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Theme: Engenharia de superfície

CORROSION RESISTANCE OF PLASMA NITRIDED AISI 420 MARTENSITIC STAINLESS STEEL: INFLUENCE OF THE PRETREATMENT AND TREATMENT TEMPERATURE*

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Abstract

Low-temperature nitriding of stainless steels is applied to obtain wear resistant surfaces without losing its corrosion resistance. The treatment consists in introducing nitrogen into the steel surface avoiding chromium nitride precipitation. The corrosion resistance of martensitic stainless steels is expected to be improved if the treatment parameters are correctly selected. It can be related to ε-$Fe_{2-3}N$ and α'_N phase formation on the treated surface. In the present work the influence of the pretreatment and treatment temperature on corrosion resistance of plasma nitrided AISI 420 steel samples is studied. Annealed, as-quenched and 400ºC-tempered samples were nitrided at 300, 350, 400, 450 and 500°C, for 6 h at 600 V. The pressure was 3 Torr and the gas mixture was composed of 70%N_2, 20%H_2 and 10%Ar, at a gas flow rate of 3.34×10^{-6} Nm^3s^{-1}. Plasma was generated using a square-wave pulsed DC power supply and the sample temperature was controlled by the duty cycle. The modified layers were characterized by optical microscopy, X-ray diffraction and microhardness measurement. The corrosion resistance was studied by electrochemical characterization, by means of Open circuit potential and Anodic polarization curves. The maximum surface hardness was achieved at 400°C. This temperature seems to be near the limit temperature for low-temperature treatment aiming to improve or at least to keep unaltered the corrosion resistance in relation to that verified for non-treated steel samples. Results confirm that the pretreatment and treatment temperature significantly affects the corrosion resistance of the treated surface.

Keywords: Low-temperature plasma nitriding; AISI 420 steel; Open circuit potential; Anodic polarization curve.

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1 INTRODUCTION

Low-temperature nitriding is a well established process to improve wear and corrosion resistance of stainless steels. The treatment results in metastable phase formation on the treated surface. Technological and scientific aspects involving this treatment have attracted the interest of many researchers and industrials. A vast number of papers can be found on the subject, most of them are focused on austenitic stainless steels (see for example [1-6]). Concerning martensitic stainless steels, the number of publications is less expressive and the AISI 420 steel is probably the most studied steel of this class of materials [7-14].

As verified for other martensitic stainless steels, the AISI 420 is applied whenever good corrosion resistance and high mechanical strength are required. However, for severe surface working conditions, its hardness and wear resistance must be improved [10-12,15]. To overcome this limitation, plasma assisted nitriding has been successfully applied [7-14,16-25].

In the last decades, studies were conducted aiming to improve martensitic stainless steels wear and corrosion resistance by applying plasma assisted technology [16-21]. Nowadays, it is well known that high-temperature treatment, usually above 400˚C, leads to a considerable decrease in the corrosion resistance of the material due to the precipitation of chromium nitride, resulting in the sensitization of the treated surface. Moreover, martensitic stainless steels present metastable structure and, as such, require careful choice of treatment conditions to avoid undesirable phase transformation during nitriding. On the other hand, if the process is carried out at low-temperatures, typically below 400˚C, the chromium nitride precipitation is avoided, and wear and corrosion resistance of the treated stainless steel surface is enhanced [18-23]. For low-temperature nitrided martensitic stainless steels, iron nitrides and a supersaturated phase, termed as nitrogen-expanded martensite, have been regularly obtained [8-12,18,22].

Usually, martensitic stainless steels are applied after heat treatment of quenching and tempering. The heat treatment affects the initial microstructure and defect density of the martensitic stainless steels, so, nitriding, as a diffusion-controlled process, is also influenced by the heat treatment for which the steel was subjected before nitriding. This dependence is more pronounced for low-temperature treatments since high-diffusion paths present lower diffusion activation energy compared to volume diffusion mechanisms. In this context, Figueroa et al. [23] have already demonstrated that the previous heat treatment induces different phase formation after nitriding the AISI 420 steel by plasma immersion ion implantation (PIII). Kochmanski and Nowacki [24] studied the influence of initial heat treatment on gas nitriding kinetics for 17-4 PH precipitation-hardening martensitic stainless steel. Similarly, Manova et al. [25-26], studying the PIII nitriding process of the AISI 420 steel, have demonstrated that the material microstructure strongly affects the nitrogen diffusivity in treated surface. Nevertheless, no article presents a systematic study of the temperature and previous heat treatment influence on the corrosion resistance of plasma nitrided martensitic stainless steels.

