

STUDY OF THE PLASMA NITRIDED LAYER HOMOGENEITY IN CYLINDRICAL HOLES OF LOW-CARBON STEEL SAMPLES

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Abstract. *The paper presents an evolution study of the plasma nitrided layer homogeneity along cylindrical holes in low-carbon steel samples. Holes of different diameters were machined-made for 2.5, 7 and 11 mm, of 102 mm length. Plasma nitriding process were carried out in a industrial vacuum-chamber at 520 °C, 24 hours, 3.5 torr, and 23 % H₂ + 47 % N₂ + 30 % Ar gaseous mixture. The microstructural homogeneity of the nitrided layer was characterized by optical and scanning electron microscopy, microhardness profile determination and x-ray diffraction patterns analysis. The possibility of the formation of the braunite layer as a consequence of the internal surface over-heating is discussed considering the eventual occurrence of the hollow cathode effect in the electrical discharge into the holes.*

Keywords: *Plasma nitriding, cylindrical holes, nitrided layer, hollow cathode effect.*

1. INTRODUCTION

Nitriding is a thermochemical treatment process, which involves the deposition and the diffusion of nitrogen into metallic materials “Gontijo et al. (2006)”. Plasma nitriding is an advanced surface modification technology which has experienced substantial industrial development over the past 30 years. This method is one of the most effective techniques for increasing wear resistance, fatigue strength, surface hardness and corrosion resistance of industrial components “Béjar et al. and Yang et al (2006)”.

In the plasma nitriding process, a glow discharge in the abnormal regime is utilized “(Chapman (1980))”. Gas mixtures are normally comprised of H₂ and N₂, in different proportions, and Ar can eventually be present. The substrate (steel samples or mechanical components) are placed on the cathode, and as a consequence of the ion and neutral species bombardment, temperatures ranging from 520 and 580 °C are frequently obtained. So, the atomic nitrogen condensate on the sample tends to diffuse into the surface, and to form a compound layer on top of the diffusion zone. In the diffusion one of iron-base materials, the nitrogen exists as single atoms in solid solution at lattice sites or interstitial positions, until the limit of nitrogen solubility in iron is exceeded. As the nitrogen concentration increases toward the surface, nitride precipitates are formed when the solubility limit of nitrogen in iron is exceeded. The surface hardness is only slightly changed by the nitrogen in solid solution, and the same occurs when it is present in the non-coherent (iron nitrides) precipitates, while the hardness increases substantially when the coherent (nitride-forming alloying elements) precipitates form.

The characteristics of the plasma nitrided layer are strongly dependent on the treatment parameters, such as gas mixture composition, temperature, time, and pressure. It is well established “Wriedt (1993)”, three different kind of nitrided layers can be obtained as a function of the H₂ + N₂ gas mixture composition:

- a) mixtures comprising N₂ < 7 vol. %: only the diffusion layer is formed;
- b) mixtures comprising 10 < N₂ < 20 vol. %: besides the diffusion layer, a γ -Fe₄N rich compound layer is also present on top of the surface;
- c) mixtures comprising N₂ > 20 vol. %: besides the diffusion layer, a ϵ -Fe₂₋₃N + γ -Fe₄N poliphasic compound layer is also present.

According to the Fe–N phase diagram “(Wriedt, 1993)”, when the treatment temperature is higher than eutectoid temperature (592 °C), nitriding occurs in the austenite field. Under slow cooling (simulating an annealing treatment), the austenite, γ -Fe(N), presents eutectoid transformation into the α -Fe(N) + γ -Fe₄N phase mixture. Otherwise, under fast cooling (simulating a quenching treatment), martensite, α' -Fe(N), can be formed from the austenite. The starting temperature of the transformation into martensite and the extent of the transformation depend on the nitrogen content and the cooling rate. If the nitrogen concentration is higher than 8.8 % at, the transformation into martensite will be completely avoided and all austenite will be retained at room temperature as a metastable phase “Schaaf (2002)”.

“Metin and Inal (1987)” have commented that interstitial nitrogen stabilizes the γ -Fe(N) phase at temperatures above 592 °C, which is in accordance with the Fe–N phase diagram “Wriedt (1993)”, and the effect of the austenite stabilizer alloying elements like N, C, Ni and Mn on the austenite field in that diagram. Although, it is important to keep in mind for alloyed steels, the eutectoid temperature of the Fe–N system tends to increase for temperatures up to 630 °C, as a consequence of the alloying elements effect on the austenite field.

