

# EFFECT OF PLASMA NITRIDING PARAMETERS ON SURFACE PROPERTIES OF LOW-TEMPERATURE NITRIDED AISI 420 MARTENSITIC STAINLESS STEEL<sup>1</sup>

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## Abstract

The nitriding mechanisms of conventional DC plasma treatments have been extensively studied and discussed, however the influence of the process variables is not yet completely understood. Thereby, aiming to contribute to the subject understanding, a series of low-temperature plasma nitriding experiments have been carried out to evaluate the process parameters effect on the surface properties of AISI 420 martensitic stainless steel. The influence of treatment temperature and time, gas mixture composition and flow rate, process pressure and applied voltage, was investigated. The treated samples were characterized by optical microscopy, X-ray diffractometry and microhardness measurements. The results indicate that critical process parameters in the development of the microstructure and phase composition of the nitrided layer are the treatment temperature and time. Moreover, the results also show that the parameters of gas mixture composition, gas flow rate, process pressure and applied voltage are also important.

**Keywords:** Low-temperature plasma nitriding; AISI 420 martensitic stainless steel; Nitrogen expanded martensite; Nitriding process parameters.

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## 1 INTRODUCTION

The AISI 420, as other martensitic stainless steel, is commonly used in applications requiring good corrosion resistance combined with high mechanical strength.<sup>(1-5)</sup> However, when severe working conditions are necessary, its hardness and wear resistance must be improved. Plasma assisted nitriding is a process that takes advantage of glow discharge in order to introduce nitrogen atoms on metallic materials surface.<sup>(6)</sup> This technique has been successfully applied to the surface engineering of austenitic and martensitic stainless steel<sup>(7-9)</sup>. Mechanical properties of the modified layer are dependent of the operation variables applied during the process, including the treatment temperature and time, gas mixture composition and flow rate, process pressure and applied voltage. Owing to the lack of information, and aiming to improve the knowledge on this subject, the effect of treatment variables on the characteristics of the modified surface layers produced on low-temperature plasma nitrided AISI 420 martensitic stainless steel samples are stressed and discussed here.

## 2 EXPERIMENTAL PROCEDURE

Cylindrical samples of AISI 420 martensitic stainless steel (presenting composition in weight % of 0.17% C, 0.70% Mn, 0.50% Si, 12.22% Cr, 0.16% Ni, 0.23% P, 0.03% S, 0.03% N, 0.01% Cu, 0.02% Co, and balance in Fe) with 10 mm in height were cut from a commercial rod of 9.5 mm in diameter, austenitized at 1050°C for 0.5 h, and then quenched in air, resulting in microhardness of 510±15 HV0.3. After heat treatment, samples were ground using SiC sandpaper ranging from 100 to 1500 grade and polished using 1 µm Al<sub>2</sub>O<sub>3</sub> abrasive suspension. Finally, samples were cleaned with alcohol in ultrasound bath and introduced into the discharge chamber, in the as-quenched condition.

The nitriding equipment consisted of a square waveform pulsed power supply of 3.6 kW and a vacuum chamber of 350 mm in diameter and 380 mm high stainless steel cylinder attached to steel plates sealed with silicone o-rings at both ends. The system was evacuated to a residual pressure of 1.33 Pa using a double stage mechanical pump. The gas mixture flux of H<sub>2</sub>, Ar and N<sub>2</sub> was adjusted by three mass flow controllers of 8.33×10<sup>-6</sup> Nm<sup>3</sup> s<sup>-1</sup>. Samples were placed in the cathode. The mean power transferred to the plasma was adjusted by varying the switched-on time (*t*<sub>ON</sub>) of the pulse. The pulse period was 240 µs. The temperature was measured by means of a chromel–alumel thermocouple inserted 8 mm in depth, into the sample support, and it was controlled by adjusting the applied *t*<sub>ON</sub>. The pressure in the vacuum chamber was measured by a capacitance manometer of 1.33×10<sup>4</sup> Pa in full-scale operation and adjusted by a manual valve.

