

## EFFECT OF THE TEMPERATURE OF PLASMA NITRIDING IN AISI 316L AUSTENITIC STAINLESS STEEL

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Key words: plasma nitriding, AISI 316L, temperature.

### ABSTRACT

*Plasma nitriding is one of the techniques used in surface engineering to increase the surface hardness and wear resistance of the austenitic stainless steels. This process, when carried out at low-temperatures (350-400°C), can increase the corrosion resistance of the produced layer, in relation to the substrate, due to the formation of the "S" phase rich in nitrogen with high resistance to pitting formation. In the present work, samples of AISI 316L austenitic stainless steel were plasma nitrided at temperatures of 400, 450 and 500°C in a d.c. plasma with a gaseous mixture of 80%H<sub>2</sub> - 20%N<sub>2</sub>. The structures and properties of the nitrided layers were investigated through optical microscopy, microhardness measurements, scanning electron microscopy coupled with EDS, and X-ray diffraction analysis. All of the layers presented an accentuated increase in their hardness, in relation to the hardness of the substrate.*

### 1. INTRODUCTION

Austenitic stainless steels are largely used in corrosive industrial environment, such as in the chemical and food industries [1]. These steels are known by its excellent corrosion resistance due to formation of a thin surface layer of oxide, however their wear and hardness characteristics are relatively poor [1,2]. Therefore, its use in applications that require resistance to wear is limited. Many attempts have been made to increase the surface hardness and the wear resistance through techniques of surface modification such as nitriding or layers deposition [3,4]. Among these techniques the plasma nitriding stands out. It accomplishes nitriding in lower temperatures than in the cases of the liquid or gaseous nitriding, it is a non pollutant process and is appropriate to increase the hardness and wear resistance of the austenitic stainless steel [5,6]. Temperatures above 500°C increase the surface hardness and the wear resistance of the layer, but, the corrosion resistance is affected, due to the precipitation of chromium nitrides, that induces the local depletion of chromium [6]. Also, the treatment temperature and total treatment time has a great influence in the stability of the solid solution of chromium in the matrix. On the other hand, when plasma nitriding is carried out in temperatures below 450°C, a thin nitrided layer called "S" phase or expanded austenite with high hardness and good pitting

corrosion resistance is obtained [3-5,7-9]. The present work investigates the effect of the nitriding temperature in the characteristics of the formed layers.

### 2. EXPERIMENTAL DETAILS

The material used for the investigation was AISI 316L austenitic stainless steel. The steel was supplied in the solubilized condition. Its chemical composition is presented in the table I.

**Table I - Chemical composition of the AISI 316L austenitic stainless steel (wt%)**

Steel	C	Mn	Si	Cr	Ni	Mo	P	S	Fe
316L	0,021	1,56	0,53	17	13	2,16	0,033	0,030	Bal.

Samples were cut with a rectangular configuration (10 x 15 x 3 mm) and in discs with 10 mm of diameter and thickness of 3 mm.

The nitriding process was carried out in a cylindrical reactor with 300mm of diameter and 300 mm of height, capable of a maximum of 800 V, either with DC or pulsed current varying from 1 to 10 kHz in frequency. Previously to the nitriding treatment the samples were ground, polished and submitted to ultrasonic cleaning on petroleum ether for 15 minutes. After the samples were placed on the cathode, the chamber was evacuated to  $8 \times 10^{-2}$  mbar and the samples were treated according to the conditions presented in the table II.

**Table II – Parameters of the plasma nitriding treatment**

Parameters	Sputtering	Nitriding
Temperature (°C)	350, 400 e 450	400, 450 e 500
Time (h)	1	5
Duty cycle (%)	62	-
Frequence (kHz)	5	-
Gas (%)	100%Ar	80%H <sub>2</sub> /20%N <sub>2</sub>

After nitriding, the cross-sectional samples of the nitrided pieces were mounted in special bakelite to ensure edge retention. Samples were ground through successive on SiC papers, grades 120, 220, 320, 400, 600, 1200 and 2000. The polishing was carried out with 0.3 and 0.05 µm alumina. For the metalographic revelation Beraha reagent was used. The microhardness tests were performed surface and in the cross-section of the layers using a hardness tester with a

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load of 25gf. X-ray diffraction (XRD) experiments were performed using a Cu K $\alpha$  ( $\lambda = 1.5418\text{\AA}$ ) source over the  $2\theta$  range from  $30$  to  $100^\circ$  at scanning rate of  $2^\circ$  per min. The microstructures were examined by optical microscopy, scanning electron microscopy (SEM) and energy-dispersive spectrometry (EDS) analysis.