So, this paper presents experimental results on DC plasma assisted nitriding of the AISI 420 steel, focusing on the influence of the previous heat treatment and nitriding temperature on the corrosion resistance of the treated surface. Corrosion resistance was evaluated by electrochemical measurements in 3.5% NaCl solution. Discussion is based on results obtained from open circuit potential and anodic polarization curves.

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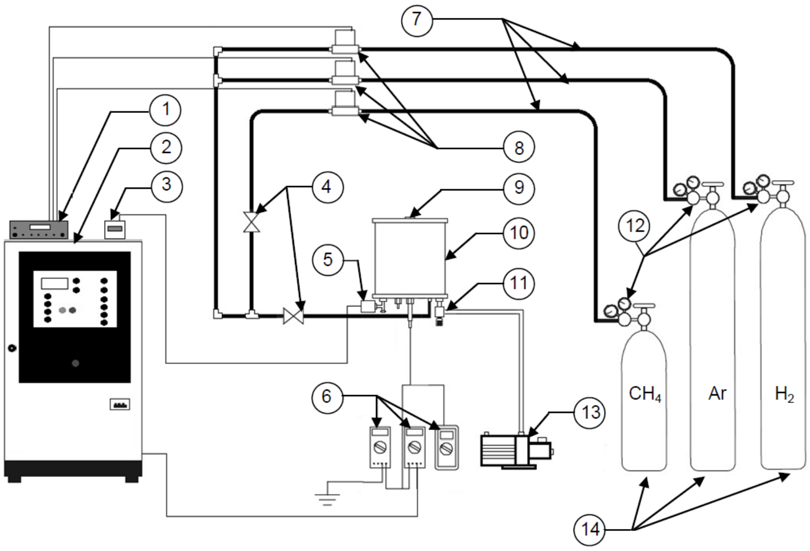
To support the discussion on corrosion resistance XRD, microstructural analysis and microhardeness measurement were also performed.

2 MATERIAL AND METHODS

Cylindrical samples of AISI 420 martensitic stainless steel with 10 mm in height and 50.8 mm in diameter were cut from a commercial rod. To obtain the as-quenched samples, they were austenitized at 1050˚C for 0.5 h and air-quenched. The tempered samples were obtained subjecting as-quenched samples to tempering at 400˚C for 1 h. Before nitriding, samples were ground using SiC sandpaper ranging from 180 to 1200 grade and mirror polished using 1 μm Al_2O_3 abrasive suspension. Finally, samples were cleaned with alcohol in ultrasonic bath and introduced into the discharge chamber. Samples presenting three different studied conditions (one as-quenched, one tempered and one annealed) were simultaneously treated, aiming to guarantee the same treatment conditions.
In order to promote ultimate cleaning and aiming to remove the native oxide layer from the sample surface, before nitriding process, specimens were sputter-cleaned for 0.5 h in a glow discharge generated in a gas mixture containing 90% H_2 + 10% Ar, at 300˚C. All plasma nitriding treatments were carried out using a gas mixture composed of 70% N_2 + 20% H_2 + 10% Ar, at a flow rate of 3.34×10^{-6} Nm^3s^{-1} and a pressure of 400 Pa. The studied temperatures were 300, 350, 400, 450 and 500˚C,and the treatment time was fixed at 6 h.
The plasma nitriding equipment consisted of a square waveform 4.2 kHz pulsed power supply and a stainless steel vacuum chamber of 350 mm in diameter and 380 mm high. The system was evacuated to a residual pressure of about 2 Pa using a double stage mechanical pump. The gas mixture composed of 99.999% purity N_2, H_2, and Ar was adjusted by three mass flow controllers of 8.33×10^{-6} Nm^3s^{-1}. A scheme of the equipment is presented in Figure 1.