Prior to nitriding, samples were sputter-cleaned using abnormal glow discharge obtained at gas mixture of 80%H<sub>2</sub> + 20%Ar, for temperature and time of 300°C and 0.5 h, respectively. For the treatment temperature influence study, plasma nitriding was carried out using gas mixture of 70%N<sub>2</sub> + 20%H<sub>2</sub> + 10%Ar, flow rate of 3.34×10<sup>-6</sup>Nm<sup>3</sup>s<sup>-1</sup>, pressure of 400 Pa, applied voltage of 600 V, time of 6 h, at temperatures of 300, 350, 400 and 450°C. To the treatment time influence study, plasma nitriding was carried out using gas mixture of 70%N<sub>2</sub> + 20%H<sub>2</sub> + 10%Ar, flow rate of 3.34×10<sup>-6</sup>Nm<sup>3</sup>s<sup>-1</sup>, pressure of 400 Pa, applied voltage of 600 V, temperature 350°C, at times of 2, 4, 6 and 12 h. On the gas mixture study, starting from a gas mixture composed by 80%N<sub>2</sub> + 20 %H<sub>2</sub>, was added amounts of 10 to 50% of argon in

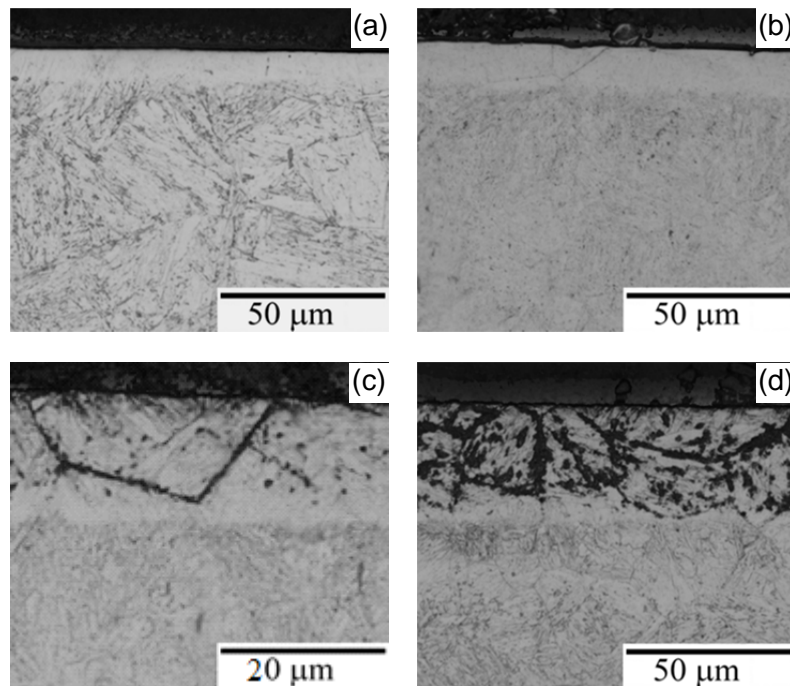
volumetric fraction to the initial composition, being treatments performed at a flow rate, pressure, applied voltage, time and temperature of  $3.34 \times 10^{-6} \text{ Nm}^3 \text{ s}^{-1}$ , 400 Pa, 600 V, 6 h and  $350^\circ\text{C}$ , respectively. For the study of gas flow rate effect, flows of 0.41, 0.83, 1.67, 3.34 and  $6.68 \times 10^{-6} \text{ Nm}^3 \text{ s}^{-1}$  (25, 50, 100, 200 and 400 sccm) were analyzed, being treatments performed at a gas mixture, pressure, applied voltage, time and temperature of 70%N<sub>2</sub> + 20%H<sub>2</sub> + 10%Ar, 400 Pa, 600 V, 6 h and  $350^\circ\text{C}$ , respectively. To the pressure influence study, pressures of 133.3, 400, 666.6 and 933.3 Pa (1, 3, 5, and 7 torr, respectively) were analyzed, being treatments performed at a gas mixture, gas flow rate, applied voltage, time and temperature of 70%N<sub>2</sub> + 20%H<sub>2</sub> + 10%Ar,  $3.34 \times 10^{-6} \text{ Nm}^3 \text{ s}^{-1}$ , 600 V, 6 h and  $350^\circ\text{C}$ , respectively. Finally, to the applied voltage study, voltages of 400, 500, 600 and 700 V were investigated, and the other parameters of gas mixture, gas flow rate, pressure, time and temperature were fixed in 70%N<sub>2</sub> + 20%H<sub>2</sub> + 10%Ar,  $3.34 \times 10^{-6} \text{ Nm}^3 \text{ s}^{-1}$ , 400 Pa, 6 h and  $350^\circ\text{C}$ , respectively. After nitriding treatments, the samples were cooled from nitriding temperature in H<sub>2</sub> + Ar gas mixture flow.

For microstructural analysis, samples were prepared by conventional metallographic procedure. After polishing, the cross-sectioned samples were etched using Vilella's reagent (95 ml of ethyl alcohol, 5 ml of hydrochloric acid, and 1 g of picric acid). Samples were examined using an Optical Microscope (Olympus BX51M). The identification of the phases present in the treated layers was carried out by X-ray diffractometry (XRD), using a Shimadzu XDR 7000 X-ray diffractometer with a CuK<sub>α</sub> X-ray tube in the Bragg-Brentano configuration. Microhardness measurement was also performed for the treated (top) and non-treated (bottom) surfaces employing a Shimadzu Micro Hardness Tester HMV2T, applying a load of 300 gf and a peak-load contact of 15 s. The presented points of the hardness profiles are a result of the mean from five measurements.

