

Plasma Nitriding of CA-6NM Steel: Effect of H₂ + N₂ Gas Mixtures in Nitride Layer Formation for Low N₂ Contents at 500 °C

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Received: October 1, 2010; Revised: December 13, 2010

This work aims to characterize the phases, thickness, hardness and hardness profiles of the nitride layers formed on the CA-6NM martensitic stainless steel which was plasma nitrided in gas mixtures containing different nitrogen amounts. Nitriding was performed at 500 °C temperature, and 532 Pa (4 Torr) pressure, for gas mixtures of 5% N₂ + 95% H₂, 10% N₂ + 90% H₂, and 20% N₂ + 80% H₂, and 2 hours nitriding time. A 6 hours nitriding time condition for gas mixture of 5% N₂ + 95% H₂ was also studied. Nitrided samples results were compared with non-nitrided condition. Thickness and microstructure of the nitrided layers were characterized by optical microscopy (OM), using Villela and Nital etchants, and the phases were identified by X-ray diffraction. Hardness profiles and hardness measured on surface steel were determined using Vickers hardness and nanoindentation tester, respectively. It was verified that nitrided layer produced in CA-6NM martensitic stainless steel is constituted of compound layer, being that formation of the diffusion zone was not observed for the studied conditions. The higher the nitrogen amounts in gas mixture the higher is the thickness of the nitrided layer and the probability to form different nitride phases, in the case γ -Fe₄N, ϵ -Fe_{2,3}N and CrN phases. Intrinsic hardness of the nitrided layers produced in the CA-6NM stainless steel is about 12-14 GPa (~1200-1400 HV).

Keywords: plasma nitriding, Low N₂ content gas mixtures, ASTM CA-6NM martensitic stainless steel, nanoindentation technique

1. Introduction

The martensitic wrought stainless steels, CA-6NM, were developed in Suisse to improve the weldability of conventional martensitic stainless steels as, for example, the ASTM CA-15. Classified by ASTM as a soft stainless steel, CA-6NM was evaluate to attend the market which needs steels with superior mechanical properties and facilities to fabricate. This stainless steel after tempering presents excellent mechanical properties, as high strength, cavitation erosion and adequate toughness, even at low temperatures. In addition, due to its high hardenability, CA-6NM is utilized in diverse applications, normally in the manufacturing of large pieces as hydraulic turbine rotors, pumps and compressors¹⁻³.

Otherwise, nitriding is a thermochemical surface treatment widely used to treat steels and alloys. The main advantages of nitriding are the improvement of wear and frictional properties, corrosion and fatigue resistance⁴. Plasma nitriding⁵⁻⁷ is one of the most versatile nitriding processes with many advantages over the conventional salt-bath and gas nitriding, and it has been widely used in many industrial applications to improve the wear and fatigue resistance.

As pointed out by literature^{8,9} the presence of alloying elements, particularly nitride formers, has a strong influence on the hardening, morphology and kinetics characteristics of the nitrided surface. The influence of nitride former elements is dependent on the degree

of interaction with nitrogen. Elements as Al and Ti have a strong interaction with nitrogen, while the interaction of Cr is dependent of the alloying element content on steel. It is considered chromium contents higher than 5.6 wt. (%) leads to strong nitrogen interaction characteristics.

Pinedo and Monteiro¹⁰ studied the plasma nitriding kinetics of AISI 420 martensitic stainless steel. Nitriding was performed at 480, 500, 520, 540 and 560 °C temperatures, to 4 hours, using a gas mixture of 75% N₂ + 25% H₂, and pressure of 250 Pa (1.87 Torr). For all the nitriding temperatures, the nitrided surface was comprised by both the compound layer and the diffusion zone, even at lower temperatures, as a result of the high nitrogen potential on the gas mixture. The maximum nitriding surface hardness was 1500 HV_{0.025}. The hardness profiles show a step shaped decrease from the maximum hardness to the core hardness. This behavior is a consequence of the complex nitriding reactions that take place at the interface, and reflects the nitrogen compositional profile across the nitrided case.