### 3. RESULTS AND DISCUSSION

Figure 1 shows the substrate austenite and the growth of the nitrided layer, with the increase of the nitriding temperatures. In the sample nitrided at  $400^\circ\text{C}$  it is observed the formation only of a white layer (fig. 1A), in the nitrided at  $450^\circ\text{C}$  emergence the CrN precipitate in the white layer (fig. 1B) and in the nitrided at  $500^\circ\text{C}$ , a substantial increase of CrN precipitation produced a second dark layer over the original white layer (fig. 1C).

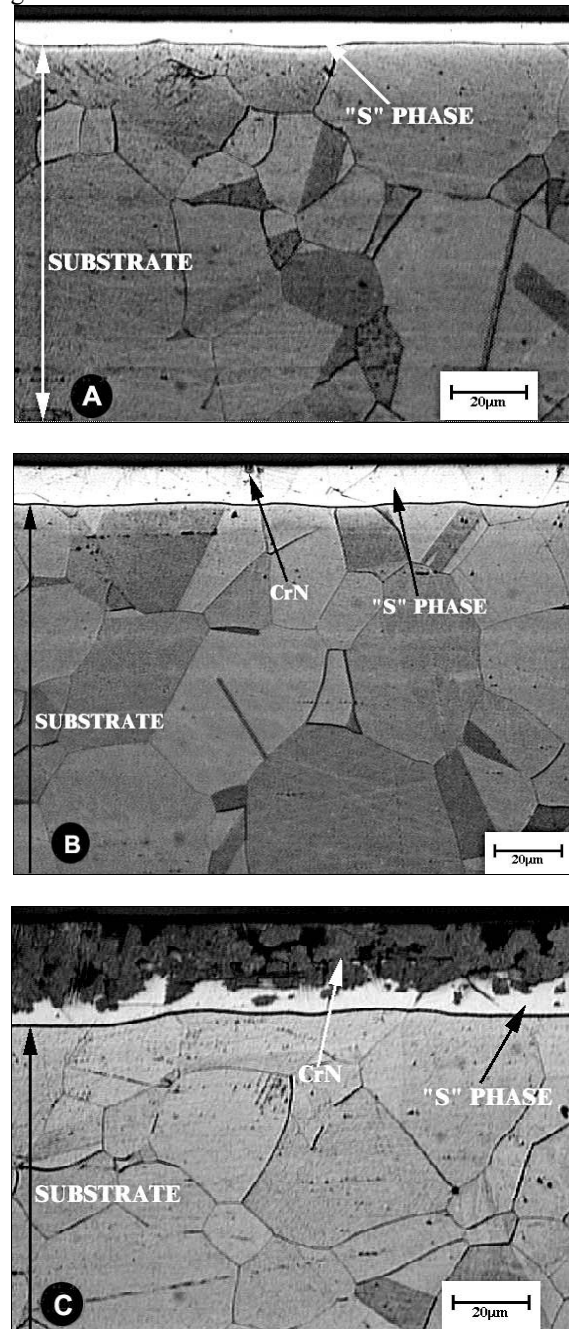
The X rays diffraction analyses (fig. 2) showed that the white layer is constituted by the phase "S" or expanded austenite ( $\gamma_N$ ). The S phase can be defined as a thermodynamically metastable, nitrogen supersaturated (20-30 at. %) solid solution with an distorted fcc structure, while in the normal austenite the maximum solid solubility of fcc  $\gamma\text{-Fe}$  is 8,7 at.% [3, 7, 9-11]. Figure 2 also show the X-ray diffraction patterns of low temperature ( $400^\circ\text{C}$ ) plasma nitrided sample. It can be seen two well defined peaks obtained in nitrided layer, indicated as  $\gamma_N$ , that appear at lower angles than the substrate face centred cubic fcc austenite (111) and (200) peaks, suggesting that the single phase (S phase) has a larger lattice parameter than the substrate austenite, and the expansion has been caused by the supersaturation of nitrogen in austenite [7, 11, 12]. Some investigators also suggested that the low temperature nitrided layer corresponds to a body centred tetragonal (bct) structure [11]. The development of high compressive residual stress in the low temperatures nitrided layer may be also responsible for the shift of the diffraction peaks from the ideal positions for an fcc lattice [1]. In the X rays diffractogram (fig. 2) it is also observed that, with the increase of the nitriding temperature to  $500^\circ\text{C}$ , chromium nitrides were detected ( $\text{Cr}_2\text{N}$ ), corresponding the formation of dark phases in the nitride layer (fig. 1C)

The formation of the "S" phase alone in the nitrided layer of the AISI 316L steel increases both the corrosion and wear resistances. On the other hand, the formation of a layer constituted by  $\text{Cr}_2\text{N}$  in the surface improves the wear resistance but it reduces the corrosion resistance of the layer and of the substrate[1-3].

