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Structural characterization of plasma nitrided interstitial-free steel at different temperatures by SEM, XRD and Rietveld method



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ABSTRACT

Plasma nitriding processes are widely used to improve surface properties of several steels and alloys. In this work, the formation of nitrides in the surface of plasma nitrided IF steels as a function of the temperature was investigated. Three cold-rolled IF steel plates were nitrided for 4 h after shot peening at three different temperatures: 450 °C, 475 °C, and 500 °C. The resultant nitrided layers were then characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), Rietveld method, and hardness measurements. Through SEM images, it was possible to visualize two main sublayers: a compound layer and a diffusion zone. Through XRD, two phases were identified in the compound layer, which were ϵ -Fe₂₋₃N and γ '-Fe₄N. The diffusion zone presented a ferritic matrix with fine precipitates, possibly α '-Fe₁₆N₂. By Rietveld, the calculated quantity of γ '-Fe₄N was 68 wt.% for the sample treated at 475 °C and 58 wt.% for the one treated at 500 °C. These values were consistent with the hardness measurements. Thus, it is suggested that higher nitriding temperatures facilitate the decreasing of γ '-Fe₄N and, consequently, the increasing of ϵ -Fe₂₋₃N in the compound layer.

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1. Introduction

Nitriding is a thermochemical process largely applied to increase the surface hardness, fatigue life, wear and corrosion resistance of iron-based alloys [1–3]. Several surface modification techniques are already well known and established, such as plasma nitriding [4–6], gas nitriding [7,8], salt-bath nitriding

[2], and laser nitriding [9]. Among these techniques, plasma nitriding is one of the most studied and industrially adopted processes, which involves the introduction of nitrogen in the structure of the material through diffusional mechanisms while the component is treated by plasma at elevated temperatures. This process has been largely applied to steels of low alloy, tool steels, and stainless steels, and is considered

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one of the most economic surface treatments [10]. A major advantage of plasma nitriding is an increased mass transfer of high-energy nitrogen molecules and ions to the surface of the material and a better control of the process parameters [11].

According to the iron-nitrogen phase diagram, the maximum nitrogen content that can be dissolved in α -Fe is approximately 0.1 wt.% [12]. Thus, during the ferritic steels nitriding, the solubility limit of nitrogen in the α -Fe matrix is exceeded and it results in the formation of iron nitrides. The precipitation of nitrides is facilitated in the surface of the component where the nitrogen concentration is higher, originating a nitride layer that can be divided in two main sublayers: the compound layer and the diffusion zone. The compound layer comprises an outer layer of close-packed hexagonal ϵ -Fe₂₋₃N phase and an inner layer of face-centered cubic γ' -Fe₄N phase [5]. In the diffusion zone, the presence of two types of nitrides can be detected, which are γ' -Fe₄N and body-centered tetragonal α'' -Fe₁₆N₂. The nitrides in the diffusion zone are distributed in the α -Fe matrix as coherent precipitates and present the form of large needles in the case of γ' -Fe₄N, while the α'' -Fe₁₆N₂ phase shows a fine plated-like morphology [2]. The precipitation of second phases during plasma nitriding is related to the nitrogen concentration in the matrix. Low nitrogen concentrations will lead to the precipitation of α'' -Fe₁₆N₂, while the formation of ϵ -Fe₂₋₃N and γ' -Fe₄N are favored by higher nitrogen concentrations [5,11,13]. Therefore, as the nitrogen content gradually decreases toward the substrate, nitride phases precipitate in the following sequence: ϵ -Fe₂₋₃N \rightarrow γ' -Fe₄N \rightarrow α'' -Fe₁₆N₂ [2]. The formation of these precipitates, as well as their quantity and distribution in the nitriding layer, depends not only on the nitrogen concentration, but also on the exposure time, temperature, and cooling rate. Understanding and controlling the formation of these precipitates is a major industrial interest. The wear and corrosion resistance of the nitrided layer depends on the type of nitride formed in the compound layer. The presence of ϵ -Fe₂₋₃N is considered tribologically desirable, since these nitrides present high corrosion resistance, adequate hardness and scuffing resistance [14], while γ' -Fe₄N is known for been a brittle phase, which is not recommended for forming processes [11,14]. In this case, the control of the proportion of these phases in the compound zone becomes very important.