In the present work, surface hardness of the plasma nitrided CA-6NM martensitic stainless steel samples was determined by nanoindentation technique, for different nitriding conditions, considering different N₂ + H₂ gas mixtures and nitriding times, and results were compared to the obtained hardness profiles and they were correlated to the phases present in the nitride layers.

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2. Materials and Methods

Samples were prepared from a cast CA-6NM martensitic stainless steel, which was received in the 22 HRC hardness tempered condition. The chemical composition in wt. (%) was 0.032% C, 12.25% Cr, 4.42% Ni, 0.63% Mn, 0.522% Si, 0.43% Mo and Fe balance, and the microstructure is comprised of martensitic matrix (α) with some dispersed austenite (γ). Before nitriding, the samples were cut for $20 \times 30 \times 10$ mm dimensions, ground and polished using $1 \mu\text{m}$ Al_2O_3 solution, in accordance with the conventional metallographic preparation.

The plasma nitriding apparatus is shown in Figure 1. Nitriding was performed at 500°C temperature, at 532 Pa (4 Torr) pressure, gas flow of 240 sccm (4.00×10^{-6} standard m^3/s), for 2 and 6 hours nitriding times, using different gas mixtures of 20% N_2 + 80% H_2 , 10% N_2 + 90% H_2 and 5% N_2 + 95% H_2 . The discharge chamber consisted of a stainless steel cylinder 350 mm in diameter and 380 mm in height. Samples were placed in the cathode and were negatively biased in a selected potential, using a square waveform pulsed power supply of 3.6 kW. The potential was specified to 660 ± 20 V and the power transferred to the plasma was adjusted by varying the time switched on (*ton*) of the pulse. The *ton* of the pulse could be varied from 10 to 220 μs and the total on/off time was 240 μs . The sample temperature was varied by adjusting the on/off time of the pulsed potential and was measured using a chromel/alumel (type K) thermocouple that is placed into the sample holder, which is inserted 12 mm into the sample. The 1.5 mm diameter thermocouple is electrically isolated with Al_2O_3 and is protected with a stainless steel cover.

Prior to nitriding, the system was evacuated to a residual pressure of 2.6 Pa (2×10^{-2} Torr). The N_2 (99.999% pure) and H_2 (99.999% pure) gas mixtures were obtained adjusting datametrics mass flow controllers whose full scale value was the same for both, in such case 500 sccm (8.33×10^{-6} standard m^3/s).

The total gas flow was set to 240 sccm (4×10^{-6} standard m^3/s) in order to maintain the specified atmosphere of the discharge. The pressure in the vacuum chamber was adjusted by manual valves and measured using a capacitance manometer of 1.33×10^4 Pa (100 Torr) full scale. Heating rates on the order of $15^\circ\text{C}/\text{min}$ was employed to reach the plasma nitriding temperature. Prior to nitriding, the samples were cleaned in a H_2 glow discharge at a pressure of 400 Pa (3 Torr) and at a temperature of 300°C during 10 minutes.

The nitrided samples were cross-section cut for microstructural analysis. The surfaces were then ground and polished with $1 \mu\text{m}$ diamond paste, and after etched by two different etchants, Vilella and 2% Nital solution. Optical microscopy analysis was performed in a Olympus PME equipment. Microhardness measurements were performed using a HMV Microhardness Tester Shimadzu equipment, with 100 g load for profiles determination and 500 g load for surface measurements. The nanoindentation technique was executed on nitrided and non-nitrided samples. The equipment utilized was a Nanoindenter XP - MTS Systems, with 40 g (400 mN) load and 10 seconds loads time. Finally, X-ray diffractometry (XRD) analysis was performed on surfaces of nitrided samples, using a Shimadzu equipment, for 1.54 nm wave-length (λ) copper tube.

