

## LOW TEMPERATURE PLASMA ASSISTED NITRIDING OF FERRITIC AND MARTENSITIC AISI 420 STAINLESS STEEL

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**Abstract.** The AISI 420 martensitic stainless steel is commonly applied in various industrial segments due to its high mechanical and corrosion resistance. The AISI 420 allows hardening by quenching and/or by thermochemical treatments like nitriding, which introduces nitrogen on the metal surface to increase its surface hardness and, therefore, its wear resistance. This treatment, when done at high temperatures, can lead to a significant reduction in the corrosion resistance of stainless steels, as a consequence of precipitation of chromium nitrides, depleting the chromium content in solid solution. In this context, low temperature plasma assisted treatment is a viable technique once it can combine, in certain process conditions, hardening and no deterioration of the corrosion resistance of stainless steels. This work presents results of the influence of treatment temperature on low temperature plasma nitriding process of AISI 420 in as-quenched and annealed condition (martensitic and ferritic phases, respectively). Samples were nitrided for a period of  $14.4 \times 10^3$  s (4 hour), using a DC plasma apparatus under a constant pressure of 400 Pa (3 Torr) with a gas mixture flow composed of 70%  $N_2$  + 20%  $H_2$  + 10% Ar, at a flow rate of  $3.34 \times 10^{-6} m^3 s^{-1}$  (200 sccm). The influence of the temperatures on the properties and thickness of the treated layer were studied for temperatures of 573, 623, 673, 723 and 773 K. The nitrided layers were characterized by optical microscopy, X-ray diffraction and microhardness measurements. The results indicate that the treatment temperature is the key parameter of the process, being essential for mechanical and corrosion properties of the treated layer.

**Keywords:** Low temperature plasma assisted nitriding, martensitic stainless steel, AISI 420.

### 1. INTRODUCTION

The AISI 420 martensitic stainless steel is commonly used in applications requiring good corrosion resistance combined with high mechanical strength, due to its chemical and metallurgical properties (Kim *et al.*, 2003; Figueroa *et al.*, 2005; Souza *et al.* (2008); Xi *et al.* (2008)a; Xi *et al.* (2008)b). However, low hardness and poor wear resistance sometimes limit its industrial applications (Alphonsa *et al.* (2002); Pinedo and Monteiro, 2004). So, despite their properties, in recent decades, researches were conducted with the aim of improving its wear and corrosion resistance, through the application of plasma assisted technology (Zhang and Bell, 1985; Ichii *et al.* (1986); Davis, 1994; Menthe *et al.* (1995)).

Nevertheless, in most of these studies, the obtained results showed a considerable decrease in the corrosion resistance of the material that occurred due to the precipitation of chromium nitride particles resulting in the depletion of chromium in solid solution into the matrix (Alphonsa *et al.* (2002); Li and Bell, 2004; Pinedo and Monteiro, 2004; Heuer *et al.* (2007); Xi *et al.* (2008)b; Czerwicz *et al.* (2009); Souza *et al.* (2009)). As a result, recent works have been developed by performing the process at sufficiently low temperatures (typically below 773 K) to prevent the precipitation of chromium carbides and nitrides, promoting enhancement of wear and corrosion resistance. In such cases, when treatment is performed at low temperatures, it produces a supersaturated phase called expanded martensite (Kim *et al.* (2003); Corengia, *et al.* (2004); Figueroa *et al.* (2005); Souza *et al.* (2008); Xi *et al.* (2008)a; Xi *et al.* (2008)b), so called when compared with expanded austenite, or S-phase, reported by Sun (2005) and Souza *et al.* (2009). Within this context, this paper presents recent experimental results on the low temperature plasma assisted nitriding process for the AISI 420 stainless steel (in as-quenched(QC) and annealed(AN) conditions), taking special attention to the influence of the temperature and sample pre-treatment on the microstructure, hardness and thickness of the treated layer.

### 2. EXPERIMENTAL PROCEDURE

The AISI 420 martensitic stainless steel round bar was received in the annealed condition, with a microstructure composed of a ferritic matrix with dispersed carbides. Samples of 10 mm in height were cut from the original bar ( $\varnothing = 9.5$  mm). Some samples were subjected to quenching heat treatment in air from the austenitizing temperature of 1323 K, keeping this temperature for 30 minutes for complete carbide dissolution. Before the thermo-chemical treatment, the samples were first fine-grounded using wet SiC paper from 240 down to 1200-grit finish and mechanically polished using a felt disc and 1  $\mu m$  size  $Al_2O_3$  abrasive suspensions. Finally, the specimens were manually cleaned with alcohol, and introduced into the treatment chamber.