1 – Mass flow control unit
2 – Power supply
3 – Digital pressure display
4 – Gas valves
5 – Capacitive manometer
6 – Multimeters
7 – Gas lines
8 – Thermal mass flow controllers
9 – Viewing window
10 – Vacuum chamber
11 – Vacuum valve
12 – Manometers
13 – Vacuum pump
14 – Gas cylinders

Figure 1. Schematic representation of the experimental setup.

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Samples were placed on the discharge cathode, being negatively biased at 600 V. The treatment temperature was measured by means of a chromel–alumel thermocouple inserted 8 mm depth into the samples holder. The mean power transferred to the plasma, and consequently the samples temperature, was adjusted by the power supply duty cycle. The pressure in the vacuum chamber was measured by a capacitive manometer of 1.33×10^4 Pa in full-scale operation and controlled by an automated throttle valve.
Nitrided samples were cross-sectioned and prepared for microstructural analysis by conventional metallographic procedure. After polishing, the samples were etched using Vilella's reagent (1 g picric acid, 4 ml HCl, 96 ml ethanol). The microstructure of samples was analyzed using an Olympus BX51M optical microscope. To identify the phases present in treated layers X-ray diffractometry (XRD) was performed using a Shimadzu XDR7000 X-ray diffractometer, with a Cu Kα X-ray tube in the Bragg-Brentano configuration. Surface microhardness measurement was performed using a Shimadzu Micro Hardness Tester HMV-2T, applying a load of 300 gf for a peak-load contact of 15 s. Finally, the electrochemical characterization was carried out with potentiostat/galvanostat (Microquimica - MQPG-01 model) equipment, using a conventional electrochemical cell with a saturated calomel reference electrode (SCE) and a platinum counter electrode. The working electrode was the AISI 420 treated sample, being the area exposed to the electrolyte (3.5 wt% NaCl) equal to 0.28 cm^2. The initial and final potentials were E_i=-0.6 and E_f=+1.0 (V *versus* SCE), respectively. For the potentiodynamic polarization, the scan rate was 0.1 $mV.s^{-1}$, starting from E_i until reaching a limit current density of 10^{-2} A/cm^2 or E_f. For the open circuit potential measurement, the potential was determined when steady condition was reached (1 hour).

3 RESULTS AND DISCUSSION

3.1 Influence of the Treatment Temperature on the Corrosion Resistance of Nitrided AISI 420 Steel

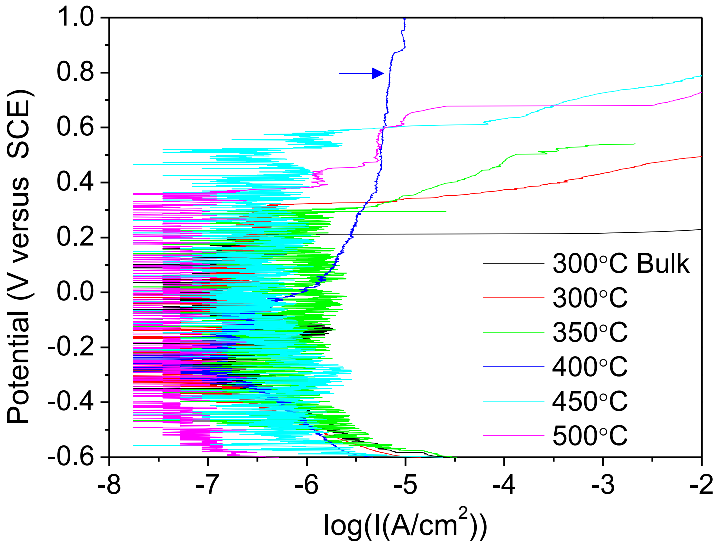

Figure 2. Anodic polarization curves at 0.1 mV/s for as-quenched samples nitrided at different temperatures, for comparison purpose, data obtained from the bulk of as-quenched sample treated at 300˚C is also presented.

