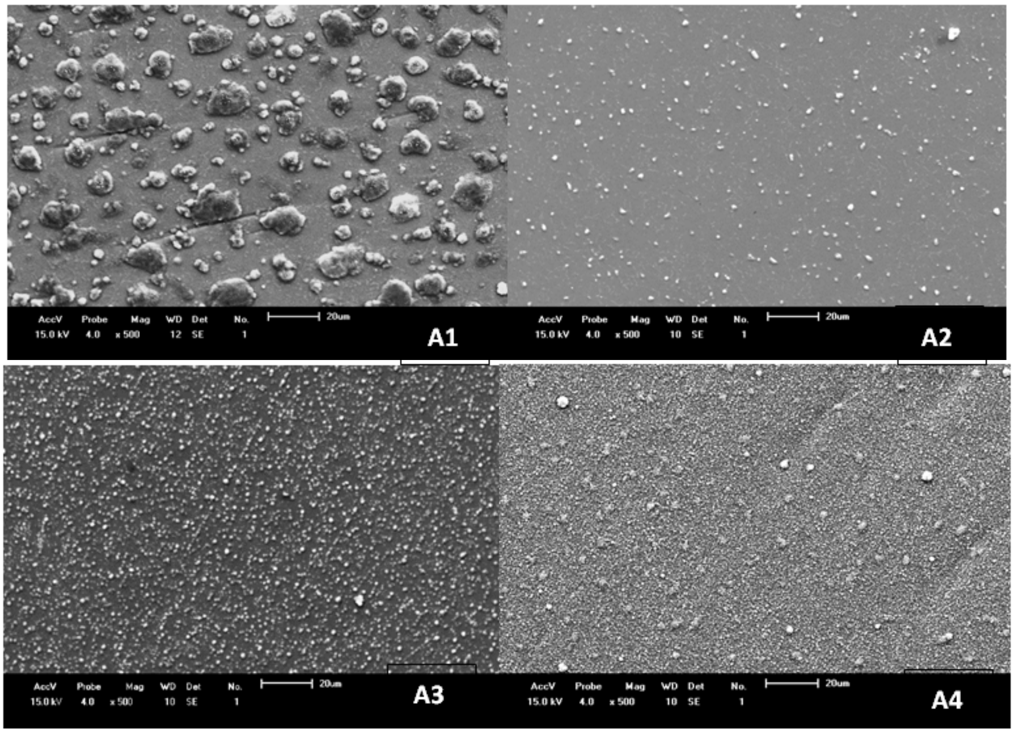

Figure 1. Micrographs of samples submitted to NGC with a magnification of 500x

Sample Characterization: The SE and EDS modes of the SEM, SHIMADZU® SSX-550 were applied during the experiment. The images were obtained with magnitudes of 100x, 500x, 1000x and 2000x, a current of 2.5 A and a voltage of 15 kV at three different points. In total, 12 images were captured per sample. Seeking the identification of the Ti6-Al7-Nb titanium alloy surface phases, the X-ray diffraction equipment of the Panalitycal® brand, Empyream model with CoKα (1.79 Å) radiation tube was used. The diffractometry was performed applying Bragg-Brentano geometry, with a scanning range from 30º to 80º with 0.01º steps. Microhardness analyses were performed through the SHIMADZU® HMV microdurometer. The measurements were taken in Vickers microhardness. According to ASTM E140-02, the tests were conducted at a constant load of 0.25 N, for 15 seconds long, and at 5 different points. Regarding roughness analysis, the rugosimeter, the Time Group Inc. and model TA 630 were used. Parameters Ra, Rp

This characteristic is also observed in Braz study when got the correlation of behavior of the species in cathodic cage with a surface reactivity them forming phases os oxynitrides [3]. Additionally, it was also possible to notice in Figure 1 that the film obtained by NGC presented a morphological characteristic, consisting of a slightly circular shape, corresponding to the titanium oxide compounds detected by EDS in area mode format.

Figure 2 displays the chemical features of the surfaces; these are associated with the uniformity degree of the formed film. The samples of conditions 1, 2 and 3 showed the TiO_2peak (highlighted in the images) slightly more intense under these specific conditions.Other elements observed in spectrum are from of Ti alloys used and in lower concentration from the stainless steel of the nitriding chamber.

