Corrosion process in NaCl/Na\textsubscript{2}SO\textsubscript{4} solutions of AISI 316L stainless steel treated by ionic nitriding

C. B. Santos\textsuperscript{*1}, M. Metzner\textsuperscript{1}, C. F. Malfatti\textsuperscript{2} and J. Zoppas Ferreira\textsuperscript{3}

This work is a corrosion study of an AISI 316L austenitic stainless steel after different plasma ion nitriding conditions. The properties of the coated AISI 316L were measured. The corrosion resistance was evaluated by cyclic voltammetry and salt spray testing. Sample surfaces were characterised by SEM and the phase determination with XRD analysis. Nanohardness was determined by using a Vickers indenter. The nitrided samples treated at 400°C, in a gaseous mixture of 5%N\textsubscript{2} and 95%H\textsubscript{2} for 4 and 5 h, had the best corrosion resistance. For the salt spray test, where the potential range is near the equilibrium potential, the nitrided material presented a reduced corrosion resistance. Through the control of the process parameters it is possible to improve the stainless steel surface hardness, combined with a good corrosion resistance. The highest value of temperature and N\textsubscript{2} proportion increased the surface roughness and hardness, though it caused a decrease in corrosion resistance.

Keywords: Stainless steel, Cyclic voltammetry, X-ray diffraction, Pitting corrosion

Introduction

Surface modification of a component for metal protection may be required for one or more of the following reasons:

(i) to prevent or reduce corrosion of the metallic substrate
(ii) to modify the physical or mechanical properties of the substrate metal
(iii) to achieve and maintain some desired decorative effect.

Although the initial choice of coating material applied for reasons (ii) and (iii) may be dictated by the particular properties required, the corrosion behaviour of the coating/substrate system must also be taken into consideration so far as it may affect the maintenance of the desired properties.\textsuperscript{1}

Materials treatment through a plasma process can significantly change the surface properties of metallic components. Ionic nitriding and carburising, plasma assisted etching and stripping, physical vapour deposition and plasma enhanced chemical vapour deposition are examples of industrial applied plasma treatments.\textsuperscript{2}

Dowling\textsuperscript{3} has reviewed plasma processing. Coatings, films and modified surfaces through plasma technology are used to enhance the machine performance of cutting tools, the mechanical properties of implantable and non-implantable devices and for decorative applications. Another application area of plasma technology is the semiconductor and food packaging industry.

The ionic nitriding process has been successfully used in the industrial sector for many years. The purpose of this process is to harden the surface of ferrous and non-ferrous materials. Austenitic stainless steels have good corrosion resistance, though a relatively low hardness limits their use in applications requiring resistance to mechanical wear. Plasma nitrided stainless steel contains γ-Fe\textsubscript{2}N and γ’-Fe\textsubscript{4}N (white layer) and chromium nitrides at the surface. Chromium nitrides decrease the corrosion resistance of a stainless steel. Under controlled conditions the plasma nitriding process at low temperature results in a formation of the so called ‘S phase’, without iron nitrides and chromium nitrides. The ‘S phase’ improves corrosion properties.\textsuperscript{4,8}

Rolinski\textsuperscript{9} showed that the tribological properties of stainless steel can be improved with the nitriding process in temperatures above 400°C with the appearance of ferrite, iron and chromium nitrides, reducing the corrosion resistance. Therefore, the nitriding temperature has a significant influence on the austenitic stainless steel behaviour in a corrosive medium.

The work reported here is a corrosion study of an AISI 316L austenitic stainless steel (SS 316L) under different plasma nitriding conditions. Changes in properties at the surface were investigated under the unnitrided and nitrided conditions, and the corrosion resistance of the samples was determined by cyclic voltammetry and salt spray tests.
The cyclic voltammetry was carried out in 0.6 M NaCl and 0.1 M NaCl/0.04 M Na₂SO₄ solutions. Zuo et al. studied the effect of different anions (PO₄³⁻, CrO₂⁴⁻, SO₄²⁻ and NO₃⁻) on metastable pitting of 316L stainless steel. The metastable pitting potential $E_m$ and the stable pitting potential $E_p$ grow with the increase in each anion’s concentration. Flies et al. used 0.05 M Na₂SO₄ solution to evaluate the corrosion behaviour of the nitrided stainless steel. The SO₄²⁻ ion can generate surface inhibition on the stainless steel.