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Figure 2 presents the anodic polarization curves for as-quenched samples treated at different temperatures. It is worth mentioning that, for these samples, tempering was simultaneous to the nitriding process. For comparison purpose, measurement of the 300˚C treated bulk material, equivalent to a non-treated surface tempered at 300˚C for 6 h, is also presented. All samples present the same magnitude for the corrosion current density, in the passive region (for the low-current region), excluding the sample treated at 400˚C (blue profile). The case of sample treatment at 400˚C merits a special attention. Even if corrosion current density in the passive region for the sample treated at 400°C is higher, when compared with other samples, no breakdown was observed up to 1.0 V, indicating that a low-corrosion rate was observed even for aggressive condition. So, according to results of Fig. 2, for very aggressive applications this treatment condition presents the best results.

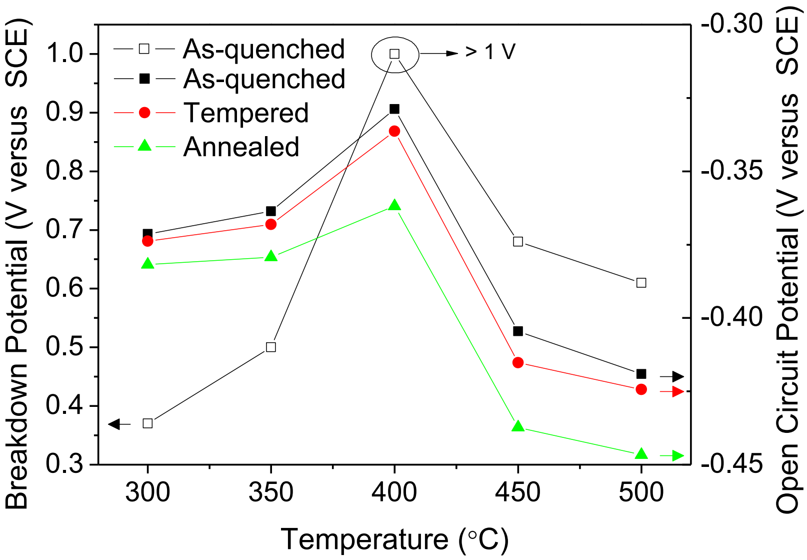

Figure 3. Influence of the nitriding temperature on the open circuit potential for as-quenched, tempered and annealed samples and on the breakdown potential for as-quenched samples.

Other important result obtained from the corrosion resistance characterization of the studied samples is the breakdown potential, which is usually related to pitting or crevice corrosion. The breakdown potential and the open circuit potential measurements for different treatment temperatures are presented in Fig. 3. For all nitriding conditions the breakdown potential is higher than the value obtained for the bulk material (tempered at 300˚C for 6 h, 0.2 V). Comparing the different treatment temperatures, the breakdown potential was increased up to 400˚C, and decreased for higher temperatures. It is important to notice that the surface composition changes for different temperatures. So, the corrosion mechanism, clearly defined as pitting for low temperature, also changes for high temperature treatments. Analysis of the corroded region is being conducted to clarify this point.
The behavior of the breakdown potential is similar to the behavior of the open circuit potential (Fig. 3). From this characterization, the noblest surface is that obtained from treatments at 400˚C. In contrast from the observed for the breakdown potential, surfaces treated at low temperature remain nobler than that treated at high temperature. For all studied conditions, the as-quenched samples are nobler than tempered samples and both are nobler than annealed samples. This result can be explained by the fact that in the annealed condition about half of the chromium content of the AISI 420 steel is in the form of chromium carbides instead of being in solid

solution. So, the formation of a chromium-rich passive layer is not expected for this case. In the case of high temperature treated surfaces, nitride precipitation also leads to reduction of chromium content in solid solution reducing the open circuit potential.