Interstitial-free (IF) steel is an interesting case for this investigation due to several reasons. This steel presents a single bcc phase, which is prone to diffusional mechanisms. Furthermore, due to their excellent formability, IF steels are largely used in the automotive industry. Surface treatment by plasma-nitriding would broaden their applicability, adding to these steels interesting surface characteristics, such as wear resistance. Nevertheless, the control of the formation of nitride zones in IF steels and the quantity of present phases still needs deeper investigation.

In the current study, the formation of nitrides precipitation in an IF steel as a function of the temperature was investigated. Scanning electron microscopy (SEM), X-ray diffraction (XRD), the Rietveld method, and hardness tests were used to characterize the morphology, phase proportions, structural parameters, and mechanical properties of the present nitrided layers.

2. Materials and methods

Commercially available Ti-stabilized IF steel manufactured by Usiminas S.A was used in this study. Small plates (20 mm \times 20 mm \times 2 mm) were extracted from a conventionally cold-rolled sheet. Its chemical composition is listed in Table 1. The plates were then shot peened according to the SAE-AMS-S-13165 standard [15], using the following parameters: stainless steel balls with diameters ranging from 0.09 mm to 0.2 mm, blast pressure of 100 Psi and 100% coverage. Plasma modification processes were conducted by Wallwork Ltd. (Cambridge, England). Samples were nitrided in a 60% Ar plus 40% N₂ atmosphere at pressure of 4×10^{-3} mbar with a voltage of 200 V, using a D.C. triode configuration in a PAPVD coating system. This concentration was chosen based on typical mixtures used for plasma nitriding [16]. The process time was 4 hour and three different temperatures were selected: 450 °C, 475 °C, and 500 °C. The samples were then cooled in air to the room temperature at a rate of approximately 1.5 °C/s.

After nitriding, the samples were cross-sectioned, mounted in Bakelite, mechanically ground, polished (down to 1 μ m), and then etched with Nital 4% (4% HNO₃-98% CH₃CH₂OH). The microstructural characterization was performed by SEM, using a FEI Inspect S50 microscope (FEI, Hillsboro, OR, USA). The samples were covered with gold and imaged using a tension of 15 kV under high vacuum.

The existing phases in the top nitrided surface were identified by XRD measurements, using a Philips PW 1710 diffractometer (Philips Instrument, Eindhoven, The Netherlands) with a Bragg-Brentano geometry and Cu K α radiation ($\lambda = 0.15418$ nm). Diffraction spectra were obtained in an angular range of 2θ between 20° and 90° with a rate of 0.02°/s. In order to quantify the nitride phases and characterize their atomic structure, Rietveld analyses [17] of XRD patterns were carried out using GSAS package [18], and the starting structural models used were based on information given in the ICSD database [19].

In order to evaluate the mechanical properties of the nitrided layers, hardness-depth curves were obtained through a Berkovich indenter. The measurements were performed on the polished cross-sections of the samples with a peak load of 1900 mN during 5 s and constant loading rate of 0.83 mN/s by using a Shimadzu DUH-W201S instrumented indentation tester (Shimadzu, Kyoto, Japan).

3. Results and discussion

3.1. SEM microstructural analysis

Fig. 1 displays the cross-sectional views by SEM for a not-nitrided sample (Fig. 1a) and for the samples exposed to different nitriding temperatures: 450 °C, 475 °C, and 500 °C (Fig. 1b-d). In the not-nitrided sample, the cross-sectional microstructure presented only grains of α -Fe and an irregular and plastically deformed surface resulted from the shot peening process. The visible plastic deformation extended to a depth of approximately 20 μ m. All nitrided samples presented an outer compound layer and an inner diffusion zone.