For parts with holes, the effect of hollow cathode can occur. This effect is characterized in cathode (or parts) that present holes or cavities. “According to Koch (1997)”, considering the several geometries and possible arrangements, the effect of hollow cathode is verified for product axp (a = distance between cathodes; p = pressure) varying between 0.375 and 3.75 cm.Torr. When this happen there is geometrical confinement of the discharge in the cavity, resulting in the increase of the current density.

The treatment pressure in plasma nitriding of parts with holes is an important point to be considered. “According to Grün and Günther (1991)”, if the pressure is high, the plasma density is high and a good penetration of the discharge into holes and cavities will be verified. This is desirable despite the fact that it can lead to an unstable plasma and high risk of arc formation. On the other hand, smaller is the pressure, lower is the probability of the full discharge penetration into holes and cavities.

Otherwise, studies have been conducted using different components of many varied geometries, dimensions and materials “Metin and Inal (1987), Pye (1994), Russet 1991, Schaaf (2002), Wriedt (1993), Brunatto (2000)”. Products with long holes of different diameters have been problematical in terms of nitride layer uniformity. The study of the nitride layer evolution in industrial plants presents an important contribution for the understanding of the relationships between the process in large scale and the characteristics of the products obtained. In this context, the present work intends to study the plasma nitriding process in a typical industrial plant, looking for to determinate two different aspects: a) the characteristics of the nitride layer in parts presenting holes with different diameters, and the respective relationships with the discharge penetration into the holes; and b) the homogeneity of the plasma nitriding process in parts strategically placed along the entire vacuum chamber, emphasizing the nitride layer evolution into the holes.

2. EXPERIMENTAL

Cylindrical samples were produced using SAE 1010 spheroidized steel bars and the chemical composition presents in average 0.09% C, 0.04% Si, 0.04% Mn, 0.017% P, 0.019% S, and Fe balance. Three different sets, all presenting samples with 30 mm external diameter and 102 mm length, were machined-made for holes of 2.5, 7.0 and 11.0 mm diameter ($\varnothing A$ at the figure 1). Figure 1 shows sample in a cross-section view. It is to be noted each sample was embedded in a SAE 4140 steel body. This procedure was necessary to place the samples in the fixing system of the vacuum chamber. The nitriding process was performed using an Eltropuls industrial plasma nitriding furnace with capacity of 660 parts per charge.

The schematic representation of the plasma experimental apparatus is showed in the Fig. 2(a). The fixing system of the parts is divided in 11 levels, and samples are placed concentrically along the ring. The vacuum chamber presents the entrance and exit of the treatment gaseous mixture in the bottom, and the gas circulation system is positioned at top of the chamber.

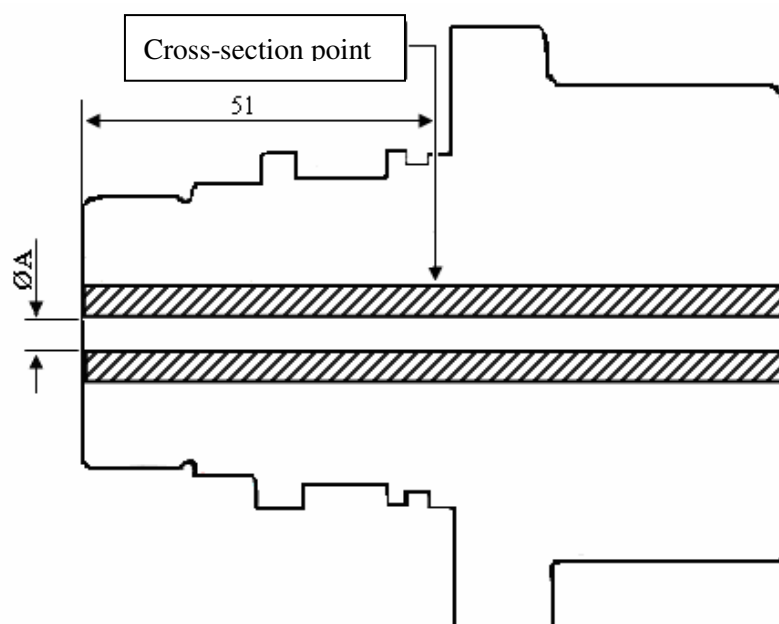


Figure 1 - Cross-section view of the sample.

