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CORROSION RESISTANCE OF AISI 316L STAINLESS STEEL NITRIDED BY THREE DIFFERENT PLASMA ASSISTED TECHNIQUES*

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Abstract
Plasma assisted surface modification methods have been used to nitride stainless steels in order to enhance hardness and therefore the lifetime of industrial components. Nevertheless, the corrosion resistance is not always preserved since it is very sensitive to the process parameters, either in implantation or in thermochemical diffusion techniques. AISI 316L stainless steel was plasma nitrided using three different techniques: Low Energy Ion Implantation (LEII), Plasma Immersion Implantation (PI3) and conventional DC pulsed plasma nitriding (DCPN). For each method several parameters were tested and some of them were selected to achieve the so called S phase of about 3 μm thickness and no nitrides precipitation. The nitrided layer was characterized with OM and SEM. Hardness was assessed on the surface with Vickers indenter and 25 g load. XRD was performed to characterize the S phase and to detect other phases if present and electrochemical corrosion tests were carried out in 3.5% NaCl solution. Although the S phase thickness in the three groups of samples was comparable, hardness was not and neither was the corrosion resistance. The PI3 samples were the hardest with the best performance in corrosion experiments, resulting in a higher breakdown potential and lower currents.
Keywords: Plasma nitriding; Stainless steel; Corrosion; Implantation.

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1 INTRODUCTION

Austenitic stainless steels has an extended use in different industries due to its good corrosion resistance [1,2]. The fields of application are wide from tanks and heat exchangers to prosthesis or instrumental devices. Nevertheless, there are several situations in which their poor tribological properties seem to be a problem. The plasma nitriding of these steels can overcome their limitations, because it is possible to form nitrogen rich layers of high hardness [3-6]. On the other hand, in order to keep a high corrosion resistance it is necessary to avoid the precipitation of CrN that usually occurs above 450ºC [7-11]. During the past twenty years different plasma assisted nitriding techniques had been established and some of them started to commercialize in an industrial scale [12-16].

The corrosion behaviour of the layers obtained by these methods is still an issue for the design of the process. The principal advantages of these treatments are the use of lower temperatures, a better control of surface structure, no sometimes, a shorter duration compared to the traditional gas nitriding. Three of the most popular methods are plasma immersion ion implantation, low energy ion implantation, and direct current pulsed plasma nitriding (or ion nitriding). There is a lot of information in the literature, overlooking these different processes and characterizing the nitride layer obtained combining different variables and setups.

In this work three different plasma assisted techniques were used to nitride AISI 316L surface with the aim of improving wear behaviour without affecting corrosion resistance, therefore low temperatures were used. Plasma Immersion Ion Implantation (PI3), Low Energy Ion Implantation (LEII) and conventional DC Pulsed Glow Discharge Nitriding (DCPPN) were carried out to modify the near surface of AISI 316L stainless steel.

2 MATERIALS AND METHODS

The samples for this work were prepared from a 25mm diameter rod bar of austenitic stainless steel AISI316L. The bar was sliced to obtain discs of 6 mm thickness. The samples were grounded with SiC paper and then mirror polished prior to nitride them. PI3 and LEII were performed in Leibniz Institute for Surface Modification (IOM), in Leipzig, Germany. DC pulsed plasma nitriding was carried out in UTN, Faculty of Concepción del Uruguay, in Argentina.

The nitriding treatments were carried out using selected process parameters to assure a nitrogen supersaturated expanded austenite phase, called S phase or γ_N, without Fe or Cr nitrides precipitation [3,6].

Process parameters are as follow: PI3 experiments were performed with 10 kV bias and 15 ms pulse during 1 hour treatment, at a temperature of 430ºC and 0.84 Pa pressure. LEII experiments used an ECR Ion source, ion of 0.8 keV energy, temperature was kept in 430ºC, and implantation was pulsed using 30% duty cycle, during 1 h. Finally, DCPPN was carried out in a 22%N_2-H_2 atmosphere, current density was kept at 1.05 mA/cm^2, temperature at 410ºC and the treatment duration was set in 6 h, with 2 h previous sputtering in Ar-H_2 atmosphere.