Table 1 – Chemical composition in weight percent of the IF steel used in this study.

C	N	Ti	Nb	P	S	Al	Si	Mn
0.005	0.006	0.049	0.002	0.012	0.0071	0.025	0.012	0.12

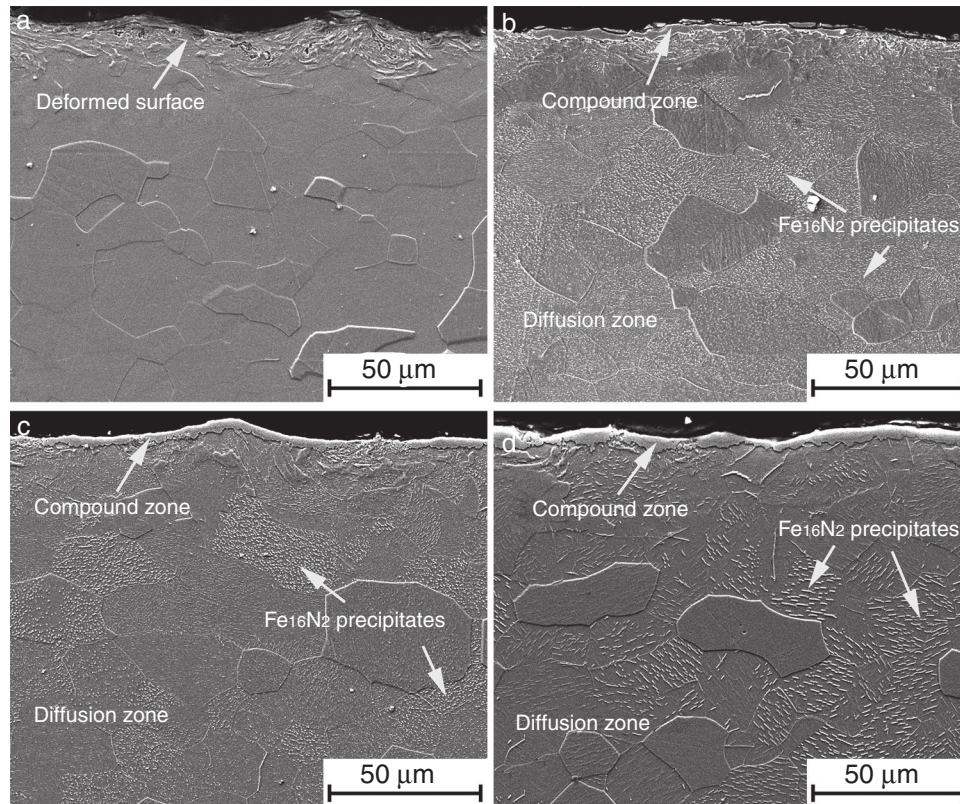


Fig. 1 – SEM cross-sectional views of the evolution of the nitride zones as a function of the temperature:(a) not treated sample, (b) treated at 450 °C, (c) treated at 475 °C, and (d) treated at 500 °C.

Through the images, the thickness of the compound zone could be measured in different points of each sample and the average values for the samples treated at 450 °C, 475 °C, and 500 °C were, respectively, 2.8 μm, 3.5 μm, and 4.8 μm. The compound layer in the sample treated at 450 °C was quite irregular, as was the thickness results. On the other hand, the compound layers in the samples treated at 475 °C and 500 °C were regular, dense, and presented increased thickness. This was expected, once the kinetics of precipitation for nitrides rich in nitrogen is favored by the highest treatment temperature. However, it is known [5] that the compound zone is divided into two nitride phases (ϵ -Fe₂₋₃N and γ' -Fe₄N), which cannot be observed by SEM. Thus, the proportion and quantities of the respective phases in the compound zone must be characterized by other techniques (e.g. XRD and Rietveld method) than SEM. The quantification of present phases in the compound layer is very important, since each phase plays a different role in the final properties of the material. The γ' -Fe₄N phase is very brittle and not desirable in forming processes [9], which make the control of its quantity a major necessity.