### Experimental

Samples of austenitic stainless steel AISI 316L (0.03C–1.87Mn–0.04P–0.02S–0.87Si–16.76Cr–12.65Ni–2.13Mo, wt.%) were heat treated at 1100°C for 1 h in the normal atmosphere. The samples were mechanically polished with increasingly fine paper grit up to 1000 and in diamond paste of 4 and 1 μm. Samples were nitrided in ionic nitriding equipment constructed by the UFRGS Physical Metallurgy Laboratory. The nitriding process was preceded by surface cleaning for ionic sputtering with 30% argon and 70% nitrogen gaseous mixture, at 1 torr pressure. The nitriding process pressure was 4 torr.

A Philips XL 20 scanning electron microscope (SEM) was used to perform surface image analysis and to measure sample thicknesses. A Philips X-Pert MPT diffractometer with Cu Kα ($\lambda = 1.5418 \text{ Å}$) radiation was used to study the phase analysis. Nanohardness was determined using a Fischerscope HV100, with Vickers indenter. In this characterisation the normal load was 25 mN and the penetration depth was 0.5 μm. The roughness of each sample was averaged from three measurements.

The corrosion resistance was determined by cyclic voltammetry using a 0.6 M NaCl and a 0.1 M NaCl/0.04 M Na₂SO₄ solution (pH 6). These tests were performed at room temperature and the scan rate was 1 mV s⁻¹. The electrochemical experiments were carried out with an EG&G PAR 273A potentiostat/galvanostat. The electrolytic cell had a three electrode configuration, with treated and untreated steel as a work electrode, platinum as a counter electrode and a saturated calomel reference electrode. The samples were also evaluated by salt spray test according to ASTM B-117.

### Results and Discussion

#### Analysis of SEM

The SEM analysis of the matrix showed an austenitic microstructure. It was possible to observe the nitrided layer for all treatment conditions. Figure 1 shows the SEM image with the morphology of the samples untreated (316L) and nitrided at 400°C for 4 h, with a gaseous mixture of 5N₂–95H₂ (316LNIT2).

The thickness of the layer (Table 2) increases with the temperature and the N₂ proportion in the gaseous mixture. These results agree with the literature. Marchev et al. have studied the formation of a single phase m-structure (nitrided layer) on the ion nitrided 300 series stainless steel. The nitrided layer had a depth dependent on variable nitrogen content. Kumar et al. used different contents of hydrogen in the gaseous mixture at the low temperature radio frequency plasma. They studied the effect of hydrogen on the growth of the ‘expanded austenite’ layer. If the partial pressure of the nitrogen is constant, an addition of hydrogen at concentrations in the range of 5–50% results in a thicker nitrided layer and enhances surface hardness compared to treatments in pure nitrogen. An excessive amount of hydrogen (~75%) in the gaseous mixture retards the nitriding process, resulting in a reduced nitrided layer thickness compared to pure treatment in nitrogen.

#### Surface roughness

Before treatment the samples had a surface roughness of 0.003 μm. Table 2 presents the values of $R_s$ (μm), surface roughness, for all nitrided samples.