The cathode was negatively biased at the voltage using a square form pulsed power supply. The power transferred to the plasma was adjusted by fixing the time switched-on of the pulse at 200 μ s, and 1800 μ s time switched-off (resulting in a pulse period of 2000 μ s). The voltage was fixed to 520 V. Nitriding was carried out using temperature of 520 °C, a gaseous mixture of 47% N₂, 23% H₂ and 30% Ar, in volume %, and a pressure of 3.5 Torr. The temperature was monitored by a calibrated chromel-alumel thermocouple embedded into the cathode. The three different set of samples were distributed and placed side by side to 120° one each other, at 3 different levels, namely (1) superior, (5) medium and (10) inferior related to the high of the chamber, in accordance with Fig. 2(b). Auxiliary heating system (hot wall) was employed to guarantee temperature homogeneity in overall chamber, in this case, the chamber wall temperature was pre-fixed at 420 °C.

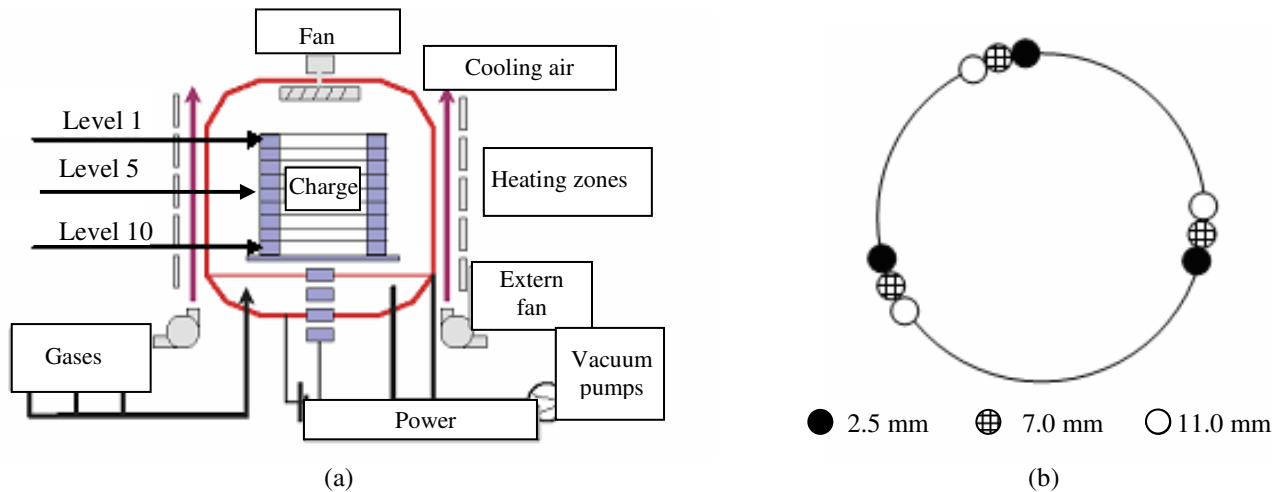


Figure 2 - Schematic representation of the plasma nitriding system: a) schematic of industrial plant; and b) arrangement of the three different set of samples (for 2.5, 7.0, and 11.0 mm hole diameter) placed in three different levels (1, 5 and 10).

After nitriding, the samples were covered for a copper coating by galvanic process to prevent the compound layer was damaged during the grinding and polishing process. After this step, the samples were sectioned in the middle, 51 mm from the external surface (Fig.1), and hot-pressed in bakelite. The surface of the substrates were mechanically ground using a sequence of 320, 400, 600 and 1000 grit wet SiC emery paper, followed by fine polishing with 1 μ m diamond, to yield a mirror surface, and then they were etched with Nital 2% (2% HNO₃-98% CH₃CH₂OH).

The microstructural homogeneity of the nitrided layer was characterized by optical and scanning electron microscopy, determination of the microhardness profile and x-ray diffraction patterns analysis. The results indicated for the thickness of the compound layer and depth of the diffusion layer are the average of the measurements which were taken in 9 samples each diameter strategically placed along the plasma nitriding oven, as previously seen.

3. RESULTS AND DISCUSSIONS

Figure 3 shows the thickness evolution of the compound layer (measurements take 51 mm from the external surface), for the three different set of samples (for 2.5, 7.0, and 10.0 mm hole diameter) placed in three different levels (1, 5 and 10), in accordance with Fig.1. It is to be noted for 2.5 mm diameter hole samples the compound layer formation is totally suppressed for every levels 1, 5 and 10 studied. The same was not observed for samples presenting 7.0 and 11.0 mm diameter holes. In both the conditions, the compound layer average thickness is about of 8.0 and 8.3 (s = 1.5) μ m, respectively in every levels. It can be noted that compound layer obtained at different positions along vacuum chamber (1, 5 and 10 levels), for diameters of 7.0 and 11.0 mm, present similar average thickness.