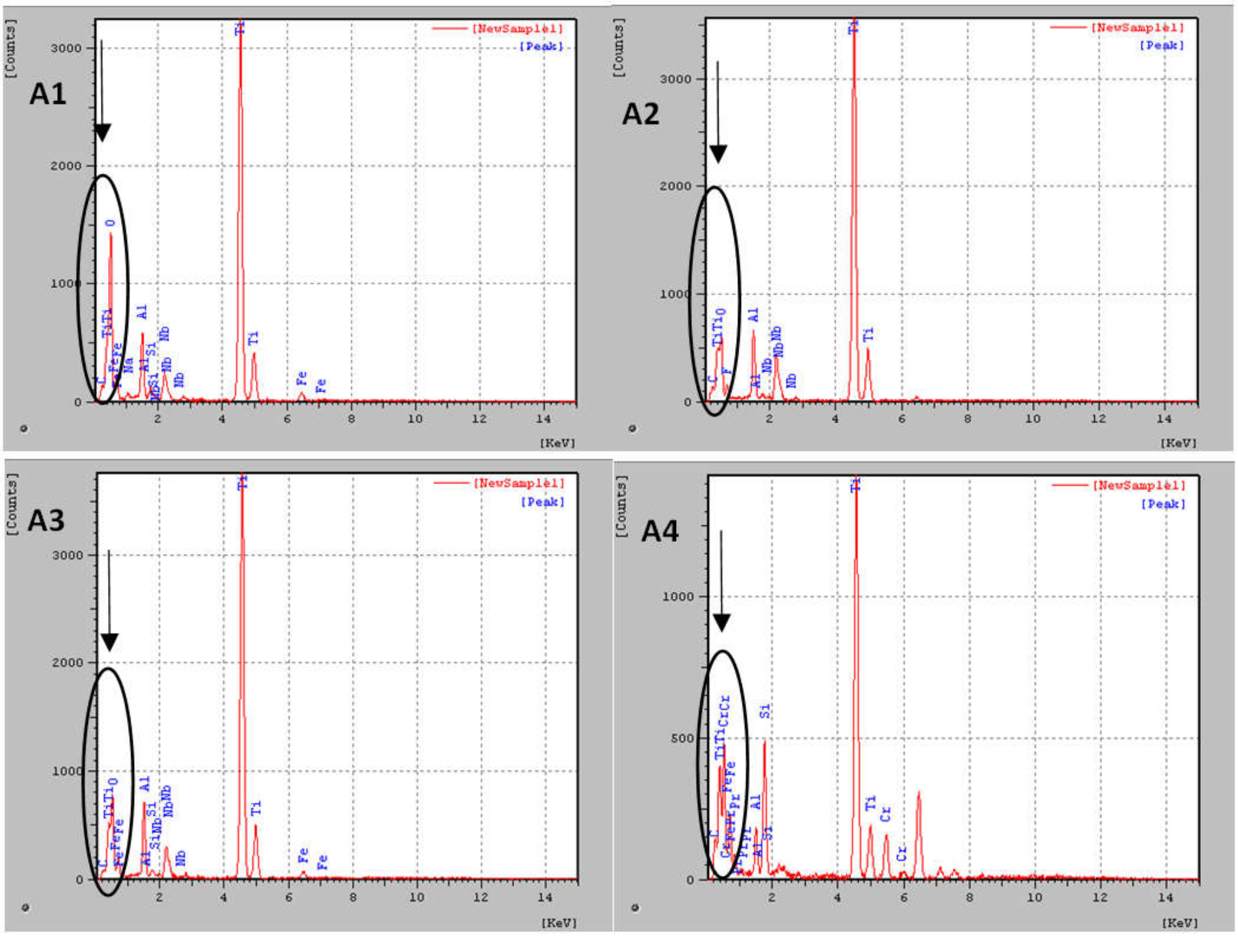

Figure 2. EDS analysis coupled to the SEM for samples treated by NGC technique

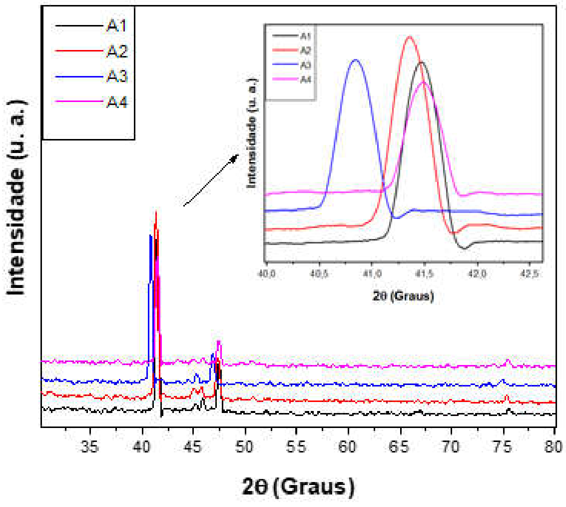

Figure 3. X-ray diffraction of the TiN film

This phenomenon indicates a dense and significant formation in terms of the amount of TiO_2 matter for NGC. This result means that the film formed by the NGC is thick. Special attention was given to the EDS of A4 since it did not display a detectable quantity of the TiO_2 compound. This aspect is related to the low values of roughness and microhardness for this particular sample (A4), diverging from the higher values obtained in the results of the other samples submitted to the same treatment.

XRD: In Figure 3, the diffractogram of the four conditions by NGC is arranged. According to this diffractogram, there is a significant displacement in the TiN peaks, especially in the sample A3 treated by NGC. This sample showed an offset towards the smallest angle. The indicated effect was probably due to the increase in the interplanar distance of the crystalline network of TiN, given it was submitted to different thermal conditions of treatment of Nitriding.

It is important to note that the existence of TiN is totally dependent on deposition conditions. Also, it is associated with the basal plane/position which the TiN structure has deposited on the substrate [4]. Another reason for this offset in sample A3 is the probable replacement of nitrogen by oxygen, detected in the ESD and affirmed by Lima [5]. Diffractograms were similar