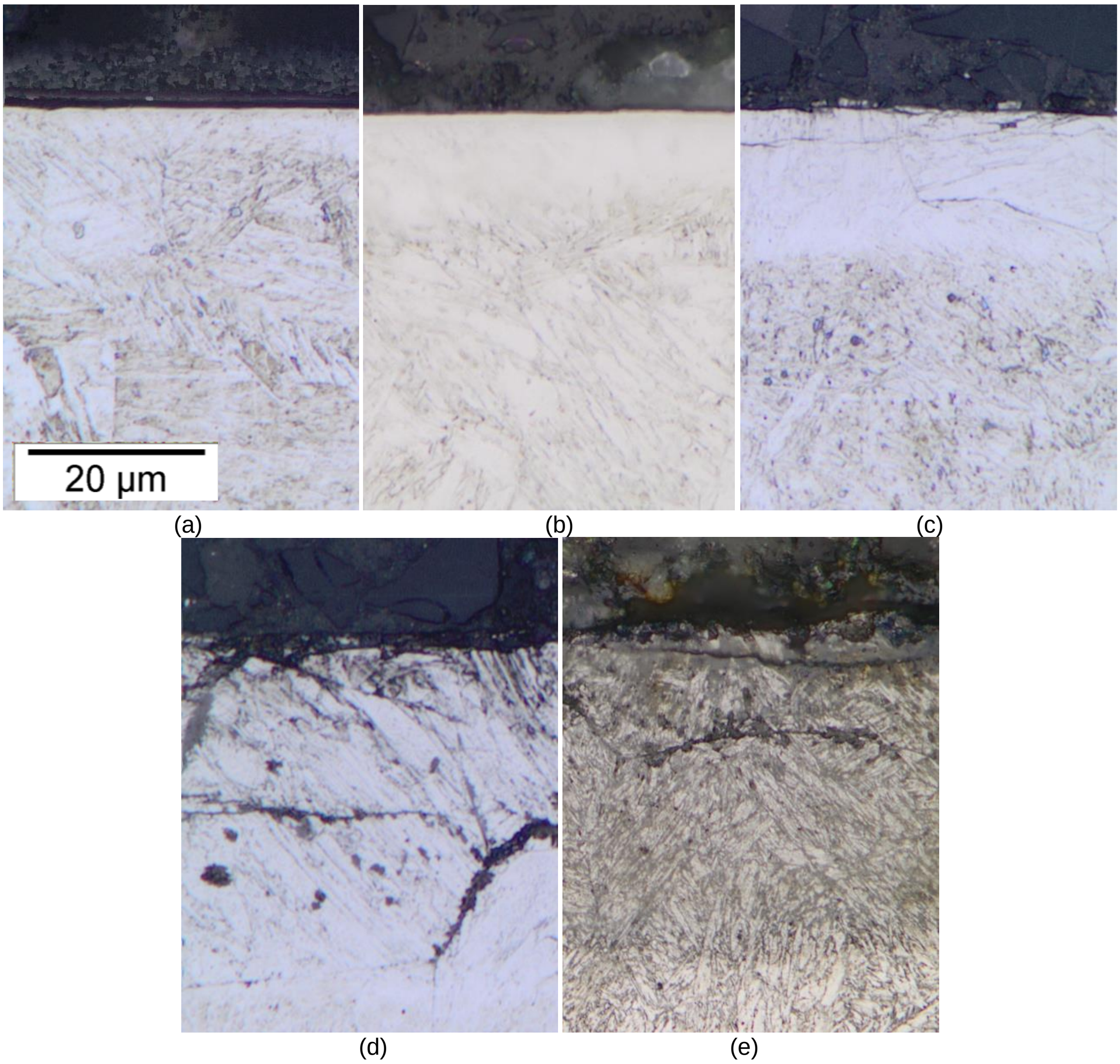

Figure 4. Cross-section micrographs for nitrided as-quenched samples. Treatment temperature: (a) 300, (b) 350, (c) 400, (d) 450 and (e) 500˚C.

The electrochemical discussed results can be understood by analyzing the cross-section micrographs (Fig. 4) and XRD patterns (Fig. 5). In fact chromium nitride precipitation starts at grain boundaries at 400˚C, being intensified for 450 and 500˚C nitriding temperature. It is evidenced by the black-aspect regions in the referred treated layers. Nitride precipitation is confirmed by the XRD diffraction patterns. Thus, for high temperature, it is expected that the chromium content in solid solution in the treated layer is not sufficient for the formation of a chromium-rich passive oxide layer protecting the surface against corrosion. Consequently, it is probable that the considerable corrosion resistance measured for high temperature treated samples is related to the corrosion resistance of chromium and/or iron nitrides present in the obtained treated layer (complex nitride formation cannot be ruled out).

