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OBTAINING NITROGEN MARTENSITE IN INTERSTITIAL FREE STEEL ENRICHED WITH CHROME

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Abstract*. Nitrogen martensite was produced by Solution Heat Treatment after Plasma Nitriding (SHTPN) process in interstitial-free steel samples enriched with chrome and treated. Pure iron samples were also treated for comparison. The SHTPN process consisted of a nitriding at 510°C for 2h, followed by a solution treatment and oil quenching. Three solution treatment temperatures (800, 900 and 1000°C for 15 minutes) were studied. Samples were characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and Vickers microhardness testing. Results show that chrome presence increases the thickness of the nitrided layer, resulting in thicker and more homogenous layers after the solubilization. In other hand, chrome-rich surfaces have presented increases in porosity. Despite of the better diffusion of the nitrogen, higher solution temperatures promotes the emergence of heterogeneous layer.*

Keywords*: IF steel, Nitrogen Martensite, SHTPN, Chrome Enrichment, Plasma Nitriding*

1. INTRODUCTION

The nitrogen solubility in α-Fe is approximately two and five times better than the carbon at temperatures of 20 and 590°C respectively; resulting in a decrease in the tendency for precipitation (Shen et al, 2006). Thus, the presence of nitrogen as an interstitial atom in iron and its alloys provides a more efficient strengthening effect than carbon. Its also can improve the corrosion (Bernardelli et al, 2010) and creep (Kim et al, 2008) properties.

Nitriding is a thermochemical treatment used for introduction of nitrogen in solid solution or nitride form, on the surface of the material. One of the most advantageous nitriding processes is by using abnormal glow discharges, which reduces the treatment time, consumption of the gases and energy, but also to obtain more uniform layers (Damin, 2015).

Nitrides formation on ferritic steels is frequently noticed due to an excess of nitrogen in the α matrix. The nitride layer is composed by two sublayers: the compound layer, which is composed by ε-$Fe_{2-3}N$ and γ'-Fe_4N nitrides and the diffusion layer, with nitrogen atoms dissolved interstitially in the matrix, also tending to form nitrides γ'-Fe_4N and α''-$Fe_{16}N_2$ (Lee et al, 2010).

The diffusion of the nitrogen present in the nitride layer for its introduction as an interstitial atom can be promoted by a solution treatment and quenching. This sequence of processes, nitriding followed by high temperatures solution and quenching, is called Solution Heat Treatment after Plasma Nitriding process, SHTPN. The high solution temperatures benefit the dissolution of the nitrides and consequent diffusion of this element in the matrix, which results in a high concentrate layer of nitrogen in solid solution. Also, the high cooling rate of this treatment favors the formation of the nitrogen martensite.

Previous work (Berton, 2014) showed that was possible to obtain the nitrogen martensite using the SHTPN technique in ferritic stainless steels, which was accompanied of an important increase in the hardness and improved the corrosion resistance. Meira (2014) has introduced nitrogen into interstitial-free steel matrix, although the capacity of nitride formation is lower compared to the alloys with chrome. In the present work is studied the influence chrome enrichment on the formation of nitrogen martensite.

2. EXPERIMENTAL PROCEDURE

Samples of interstitial-free steel were treated in the present work. The measured chemical composition (wt %) was 0.004 C; 0.137 Mn; 0.007 P; 0.007 S; 0.085 Si; 0.024 Al; 0.035 Nb; 0.037 Ti; 0.003 N. Before the treatments, the samples (30x30x7 mm) were grinded up to 1200 grift and polished in 1 µm diamond suspension.

In the present work were performed two routes of treatment: In the first one, the samples were enriched and submitted to SHTPN process; in the second, the samples were just treated by SHTPN process. The parameters of treatments are presented in Table 1.