The phases obtained were investigated with X-ray diffraction (XRD) in Bragg – Brentano geometry using CuKα radiation. The thickness of the nitrided layer was measured by the observation of polished cross sections, etched with Marble reagent, to reveal the microstructure.

The wear tests were carried out in a dry sliding situation using a pin on disk self-designed machine. Normal load was fixed in 4 N, tangential velocity in 10 cm/s, a Si_3N_4 ball was used as counterpart, radius was 7mm and the total sliding distance was 700 m. The wear track was measured using a surface roughness meter acting as profilometer and from the mean value of six cross sections; the volume loss of the sample was calculated, assuming cylindrical symmetry.

Electrochemical tests were carried out at room temperature and atmospheric pressure, in a three electrode cell. The tested sample was slightly polished to eliminate any air formed oxide, and was used as the working electrode in each test. As auxiliary and reference, a platinum wire and a saturated calomel were used. The tested area was restricted pressing an O-ring to the sample surface, giving an area of $0.41cm^2$. The electrolyte was 3.5 wt% NaCl water solution saturated with air. To evaluate the localized corrosion resistance, cyclic potentiodynamic polarization experiments were carried out with a sweep rate of 1mV/s. The reversal of the potential was done at a fixed, arbitrary chosen current density of 200 µA/cm^2. This potential was called E_{200}.

## 3 RESULTS AND DISCUSSION

3.1 Microstructure and Hardness

After the nitriding processes some samples were cut and mounted to observe the nitrided layer, while on others hardness was measured on the surface and XRD analysis was carried out. Table 1 shows the average nitride layer thickness and average hardness in each case. In this work, the processes variables were controlled in order to have comparable thicknesses between the different nitriding techniques. In this way, a better comparison between the layers can be done.

Table 1. Hardness, thickness and (111) peak position of the nitrided layers

SAMPLE	HV 0,05	γ_N width [µm]	XRD (111) 2θ
LEII	525±5	3.8	40.3
PI3	846±7	4.0	39.4
DCPPN	590±10	6.5	41.5

Figure 1 shows the XRD diffraction patterns. All the samples show the particular shift of the peaks to lower angle, due to the presence of the expanded austenite. No other species, like CrN, are present in the nitrided samples. As the thickness is similar, we attribute the difference in the peak shift to a larger lattice expansion due to the mean ion energy in each process. As the two implantation methods (PI3 and LEII) are more energetic they produce the major lattice expansion and the highest shift to lower angles is observed, especially in the (111) peak. In the LEII samples a signal form the austenite could also be detected, because the layer is the thinnest.

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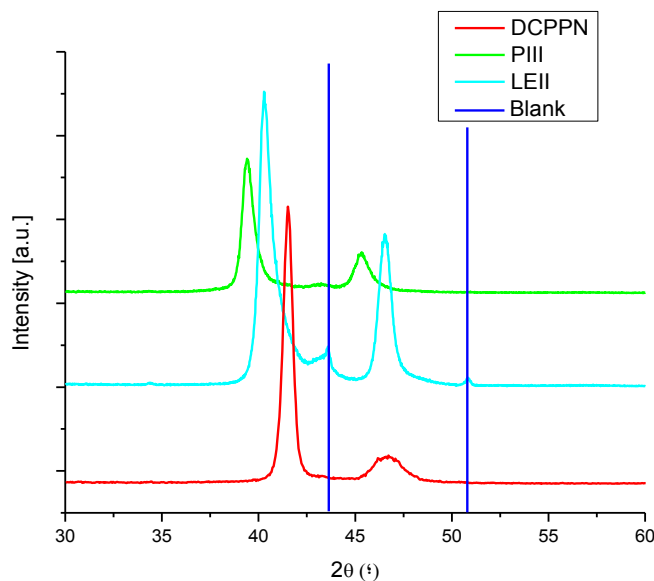
Figure 1. XRD diffraction patterns of the three nitrided samples with vertical black lines indicating the (111) and (200) peaks positions for the untreated steel.

3.2 Wear

Regarding pin on disk experiments all the treated samples had a better behaviour than the untreated material but the behaviour of the PI3 sample was remarkable since it had the minor volume loss with a nitrided layer only 4 μm thickness. As expected, wear loss was also in relation to hardness. It was verified that in all cases the wear track depth was not bigger than the nitrided layer thickness. Results are presented together with corrosion data in Table 2.

