Nitriding in Cathodic Cage of Stainless Steel AISI 316: Influence of the Sample-Cage Walls Distance

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Abstract

The aim of this work is to perform a systematic study about sample position influence of a new plasma nitriding process called cathodic cage plasma nitriding (CCPN). It was studied the nitrided layers properties as function of the distance between cage wall and samples. In this technique the samples are kept on floating potential, inside a cage, that acts as a cathode and shields the samples from the cathodic potential. Cylindrical austenitic stainless steel AISI 316 samples were placed in different positions on the alumina plate inside the cathodic cage. The nitrided samples were characterized by optical microscopy, x-rays diffraction and microhardness measurements. The results shows that for samples near wall cage exhibit higher layer thickness This results must be due to compromise between mean path free and sputtering rate that changes in the depositon rate depending on how far the samples surface are from the cage walls.

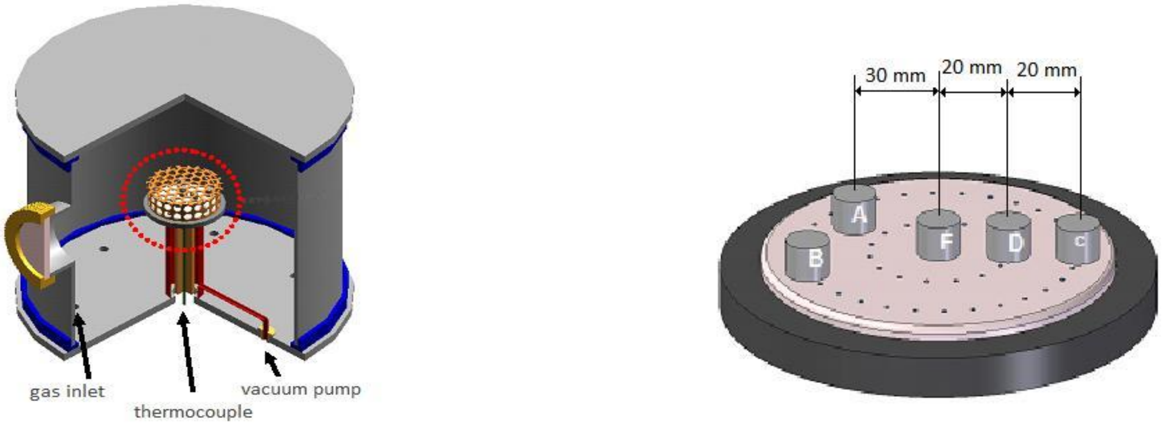
Introduction

All kinds of stainless steel are of great use in engineering due to their high corrosion resistance, although they process low were resistance and reduced hardness. These two last properties are significantly improved through ionic plasma nitriding [2-4]. As it is well known, when the nitriding of austenitic stainless steel is carried out at temperatures higher than 723 K it produces layers of high were resistance and surface hardness, while the corrosion resistance decrease significantly due to precipitation of chromium nitride, with a consequent reduction of the chromium content in the matrix. In contrast, when the nitriding is carried out at temperatures lower than 723 K a supersatured phase with nitrogen is formed which is called expanded austenitic or S-phase, which possess high hardness and were resistance besides a great resistance to corrosion [5,6]. It is observed that in the conventional nitriding process, called direct current plasma nitriding (DCPN), the nitriding layer is not uniform because edge effect and area to volume ratio. We show that this effect there is not occurring in the cathodic cage plasma nitriding [1]. It was also observed that in this process, nitriding layers with properties as good as layers obtained by DCPN, but with some improvements, such as bigger thickness, better uniformity, higher hardness and the elimination of the so called border effect [1,9]. In this study the objective is to identify the influence of the sample position inside the cage on the nitriding layers properties.

Materials and methods

The material used in this study was austenitic stainless steel 316, supplied by the Villares Metals Co., annealed (hardness 240 HV).

The stainless steel AISI 316 samples were machined in cylindrical form, 8 mm x 8 mm (diameter x height) previously annealed, grounded with 320, 400, 600 and 1200 mesh grinding papers and polished on a felt disc with 1,0 and 0.3 µm diamond suspensions. They were then ultrasonically cleaned in an acetone bath, before being placed into the nitriding chamber. The nitriding system consists of a power source (maximum tension 1500 V, current 2A), a cylindrical stainless steel vacuum chamber (Figure 1) with 40 cm in diameter and 40 cm in height. A stainless steel cathodic cage with 112 mm diameter and 25 mm height was placed on the cathode. The cage has holes with diameter of 8 mm, 9.2 mm distance between centers and 0.8 mm thickness.