The chrome enrichment was performed by a cathodic sputtering, where a plate (100x100x5 mm) of AISI 409 stainless steel (0.006 C, 10.91 Cr, 0.02 Co, 0.02 Cu, 0.21 Mn, 0.04 Mo, 0.21 Ni, 0.03 P, 0.001 S, 0.17 Ti,) was used as target. A pulsed plasma source with pulse width modulation was employed for all treatments, being the temperature control performed by the t_{on} values.

Table 1. Parameters of the thermochemical surface-treatments of the IF steel.

Parameters	Chrome Enrichment	Sputtering Cleaning	Plasma Nitriding
Time (h)	3	1	2
Temperature (°C)	1200	160±10	510±10
Flow (cm^3/min)	240	200	200
Atmosphere	80%Ar + 20%H_2	100%H_2	80%N_2 + 20%H_2
Pressure (Torr)	2	1,5±0.2	3±0.2
Power (V)	700	400	600
t_{on} (µs)	180	220-250	95-195
t_{off} (µs)	-	250	250

The solution step of SHTPN process was done in a salt bath at three different austenitizing temperatures, 800, 900 and 1000°C, with time of 15 minutes, followed by an oil quenching. The metallographic analyses were performed according to the conventional metallography techniques: cutting; grinding up to 1200 grift and; polishing with 1 µm and 0.25 µm diamond paste. The microstructure was revealed using Nital 10% etch, which analysis were carried out by scanning electron microscopy (SEM) and optical microscopy (OM). The SEM results were performed on the Carl Zeiss EVO MA 15, equipped with Oxford X-Max EDS detector. The microhardness vickers testing was made using a Shimadzu Microhardness Tester HMV-2, applying 50gf. Hardness profiles correspond an average of three measurements and other hardness results correspond an average of ten measurements.

3. RESULTS AND DISCUSSION

The enrichment treatment was efficient to obtain a chrome-enriched ferritic layer in the IF steel surface, as can be seen in the Fig. 1. As predicted by the Fe-Cr system, and according to the EDS analysis, the samples has approximately 8% of chrome in this layer 105 µm thick.

IF samples only nitrided, present a typical γ' needles formation over more than 200 µm in the nitrided layer, which can be observed in Fig. 2. The effect of chrome addition is well observed in the Fig. 3. The morphology of the nitride layer of the IF Cr-rich surfaces shows, in addition of γ' nitrides needles, there are plate like precipitates, characteristic of α" nitrides. It can also be noted that α" nitrides were more concentrate in deepest sections. This finding is in accord with the stoichiometry of this nitride which contains less nitrogen than γ'. Meira (2014) has observed the higher affinity of the nitrogen with chrome than to iron, resulting high concentration of phases rich in chrome, as ε and CrN after nitring. The increase in nitrogen content leads to iron nitride precipitation, which in accordance with de Fe-N system, the equilibrium iron nitrides are the Fe_4N (γ'), with needles morphology, and $Fe_{2\text{-}3}N$ (ε) (Oliveira, 2002). Still, according to Oliveira (2002), for certain substrate compositions and processing parameters a metastable nitride is formed before the γ' precipitation, the $Fe_{16}N_2$ (α"), a face centered tetragonal nitride, which has a plate like morphology.

Fig. 4, 5 and 6 shows the morphology of IF samples after SHTPN process, having the solution step at 800, 900 and 1000°C, respectively. It can be observed that the surface layer is composed mainly by nitrogen martensite. As result of greater diffusion, the increasing in temperature results in thicker layers. In other hand at 800°C the layer is much easily distinguished than at 900°C and 1000°C, where the layers have martensite crystals more dispersed.

For the IF steel enriched and treated by SHTPN process (Fig. 7, 8 and 9), as observed for the IF only treated by SHTPN, the mainly structure of nitrogen martensite was verified. Again, the increase of the solution step temperature, led to an increase in layer thickness. It can be also observed the occurrence of porosity, mainly for the temperature of 900°C. This refers to the chromium capture during the nitriding process for the formation of chrome nitrides, which can be associated with the nitrogen evolution in gas state as proposed by Borges and Rocha (2011). In this way, the samples enriched and treat by SHTPN process were more susceptible to $N_{2(g)}$ evolution and consequently pore formation than the samples only treated by SHTPN process.