### 3 RESULTS AND DISCUSSION

#### 3.1 Treatment Temperature Study

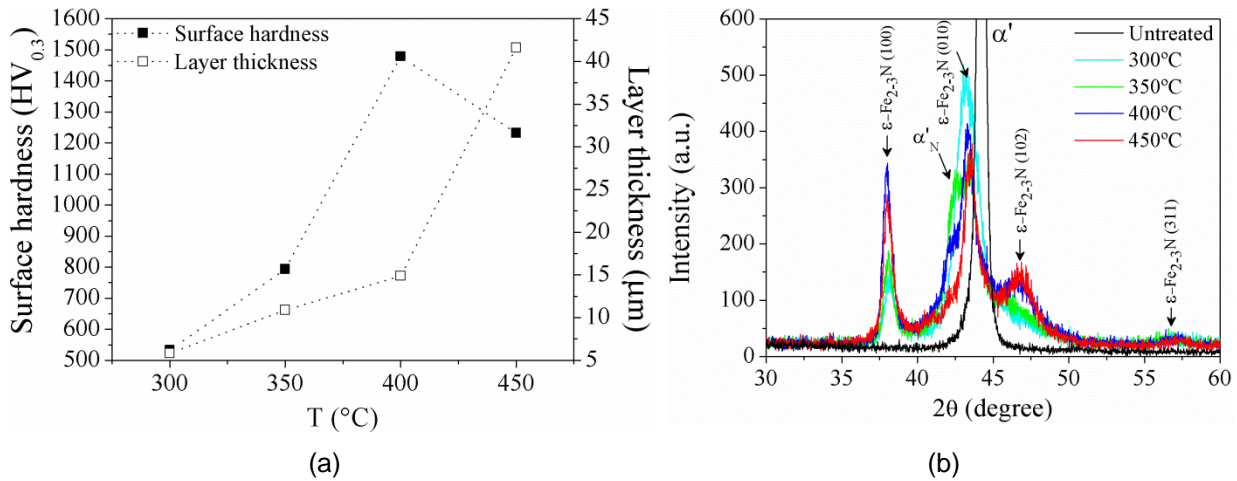
The cross section micrograph of samples plasma nitrided at 300, 350, 400 and  $450^\circ\text{C}$  are shown in Fig. 1 (a, b, c and d), respectively. It can be observed that for the lower treatment temperatures (300 and  $350^\circ\text{C}$ ) the nitrided layer presents higher resistance to the etchant if compared to the material bulk, while for the higher temperatures (400 and  $450^\circ\text{C}$ ) the layer presents lower resistance to the etchant if compared to the bulk material. It is an evidence of chromium nitride precipitation causing sensitization, what is well confirmed for the sample treated at temperature of  $450^\circ\text{C}$  (Fig. 1 (d)).



**Figure 1.** Cross section of samples plasma nitrided at (a) 300, (b) 350, (c) 400 and (d) 450°C. Treatments carried out for 6 h under a gas mixture composed by 70%N<sub>2</sub> + 20%H<sub>2</sub> + 10%Ar, at flow rate of  $3.34 \times 10^{-6} \text{ Nm}^3 \text{ s}^{-1}$ , pressure of 400 Pa and applied voltage of 600 V.

The evolution of surface hardness and thickness as a function of the nitriding temperature are present in Fig. 2 (a). The thickness grows with temperature obeying a parabolic behavior. The hardness grows with the temperature up to 400°C. This growth can be due to the actual hardness of the treated layer and also to the layer thickness. After chromium nitride precipitation, which has been enhanced to the 450°C nitriding temperature, and accompanied by the expanded martensite reduction, the hardness decreases, indicating that  $\alpha'_N$  has an important hardening effect in low temperature nitriding of martensitic stainless steel.

X-ray diffraction patterns of samples plasma nitrided at different temperatures are presented in Fig. 2 (b). Comparing the obtained XRD patterns, it can be visualized that for low temperature nitriding conditions the main phases are  $\epsilon$  iron nitride and nitrogen expanded martensite ( $\alpha'_N$ ). For high temperature nitriding peaks of CrN are also observed, confirming the observed sensitization.