3. Results and Discussion

Figure 2 shows typical microstructures after the nitriding treatments, which were etched by Vilella (Index 1) and Nital (Index 2). It is possible to verify the Nital etching made possible to reveal the nitrided layers for all the studied conditions. The same was not verified for the respective substrate bulks. This result clearly indicates as the nitriding process develops, the chromium alloying element is kept

in solid solution in the substrate bulk, and the stainless characteristic is kept unaltered in such region. Otherwise, in the nitrided layer, the nitrogen diffusion into surface, allied to the high chromium-nitrogen affinity at the considered temperature tends to result in chromium nitride precipitation. Such assumption is in accordance with the X-ray diffraction results presented ahead. As a consequence of the strong solid solution chromium depletion close to surface, the nitrided layer was also revealed using Nital etchant. It is to be noted Nital is a non-adequate etchant for stainless steels. Such result must be emphasized, since the use of Nital solution, in this case, would permit to indicate if the surface was nitrogen sensitized due to the nitriding treatment for the considered material. Moreover, such result indicates Nital solution as etchant could be utilized as a direct method to determine if the stainless characteristic of the stainless steel in the nitrided layer region is maintained unaltered after nitriding treatments. The above mentioned is based confronting both the nitrided layer and bulk regions aspects at micrographs shown in Figure 2a2, b2, c2, d2. In addition, the use of Nital solution facilitated the determination of the nitriding depth in the present work. Otherwise, Vilella etchant was responsible by etching similarly the nitrided layer and bulk regions, resulting in visual contrast slight differences of both the regions, as shown in Figure 2a1, b1, c1, d1.

It is to be emphasized nitriding layer is normally composed of compound layer and diffusion zone. For the processing conditions and characterization techniques adopted in the present work it was

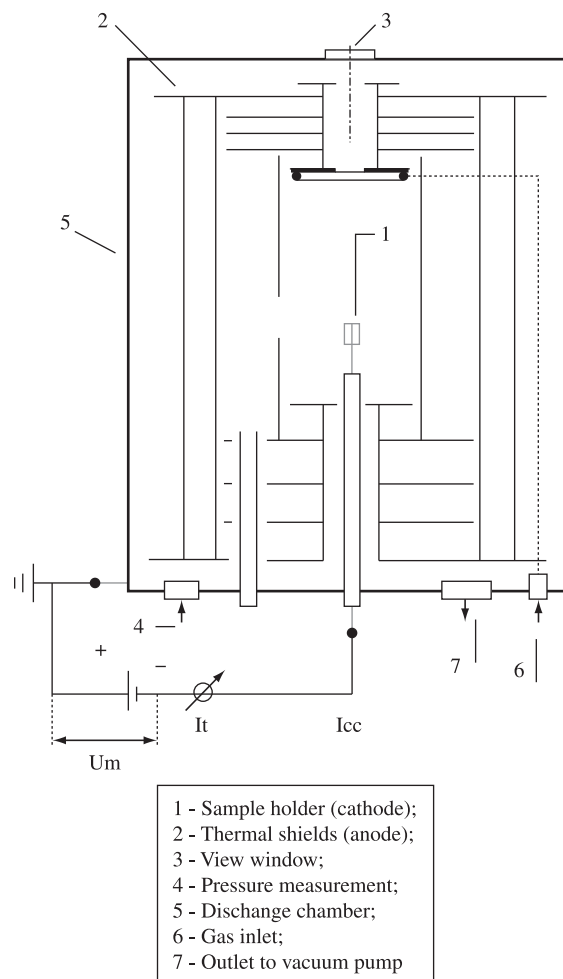


Figure 1. Plasma nitriding apparatus representation.