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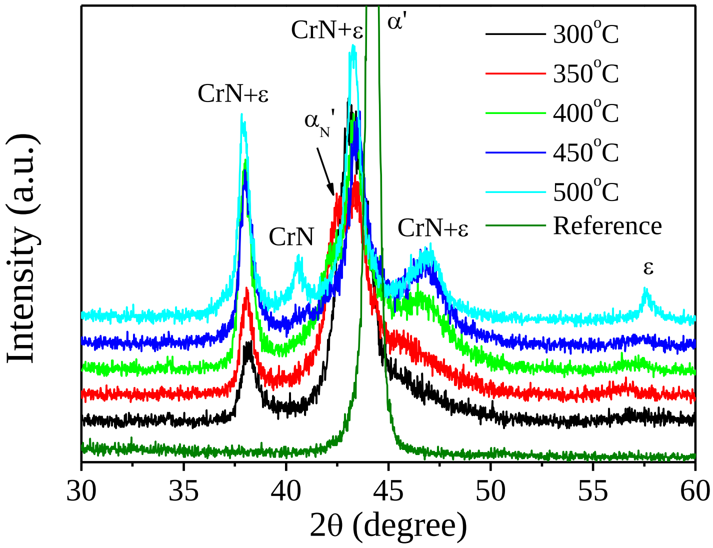

Figure 5. X-ray diffraction patterns for as-quenched samples nitrided at different temperatures. Data obtained from the bulk of a non treated as-quenched sample is also presented (reference).

Another important result, the hardness of the treated surface, is presented in Fig. 6. It seems that the best mechanical property (high hardness in this case) and the best corrosion resistance were obtained for a same treatment condition, which was 400°C. Moreover, for a given temperature the higher harness was obtained for as-quenched samples and the lower hardness was obtained for annealed samples. It can be attributed to the higher content of Cr in solid solution in the as-quenched samples, favoring N-expanded martensite formation. For higher temperatures it is to be considered that the martensite tends to be decomposed, which would explain why the hardness value of the three pretreatment conditions tends to a same value.

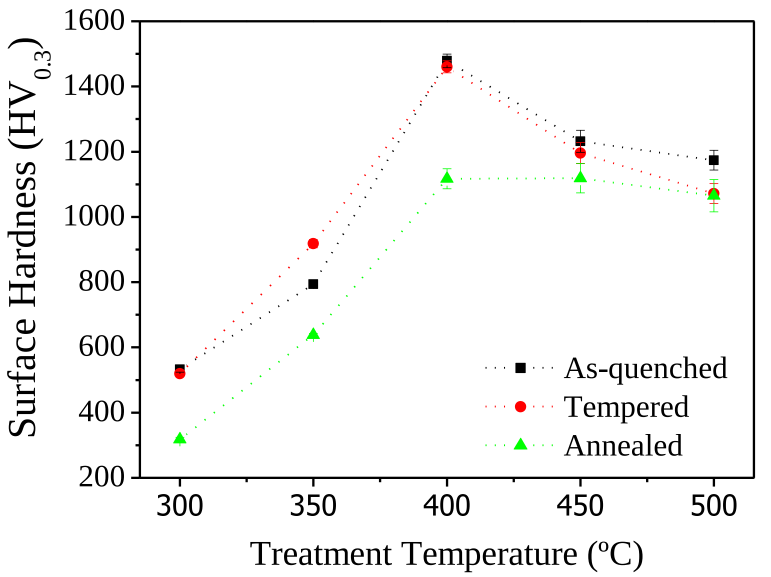

Figure 6. Surface hardness for as-quenched, tempered and annealed samples nitrided at different temperatures.