Under the compound layer it is possible to visualize the presence of a diffusion zone for the three treated samples (Fig. 1b–d), where the nitride precipitates are distributed in

the ferritic matrix. The main difference among the samples treated at different temperatures is the morphology of these precipitates. At 450 °C, the precipitates are finer and more numerous. With the increase of the temperature, the precipitates became bigger and well defined. As discussed previously, it is expected two types of precipitates to be formed in the diffusion zone, which are γ' -Fe₄N and α'' -Fe₁₆N₂. The γ' -Fe₄N phase is related to higher temperatures and longer nitriding times and presents the shape of long needles, normally located close to the compound layer as demonstrated by Gontijo et al. [5]. On the other hand, the α'' -Fe₁₆N₂ phase is a metastable structure and its formation is attributed to lower temperatures and faster cooling rates, having a plated-like morphology, which are finely distributed in the matrix [2]. Observing Fig. 1b–d, it is suggested that only α'' -Fe₁₆N₂ phase was formed in the diffusion zone, since large needles of γ' -Fe₄N are absent in all nitrided samples and the morphologies are quite different from those published by Gontijo et al. [5], which presented a considerable amount of γ' -Fe₄N. Furthermore, those authors related the formation of γ' -Fe₄N to low cooling rates and suggested that this nitride precipitates mainly during the cooling process. The cooling rate used in this work was fast, which may explain the absence of γ' -Fe₄N.

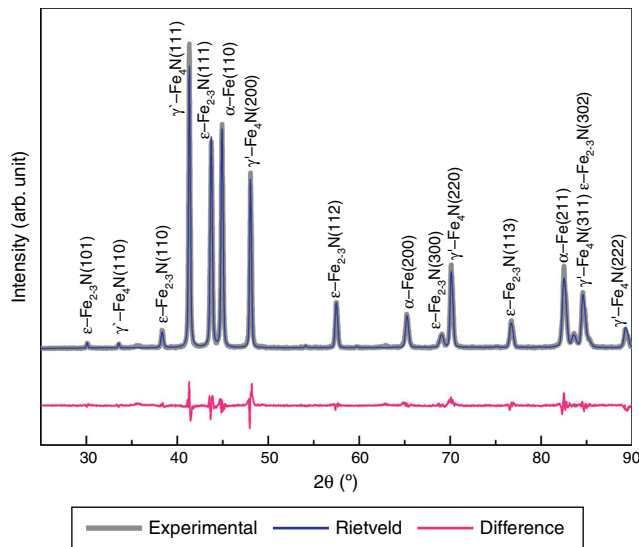


Fig. 2 – XRD pattern and Rietveld refinement for the nitrated sample at 450 °C.

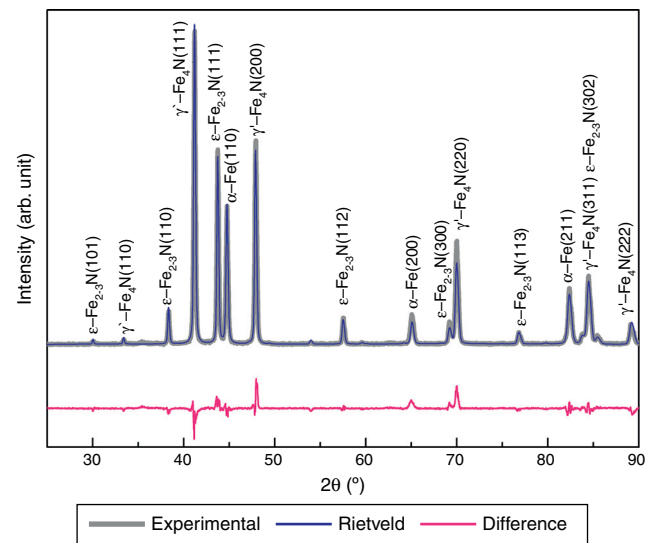


Fig. 4 – XRD pattern and Rietveld refinement for the nitrated sample at 500 °C.