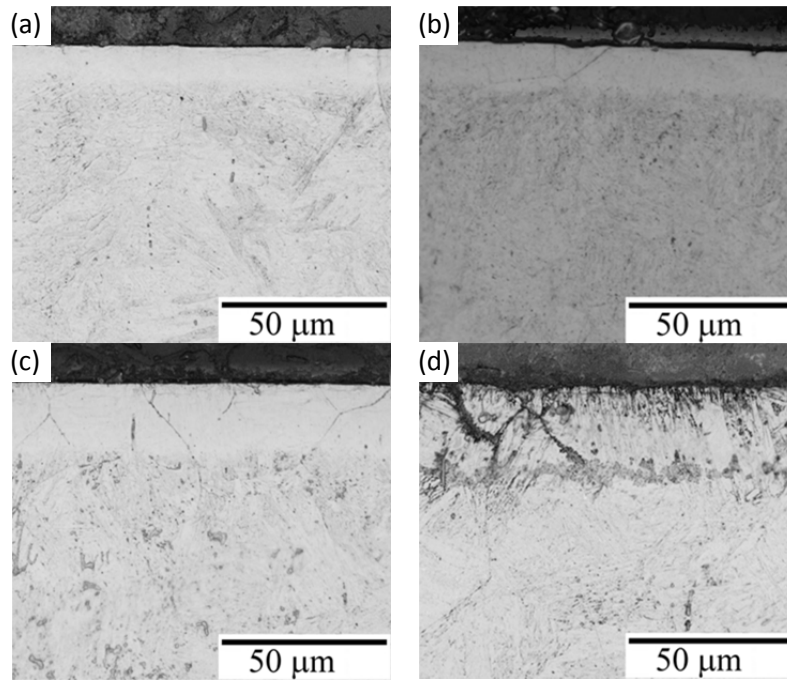


**Figure 2.** (a) Hardness and thickness of the nitrided layer as a function of treatment temperature; and (b) XRD patterns of samples treated at 300, 350, 400 and 450°C. Treatments carried out for 6 h under a gas mixture composed by 70%N<sub>2</sub> + 20%H<sub>2</sub> + 10%Ar, at flow rate of  $3.34 \times 10^{-6} \text{ Nm}^3 \text{ s}^{-1}$ , pressure of 400 Pa and applied voltage of 600 V.

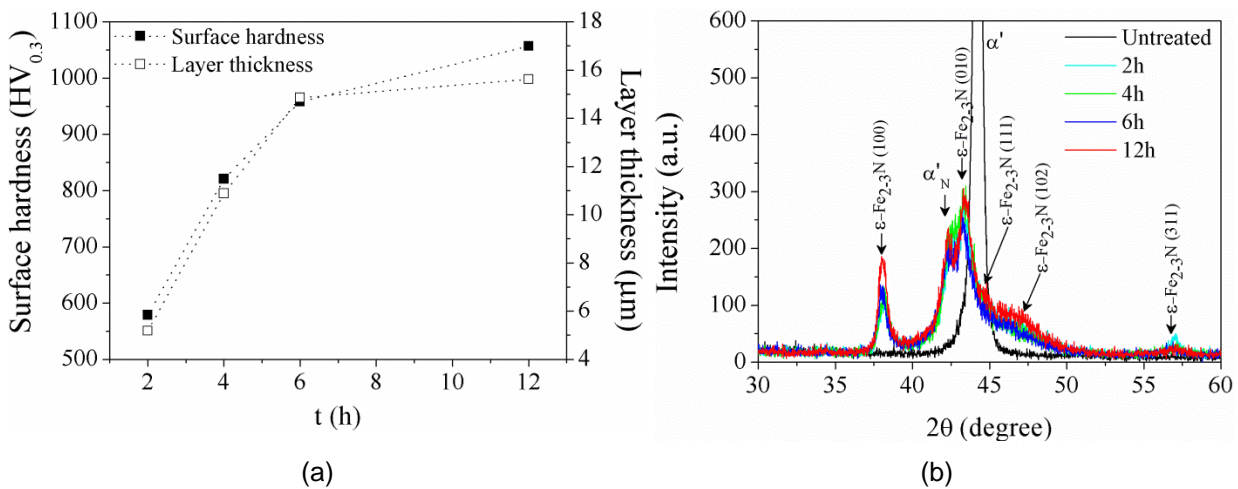
### 3.2 Treatment Time Study

In Fig. 3 (a,b,c, d) the cross section micrographs of as-quenched samples treated at 350°C for 2, 4, 6 and 12 h are showed. It can also be observed that for 4 h treatment a slight sensitization starts at the grain boundaries, being intensified for 6 h. For 12 h the sensitization is generalized in the entire nitrided layer. Again this sensitization is attributed to chromium nitride precipitation.