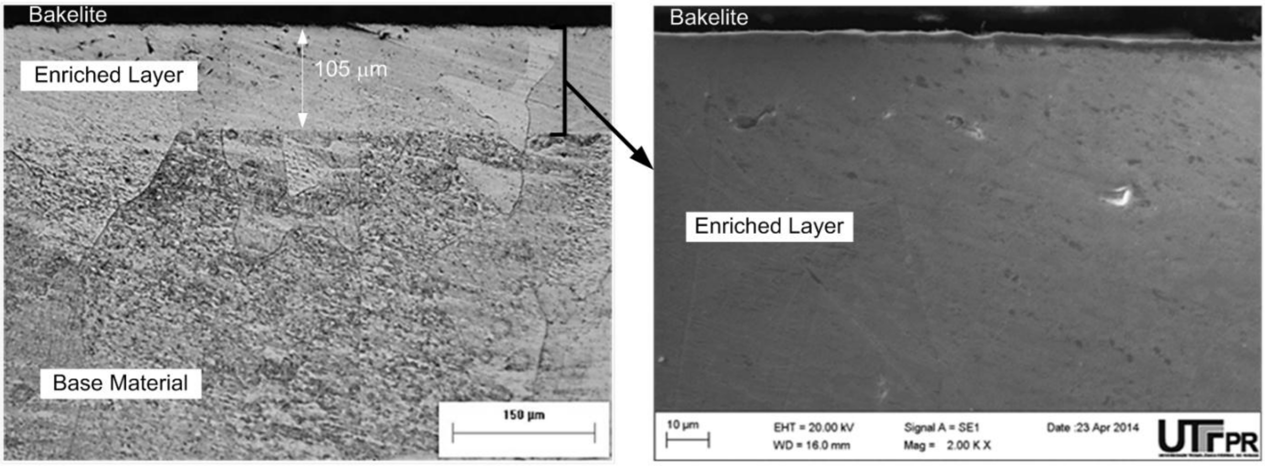

Figure 1. IF steel chrome-rich layer by cathodic sputtering.

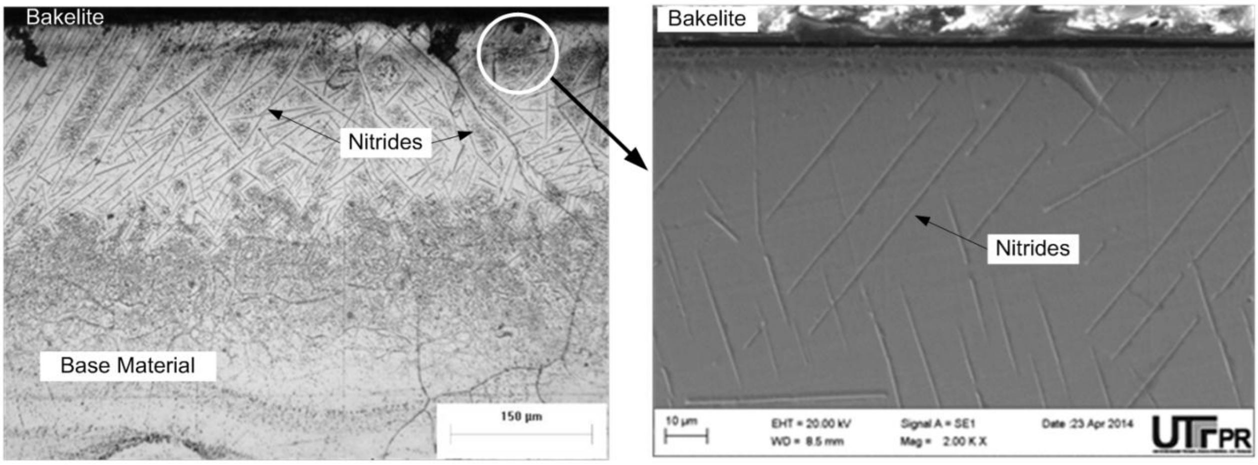

Figure 2. IF steel nitrided layer.