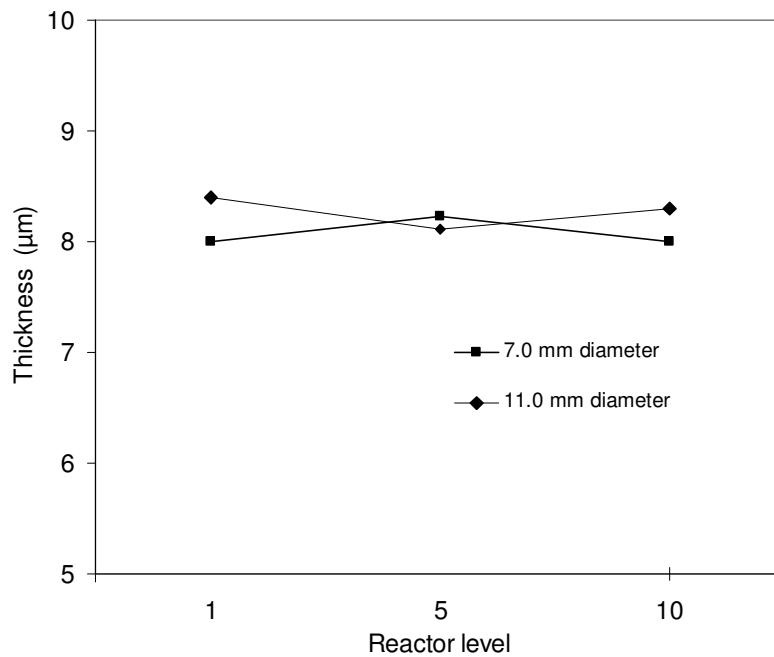


Figure 3 - Thickness evolution of the compound layer for the three different set of samples (for 7.0 and 11.0 mm hole diameter) placed in three different levels (1, 5 and 10).

Figure 4 shows the evolution of the nitride precipitates depth, which was obtained by metallographic analysis (measurements taken 51 mm from the external surface), for the three different set of samples (for 2.5, 7.0, and 10.0 mm hole diameter) placed in three different levels (1, 5 and 10). Likely of verified on the compound layer evolution (Fig. 3), for samples presenting 2.5 mm diameter holes, the nitrides precipitates were not found in every levels 1, 5 and 10. The same was not observed for samples presenting 7.0 and 11.0 mm diameter holes. In both the conditions, for every positions studied, it can be observed a diffusion zone. It is to be noted for 7.0 and 11.0 mm diameter holes, the depth of which the nitrides precipitates occur in the level 1, 5 and 10 is 855 (s =60), 858 (s =60) and 860 µm (s =60 µm), respectively. These results are better evidenced on SEM cross-sectional micrographs (Fig. 5) and optical cross-sectional micrographs (Fig. 6).