Fig. 4 (a) presents the evaluation of surface layer thickness and hardness as a function of treatment time. It can be noted that both the thickness and hardness increasing with the treatment time. As previously mentioned, the hardness growth can be due to the actual hardness of the treated layer and also to the layer thickness. Fig. 4 (b) present the X-ray diffraction pattern obtained for samples plasma nitride at 350°C at 2, 4, 6 and 12 h. As for the temperature variation study, here the main phases present were ε iron nitride and expanded martensite ( $\alpha_N$ ).



**Figure 3.** Cross section of samples plasma nitrided at (a) 2, (b) 4, (c) 6 and (d) 12 h. Treatments carried out at 350°C under a gas mixture composed by 70%N<sub>2</sub> + 20%H<sub>2</sub> + 10%Ar, at flow rate of  $3.34 \times 10^{-6} \text{ Nm}^3 \text{ s}^{-1}$ , pressure of 400 Pa and applied voltage of 600 V.



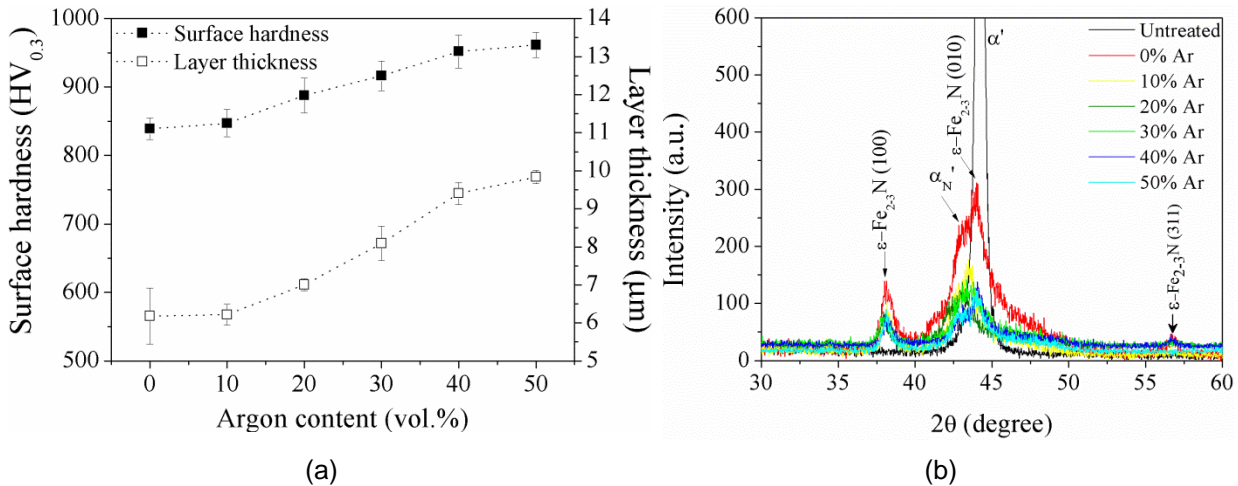
**Figure 4.** (a) Hardness and thickness of the nitrided layer as a function of treatment time; and (b) XRD patterns of samples treated at 2, 4, 6 and 12 h. Treatments carried out at 350°C under a gas mixture composed by 70%N<sub>2</sub> + 20%H<sub>2</sub> + 10%Ar, at flow rate of  $3.34 \times 10^{-6} \text{ Nm}^3 \text{ s}^{-1}$ , pressure of 400 Pa and applied voltage of 600 V.

### 3.3 Gas Mixture Study

Cross section micrographs of the samples treated at different gas mixtures, presented similar characteristics to the obtained for 350°C condition of the treatment temperature study (previously presented in Fig. 1(b)), *id. est.*, the occurrence of a thin and continuous precipitation-free layer for all studied conditions.

Fig. 5 (a) shows measurements of the nitrided layers thickness and hardness as a function of the Ar content in the gas mixture. The higher the argon content the higher is the nitrided layers thickness and hardness. From these results, we can infer that