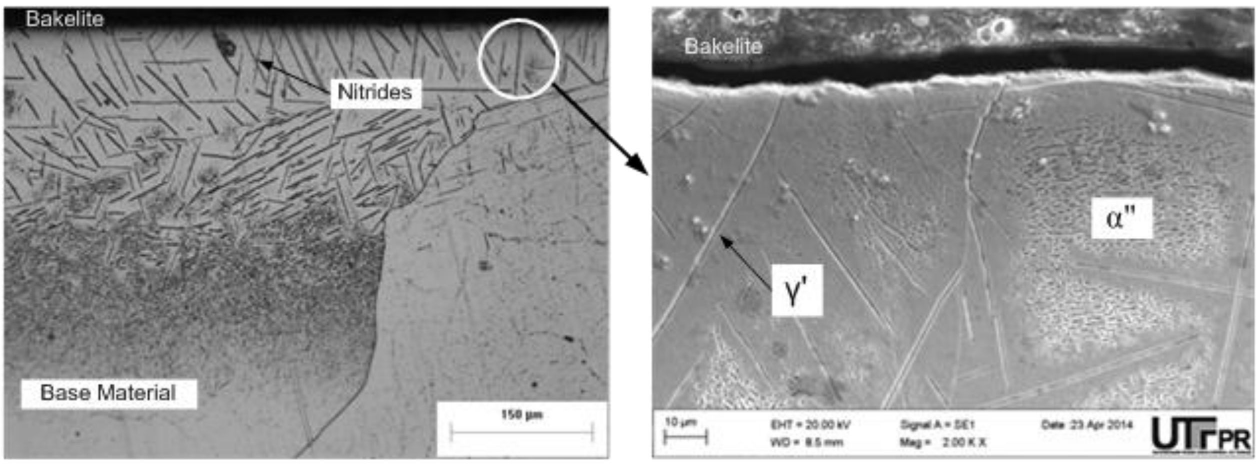

Figure 3. IF steel enriched and nitrided layer.

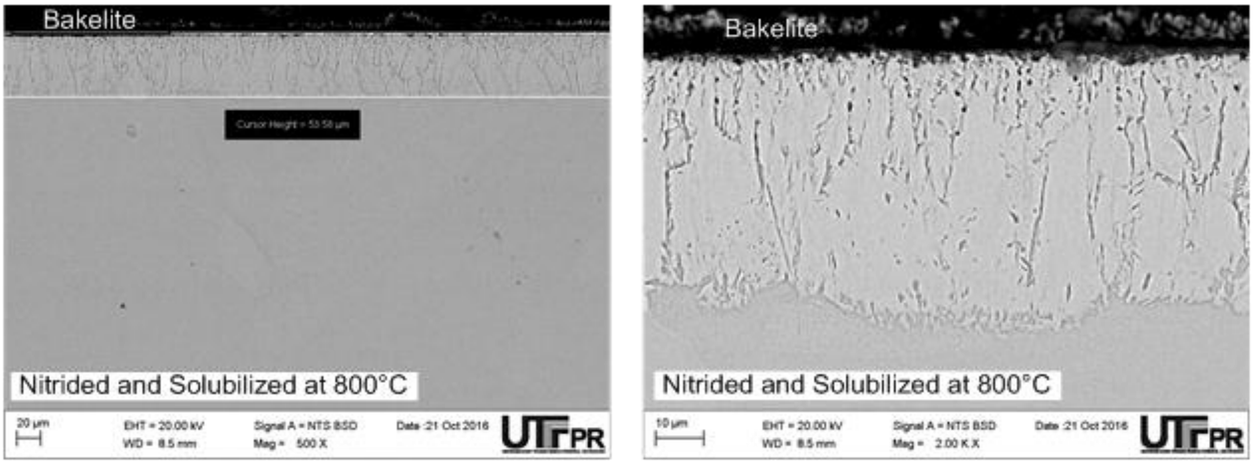

Figure 4. IF steel after SHTPN at 800°C.