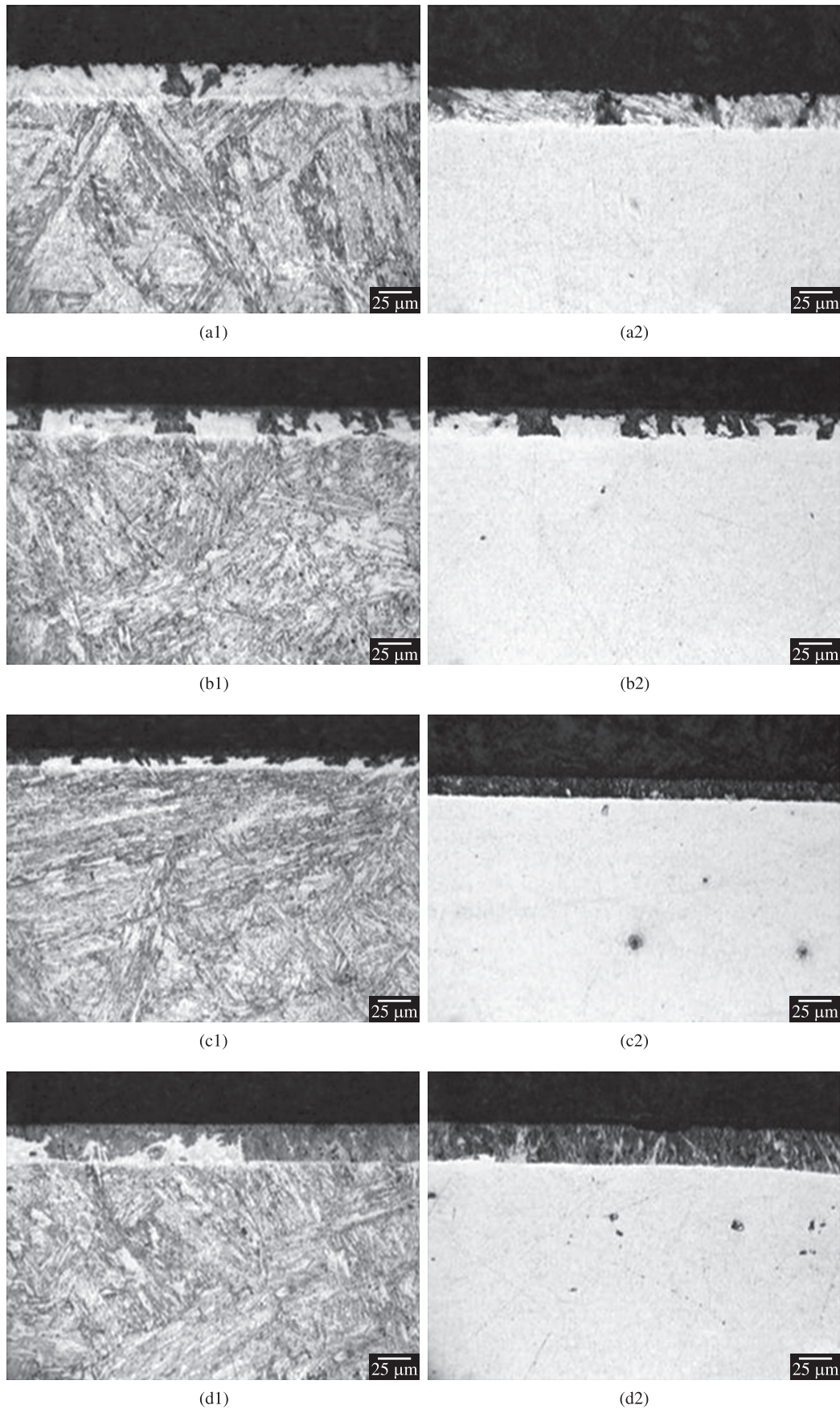


Figure 2. Micrographies for different nitriding conditions: a) 20% N_2 – 2 hours; b) 10% N_2 – 2 hours; c) 5% N_2 – 2 hours; and d) 5% N_2 – 6 hours (Index 1: etched with Vilella; and Index 2: etched with Nital 2%).

not possible to observe any diffusion zone. Such fact could be related to its very small thickness, due to short nitriding times utilized here. This assumption is in agreement with Li and Bell results¹¹, which demonstrated a very thin diffusion zone was obtained in martensitic stainless steel for 20 hours nitriding time at 500 °C (10 and 3.33 times higher, and at the same nitriding temperature utilized here).