The equipment employed in the experimental work was a DC-pulsed glow discharge apparatus. It consists of a cylindrical vacuum chamber of 350 mm diameter, 380 mm high stainless steel attached to steel plates and sealed with o-rings at both ends. The system was evacuated down to a residual pressure of 1.33 Pa ( $10^{-2}$  Torr) by using a double stage mechanical pump. The gas mixture of H<sub>2</sub>, N<sub>2</sub> and Ar was adjusted by three mass flow controllers of  $8.33 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$  (500 sccm – standard cubic centimeters per minute) in full scale.

Aiming to treat four samples at the same time, an AISI 1020 steel support was constructed with external diameter of 55 mm, containing four holes of 10 mm placed at a distance of 20 mm from the support center (Fig. 1). This support operates as the cathode of DC glow discharge, being negative biased by using a square wave form pulsed DC power supply. The peak voltage was set to 600 V. The pulse period ( $t_{\text{ON+OFF}}$ ) used was 240  $\mu\text{s}$  and the power transferred to the plasma was adjusted by varying the time that the pulse was switched on ( $t_{\text{ON}}$ ). So, the temperature of the sample was controlled by adjusting the pulse voltage width. The temperature was measured by means of a chromel–alumel (K-type of 1.5 mm diameter) thermocouple inserted 6 mm depth of into the sample support. A previous study was realized to evaluate the thermal gradient through the support concluding that it is negligible.

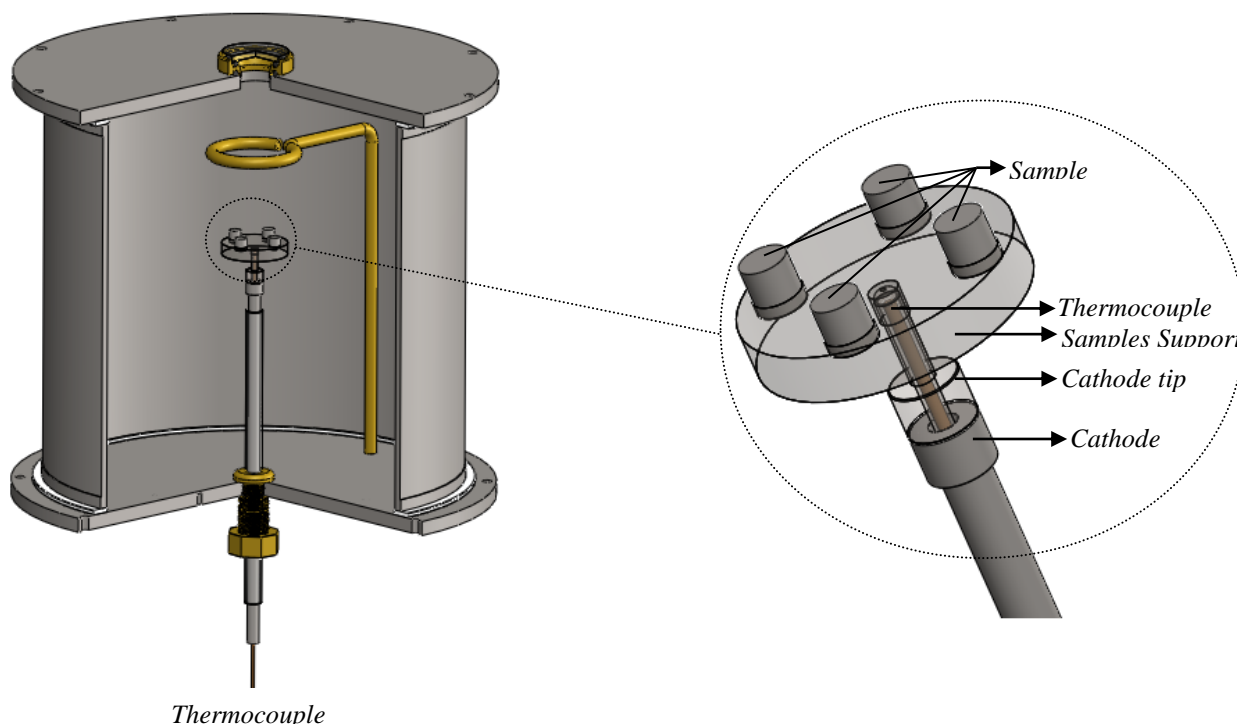


Figure 1. Schematic representation of the vacuum chamber and of the sample support configuration applied in the plasma assisted low temperature nitriding treatment.