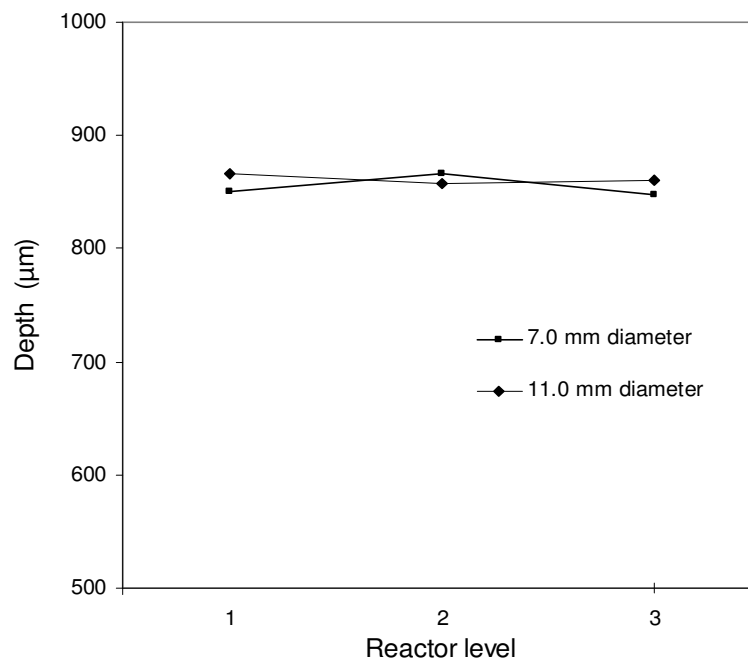
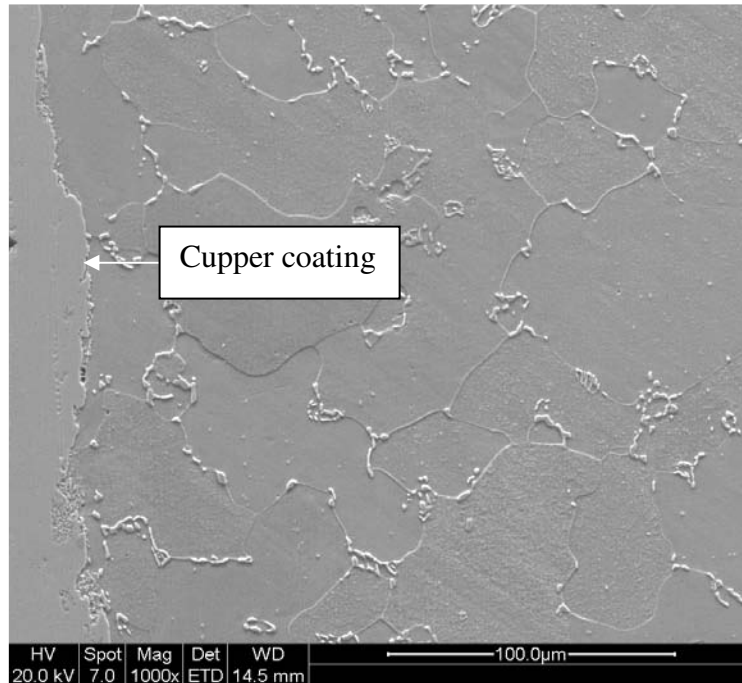
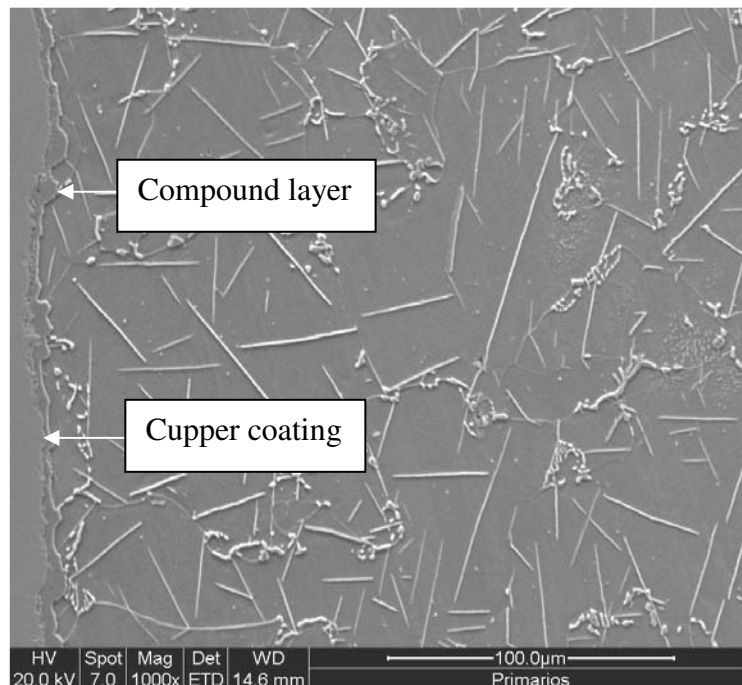


Figure 4 - Evolution of the nitride precipitates depth for the three different set of samples (for 7.0 and 11.0 mm hole diameter) placed in three different levels (1, 5 and 10).