Table 1 shows the thickness of the nitriding layer obtained for all the studied conditions. It can be verified the higher the nitrogen content in gas mixture the higher is the thickness of the nitriding layer, the same occurring for higher nitriding times. Thicknesses of 25.0, 20.0 and 12.5 μm were measured for 20, 10 and 5% N_2 gas mixtures and 2 hours processing conditions, respectively. The increase of nitriding time for 6 hours, using 5% N_2 gas mixture, resulted in thickness of 25.0 μm . Table 1 also presents hardness measurements of the samples surface. Hardness values of 1240, 1172 and 950 $\text{HV}_{0.5}$ were determined for nitrided layers produced after nitriding times of 2 hours and using gas mixtures containing 20, 10 and 5% N_2 , respectively. The compound layer produced using 5% N_2 showed lesser hardness than 1200-1300 HV probably due to the elastic-plastic deformation field which reaches non-nitrided substrate (the bulk), as a consequence of the high testing load that was utilized, in the case 500 g, and the small layer thickness, which was only of 12.5 μm , as previously presented. In such case, hardness tests must be carried out applying low loads to prevent this kind of error in measurement. It is to be noted different studies have recommended that maximum penetration depths do not reach 1/10 and 1/20 of the layer thickness, respectively, for very hard and soft materials^{12,13}. Otherwise, the

increase of nitriding time for 6 hours, using 5% N_2 gas mixture, resulted in hardness of 1173 $\text{HV}_{0.5}$ (Table 1).

Figures 3 and 4 show hardness profiles of processed samples as a function of the gas mixture and nitriding time, respectively. Hardness values of 800, 800 and 500 $\text{HV}_{0.1}$ were measured at depth of 10 μm , inside the compound layer, for 20, 10 and 5% N_2 gas mixtures and 2 hours processed conditions, respectively. The increase of nitriding time for 6 hours, using 5% N_2 gas mixture, resulted in hardness of 1100 $\text{HV}_{0.1}$ at depth of 10 μm , inside the compound layer. For all studied conditions, measurements performed at 30 μm depth, comprising the hardness of the bulk, indicated values on the order of 300 $\text{HV}_{0.1}$.

Figure 5 presents result of nanoindentation as a function of the indenter penetration, which was obtained by varying the applied loads up to 40 g (400 mN). For non-nitrided condition, the high hardness values about 4 - 5 GPa (\sim 400 - 500 HV), related to indenter penetrations up to 500 nm, could be probably explained by the occurrence of surface work hardening generated during polishing step, at the sample preparation procedure, which would be in accordance with Pethica et al. study¹⁴. For higher loads resulting in 2250 to 2500 nm indenter depth, the measurements values tend to the substrate bulk hardness, in the case 3 GPa (\sim 300 HV). For 20, 10, and 5% N_2 , and 2 hours nitriding conditions, the values of 13 (\sim 1300 HV), 14 (\sim 1400 HV) and 12 GPa (\sim 1200 HV), respectively, are in agreement with the expected for surface hardness measurements. Confronting such results and the obtained by Vickers hardness tester (Table 1), nanoindentation resulted in higher measurement values to the last two nitriding conditions (10 and 5% N_2). This fact is related to the smaller thickness of the respective compound layers and the strong differences in the applied loads in both the characterization techniques, in the case 40 g maximum load and 500 g for nanoindentation and Vickers hardness measurement techniques, respectively. In such case, the very high applied load utilized for hardness determination results in a higher penetration of the Vickers indenter, which probably overtook the compound layer, entering in the substrate bulk region. Finally, for 5% N_2 and 6 hours nitriding condition, values of 12 GPa (\sim 1200 HV) obtained for penetrations higher than 500 nm are in agreement with microhardness measurements (Table 1). The small hardness values for penetrations up to 500 nm are probably due to the surface roughness, as a consequence of the longest time that the sample was exposed to plasma species bombardment.