The plasma nitriding was very effective in increasing the surface hardness, when compared with the substrate hardness previously to the nitriding, (200HV).

In figure 3, the microhardness profiles are presented as a function of depth of the nitrided layers. It is verified that the nitriding temperature affects the surface hardness significantly, in all of the layers. The nitrided layer obtained at  $500^\circ\text{C}$  presented higher microhardness values ( $\sim 1050\text{HV}$ ) in relation to the samples nitrided at  $400^\circ\text{C}$  ( $\sim 853\text{HV}$ ) and  $450^\circ\text{C}$  ( $\sim 950\text{HV}$ ), as well as a larger case depth, probably due to formation of chromium nitrides (see figure 1C) and

the high nitrogen concentration on the white layer, as shown in figures 4 and 5.



**Figure 1 - Optical micrographs of the cross sections of AISI 316L steel plasma nitrided for 5 hours. (a)  $400^\circ\text{C}$ , (b)  $450^\circ\text{C}$ , (c)  $500^\circ\text{C}$ .**

Figure 4 display the N punctual mappings obtained by EDS in the layer of the sample nitrided at  $500^\circ\text{C}$ . It can be observed a high concentration of that element in the nitrided layer [13]. Beneath the nitrides layer ( $20\mu\text{m}$ ), it is verified an abrupt fall in the content of nitrogen. Later, N increases until the depth of  $40\mu\text{m}$ , forming the phase "S", what allowed the maintenance of high levels of hardness up to depth of  $40\mu\text{m}$ . From that depth on, it is verified a gradative fall of the N content up to approximately  $75\mu\text{m}$ , when the austenitic substrate is reached.

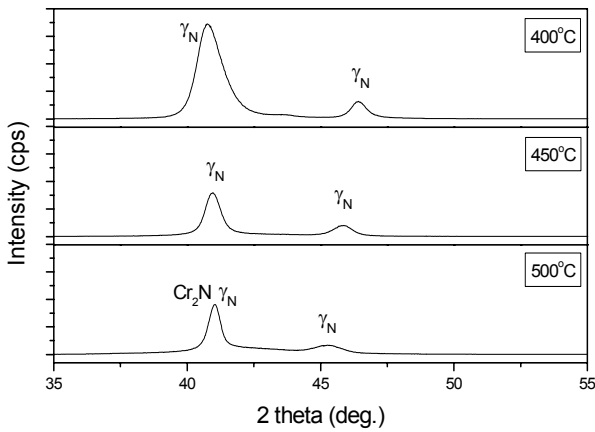


Figure 2 - X-ray diffraction patterns of AISI 316L steel nitrided at 400, 450 and 500°C.

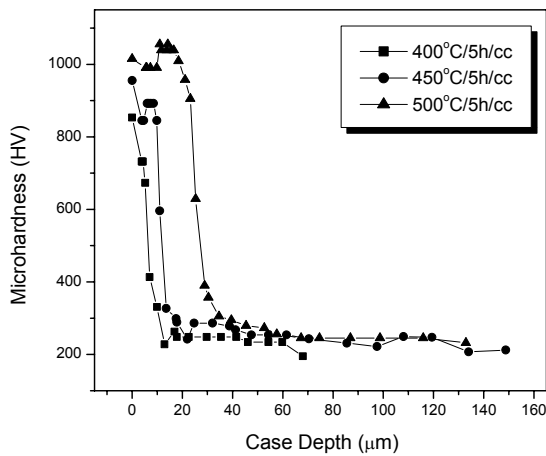


Figure 3 - Hardness depth profiles obtained in AISI 316L steel plasma nitrided at 400, 450 e 500°C.