3.2. XRD and Rietveld structural characterization

Figs. 2-4 show the XRD patterns and respective Rietveld refinements for the samples nitrated at 450 °C, 475 °C, and 500 °C. For all conditions, three phases were identified: ϵ -Fe_{2.3}N (ICSD card #79982), γ' -Fe₄N (ICSD card #79980), and α -Fe (ICSD card #159354). It is noticed that the relative intensities of the peaks change from one condition to another, meaning that the final proportion of these phases varies in response to different treatment's temperature. The presence of the α -Fe pattern means that the X-ray beam crossed through the compound layer and reached the diffusion zone, which presents a ferritic matrix. The absence of peaks related to α' -Fe₁₆N₂ can be explained by its morphology (finely distributed in the ferritic matrix) and only advanced techniques can detect this precipitates, such as transmission electron microscopy (TEM),

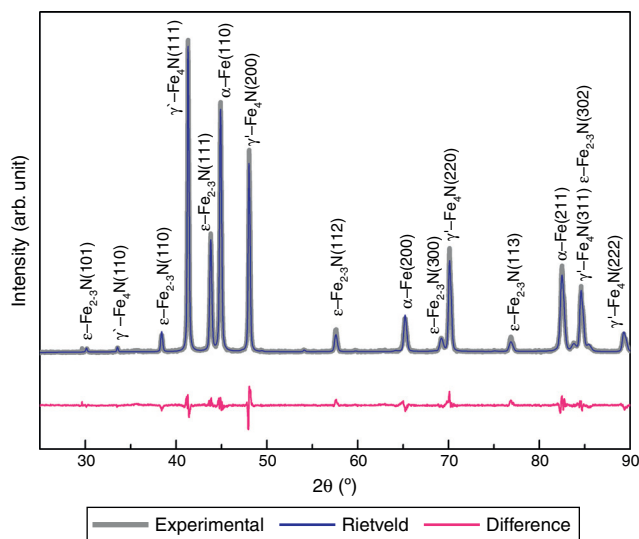


Fig. 3 – XRD pattern and Rietveld refinement for the nitrated sample at 475 °C.

field-ion microscopy (FIM), and atom probe microscopy. As discussed in Section 3.1, the SEM micrographs indicated only the presence of α' -Fe₁₆N₂ precipitates in the diffusion zone. Thus, the total amount of ϵ -Fe_{2.3}N and γ' -Fe₄N detected by XRD is attributed only to the compound layer.

Once it is known that the proportion of ϵ -Fe_{2.3}N and γ' -Fe₄N varies in the compound zone according to the temperature of nitriding, the Rietveld Method was applied to refine the atomic structure of the present phases and to quantify them. The Rietveld method is a mathematical approach based on X-ray powder diffraction patterns [20]. It implies in approximations when one is applying this method to non-powdered samples, mainly due to the presence of texture in the analyzed surface. Another important issue is the applicability of this method to layered structures, such as nitrated steels. According to Lutterotti et al. [21], the outer layer (i.e. ϵ -Fe_{2.3}N) absorbs part of the intensity from the inner layer (i.e. γ' -Fe₄N). Those authors proposed an absorption correction factor to compensate this effect on the intensity. GSAS software also presents absorption functions, which were used in this work. Nevertheless, taking into account that the Rietveld method is based on powder diffraction, any approach applied to compensate the effects of multilayered materials on the intensity is an approximation. Anywise, the Rietveld method has been used by many authors [5,22,23] through the years to quantify phases in nitrated materials with satisfactory results.