in all conditions so only A1 was analyzed in more detail can be extrapolate for the others. The presence of TiN was evidenced in 3 different stoichiometric proportions (Figure 4 and Table 2). All conditions (A1, A2, A3 and A4) are in accordance with the diffractogram of Figure 4 showing a structured nitride film, with the phases δ - TiNx, ε - Ti2N.

Microhardness: Figure 5 shows the mean microhardness profile for all NGC treatment conditions as well as the standard sample. The increase in surface hardness is due to film formation during NGC treatment. Similar results were obtained by Braz[3], who states that the cathodic cage provides a higher reactivity of the nitriding surface-atmosphere interface. Samples A1, A2 and A3 demonstrated a gradual increase in their hardness, with emphasis on condition 3, which revealed the highest value of superficial hardness among all conditions.

to the classes N2 and/or N3, defined by the norm 8404/1984 [7]. This range also shows information about the machining process to which the samples were subjected to super-finishing, lapidation and/or polishing of their surfaces.

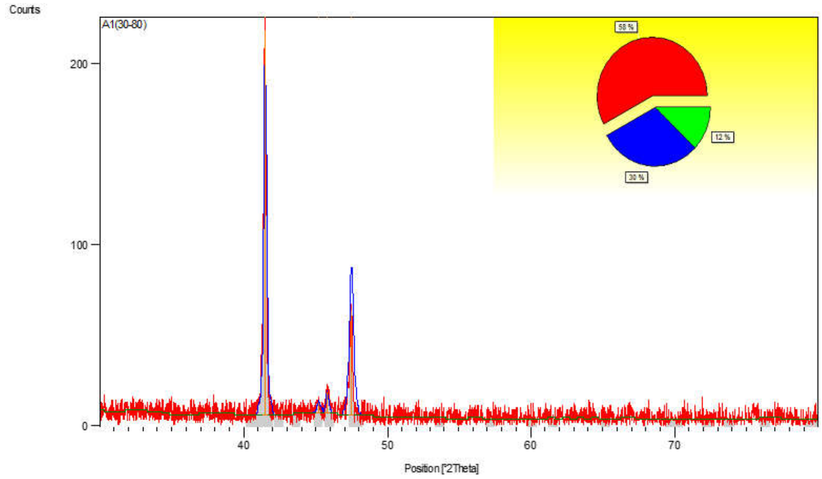

Figure 4. Detailed analysis of sample A1 diffractogram

Table 2. Data related to TiN Phases observed in diffractogram A1

Color	Referencecode	Points	Phasename	Displacement[°2Th.]	Escale factor	Chemical formula
(red)	01-074-1214	8	Osbornite, syn	0,000	0,202	Ti N
(blue)	01-084-1123	12	TitaniumNitride	0,000	0,069	$Ti_3N_{1.29}$
(green)	01-076-0198	6	TitaniumNitride	0,000	0,044	Ti_2N