(a) **(b)**

Figure 1 – (a) The plasma nitriding reactor scheme and (b) spatial distribution of the samples

The samples were pre-treated in hidrogen for 20 minutes at a temperature of 573 K and pressure of 200 Pa in order to eliminate contaminants such as oxides and/or grease/fat adsorbed on the surface. After pre-treatment the samples were treated during 5 hours, at 723K for pressures of 120 and 250 Pa. The nitriding atmosphere mixture of (80% N_2/ 20% H_2) with a flow rate of 20 sccm, regulated with a mass flow controller manually adjusted. After the nitriding process the samples were cooled down slowly inside the chamber to a temperature of 353 K in order to prevent oxidation. Then they were prepared for metallography analysis and etched in a solution containing 50%HCl+25%HNO_3+25%H_2O (água régia) and Beraha II for microstructural .observation.

The composition and texture were analyzed using X-ray diffraction (XRD). The referred analysis were carried out using Cu*Kα* (wave length: 0.154 nm) and Mo-*Kα* (λ = 0.07094 nm) lines operated at 40 KV using a Shimadzu XRD-6000 instrument. An optical microscope (Olympus BX60M) and SEM (Philips, model XL 30 ESEM) were used to observe and measure the layer thickness and to evaluate its texture and uniformity. Microhardness measurement profiles were carried out on the top surface of the nitrided samples in order to evaluate uniformity of the layers.

Results and Discussion

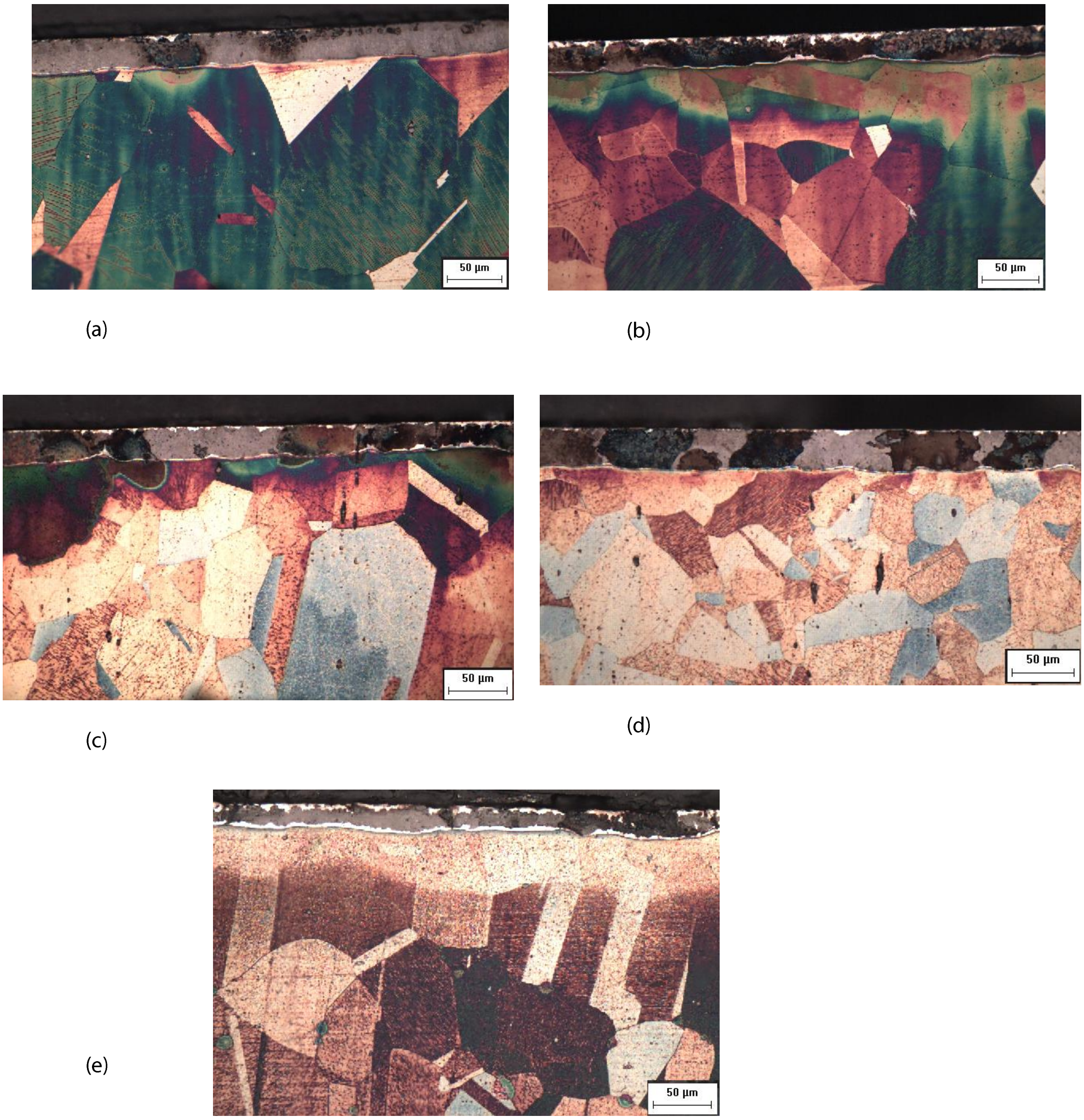
The surface hardness and layer thickness measurements data for samples treated in different positions A_{30}, B_{40}, C_{40}, D_{20}, E_{center} (fig. 1b) under pressures of 120 and 250 Pa, are presented in table 2.