Table 1. Compound layer thickness and the respective surface hardness values for different nitriding conditions.

Nitriding condition	Thickness of compound layer (μm)	Surface hardness ($\text{HV}_{0.5}$)
20% N_2 - 2 hours	25.0	1240
10% N_2 - 2 hours	20.0	1172
5% N_2 - 2 hours	12.5	950
5% N_2 - 6 hours	25.0	1173
Non-nitrided	-	250

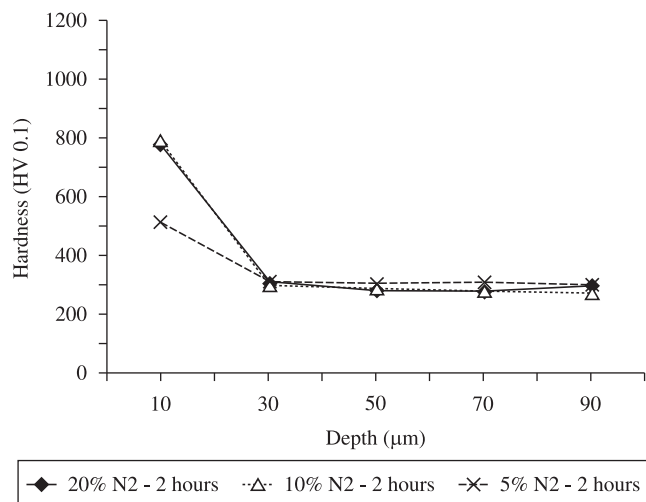


Figure 3. Hardness profiles of processed samples as a function of the gas mixture.

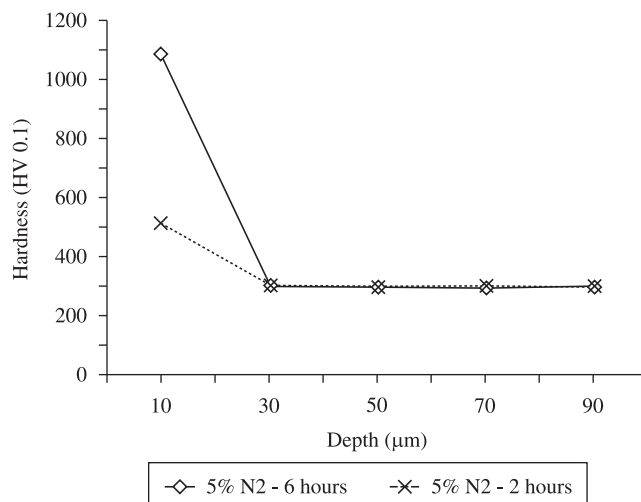


Figure 4. Hardness profiles of processed samples as a function of the nitriding time.