Before the nitriding treatment, samples were sputter-cleaned in a gas mixture of 90% H<sub>2</sub> + 10% Ar at 573 K for 30 minutes, which would remove the native oxide layers from the surface of the samples. Then, the AISI 420 stainless steel samples were plasma nitrided in a gas mixture of 70% N<sub>2</sub> + 20% H<sub>2</sub> + 10% Ar at 573, 623, 673, 723 and 773 K for 4 h. The treatment pressure was measured with a capacitance manometer of  $1.33 \times 10^4$  Pa (100 Torr) in full-scale operation and controlled at 400 Pa (3 Torr) by mean of a manual valve. After the completion of the nitriding process, samples were cooled in the chamber down to room temperature under Ar-H<sub>2</sub> gas mixture flow. The parameters used in experiments are given in Tab. 1.

Table 1. Studied parameters for plasma assisted nitriding treatments.

<i>Parameter</i>	<i>Sputter-cleaning</i>	<i>Plasma nitriding</i>
Temperature (K)	573	573, 623, 673, 723, 773
Voltage (V)	600	600
Total pressure (Pa)	400	400
Time (h)	0.5	4
Treatment gas (vol.%)	90% H <sub>2</sub> + 10% Ar	70% N <sub>2</sub> + 20% H <sub>2</sub> + 10% Ar
Gas flow ( $\text{m}^3 \text{ s}^{-1}$ )	$3.34 \times 10^{-6}$	$3.34 \times 10^{-6}$

After treatment samples were characterized. The phase evolution was studied by X-ray diffraction analysis using a Shimadzu XDR7000 x-ray diffractometer with Cu  $K\alpha$  radiation and with a scan speed of 1 deg/min. The surface microhardness of the nitrated layer was measured using a Shimadzu Micro Hardness Tester HMV-2T with a load of 300 gf. The cross-sectioned samples, after metallographic preparation and chemical etching with Vilella for 25 seconds, were analyzed with an Olympus BX51M optical microscopy in order to determine microstructural evolution of the nitrated layers formed on the AISI 420 stainless steel at different temperatures.

### 3. RESULTS AND DISCUSSIONS

#### 3.1. Microhardness

Surface microhardness of ferritic and martensitic nitride samples for a treatment time of 4 hours and different treatment temperatures are shown in Fig. 2.

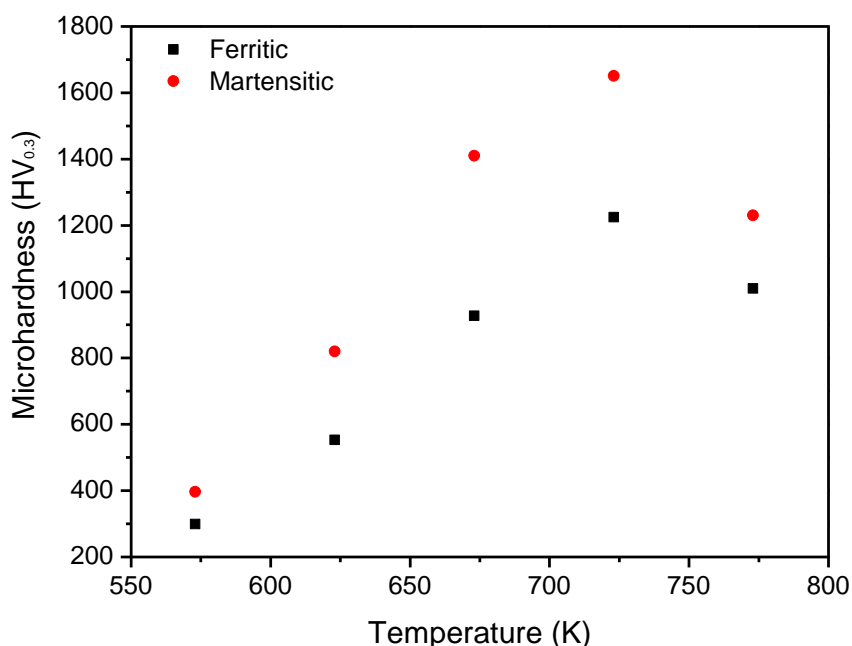


Figure 2. Evolution of nitrated surface microhardness as a function of the temperature. Samples treated for 4 h at a gas mixture composition of 70%  $N_2$  + 20%  $H_2$  + 10% Ar, flow rate of  $3.34 \times 10^{-6} m^3 s^{-1}$  and pressure of 400 Pa.