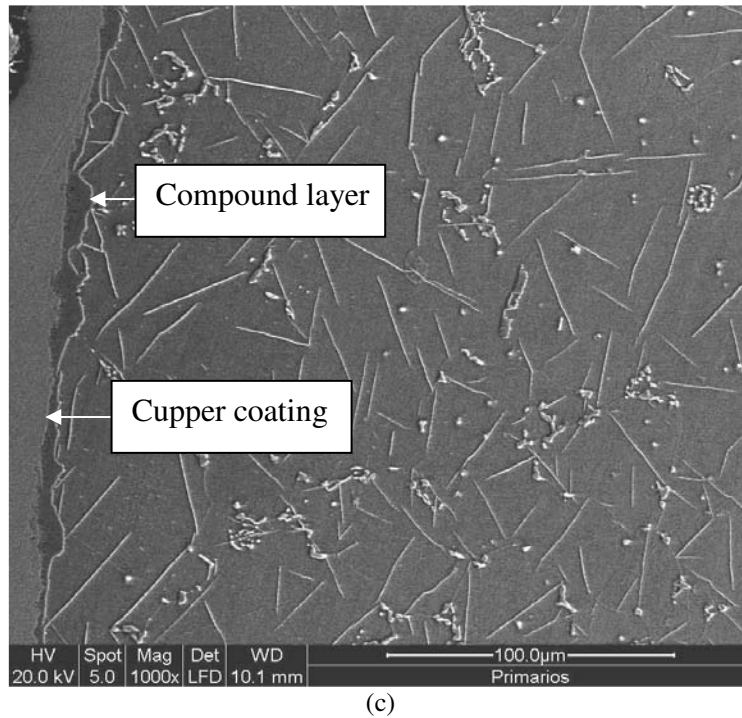
Figure 5 shows the SEM cross-sectional micrographs of the steel samples presenting diameters holes of 2.5, 7.0 and 11.0 mm. Fig.5(a) confirms the results evidenced on Fig. 3, since there is no compound and diffusion layer on the internal surface of the sample. Otherwise, it can be observed these layers occurring for samples presenting diameters holes of 7.0 and 11.0 mm (Fig. 5b, and Fig. 5c, respectively), being in accordance with the results verified for Fig.3.



(a)



(b)



(c)

Figure 5 - SEM cross-sectional views of the nitrides precipitates in level 1 of steel nitrided for (a) diameter 2.5mm, (b) diameter 7.0 mm and (c) diameter 11.0 mm.

It can be observed in Figure 6, for a sample presenting 7.0 mm diameter hole, the precipitation in the form of short needles (α' - Fe_{16}N_2 phase) occurring preferentially near to the ferrite matrix and those in the form of elongated needles (γ' - Fe_4N phase) occurring near to the compound layer “Gontijo et al. (2006)”. The same was equally verified for samples presenting 11.0 mm diameter. The elongated nitride needles appear up to 400 μm from surface, being that for depths higher than 400 μm , only short nitride needles can be verified. On the other hand, for samples presenting 2.5 mm diameter, differently of the others, both the elongate and short needles was not found. It’s possible the electrical discharge (plasma) did not enter into this hole, which could explain the different microstructure obtained.

In every set of the samples studied, it was observed no presence of the a transformed austenite (γ), what guarantees that the nitriding did not happen in the austenitic field, and therefore the hollow cathode discharge was not developed into the holes. The hollow effect could result in overheating of the surfaces exposed to the plasma, leading easily to increase the surface temperature to values higher than 592 °C.

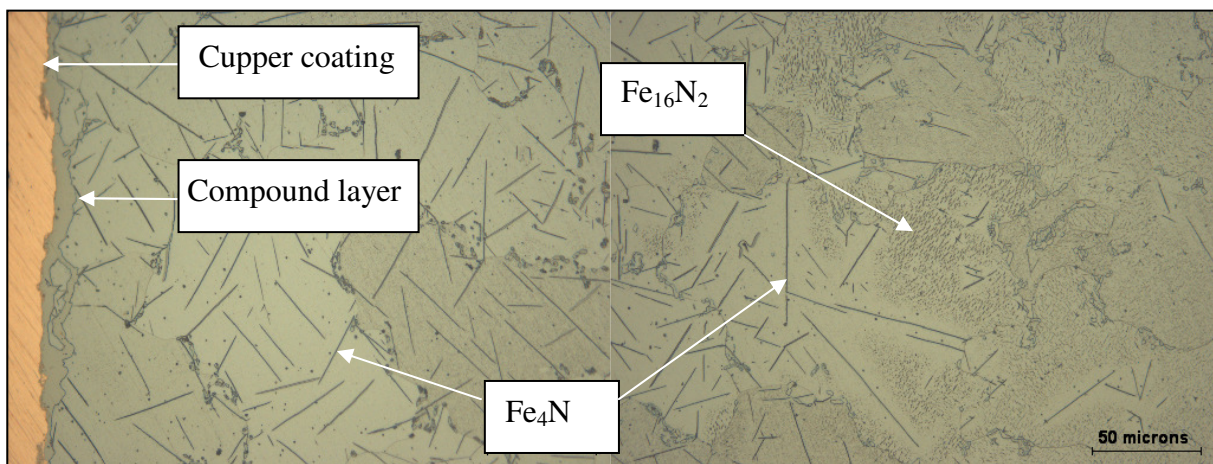


Figure 6 - Optical micrographs cross-sectional views of steel nitrided in level 5 for diameter 7.0 mm