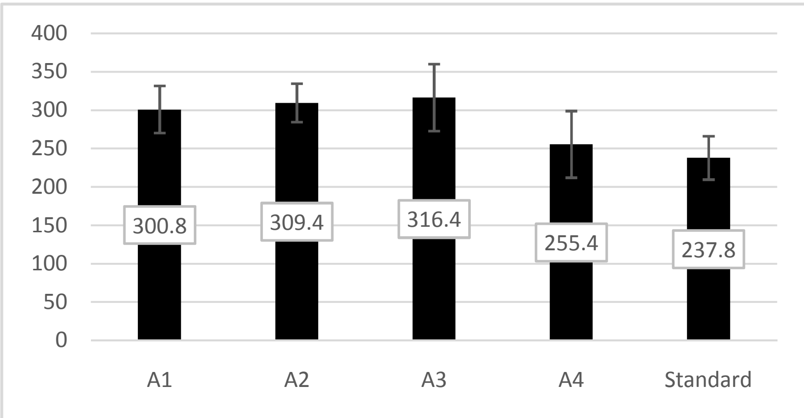

Figure 5. Vickers microhardness values for CCN treatment conditions A1, A2, A3 and A4

Table 3. Roughness data for NGC and the standard

	Ra	Rz	Rp	Rp/Rz
Samples	**Mean**	**Mean**	**Mean**	**Mean**
A1	0.07 ± 0.03	0.52 ± 0.16	0.21 ± 0.02	**0.40** ± 0.12
A2	0.10 ± 0.03	0.48 ± 0.11	0.20 ± 0.01	**0.41** ± 0.09
A3	0.14 ± 0.01	1.02 ± 0.07	0.58 ± 0.05	**0.57** ± 0.65
A4	0.11 ± 0.03	0.93 ± 0.15	0.31 ± 0.06	**0.33** ± 0.42
Standard	0.15 ± 0.02	0.85 ± 0.08	0.37 ± 0.07	**0.43** ± 0.85

Sample A4 diverged from the expected results for hardness. However, the EDS results show that the only sample that did not present relative/intense peaks to TiO_2 was A4, confirming the decay of the hardness observed in Figure 5. Another relevant aspect justifying the A4 hardness anomaly is shown by Araújo [6], where is stated that the deposition of Ti does not bring much nitrogen to the surfaces of the samples, reflecting in the low value of hardness observed in A4.

Roughness: The measurement data (Ra and Rp/Rz) of roughness for the samples and the standard are arranged in Table 3. The ratio between peaks and valleys (Rp/Rz) was relatively low in relation to the standard, except for sample A3. The Ra values were within the range of 0.05 µm to 1 µm for all samples, which is low compared to the standard. The value range for Ra revealed that the surfaces belong

Sample 1 obtained the lowest value of Ra, meaning that its condition was the best for film deposition, since in the SEM analyses the film image was the one that most evidenced the presence of titanate oxides, and the one that presented the most intense peak for TiO_2 in EDS analysis. Sample A3 was at the boundary between the rounded and pointed condition, where the parameter that defines the appearance of rounded peaks in the ratio Rp/Rz can not exceed the value of 0.5 µm[8].Considering this data, the surface has pointy peaks and also revealed the highest value for Ra for the samples submitted to NGC, thus showing that this surface also had a good deposition of the film ratified by the X-ray peak displacement and in its ESD analysis. Sample 4 presented the smallest of the values observed in the samples submitted to other NGC conditions, and value of Ra within the range provided above. This was the smallest amount identified and, once again, corroborated the anomalies that were presented by the sample 4. The lower roughness value for the A4 confirms its low surface hardness value discussed in the previous topic. It was also ratified in the analysis of ESD by showing that it was the only NGC condition that did not form sharply TiO_2 on the surface.

CONCLUSIONS

The EDS analysis verified the formation of TiOx in the nitrided layer with various intensities. The presence of TiN in all samples submitted to CCN was ratified by the diffractogram presented in the XRD analysis.The NGC technique subsequently allowed the formation of an oxynitride film on the Ti_6Al_7Nb alloy, showing satisfactory results in nearly all conditions of treatment time and temperature, except for condition 4. The best uniformity for the emission of films on display in the broader tests of SEM and EDS analyses directly influencing their levels of microhardness and surface roughness and differing only in the A4 sample. The sample A3 was more than satisfactory and coherent in the results by SEM, EDS, XRD, microhardness, except for a roughness analysis, for this condition, an Rp/Rz ratio for sharp peaks, not ruling out the possibility of overcoming the conditions of treatment and not exclude as a condition of consistency as the expectations of the results have already been.

Acknowledgments

The authors thank the academic and financial support of FAPEPI, IFPI.

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