From Fig. 2 it can be noticed that the surface hardness varies with temperature, achieving its maximum for 723 K both for martensitic and ferritic samples. The surface hardness can be interpreted as an apparent hardness since, spatially at low temperature, the indentation depth is not negligible with respect to the layer thickness. So the increase in the surface hardness from 573 to 723 K can be attributed not only for the increase in the nitrogen content in the related layer but also to the increase of the layer thickness. The decrease in the surface hardness from 723 to 773 K may be credited to the reduction of compressive stress and solid solution hardening of nitrogen when chromium nitrides are precipitated. Similar results are presented by Corengia *et al*, 2004.

For all the studied conditions the martensitic sample presents higher hardness when compared to the ferritic samples. For low temperature the bulk hardness difference would play an important role in the observed difference since the treated layers are thin in comparison to the indentation depth. For relatively high temperature (673-773 K) the difference can be explained by the difference in the chromium content in solid solution that is significantly higher for the martensitic samples. This higher unbounded chromium concentration contributes to the layer hardness by enhancing the nitrogen solid solution super-saturation at low temperature and by hard chromium nitrides precipitation at high temperature.

#### 3.2. Microstructures

Optical micrograph of cross-sectioned ferritic and martensitic AISI 420 samples, nitrated at 723 and 773 K during 4 hours are presented in Fig 3.