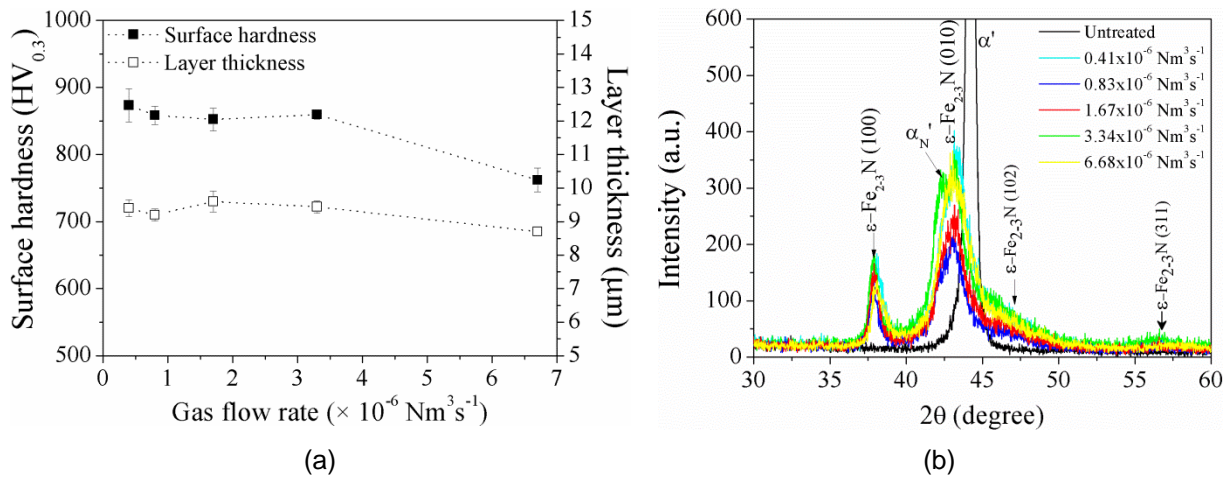
the argon has an important role in the dissociation of molecular nitrogen and formation of reactive nitrogen radicals. It follows that increasing the argon content, promotes an increased formation of reactive nitrogen radicals. Thus, the higher the supply of reactive nitrogen to react with the material surface. Fig. 5 (b) present the X-ray diffraction patterns of samples plasma nitrided under different argon compositions in gas mixture. Comparing the obtained XRD patterns, it can be visualized that the main phases are  $\epsilon$  iron nitride and nitrogen expanded martensite ( $\alpha'_N$ ).



**Figure 5.** (a) Hardness and thickness of the nitrided layer as a function of gas mixture; and (b) XRD patterns of samples treated at different gas mixtures conditions. Treatments carried out at 350°C for 6 h under a flow rate of  $3.34 \times 10^{-6} \text{ Nm}^3 \text{ s}^{-1}$ , pressure of 400 Pa and applied voltage of 600 V.

### 3.4 Gas Flow Rate Study

Cross section micrographs of the samples treated at different gas flow rates conditions, presented similar characteristics to the obtained for 350°C condition of the treatment temperature study (previously presented in Fig. 1(b)), *id. est.*, the occurrence of a thin and continuous precipitation-free layer for all studied conditions. Fig. 6 (a) present the the nitrided layer thickness and hardness variation as a function of the gas flow rate. It is found that both hardness and thickness exhibit similar values to the conditions of  $0.41$ ,  $0.83$ ,  $1.67$  and  $3.34 \times 10^{-6} \text{ Nm}^3 \text{ s}^{-1}$  (25, 50, 100 and 200 sccm, respectively). Moreover, the  $6.68 \times 10^{-6} \text{ Nm}^3 \text{ s}^{-1}$  (400 sccm) condition shows a reduction in the hardness and layer thickness as compared the other conditions. This reduction can be explained by the shorter time residence of the plasma species on the nitriding chamber, for this condition (3 seconds, whereas for  $0.41$ ,  $0.83$ ,  $1.67$  and  $3.34 \times 10^{-6}$  conditions, the residence time are 41.7, 25, 12.5 and 6.3 seconds). The reduction on the residence time reflects in a reduction of the reactive species reaction time with the surface material, and thus a lower nitrogen diffusion of nitrogen. Fig. 6 (b) presents the X-ray diffraction patterns of samples plasma nitrided under different gas flow rate conditions. Just as observed for the other studies, the main phases present are  $\epsilon$  iron nitride and nitrogen expanded martensite ( $\alpha'_N$ ).