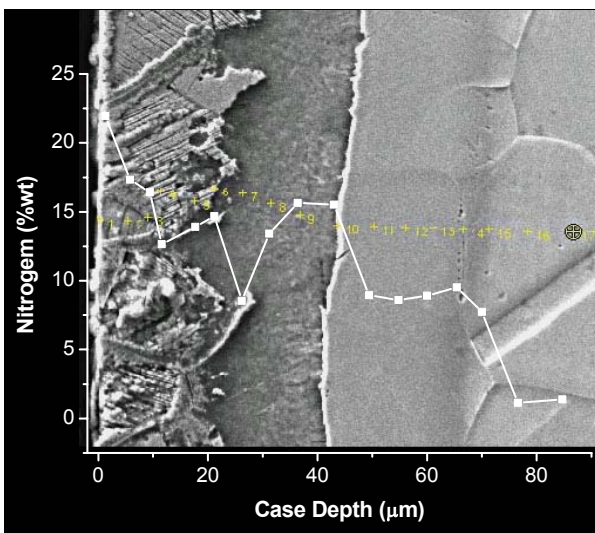


Figure 4 - Cross-section SEM micrographs and nitrogen profile (EDS) in the nitrided sample of AISI 316L steel at 500°C.

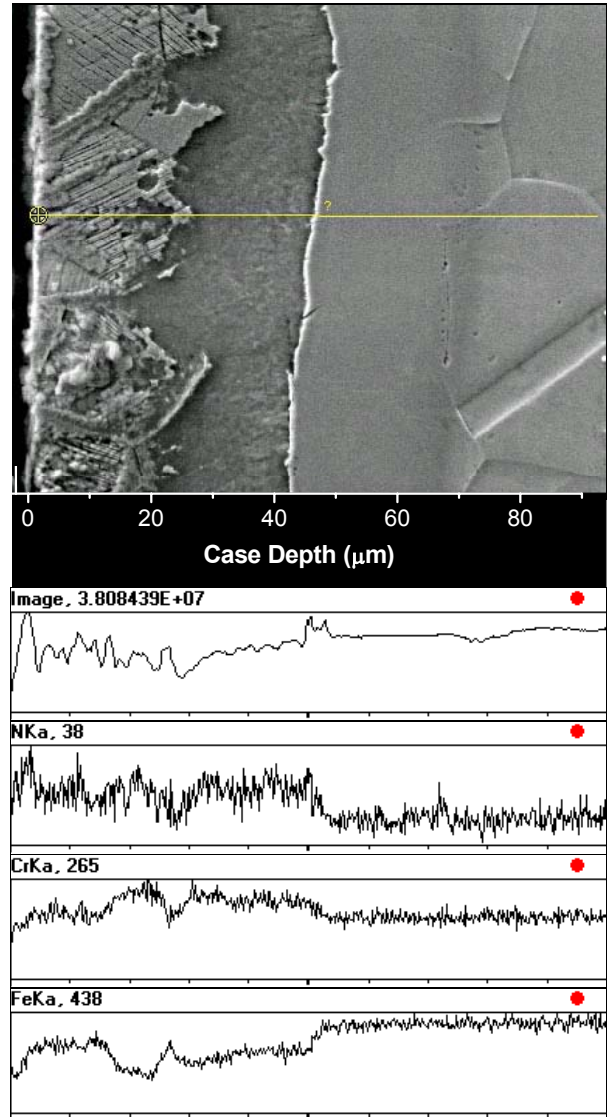


Figure 5 - EDS line profile of N, Cr, Fe in the nitrided layer at 500°C of AISI 316L steel.

Figure 5 shows the results of the EDS line profile analysis of N, Cr and Fe in the plasma nitrided area at 500°C. It can be seen that the intensities of the lines of nitrogen and chromium in the layer are higher, while that of iron is lower, confirming and justifying the results obtained in the analyses of X rays (fig. 2) and microhardness profiles (fig. 3). Such fact is due to the presence of chromium nitrides in the most external part of the layer and to the high saturation of nitrogen internally.

#### 4. CONCLUSION

The nitriding carried out at the temperatures of 400, 450 and 500°C were effective in the production of nitrided layers. In the AISI 316L steel studied, was confirmed the presence of the phase "S" in all layers (expanded austenite) and with increase temperature occurred the formation of chromium nitrides in the nitrided layer. All of the layers presented an accentuated increase in their hardness, in relation to the hardness of the substrate.

The thickness and hardness of the nitrided layer rises with increasing nitriding temperature.

## 5. ACKNOWLEDEMENT

The authors wish to thank to FAPESP (project nº 1995/0677-0), CAPES for financial support and Acesita S. A. for supplying the steel.

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