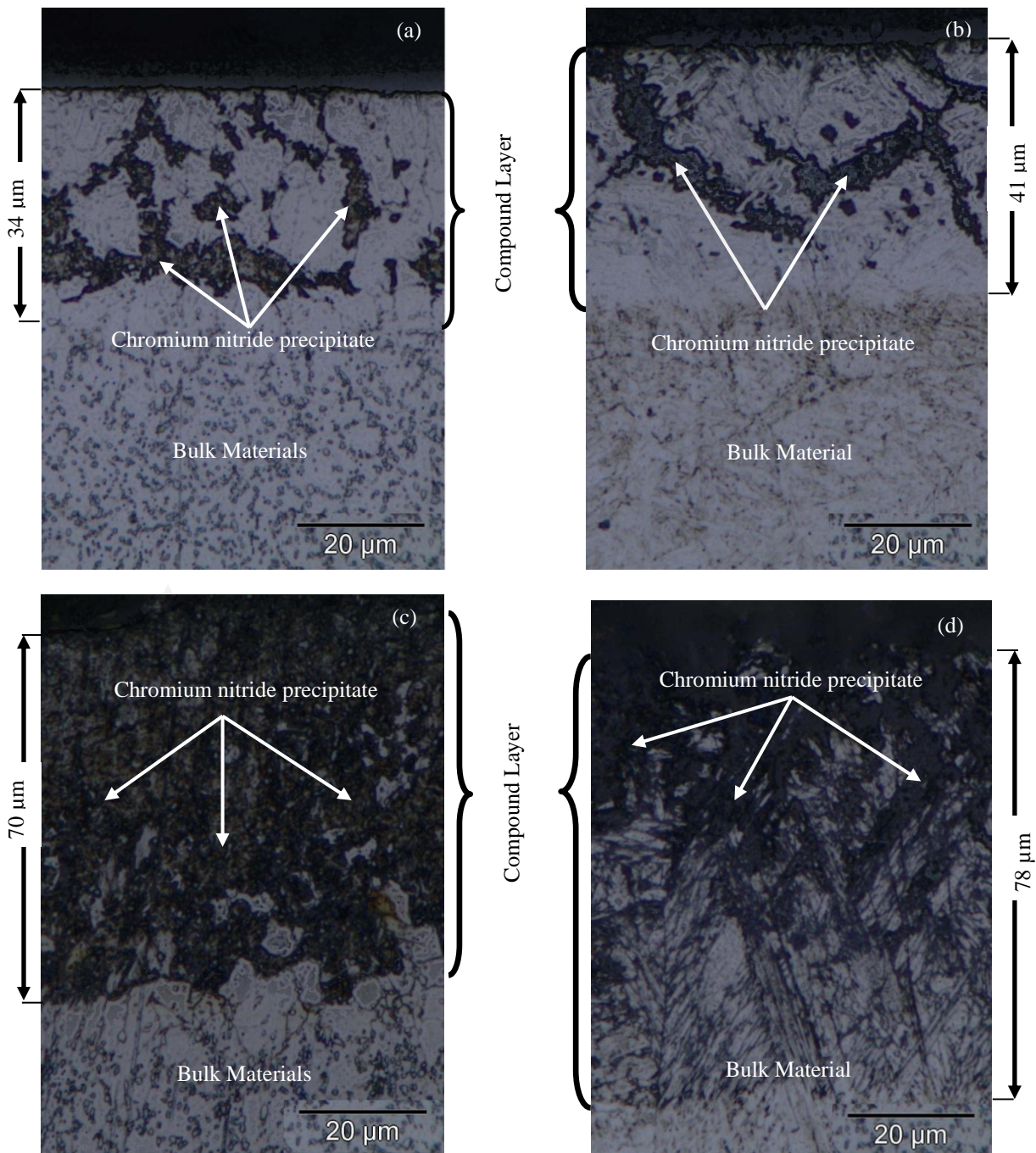


Figure 3. Cross-section optical micrograph of AISI 420: (a) Ferritic sample treated at 723 K; (b) Martensitic sample treated at 723 K; (c) Ferritic sample treated at 773 K; and (d) Martensitic sample treated at 773 K. Samples treated for 4 h at a gas mixture composition of 70% N<sub>2</sub> + 20% H<sub>2</sub> + 10% Ar, flow rate of  $3.34 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$  and pressure of 400 Pa.

In the context of this work, samples presented in Fig. 3 can be considered as treated at high temperature, since chromium nitrides precipitation occurs. It is evidenced by lower resistance of the treated layer to the etchant indicating solid solution chromium depletion. For samples treated at 723 K, chromium nitrides precipitation is mainly observed in the grain boundary, for samples treated at 773 K it is observed in the whole layer. When comparing ferritic and martensitic samples at the same temperature it is observed that the ferritic ones are easily sensitized, what can be attributed to the effect of chromium in enabling nitrogen solid solution matrix super-saturation.



Optical micrograph of cross-sectioned ferritic and martensitic AISI 420 samples nitrided at 573 and 673 K during 4 hours are presented in Fig 4.