Table 2 – Layers thicknesses and microhardness of the nitride layers as a function of the work pressure and sample position inside the cage (5 h, 723 K and 80% N2+20% H2)

Presure [Pa]	Sample Position	Nitriding Layer Thickness [μm]	Microhardness [$HV_{0,1}$]
250	A_{30}	26,6	1175
	B_{40}	28,3	1216
	C_{40}	28,2	1115
	D_{20}	24,4	1305
	E_{center}	22,2	1213
120	C_{40}	61,9	978
	D_{20}	56,7	953
	E_{center}	51,4	931

This data show that samples treated by the cathodic cage technique under the lower pressure (120 Pa) develop nitrided layers thicker than the samples treated at the pressure of 250 Pa, as it was observed in previous study [1,7]. This can be explained assuming that both the deposition by sputtering as well as the mean path free of the active species produced on the cage walls and transferred to the sample surface, play important role in the overall process. For lower working pressure we have lower sputtering rate but long mean free path of the species from cage hole to the sample surface, increasing the deposition rate and resulting on thicker layers compared to the higher pressure. This value also is higher than DCPN, contributing to idea that in the CCPN the deposition is the predominant process and overall species deposited on the sample surface are not subsequently sputtered from it. It was observed that in DCPN, for a nitriding temperature of 723 K, the growth rate of nitride layer is 3.0 μm/h [11] while in CCPN this value is between 12.0 μm/h (150 Pa) and 5.0 μm/h (250 Pa). Comparing the nitride layer thickness for sample at different position it can be observed (Table 1) that there is a light increase in the layers thickness for the samples placed in positions B_{40} and C_{40} (the nearest the cage wall) produced by the superposition of the species flow originated on the top and lateral cage walls.

The micrograph for the samples nitrided under a pressure of 250 Pa (fig. 2) shows some difference concerned with dark and white regions in the nitride layer especially when we compare the layer formed in the sample placed on the position E_{center} with the others. For this sample the micrography presents white regions what is an indication of the presence of phase-S (expanded austenite) whereas, for example, for the sample placed on position A the micrography presents almost only dark regions, what suggest the presence of nitrites.



(a)

(b)

(c)

(d)

(e)

Figure 2 – Micrographs of samples treated under a pressure of 250 Pa at temperatures of 723 K during 5 hours placed at different radial positions 30 mm (a), 40 mm (b), 40 mm (c), 20 mm (d) e center (e).

The X-ray diffractograms presented in figure 3 show that for the samples of larger thickness layers (B_{40},C_{40}) there is a predominance of iron nitrites [12], what confirm the the micrograph analisys, and should be caused by the fact that the nitriding species reach the sample surface with larger energy and intensity, since they are originated in the cathodic cage walls, which are very close to the sample surface.