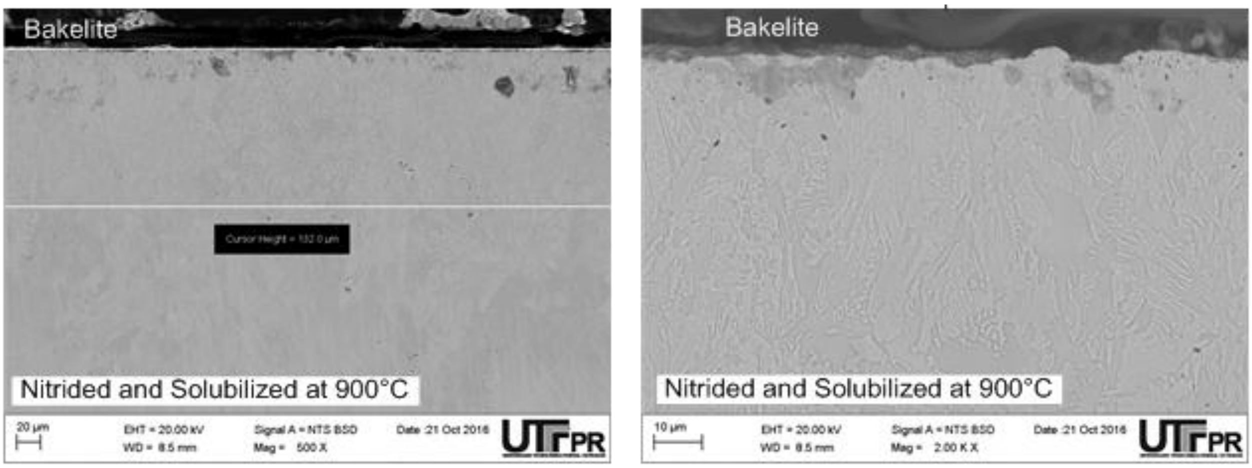

Figure 5. IF steel after SHTPN at 900°C.

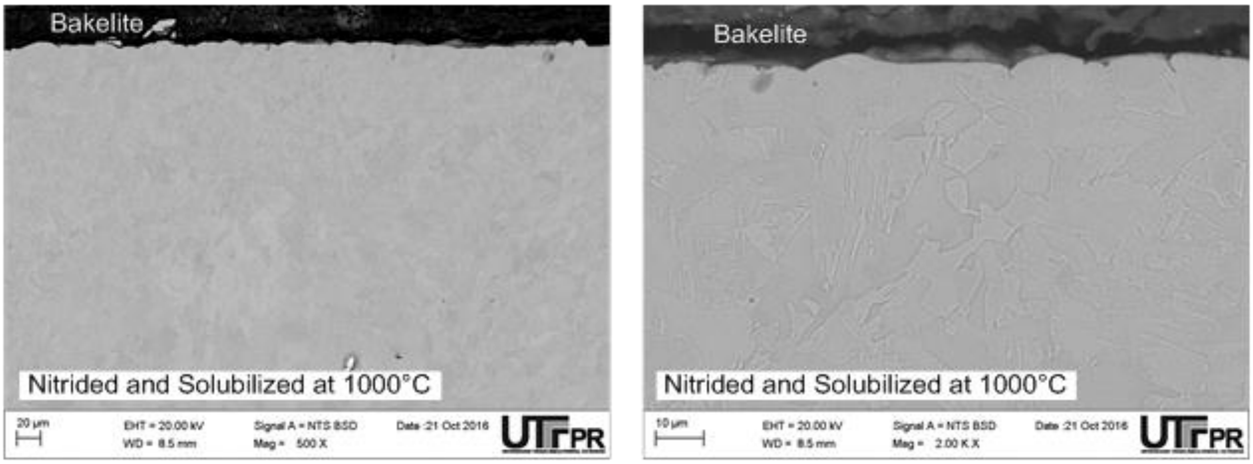

Figure 6. IF steel after SHTPN at 1000°C.