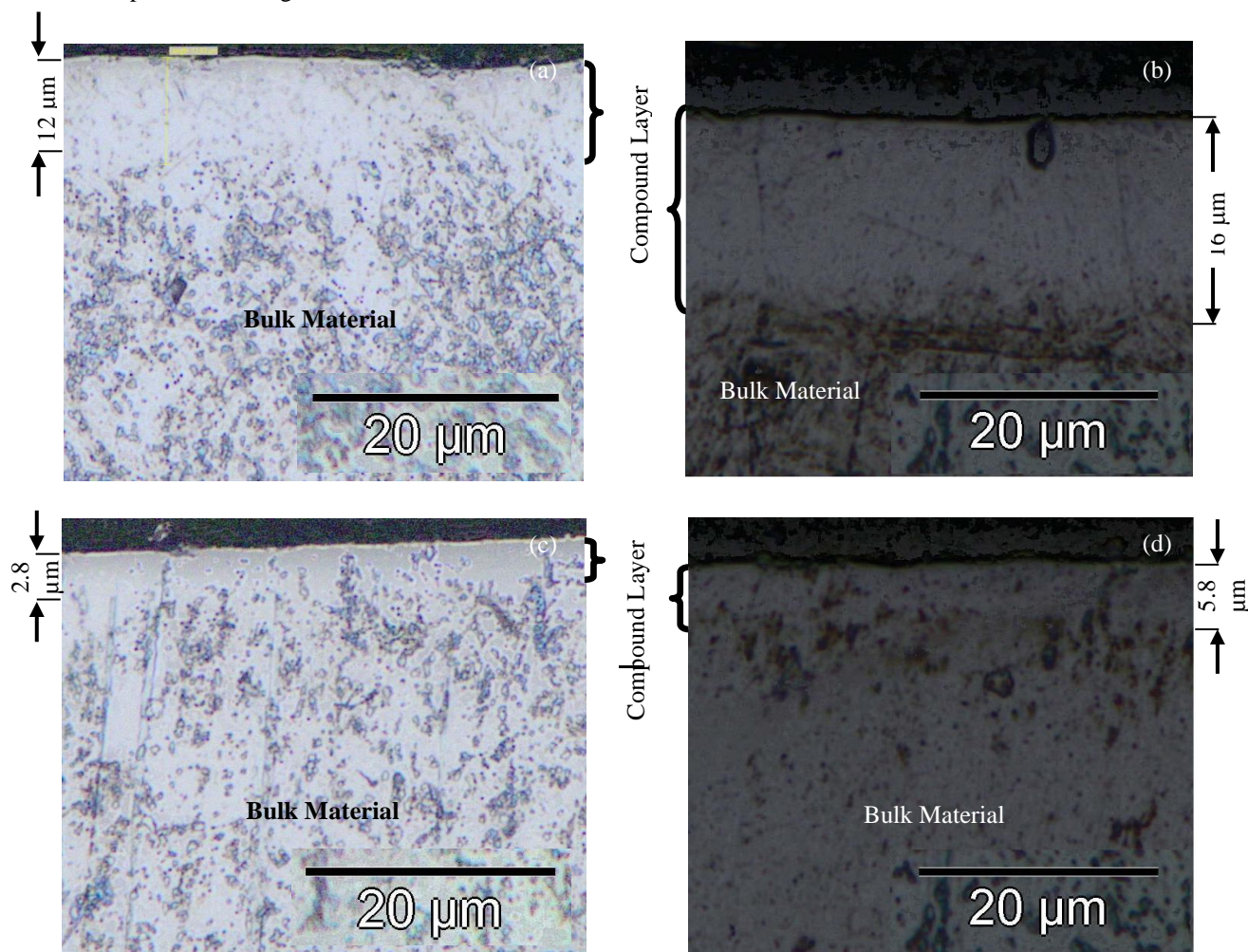


Figure 4. Cross-section optical micrograph of AISI 420: (a) Ferritic sample treated at 673 K; (b) Martensitic sample treated at 673 K; (c) Ferritic sample treated at 573 K; and (d) Martensitic sample treated at 573 K. Samples treated for 4 h at a gas mixture composition of 70% N<sub>2</sub> + 20% H<sub>2</sub> + 10% Ar, flow rate of  $3.34 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$  and pressure of 400 Pa.

From cross-section optical micrograph showed in Fig 4, it can be considered that for the presented temperatures the samples were low temperature nitrided, avoiding chromium nitrided precipitation and chromium content depletion in solid solution. Another interesting feature observed in Fig. 4 is that the treated layer is more resistant to the etchant, evidencing that the treated layer is even more resistant to corrosion than the bulk material. So, it is expected that low temperature plasma assisted nitriding is effective on preventing the decrease in the corrosion resistance, probably promoting an enhancement on this property.

Comparing the layer thickness for ferritic and martensitic samples at the sample temperature, Fig. 3 and Fig. 4, it is clear that the layer is always thicker for martensitic samples. It is attributed to high diffusion path, more present in martensitic samples, allowing deeper nitrogen diffusion.

X-ray diffraction patterns are presented in Fig. 5. Fig. 5(a) shows that the untreated sample has three diffraction peaks of martensite:  $\alpha$  (110),  $\alpha$  (200) and  $\alpha$  (211) in the range of 30°–90°. Fig. 5(b) indicates that the 573 K nitrided surface mainly consists of  $\epsilon$  iron nitride and expanded martensite. At angles of 44.8°, 64.9° and 82.2° in Fig. 5(b), diffraction peak of supersaturated nitrogen solid solution are present, the so called expanded martensite ( $\alpha_n$ ), according to the literature (Kim *et al.*, 2003; Corengia, *et al.*, 2004; Figueroa *et al.*, 2005; Souza *et al.*, 2008; Xi *et al.* 2008a; Xi *et al.* 2008b). Nitrogen solid solution causes expansion of the  $\alpha$  lattice structure shifting the (110), (200) and (211) peaks toward a lower diffraction angle.  $\alpha_n$  and  $\epsilon$  phases are responsible to the high surface hardness values that can be observed in Fig. 2. No CrN peak was detected by XRD analysis, which confirms that 573 K nitriding prevents the formation of chromium nitride in the surface layer of AISI 420 stainless steel.