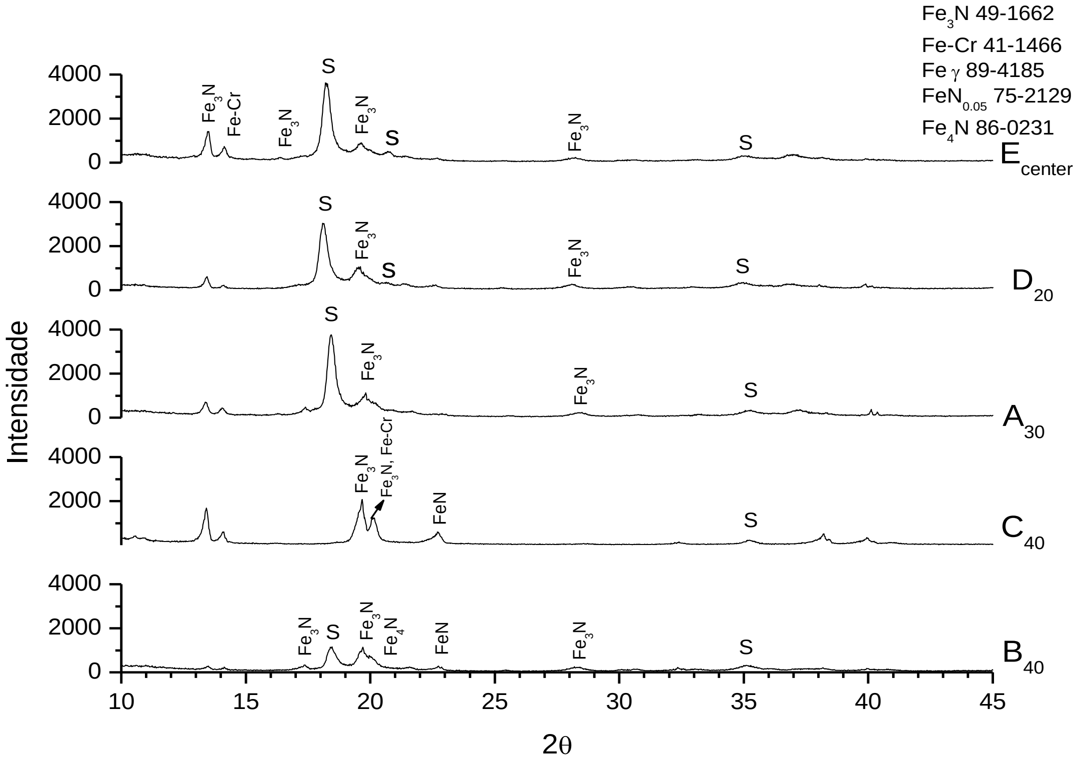
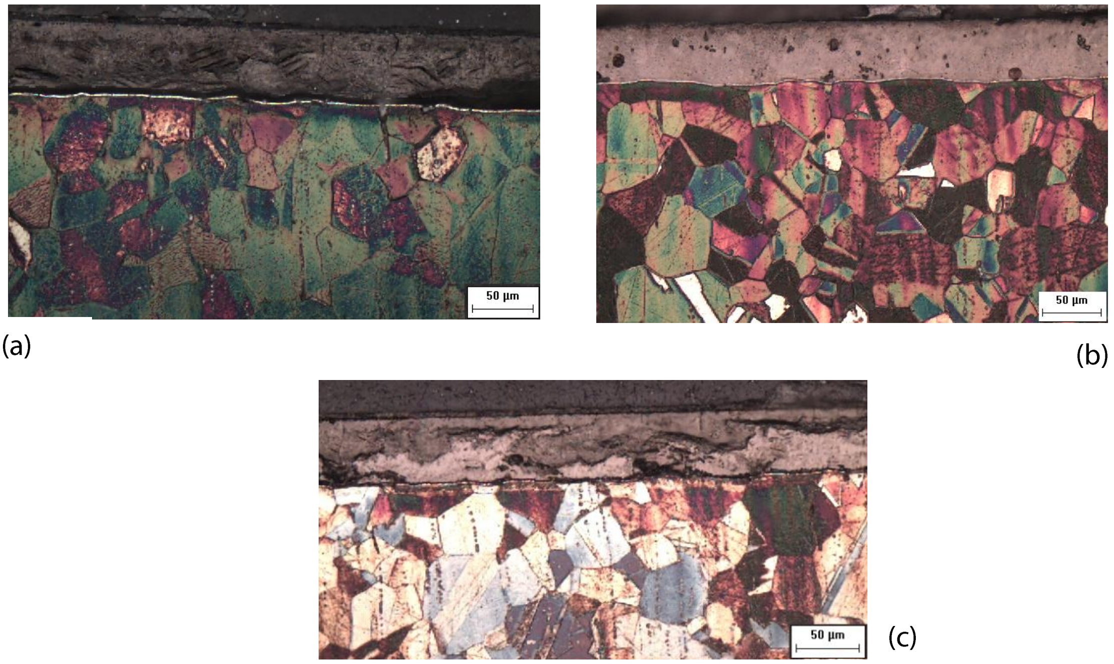


Figure 3 – X-ray difractograms [Mo-$K\alpha$ (λ = 0.07094)] for samples nitrided at 723K, during 5 hours under a pressure of 250 Pa, placed at different positions inside of the cathodic cage.