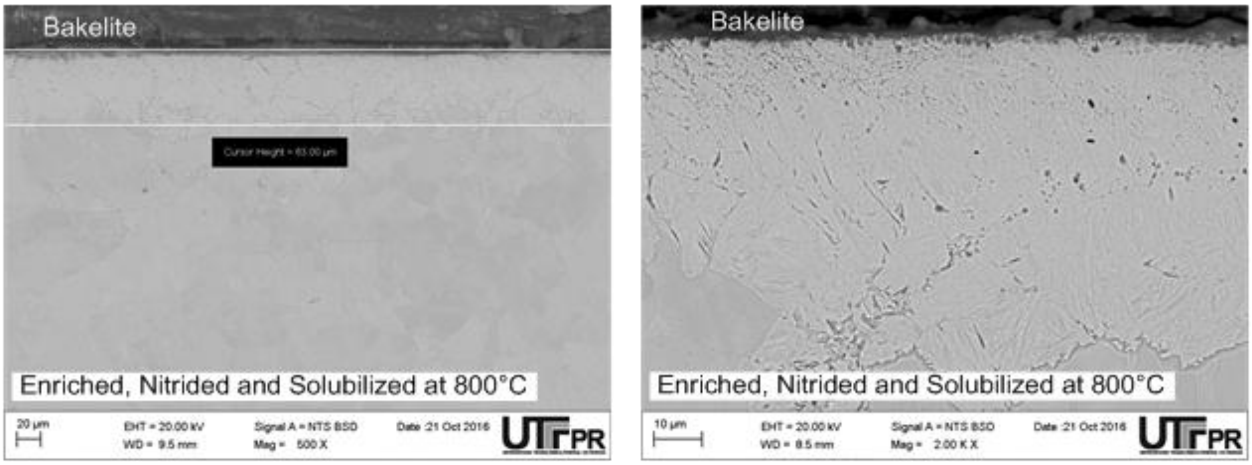

Figure 7. Chrome-enriched IF steel after SHTPN at 800°C.

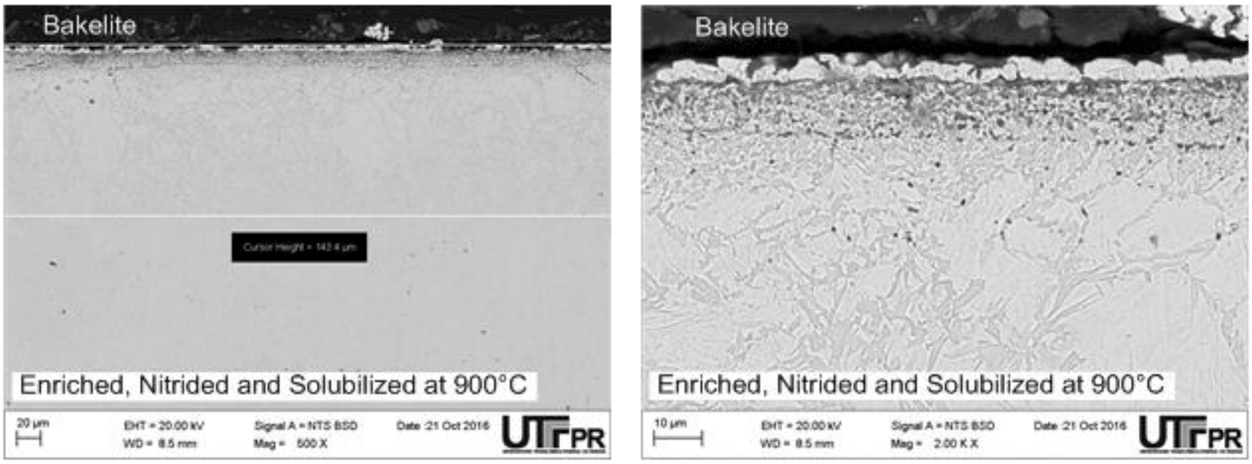

Figure 8. Chrome-enriched IF steel after SHTPN at 900°C.