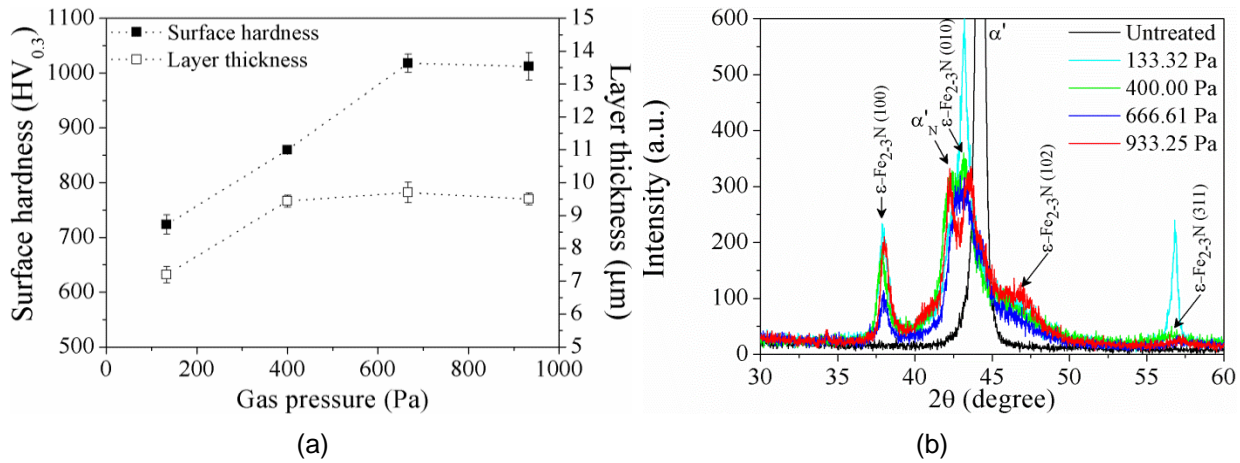


**Figure 6** (a) Hardness and thickness of the nitrided layer as a function of gas flow rate; and (b) XRD patterns of samples treated at 0.41, 0.83, 1.67, 3.34 and 6.68 × 10<sup>-6</sup> Nm<sup>3</sup>s<sup>-1</sup>. Treatments carried out at 350°C for 6 h under a gas mixture of 70%N<sub>2</sub> + 20%H<sub>2</sub> + 10%Ar, pressure of 400 Pa and applied voltage of 600 V.

### 3.5 Gas Pressure Study

Cross section micrographs of the samples treated at different gas pressures conditions presented similar characteristics to the obtained for 350°C condition of the treatment temperature study (previously presented in Fig.1(b)), *id. est.*, the occurrence of a thin and continuous precipitation-free layer for all studied conditions. The evolution of surface hardness and thickness as a function of the pressure are present in Fig. 7 (a). The thickness grows with pressure up to 400 Pa (3 torr), remaining stable for 666.6 and 933.3 Pa (5 and 7 torr). Moreover, it can be seen that the hardness increases in the range of 133.3 to 666.6 Pa (1 to 5 torr), stabilized between 666.6 to 933.3 Pa (5 and 7 torr). The lower mean free path at higher pressures results in less energetic collisions, and so has energetic changing in the plasma created species when the pressure is augmented. The lower hydrogen reactive creation is direct indicative of lower concentration of atomic Hydrogen. To relate this result, two hypothesis can be considered. First, at higher concentrations the atomic hydrogen inhibits the plasma nitriding by capture of nitrogen atoms in the gaseous volume. Second, hydrogen atoms reaching the sample surface are able to depleting the nitrogen in recombination reactions. Fig. 7 (b) presents the X-ray diffraction patterns of samples plasma nitrided under different gas pressure conditions. Just as observed for the other studies, the main phases present are ε iron nitride and nitrogen expanded martensite (α'<sub>N</sub>).



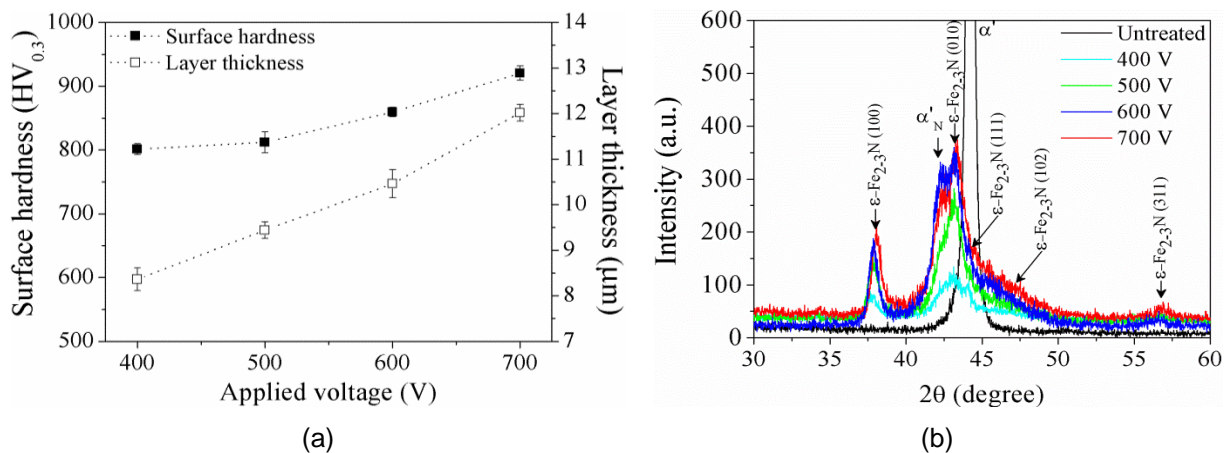


**Figure 7.** (a) Hardness and thickness of the nitrided layer as a function of gas pressure; and (b) XRD patterns of samples treated at 200, 400, 800 and 1200 Pa. Treatments carried out at 350°C for 6 h under a gas mixture of 70%N<sub>2</sub> + 20%H<sub>2</sub> +10%Ar, at flow rate of  $3.34 \times 10^{-6} \text{Nm}^3 \text{s}^{-1}$ , and applied voltage of 600 V.