The phase composition in 623 and 673 K nitrided surface layer was also dominantly  $\epsilon$ , and  $\alpha_N$  (Fig. 5(c-d)). Chromium nitride precipitate was not detected for these nitriding parameters. The phase composition for 723 K and 773 K nitrided layer presents  $\epsilon$ , CrN and  $\alpha_N$  phases (Fig. 5(e-f)). Chromium nitride precipitation was detected in these nitriding conditions, in consonance with the present in Fig. 3.

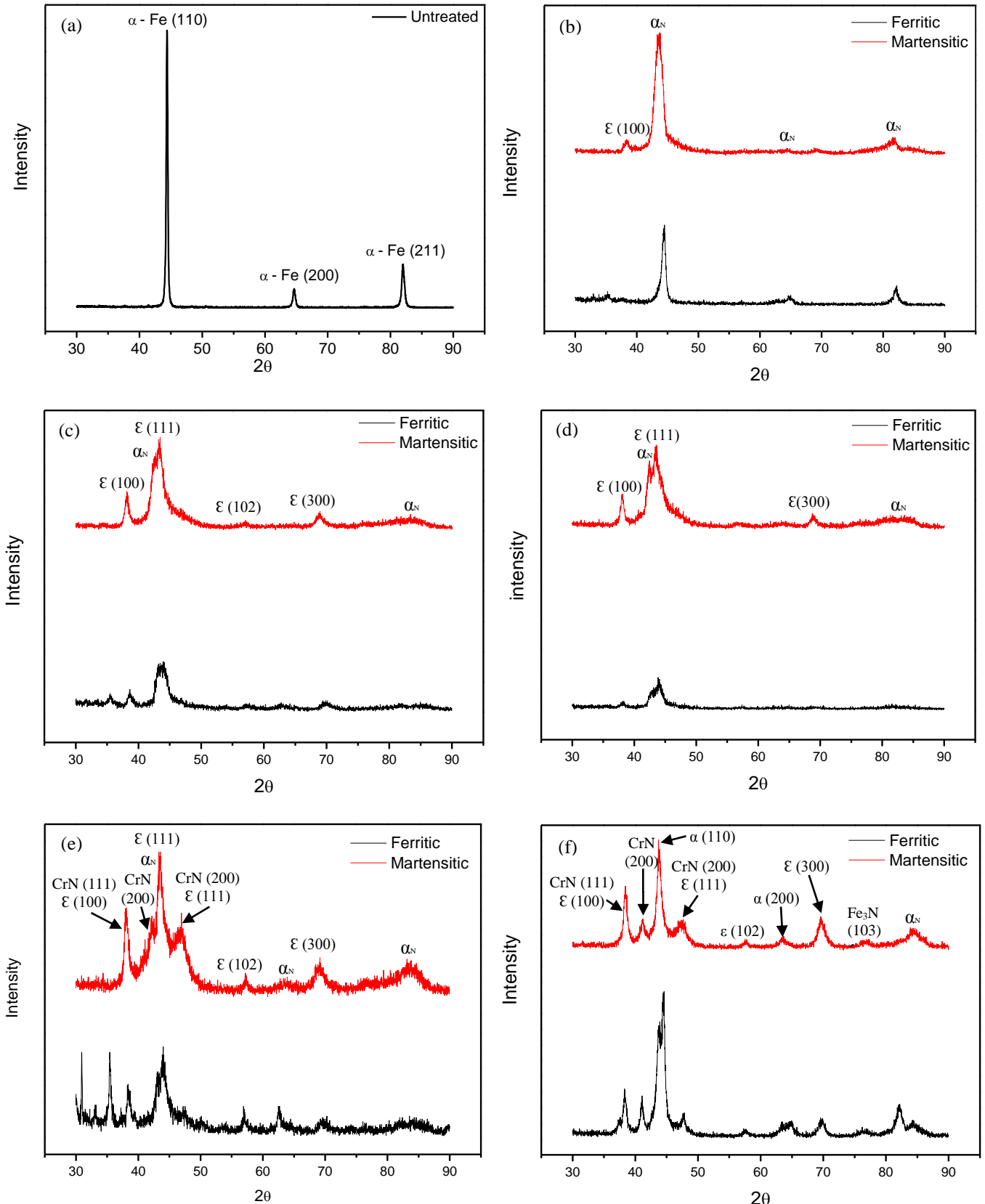


Figure 5. X-ray diffraction patterns for the plasma nitride AISI 420 stainless steel. (a) Untreated sample; (b) 573 K nitride samples; (c) 623 K nitride samples; (d) 673 K nitride samples; (e) 723 K nitride samples and (f) 773 K nitride samples. Samples treated for 4 h at a gas mixture composition of 70%  $N_2$  + 20%  $H_2$  + 10% Ar, flow rate of  $3.34 \times 10^{-6} m^3 s^{-1}$  and pressure of 400 Pa.