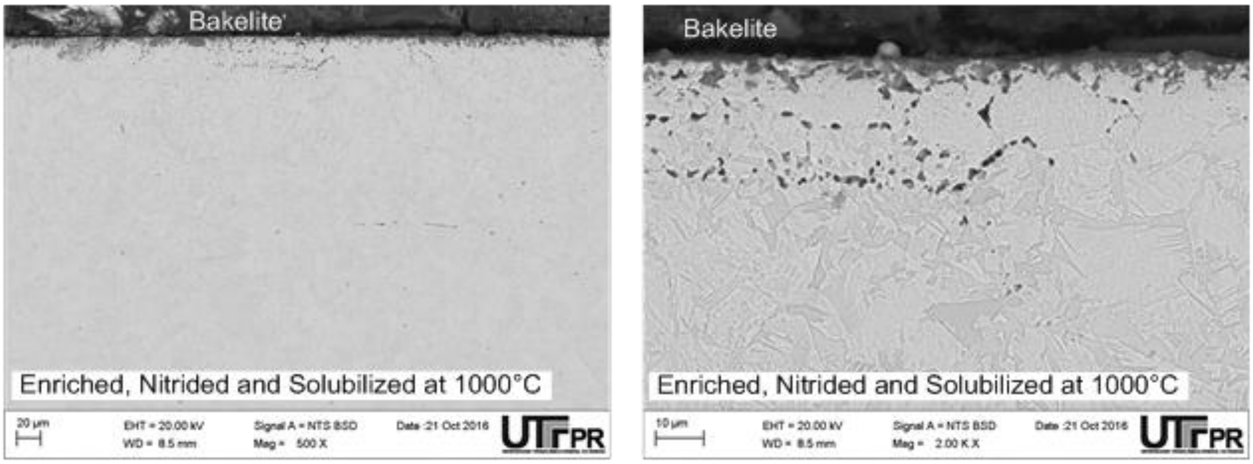

Figure 9. Chrome-enriched IF steel after SHTPN at 1000°C.

The Fig. 10 gives the results of the chemical analyses in function of the depth of the samples enriched-nitrided after SHTPN. For the sample treated at 800°C, Fig. 10a, there is a decrease in the percent of chrome in the surface, as well as for 1000°C, Fig. 10c. The smaller chrome content in the surface at 1000°C is a result of the better diffusion of this element towards the bulk of the sample. Different from the treatment at others temperatures, for the sample solubilized at 900°C, Fig. 10b, the highest concentration of chrome is in the intermediary porous layer observed in Fig. 8.

Fig. 11 shows the hardness-depth profiles. If compared to the bulk, the hardness level near the surface (mainly until 50 µm deep) increases for all treatment conditions and especially for the samples enriched and treated by SHTPN process (Fig. 11b). This figure shows the higher value for the sample treated at 800°C, what is consistent with the highest percent of chrome in this area, presented by Fig. 10a, that favored a higher nitrogen concentration. For the samples only treated by SHTPN process, presented in Fig. 11a, the higher hardness value is also relative to the treatment at 800°C. For the temperatures of 900 and 1000°C the transition of hardness values between the surface and the core is less noticeable, if compared with the samples previously enriched, indicating that the chrome retards the diffusion of the nitrogen towards the core.