The structural results of the best fits are shown in Table 2. The parameters R_{wp} , R_{exp} , χ^2 , and R-Bragg indicate the quality of the fitting and are graphically represented by the different lines in Fig. 2. R_{wp} is an index used to measure the refinement's convergence. Values of R_{wp} below 15% are desirable. R_{exp} is the amount statistically expected to R_{wp} and χ^2 (goodness of fitting) is the ratio between R_{wp} and R_{exp} . The R-Bragg parameter takes into account structural information, such as lattice parameters, to evaluate the quality of the refinement.

The α -Fe phase was considered during the refinement only to maintain the quality of the analyses. The weight percentage

Table 2 – Structural parameters from Rietveld analyses of XRD patterns of the samples nitrided at 450 °C, 475 °C, and 500 °C.

	Sample nitrided at 450 °C	Sample nitrided at 475 °C	Sample nitrided at 500 °C
R_{wp} (%)	12.55	12.92	15.12
R_{exp} (%)	5.50	6.49	4.86
χ^2	2.28	1.99	3.11
R-Bragg	0.08	0.08	0.13
a_e (Å)	4.722	4.714	4.706
c_e (Å)	4.391	4.387	4.384
ρ_e (g/cm ³)	7.11	7.14	7.12
$a_{\gamma'}$ (Å)	3.804	3.804	3.804
$\rho_{\gamma'}$ (g/cm ³)	7.16	7.16	7.15

related to this phase was removed from the final data treatment afterwards. From Rietveld analyses it can be observed that the cell parameters (and consequently the theoretical density) are quite similar to those contained in the crystallographic database [19]. No significant variations in the lattice parameters of the nitrides in the compound layer were found among the samples.

The quantitative results (phases concentrations in wt.%) calculated by the Rietveld method for the compound layers are depicted by the chart in Fig. 5. Observing the quantities of ϵ -Fe₂₋₃N, the following behavior is observed: from 450 °C to 475 °C the quantity of ϵ -Fe₂₋₃N decreases. However, at 500 °C, the quantity of ϵ -Fe₂₋₃N phase is increased in comparison with the quantity of the same phase in the sample treated at 475 °C. At all nitriding conditions, the ϵ -Fe₂₋₃N phase was still in minority. It can be explained by the fact that the formation of nitrides with higher nitrogen percentage, which is γ' -Fe₄N in this case, is favored by the plasma nitriding process. Previous studies reported the importance of the presence of ϵ -Fe₂₋₃N in the wear and corrosion resistance of the nitrided materials [6]. Although ϵ -Fe₂₋₃N was not the majoritarian phase in the samples studied in this work, its concentration was 42% in the sample nitrided at 500 °C, which is a considerably higher fraction when compared with results from other works performed on low carbon steels [5,6]. This indicates the importance of

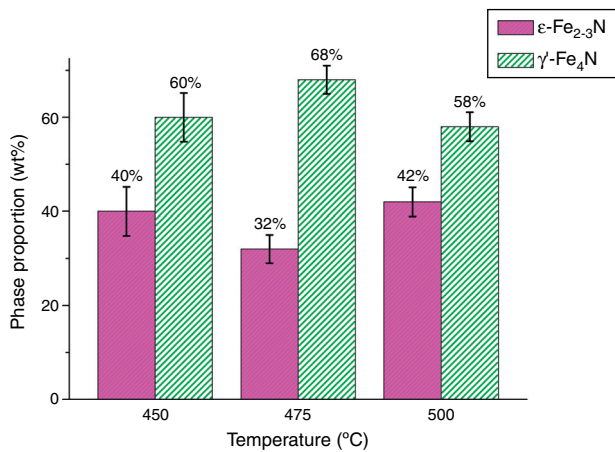


Fig. 5 – Weight percentage of the phases contained in the compound layer as a function of the nitriding temperature. The error bars indicate the standard deviation calculated by GSAS.

searching alternatives to vary nitriding parameters in order to obtain more suitable microstructures.