3.3 Corrosion

The result of the polarization tests are plotted in Figure 2. The passive current density is lower and the reversal potential is higher for all the nitrided samples compared to the untreated specimen. The best localized corrosion resistance compared to the blank is shown by the PIII and the DCPPN samples reaching E_{200} values of around 1V and 0.9V (E_{200} blank = 0.3V).

**Table 2.** Wear and corrosion data compared to untreated steel (blank)

SAMPLE	Volume loss [mm^3]	Corrosion (E_{200}) [V])
LEII	19.0	0.51
PI3	12.2	0.90
DCPPN	31.2	1.00
Blank	44.6	0.34
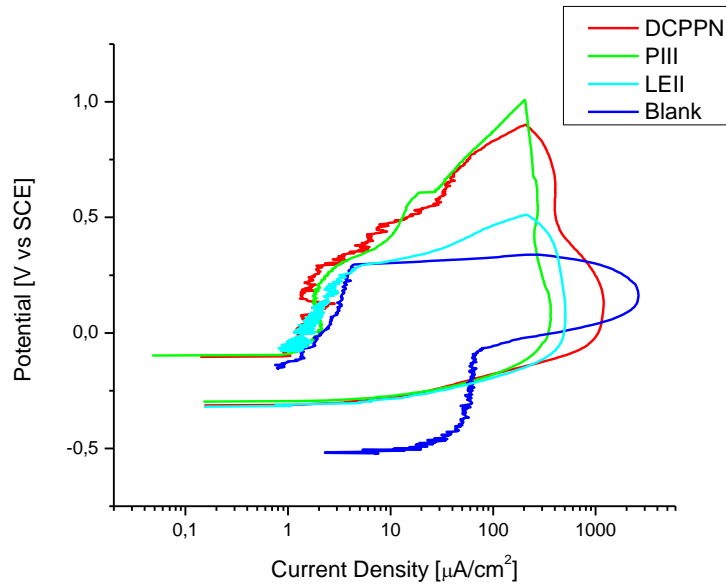
Figure 2. Cyclic polarization curves of all treated samples and the untreated steel (blank)

From optical microscopic observation it was determined that the corrosion morphology is similar for all the nitrided processes: black spots surrounded by shallow corrosion products (Figure 3).

These black spots are related to the presence of inclusions in the base alloy. The properties of the passivating films are being under study in order to go further in an explanation of the observed behavior.
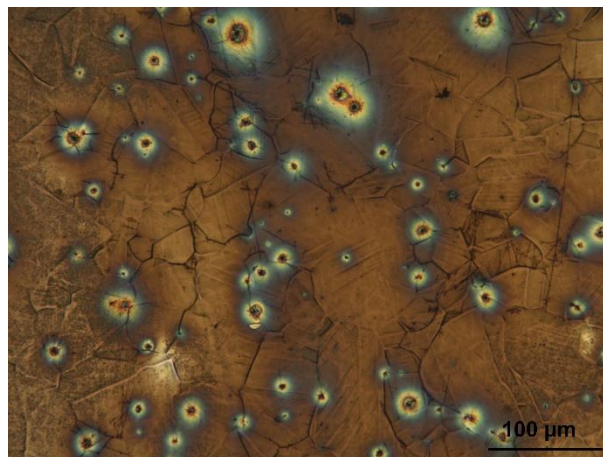
Figure 3. Optic micrograph of the nitrided steel surface after the corrosion test

4 CONCLUSION

From the wear and corrosion tests, the best behaviour corresponds to the "high density" layer of PI3, 4 μm and almost 850 HV in hardness. With DCPNN thicker layers can be obtained with more treatment time, then hardness and wear resistance will be increased, even sustaining corrosion resistance. But the advantage of the implantation is the short duration of the nitriding treatment to obtain the expanded austenite phase and a high nitrogen concentration in a not very thick layer. It remains still an issue if DCPNN can make such a nitrided layer applying other process parameters than usual.

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The corrosion attack morphology is similar in all the nitrided samples. More work has to be done in order to go deeper in the basics mechanisms behind this behaviour.

Aknowledgements

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