### 3.3. Layer thickness evolution

From the nitriding depth data, the nitrogen diffusion activation energy was calculated by an Arrhenius plot. Linearizing the related equation Eq. (1) and considering the diffusion coefficient independent of the treatment time it is obtained that:

$$\ln d = cte - \frac{Q}{2R} \cdot \frac{1}{T} \quad (1)$$

Where: d is the layer thickness

Q is the activation energy for nitrogen diffusion

R is the ideal gas constant

T is the absolute temperature

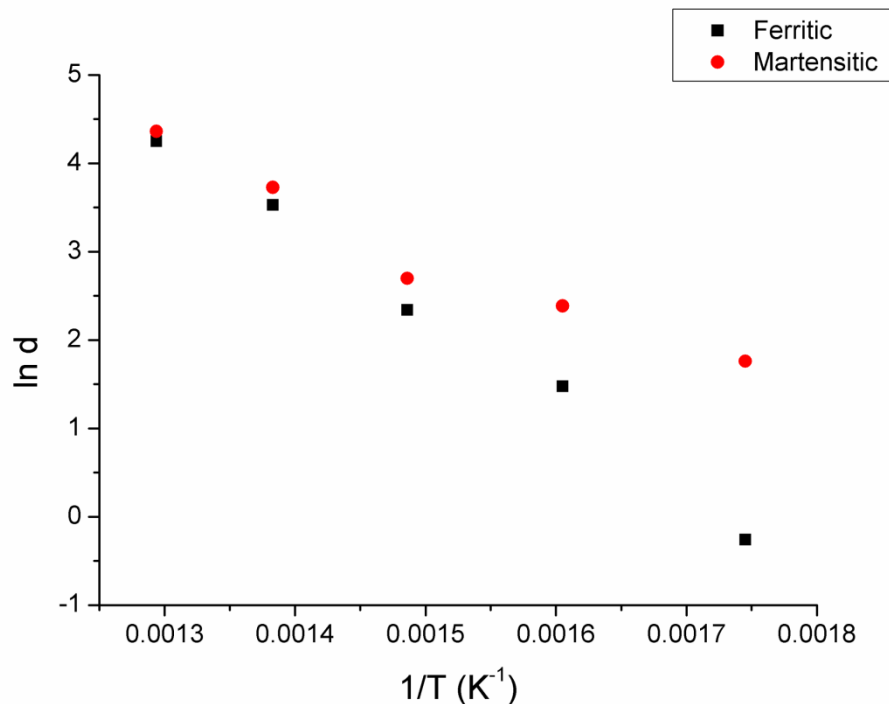


Figure 6. Arrhenius plot of the layer thickness. Determination of the activation energy for nitrogen diffusion. Samples treated for 4 h at a gas mixture composition of 70% N<sub>2</sub> + 20% H<sub>2</sub> + 10% Ar, flow rate of 3.34 × 10<sup>-6</sup> m<sup>3</sup> s<sup>-1</sup> and pressure of 400 Pa.

Considering Arrhenius-type behavior, the activation energy for nitrogen diffusion was calculated using linear regression (Pinedo and Monteiro, 2004). The activation energy for the ferritic sample was 164.3 kJ/Mol and for the martensitic sample was 144.3 kJ/mol (for high temperature) and 60.5 kJ/mol (for low temperature), this explain why in the martensitic samples the layer was thicker. It also agrees with the hypothesis of higher influence of high diffusion paths (low activation energy) for martensitic samples.

### 4. CONCLUSIONS

From this work it can be concluded that:

1. The highest surface hardness was achieved for treatments carried out at 723 K in martensitic AISI420 samples. The surface hardness decreases for 773 K when strong nitride precipitation occurs, indicating that the hardening effect of nitrogen in solid solution is higher that of chromium nitride precipitation.
2. For all studied condition the treated layer was thicker for martensitic samples, what is attributed to high diffusion paths present in higher density in martensitic samples.
3. The metallographic examination of samples cross-section has revealed that the low temperature nitred layer is more resistant to etching than the substrate, indicating the potential of the process to enhance the corrosion resistance of ferritic and martensitic stainless steel, showing also no detectable precipitation of chromium nitrides.

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