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3.2 Influence of the Pretreatment on the Corrosion Resistance of Nitrided AISI420 Steel

Anodic polarization curves obtained for the 300˚C nitrided samples with different previous heat treatment are presented in Fig. 7. The breakdown potential values of Fig. 7 are presented in Fig. 8, for comparison purpose, and the value obtained for the bulk of the as-quenched samples is also presented. The lowest open circuit potential obtained is that of the annealed samples (0.02 V), which is expected to have the lowest content of Cr in solid solution. Comparing the as-quenched bulk material and treated surface, it can be noticed that treated surface presents higher corrosion resistance than the bulk (breakdown potential of 0.20 and 0.37 V respectively). It is in accordance with the microstructure observed in the cross section micrographs of the treated samples (Fig. 9), where it can be observed that the treated layer presents a white aspect indicating higher resistance to the etching than that verified for the bulk material.

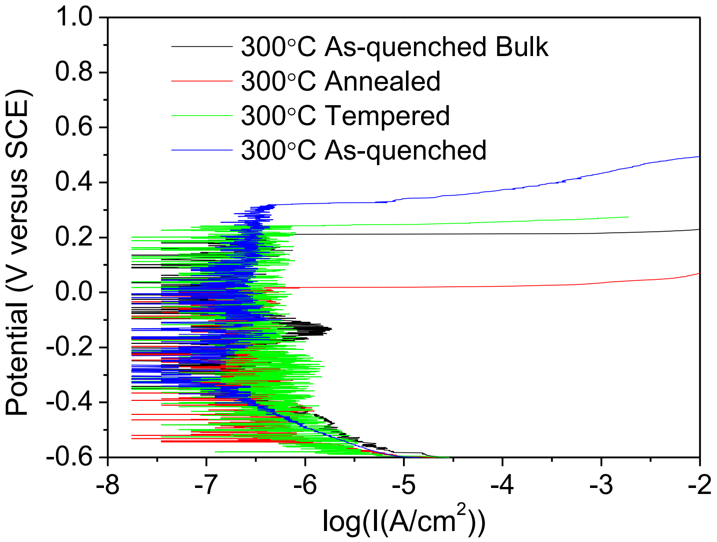

Figure 7. Anodic polarization curves at 0.1 mV/s for 300˚C-nitrided samples with different pretreatments. Data obtained from the bulk of as-quenched sample is also presented.

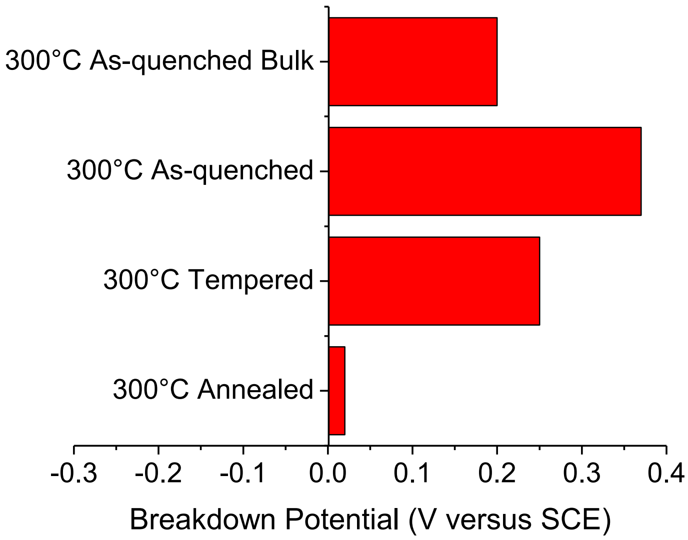

Figure 8. Breakdown potentials for 300˚C-nitrided samples with different pretreatments and data obtained from the bulk of as-quenched sample.