Fig. 7 presents the X-ray diffractograms of the internal surface of a plasma nitrided sample presenting 11.0 mm diameter hole. The results indicate the presence of a polyphasic layer, compound of ϵ -Fe_{2.3}N and γ' -Fe₄N phases, as indicated, which could be expected for the studied conditions.

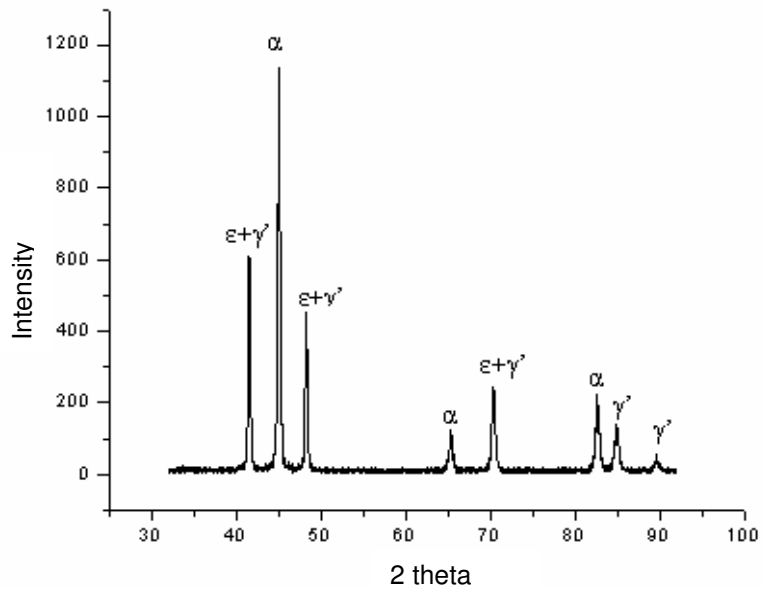
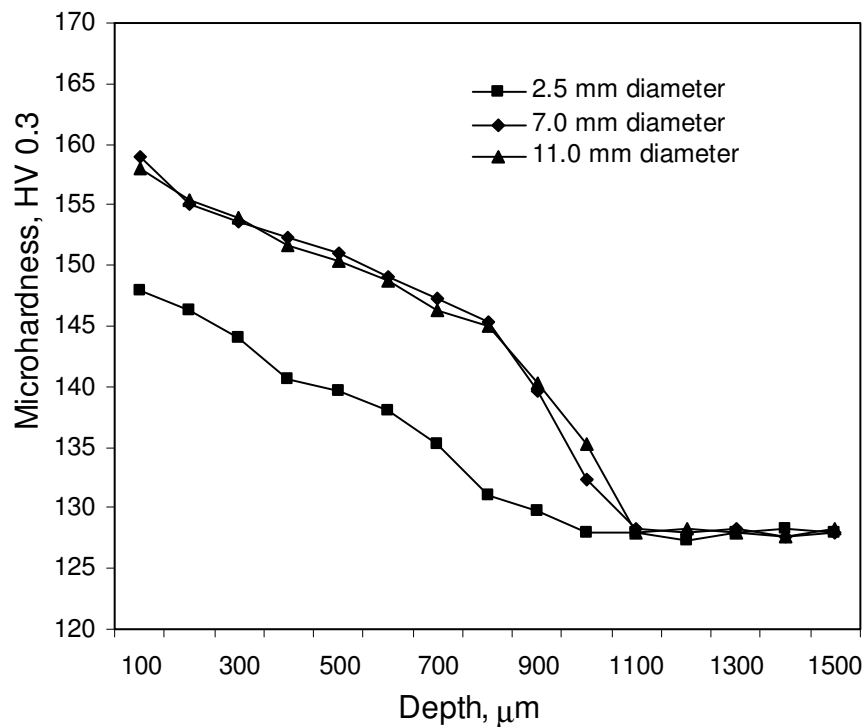


Figure 7 - X-ray diffractograms of the internal surface, for a steel nitrided in level 5, for a sample presenting 11.0 mm diameter hole.