The micrographs of samples treated under the pressure of 120 Pa (fig. 4) shows nitrided layers do totally dark in contrast with the samples nitrided under the pressure of 250 Pa, what means that the expanded austenite is absent. This fact is confirmed by the X-ray analysis (fig. 5) and this is probably responsible for the systematic reduction in the surface hardness (table 1), when compared with the samples treated under the pressure of 250 Pa.



(a)

(b)

(c)

Figure 4 – Micrographs of samples treated under pressure of 120 Pa at the temperatures of 723 K during 5 hours placed on different positions (a) C_{40}, (b) D_{20} e (c) E_{center}.

The difractograms presented in figure 5, for samples nitrided at a pressure of 120 Pa and at a temperature of 723 K, placed on different positions, inside of the cathodic cage, are nearly the same. Moreover, they do not present characteristic peaks of phase-S and it do not present intensity variation for the peaks characteristics of iron nitrite [γ' – Fe$_4$N]. This is an indicative that does not exist thermal gradient in the interior of the cathodic cage, since any increase in the treatment temperature should causes an increase of the intensity of the peaks of iron nitride, γ' – Fe$_4$N [13].

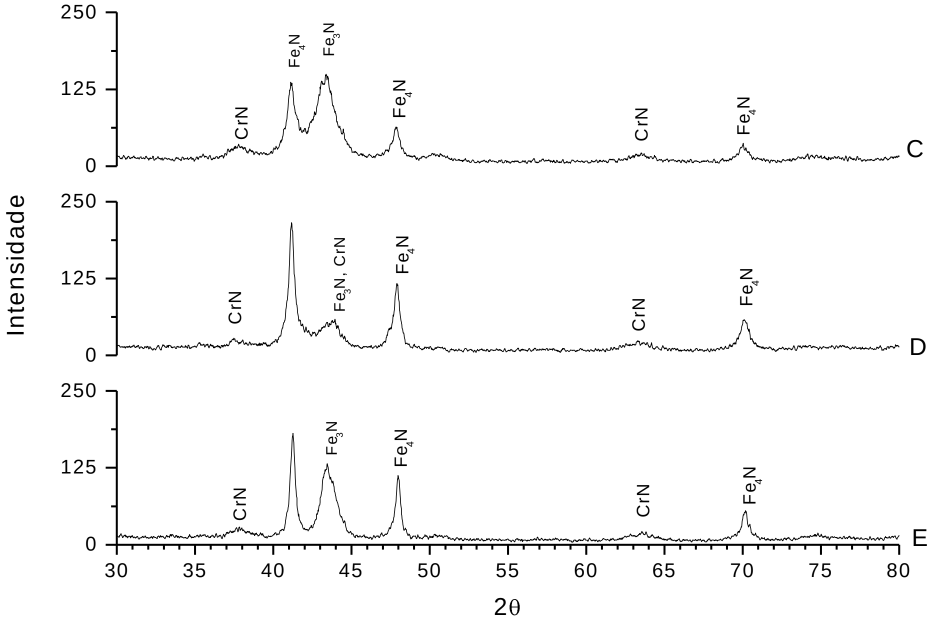


Figure 5 – X-ray difractograms for samples nitrided at 723K, during 5 hours under a pressure of 250 Pa, placed at different positions (C_{40}, D_{20}, E_{center}) inside of the cathodic cage.

Conclusions

Samples nitrided at lower pressure (120 Pa) present ticker nitrided layers than at higher pressure (250 Pa). A probable explication for this is because the mean free path of the particles from hole to sample surface is higher.

The growth rate of nitrided layer in this process is higher than in DCPN for both (150 Pa and 250 Pa) pressure used in this work.

S-phase is only present for sample nitrided at 250 Pa and positioned near cage center (beween 0 and 30 mm). A probable explication for this is that the time for temperature decreasing is higher, resulting in S-phase formation.

The growth rate of nitride layer for samples near cage wall is higher than samples near center because in the first case the sum of the contributions of species from the top and sides of the cages is larger.

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