Some careful considerations must be done about these findings: (1) the compound layer formed at 450 °C is thin and very irregular as shown in Fig. 1b, what may compromise the accuracy of the quantification process. (2) Thus, when analyzing only the two conditions where consolidated and well-formed compound layers were obtained (475 °C and 500 °C) one may suggest that higher temperatures help the formation of ϵ -Fe₂₋₃N. Gontijo et al. [5] found similar tendency for longer nitriding times. In this case, enough time was given to form nitrides what is facilitated by kinetics at higher temperatures.

3.3. Hardness measurements

As discussed previously, γ' -Fe₄N is a hard and brittle phase, not being adequate for forming processes [11,14]. Attempts to decrease its quantity in the compound layer may be welcome to improve the properties of nitrided low-carbon steels, such as IF steels. Fig. 6 depicts the hardness profile of the samples studied in this work from the surface to a depth of 600 μm. It is observed that the sample treated at 500 °C presents lower hardness values near the surface compared with the sample treated at 475 °C. This is consistent with the Rietveld results, which presented a decreased percentage of γ' -Fe₄N in the compound layer from 475 °C to 500 °C. Thus, the hardness measurements reinforce the results found by the Rietveld analysis, indicating that this methodology may

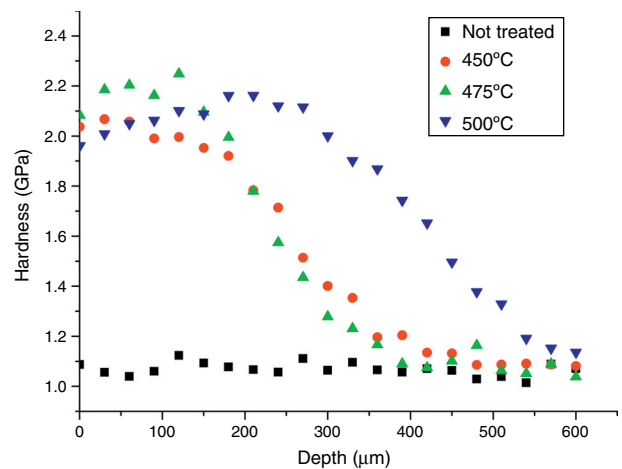


Fig. 6 – Hardness-depth profiles of the studied samples.

be applied satisfactorily to control phase quantities in the compound layer of nitrided low-carbon steels.

4. Conclusions

Plasma nitriding of IF steel plates at different temperatures (450 °C, 475 °C, and 500 °C) was studied by SEM, XRD, Rietveld method, and hardness measurements. The following conclusions were drawn:

- From the SEM images, it was observed that the resultant nitrided layers were divided in two sublayers: compound layer and diffusion zone. The compound layer was composed by ϵ -Fe₂₋₃N and γ' -Fe₄N according to the XRD patterns, while the morphology of the diffusion zone was depicted only by fine plated-like nitrides α'' -Fe₁₆N₂ distributed in a ferritic matrix.
- The thickness of the compound layer increased with the nitriding temperature. At 450 °C the compound layer was irregular and consequently the measurements of its thickness and phase quantities were damaged. On the other hand, at 475 °C and 500 °C, dense and well-formed compound layers were found.
- The proportion of the phases in the compound layer varied from one condition to another. From 475 °C to 500 °C the quantity of γ' -Fe₄N, which is the hardest phase in this layer, decreased from 68% to 58%. These results were reinforced by hardness measurements. It suggests that higher nitriding temperatures facilitate the decreasing of γ' -Fe₄N and, consequently, the increasing of ϵ -Fe₂₋₃N in the compound layer. Furthermore, the Rietveld Method resulted as an interesting tool to control the quantity of phases in nitrided steels.

Conflicts of interest

The authors declare no conflicts of interest.

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