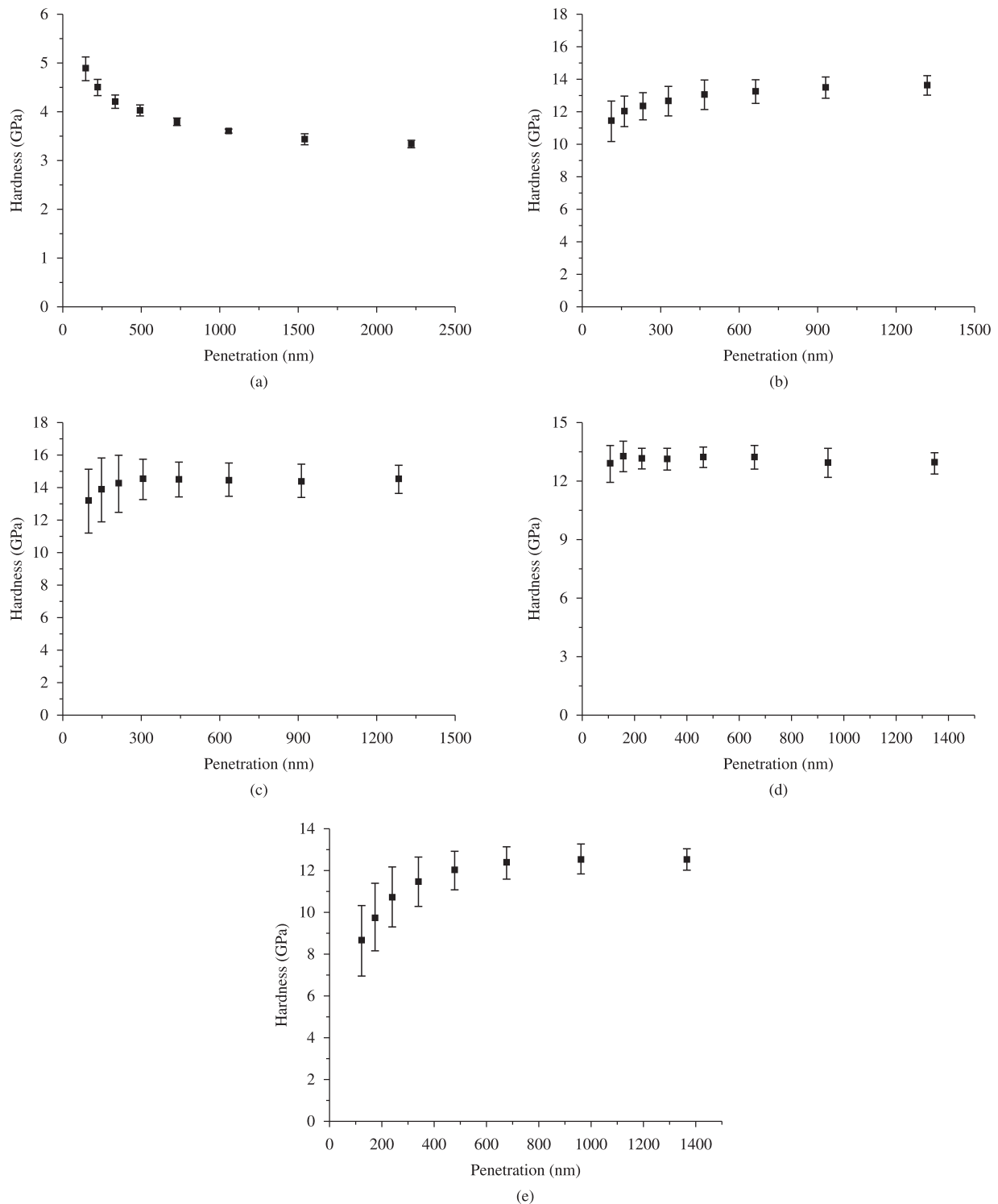


Figure 5. Nanoindentation results for different nitriding conditions: a) Non-nitrided; b) 20% N_2 - 2 hours; c) 10% N_2 - 2 hours; d) 5% N_2 - 2 hours; and e) 5% N_2 - 6 hours.

The effect for which smaller hardness values are verified for small penetrations in the nitrided layer was also verified for all nitriding conditions comprising 2 hours nitriding time (Figure 5b, c, d). The variation of the hardness values along the first 300 nm is higher as the nitrogen content in gas mixture is increased, which results in stronger sputtering effect, leading to the obtainment of a higher roughness surface.