### 3.6 Applied Voltage Study

Cross section micrographs of the samples treated at different applied voltages, presented similar characteristics to the obtained for 350°C condition of the treatment temperature study (previously presented in Fig. 1(b)), *id. est.*, the occurrence of a thin and continuous precipitation-free layer for all studied conditions.

The evolution of surface hardness and thickness as a function of the applied voltage are present in Fig. 8 (a). It can be seen that the nitrided layer hardness and thickness increases with increasing applied voltage. This is due to the greater attraction force of the ions in the cathode sheath region, increasing the acceleration of electrically charged specimens and, consequently, increasing the number of collisions resulting in an increased production of reactive nitrogen radicals. Fig. 8 (b) presents the X-ray diffraction patterns of samples plasma nitrided under different applied voltages conditions. Just as observed for the other studies, the main phases present are ε iron nitride and nitrogen expanded martensite (α'<sub>N</sub>).



**Figure 8.** (a) Hardness and thickness of the nitrided layer as a function of applied voltage; and (b) XRD patterns of samples treated at 400, 500, 600 and 700 V. Treatments carried out at 350°C for 6 h under a gas mixture of 70%N<sub>2</sub> + 20%H<sub>2</sub> +10%Ar, at flow rate of  $3.34 \times 10^{-6} \text{Nm}^3 \text{s}^{-1}$ , and pressure of 400 Pa.

## 4 CONCLUSION

A study of low-temperature plasma nitriding was performed aiming to determine the effect of the nitriding treatment parameters on the surface properties of AISI 420 martensitic stainless steel samples. The main conclusions of the work can be listed as follows:

- Low temperature plasma nitriding of AISI 420 steel leads to formation of very hard surface layer;
- At lowest nitriding temperatures and times, a precipitation-free layer is produced. At higher nitriding temperatures and times, the great chromium mobility promotes the occurrence of CrN precipitates. The occurrence of CrN precipitation reduces the chromium content in solid solution, promoting a reduction in material corrosion resistance and also causes sensitization. Similarly, the reduction of nitrogen in solid solution is accompanied by a reduction of the compressive residual stress in the martensite crystal lattice, thereby decreasing the hardness of the modified surface;
- The increase of argon content in the gas mixture for the investigated range, results in an increased nitride layer thickness. Surface hardness are also increased correspondingly;
- Surface hardness and layer thickness remains constant for gaseous flows in the range  $0.41$  to  $3.34 \times 10^{-6} \text{ Nm}^3\text{s}^{-1}$ , and present a reduction for the flow of  $6.68 \times 10^{-6} \text{ Nm}^3\text{s}^{-1}$ , when compared to other conditions.
- The variation in treatment gas pressure leads to changes in the surface characteristics of the treated samples. Gas pressures of 133.3 to 666.6 Pa are responsible by most promising results of the nitrided layer thickness and hardness;
- The variation of the applied voltage in the studied range influences the surface characteristics of treated samples. The nitrided layer thickness and hardness, increases with increasing of the applied voltage;

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## REFERÊNCIAS

- 1 XI, C.X., LIU, D.X., HAN, D. Acta Metallurgica Sinica (English Letters), v. 21, p. 21–29, 2008.
- 2 XI, C.X., LIU, D.X., HAN, D. Surface and Coatings Technology, v. 202, p. 2577–2583, 2008.
- 3 KIM, S.K. et al. Surface and Coatings Technology, v. 163-164 (2003) 380–385.
- 4 PINEDO, C.E., MONTEIRO, W.A. Surface and Coatings Technology, v. 179, p. 119–123, 2004.
- 5 ISFAHANY, A.N., SAGHAFIAN, H., BORHANI, G. Journal of Alloys and Compounds, v. 509, p. 3931–3936, 2011.
- 6 HUDIS, M. Journal of Applied Physics, v. 44, p. 1489-96, 1973.
- 7 CZERWIEC, T. et al. Plasma Process and Polymers, v. 6, p. 401–409, 2009.

- 8 FEWELL, M.P. et al. Surface and Coatings Technology. v. 131, p. 300, 2000.
- 9 LIANG, W. et al. Surface and Coatings Technology. v. 131, p. 563–567, 2000