Figure 8 shows microhardness profiles obtained from cross-sections of treated specimens at levels 1 and 10, for different diameters studied (2.5, 7.0 and 11.0 mm). The results indicate for all studied conditions, the presence of a higher microhardness values near the surface, which tend to decrease at the case/core interface to substrate. Although the samples with 2.5 mm diameter hole present lower microhardness than the other cases, it was verified a slight increase in microhardness near the surface, since it did not present nitride precipitates, what can be explained by the presence of nitrogen only in solid solution.



(a)

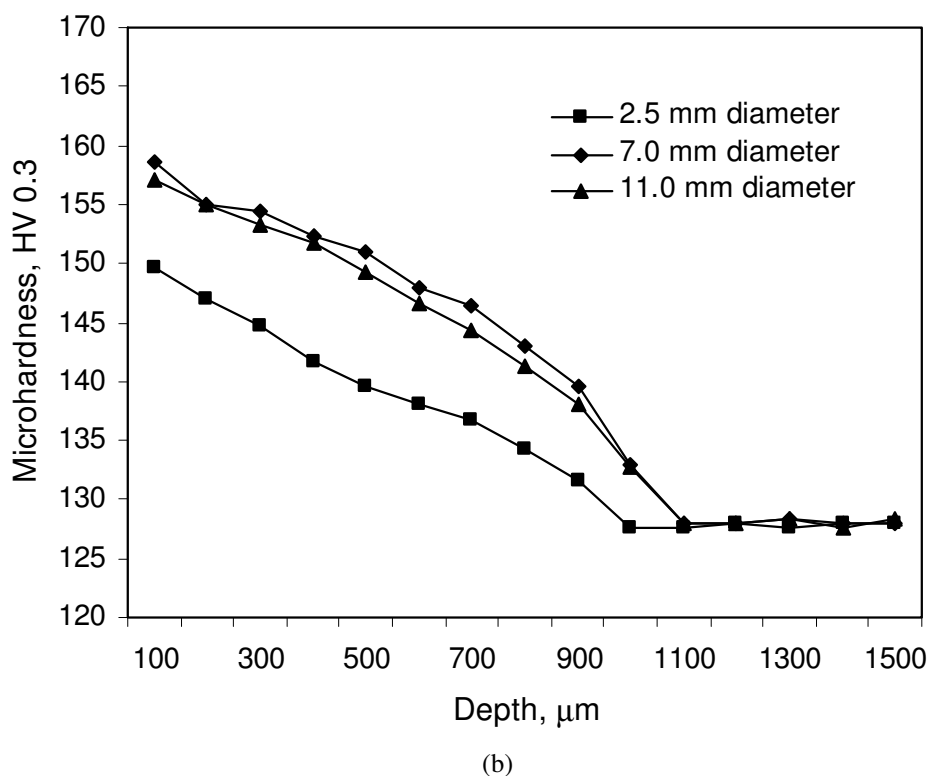


Figure 8 - Microhardness profiles for samples presenting different diameters, after ion nitriding, for workpieces placed at: a) level 1; and b) level 10.

4. CONCLUSIONS

It was observed significant differences the thickness of the compound layer with different diameters.

The compound layer consists of a thin ϵ - $\text{Fe}_{2.3}\text{N}$ layer over a thick γ' - Fe_4N layer.

The diffusion zone is constituted by two regions: one at the top, with the same thickness for the three diameters, is formed mainly by long needles of γ' - Fe_4N and a second region on the bottom formed by small needles of α'' - Fe_{16}N_2 .

The diameters 7.0 and 11.0 presented similar microhardness in every level. In both diameters, for every level studied indicated the presence of the diffusion zone with two types of nitrides, α'' - Fe_{16}N_2 and γ' - Fe_4N , in the form of short and elongated needles, respectively. In every holes was observed no presence of the a transformed austenite (γ), what guarantees that the nitriding did not happen in the austenitic field and therefore the electric discharge did not developed for a hollow cathode discharge.

The diameter of 2.5 mm presented inferior microhardness compared with other diameters in every level. In that diameter, the discharge didn't enter and the compound layer and diffusion zone with nitrites precipitates were not found.

Considering the gases feed system, along of the reactor presents the layer homogeneity the in every diameter holes.

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