Figure 6 presents a comparative of the X-ray diffraction patterns obtained for different nitriding conditions. In the start material, two identified phases are present, in the case α -(FeCr phase, corresponding to a cubic martensite, which is a typical tempering product) and γ -(FeCrNi phase, which is normally present in the CA-6NM stainless steel, for relative amounts up to 5%). All nitriding conditions resulted in formation of chromium nitride (CrN phase)

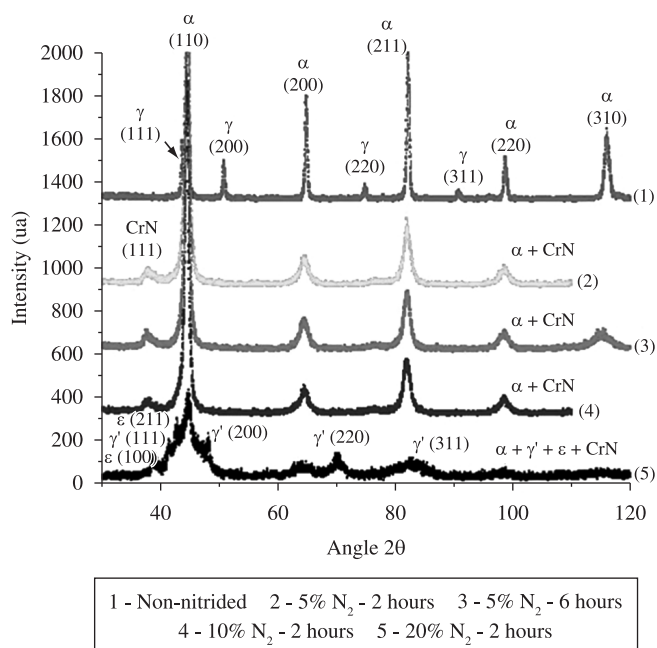


Figure 6. X-ray diffraction patterns for plasma nitrided CA-6NM stainless steel surfaces in different conditions.

and in the start phases peak enlargement. The peak enlargement is more evident for α -(FeCr) phase, and the obtainment of expanded martensite has been considered in the present case. In addition, it is to be noted the 20% N_2 and 2 hours nitriding condition also resulted in the formation of iron nitrides, which were identified as γ' -Fe₄N and ϵ -Fe_{2,3}N phases.

The fact the iron nitrides precipitation only occurred for the highest % N_2 gas mixture must be explained. Considering the iron nitrides are metastable phases, results indicate the probability of γ' -Fe₄N and ϵ -Fe_{2,3}N formation is very small for nitriding conditions comprising lower % N_2 gas mixtures. In such case, smaller amounts of nitriding reactive species could be available in glow discharge for 5 and 10% N_2 gas mixtures. An assumption the nitriding reactive species as atomic nitrogen would preferentially react with chromium alloying element, in the compound layer, is supported by the fact the chromium forms stable nitrides, which present negative formation Gibbs Free Energy Variation (ΔG) for the specified nitriding temperature. So, the higher the nitrogen amounts in gas mixture the higher is the probability to form different nitrides in compound layer. It is to be noted the same argument, *id est.*, a higher amount of available nitriding reactive species for higher % N_2 gas mixtures can be utilized to explain the nitrided layer thickness evolution as function of gas mixture as previously presented (Table 1).

4. Conclusions

The main conclusions of the present work can be listed as follows:

- The higher the nitrogen amounts in gas mixture the higher is the probability to form different nitride phases in compound layer, in the case γ' -Fe₄N and ϵ -Fe_{2,3}N and CrN phases, and the higher is the thickness of the nitrided layer, for the studied conditions;

- The hardness of the nitrided layers formed on CA-6NM stainless steel surface ranged from 12 to 14 GPa at penetration depths about 500 nm;
- The nanoindentation hardness results are in accordance with Vickers hardness measurements for the studied nitrided layers.
- The hardness values as a function of the indenter penetration, for penetrations smaller than 500 nm, are strongly dependent of the studied processing conditions; and
- Nitral solution as etchant could be utilized as a direct method to determine if the stainless characteristic of the stainless steel in the nitrided layer region is maintained unaltered after nitriding treatments.

Acknowledgments

The authors would like to thank the Brazilian Agency CNPq for financial support to perform this research, and LACTEC-UFPR by supplying the CA-6NM stainless steel samples.

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