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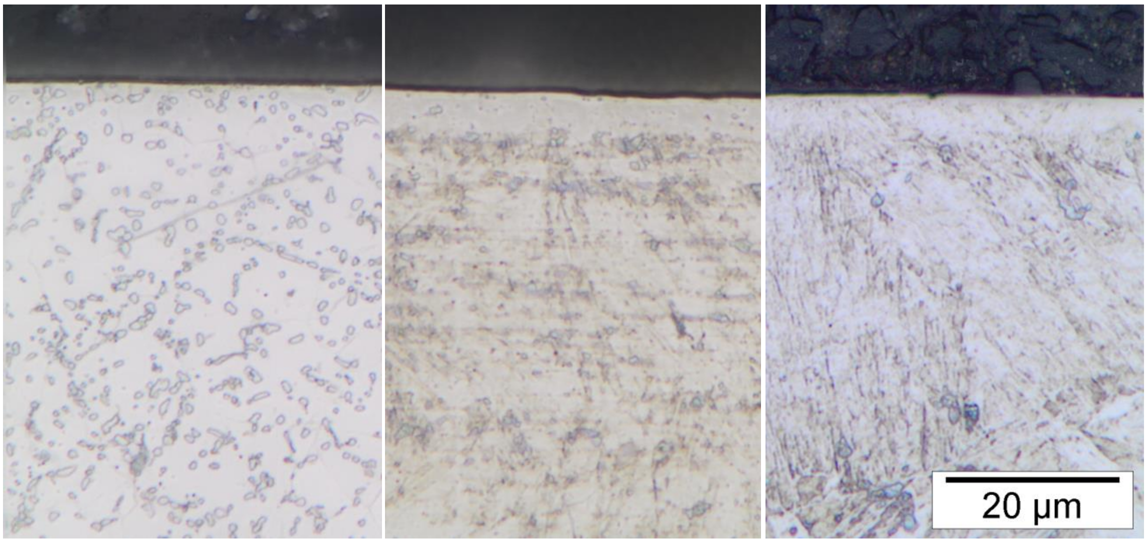

annealed tempered as-quenched

Figure 9. Cross-section micrographs for 300˚C-nitrided samples with different pretreatments.

Finally, XRD patterns of Fig. 10 demonstrate no evidence of chromium nitride precipitation. On the other hand, higher tendency of N-expanded martensite formation, related to the peak position shift, was confirmed for as-quenched samples, as it should be expected since as-quenched samples present higher Cr content in solid solution.

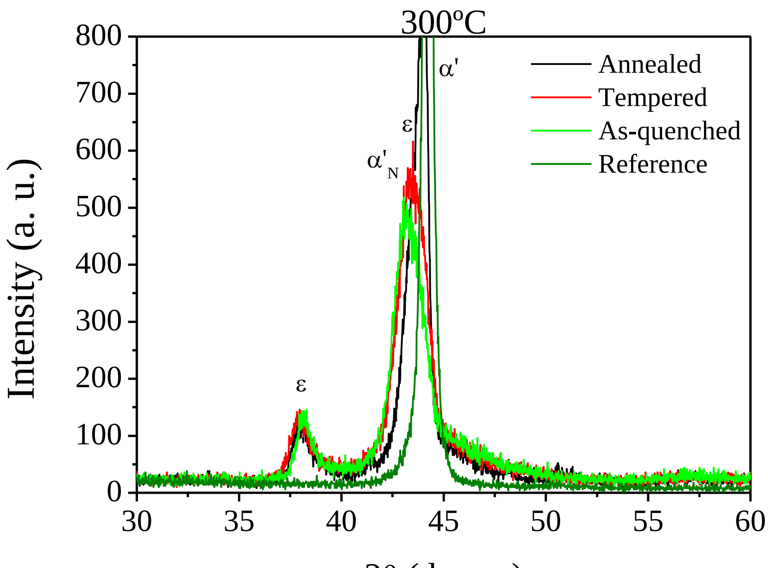

Figure 10. X-ray diffraction patterns for 300˚C-nitrided samples with different pretreatments Data obtained from a non-treated as-quenched sample is also presented (reference).

4 CONCLUSION

Electrochemical measurements were performed for AISI 420 nitrided samples obtained at different treatment temperature and for samples with different previous heat treatment. It can be concluded that the nitriding process improves the nobleness (open circuit potential) and the breakdown potential for temperatures up to 400˚C, indicating an increase of the surface corrosion resistance for the related nitrided samples. Concerning the tested previous heat treatment, the as-quenched samples presented the best results and annealed samples the worst results. So, from the

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technological point of view it can be concluded that whenever possible it is strongly recommendable to perform simultaneous tempering and low-temperature nitriding plasma assisted processing.

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