### Table 1 Nitrided layer with gaseous mixture of 5N₂–95H₂ and 76N₂–24H₂, treated for 4 h under following conditions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gaseous mixture</th>
<th>Temperature, °C</th>
<th>Voltage, V</th>
<th>Current, A</th>
</tr>
</thead>
<tbody>
<tr>
<td>316LNIT1</td>
<td>5%N₂ and 95%H₂</td>
<td>375</td>
<td>385</td>
<td>0.28</td>
</tr>
<tr>
<td>316LNIT2</td>
<td>5%N₂ and 95%H₂</td>
<td>400</td>
<td>524</td>
<td>0.32</td>
</tr>
<tr>
<td>316LNIT3</td>
<td>76%N₂ and 24%H₂</td>
<td>400</td>
<td>296</td>
<td>0.48</td>
</tr>
</tbody>
</table>
It is possible to observe the roughness value increasing as a function of the parameters. Ionic nitriding is a process that involves particle acceleration towards the cathode (sample), thus surface roughness increases with the temperature and the nitrogen content in the gaseous mixture in the process.

**Phases determination**

Figure 2 shows the X-ray patterns of the non-treated samples (Fig. 2a) and those treated at 400°C, time of 4 h and gaseous mixture of 5N2–95H2 (Fig. 2b). γ-Fe phase peaks can be observed in both samples and the S phase in the nitrided sample. The diffractograms have not shown the presence of chromium nitride.

The untreated sample shows phase γ-Fe (111), (202) and (021). From Fig. 2b it can be seen that for the plasma nitrided sample, the peaks were shifted to lower angles. Xu et al.14 associated the shift and broadening of the peaks with the ‘expanded austenite’ (γN phase) produced by nitrogen supersaturation and associated stress caused by the nitrogen remaining in solid solution in fcc lattice.

**Nanohardness measurements**

Nanohardness measurement, used for thin layer analysis, minimises the substrate effect in the measurement of surface hardness. Values shown in Table 2 demonstrate the efficiency of the plasma nitriding process at increasing the surface hardness of austenitic steel. The increase in temperature and N2 proportion in the gaseous mixture had a positive effect, increasing the surface hardness of the metal base, as also observed for the surface roughness values. This result agrees with those obtained by Wang et al.15

**Cyclic voltammetry in NaCl**

Figure 3 shows the cyclic voltammetry tests carried out in NaCl 0-6M medium. The untreated sample showed a passive region up to 400 mV, with an increase in current density at this potential. This behaviour associated with hysteresis after the return cycle is typical of localised corrosion (pitting and crevice). Pitting corrosion on the surface can be seen in Fig. 4, but this potential cannot be classified as a pitting potential \( E_p \) because the sample showed also crevice degradation in a combined process. The highest current density was 100 mA cm\(^{-2}\) at 1600 mV.

Figure 5 shows a cross-section of the untreated sample, where a 75 µm deep pitting can be observed. Regarding the nitried samples, the cyclic voltammetry curves show a corrosion resistance improvement in the sample treated at 400°C in the 5%N2 and 95%H2 mixture (316LNIT2), when compared to the untreated sample. For two other nitried conditions, besides resistance to corrosion being higher than in the untreated sample, a more pronounced current density hysteresis than the 316LNIT2 sample is shown. This hysteresis is more evident for the 316LNIT3 sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nitrided layer thickness, µm</th>
<th>Roughness, µm</th>
<th>Nanohardness, GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>316L</td>
<td>...</td>
<td>0.003</td>
<td>2.003</td>
</tr>
<tr>
<td>316LNIT1</td>
<td>4.5</td>
<td>0.440</td>
<td>8.832</td>
</tr>
<tr>
<td>316LNIT2</td>
<td>6.5</td>
<td>0.895</td>
<td>8.431</td>
</tr>
<tr>
<td>316LNIT3</td>
<td>7.8</td>
<td>1.128</td>
<td>10.355</td>
</tr>
</tbody>
</table>
The SEM images of Fig. 6 present the degree of surface degradation after cyclic voltammetry for the 316LNIT2 nitried sample. The nitried sample with gaseous mixture of 5%N₂ and 95%H₂ (Fig. 6) presents a lesser, superficial attack when compared to the sample treated in 76%N₂ and 24%H₂ atmosphere (Fig. 7). The surface analysis (SEM) shows pitting with a size of 25 μm (316LNIT1 and 316LNIT2) and no small pittings around the attack. This behaviour indicates an increase in the localised corrosion resistance. The nitried samples did not show any crevices at this test condition.