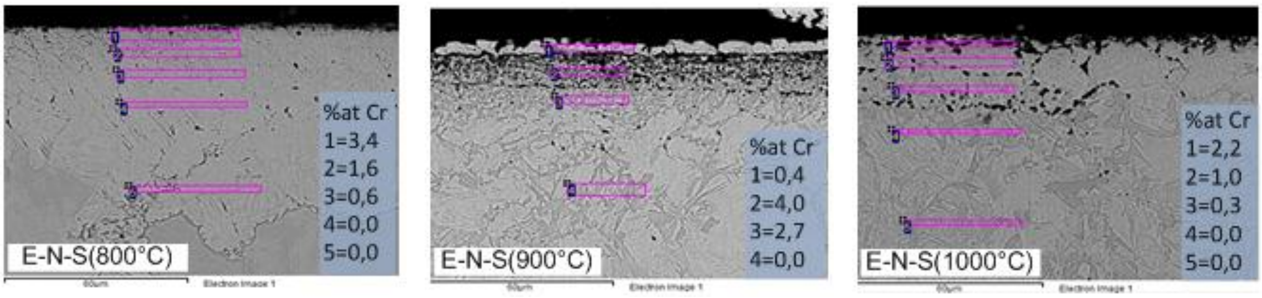

Figure 10. Results of the energy dispersive spectroscopy (EDS) of the IF steel chrome-enriched, nitrided and solubilized (ENS), (A) 800°C, (B) 900°C and (C) 1000°C.

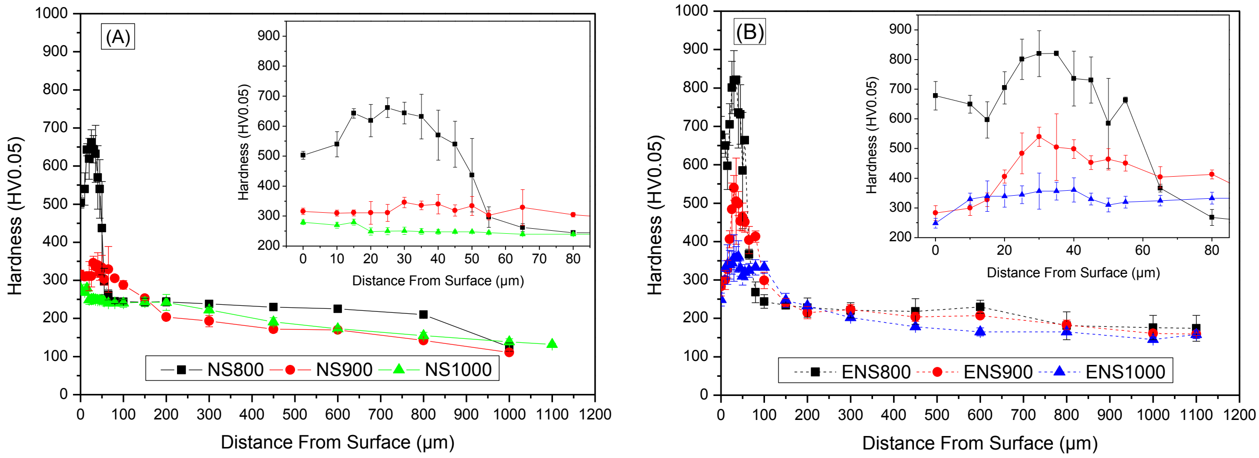

Figure 11. Hardness profiles along thickness direction of IF steel, (A) nitrided and solubilized (NS) and (B) enriched, nitrided and solubilized (ENS).

4. CONCLUSIONS

The formation of nitrogen martensite on the interstitial-free steel enriched with chrome, nitride and solubilized, as the steel only nitride and solubilized was investigated in this study. The results show that the chrome enrichment by a cathodic sputtering was effective to promote the diffusion of the element towards the core of the ferritic matrix, along with an increase of the thickness of the nitrided layers in approximately 10µm for 800 and 900°C conditions. After the solution treatment, the enrichment also promoted more homogeneous microstructure along the surface layer, however can lead to the occurrence of porosity. The oil-quenching treatment following the nitriding has allowed the formation of the nitrogen martensite. The enrichment with chrome provides an increase in the hardness for all solution temperatures.

5. ACKNOWLEDGEMENTS

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