Three important aspects can be observed in the results: the nitriding plasma process increases the passive range of AISI 316L and the pitting and crevice corrosion resistance. The potential of oxygen evolution was moved to the more positive values. This potential value is 1100 mV.

The 316LNIT3 sample, obtained with a N₂ rich atmosphere, showed poor resistance in the NaCl solution, with a lower corrosion resistance among treated samples. Figure 7 shows a corrosive attack on the grain boundary of the 316LNIT3 sample.

Cyclic voltammetry tests in NaCl/Na₂SO₄.

The cyclic voltammetry curves were carried out in 0-1M NaCl/0.04M Na₂SO₄ solution to verify the pitting potential of the samples. The choice of SO₄²⁻ combined with Cl⁻ had the purpose of producing a surface attack without crevice corrosion and thus enabling the determination of the pitting potential Ep. The solution did not cause crevice attack in the untreated and nitried samples.

Figure 8 shows the cyclic voltammetric curves of the untreated stainless steel and nitried samples. Sample 316L showed passive behaviour up to 608 mV (Eₚ). It can be seen that the material surface showed pitting corrosion in Fig. 9. The highest current density was 172 mA cm⁻² at 1600 mV.
The electrochemical test presented a corrosion resistance increase on the sample treated at 400°C in the 5%N₂ and 95%H₂ mixture (316LNIT2), when compared to the untreated sample. The nitrided sample had a passive behaviour up to 1300 mV (Eₚ). A similar behaviour can be observed for the sample treated at 375°C in the 5%N₂ and 95%H₂ gaseous mixture (316LNIT2). The sample nitrided with the mixture of 76%N₂ and 24%H₂ (316LNIT3) had a small change in the current density hysteresis. All samples treated showed a significant increase in their passive region when compared to the untreated sample.

The micrographs of Figs. 10 and 11 present the degree of surface degradation after cyclic voltammetry for two nitrided samples. Neither of the samples showed any crevice attack in these tests. The nitrided samples with gaseous mixture of 5%N₂ and 95%H₂ present a lesser, superficial attack when compared to the sample treated in a 76%N₂ and 24%H₂ atmosphere, as above. This behaviour indicates an increase in the pitting corrosion resistance for the nitrided stainless steel.

**Salt spray tests (ASTM B-117)**

All samples remained in the chamber test for up to 720 h to evaluate corrosion behaviour. The 316LNIT1 sample presented corrosion points over the material surface after 336 h in the test chamber. After 720 h exposure the 316LNIT1 sample showed surface red rust, with a light pitting corrosion.

The 316LNIT2 sample presented some red rust points after 720 h in the chamber test for the 316LNIT2 samples, as can be seen in Fig. 12a.
Figure 12b presents the 316LNIT3 sample after 168 h in the chamber test with a surface degradation beginning at the grain boundary. This sample presented red rust points after 24 h in the chamber test.

The untreated sample (316L) showed the best corrosion resistance in the salt spray test, since there were no corrosion points after 720 h in the salt spray chamber. This result indicates that the nitrided material does not show a good corrosion resistance behaviour at the potential range near the equilibrium potential.

Conclusions
The plasma nitriding process provided an increase in the steel hardness and roughness with temperature. Through X-ray diffraction the presence of chromium nitrides was not detected in the nitrided layer, but it was possible to observe the formation of the S phase for all nitriding parameters. The nitrided samples treated at 400°C, in a gaseous mixture of 5%N2 and 95%H2, for 4 and 5 h showed the best corrosion resistance. For the salt spray test, where the potential range is near the equilibrium potential, the nitrided material presented a decrease of corrosion resistance. Through control of the process parameters it is possible to improve the stainless steel superficial hardness, combined with a good corrosion resistance. The highest value of temperature and N2 proportion increased the surface roughness and hardness, although it caused a decrease in corrosion resistance.

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References: