Original Article

Influence of plasma nitriding pressure on microabrasive wear resistance of a microalloyed steel

Henver Effgen Ludovico Ramos, Adonias Ribeiro Franco Jr.*, Estéfano Aparecido Vieira

Coordenadoria de Metalurgia, Instituto Federal de Educação, Ciência e Tecnologia do Espírito Santo (IFES), Campus Vitória, Avenida Vitória, 1729, Zip Code: 29040-780, Vitória, ES, Brazil

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ABSTRACT

Microalloyed steels have been studied not only by the advent of the pre-salt, but also by the continuous search for improvement of their tribological properties. In this work, the influence of the plasma nitriding (PN) pressure on the nitried layer formed on top of an API 5L X70 microalloyed steel was studied. PN treatments were carried out using a pulsed plasma reactor at temperatures of 410 °C and 440 °C, in a gas mixture of N2 and H2, for 3 h and under different pressures. Results showed that the pressure has a significant effect on the uniformity and width of the plasma sheath and, consequently, on the structure and thickness of the resulting nitried layer. It has been observed that higher pressures and temperatures have led to the formation of nitried layers containing a thinner white layer and without nitride needles. The best wear results were offered by the thicker nitried layers, besides thinner white layer. This type of structure can be produced when PN treatments are performed using low-width plasma sheaths.

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1. Introduction

The growing demand for natural gas as an environmentally clean source of energy has stimulated, in recent years, the search of new technologies and/or new materials, or the improvement of existing technologies. Microalloyed steels have gained special attention due to the increasing use in long transport lines of high pressure gases and with the advent of the pre-salt, where they can be exposed to corrosive environments [1]. These steels can also be applied to ore transport pipelines, where abrasive wear resistance is very important.

A combination of good mechanical strength and toughness is obtained through a suitable thermo-mechanical processing, enabling the formation of acicular ferrite in the material structure [2,3]. Plasma nitriding (PN) is a good choice to increase the fatigue life, wear and corrosion resistance of microalloyed steels without changing the properties of the material in the core [4–6]. Recently, PN also has been applied for improving wear resistance of non-ferrous metals such as titanium, aluminium and their alloys [6,7].

Due to the costly process and some technological difficulties, industrial ascension of the PN process began only in the mid-1960s, with the evolution of vacuum technology, as well
as the development of electronic devices. Unlike the gaseous and liquid processes, the generation of hazardous waste is mitigated in the PN process, because treatment atmosphere uses small amounts of nitrogen and hydrogen, in addition to reduced processing time and greater control over the growth of the nitrided layer [7–10].

A gas atmosphere, usually consisting of nitrogen and hydrogen, or cracked ammonia, at pressures between 1 and 10 Torr, is used in the PN process. The ions generated by the potential difference between the anode (chamber) and the cathode (part) are accelerated against the surface, allowing the formation of atomic nitrogen that diffuses from surface towards the core of the part, resulting in the formation of a hardened layer [11].

Although the pressure is an important parameter in the PN process, there is a lack of work in the literature reporting its effect on the properties of steels [12,13]. The objective of this work was to evaluate the influence of different PN pressures on the thickness and structures of the nitrided layer produced on the API 5L X70 microalloyed steel surface.

2. Materials and methods

2.1. Material

Samples 3 cm long, 2 cm wide and 4 mm thick were cut from an API 5L X70 microalloyed steel pipeline [14]. The microstructure is composed of bands of pearlite in a ferrite matrix, and its grain size is ASTM no. 10. Previously to PN, samples were grounded and polished using 1.0 µm alumina.

2.2. Plasma nitriding

PN treatments were conducted in a pulsed plasma reactor, named SDs soluções mod Thor NP 500. Prior to nitriding, the samples were cleaned by cathodic sputtering at 150 °C and 1 Torr under H₂ atmosphere for 30 min. For PN treatments, the following conditions were used: temperatures of 410 and 440 °C, in the interval of 3 h, in gas atmosphere composed of 20% of H₂ and 80% of N₂, with a flow-rate of 400 sccm and different pressures of nitriding, as shown in Table 1. After the treatments all the samples were cooled to room temperature under vacuum pressure.

### Table 1 - Conditions used for PN experiments.

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>Pressure (Torr)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.5</td>
<td>410</td>
</tr>
<tr>
<td>2</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2.5</td>
<td>440</td>
</tr>
<tr>
<td>5</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>4.6</td>
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</tr>
</tbody>
</table>

2.3. Microstructural characterization and phase identification

After PN treatments, samples were cross-sectioned using a low speed cutting machine and then assembled into Bakelite, grounded and polished. The microstructures of the nitrided layers were revealed by etching in 2% Nital (2 ml of HNO₃ and 98 ml of ethanol) during 5 s. A Zeiss scanning electron microscope (SEM), model EVO MA10, was used for microstructural characterization of the nitrided layers and the formed phases were identified using a Bruker diffractometer, model D2phaser.

2.4. Vickers hardness test

To determine the hardness profiles of the nitrided layers, Vickers hardness tests were performed using a Shimadzu DUH-2115 dynamic ultra-microhardness tester. All measurements were made in the cross section of the samples, starting from the nitrided surface towards the core of the material. Indentations were performed at spacings of 25, 50, 100, 150 and 200 µm, with a test load of 500 mN, for 20 s.

2.5. Micro-scale abrasive wear test

Wear tests were performed using a CSM CALOWEAR “free ball” micro-abrasion apparatus with a 25.4 mm diameter AISI S2100 martensitic steel ball. The rotation of the drive shaft, which causes the sphere to move, was set at 150 rpm, the applied load was 0.27 N and the abrasive slurry was made of silicon carbide (SiC), with particles of size of about 5 µm at a concentration of 0.75 g/cm³ (75 g of SiC dissolved in 100 ml of distilled water) and with approximately 24 drops per minute.

The wear coefficient (K) were established using Eq. (1) (Archard equation) [15,16]:

\[
K = \frac{V}{l \cdot F_N}
\]

where \(V\) is the volume of worn material, \(F_N\) is the normal force applied to the surface of the sphere and \(L\) is the sliding distance.

The values for the wear coefficient were obtained when steady-state wear regime was reached.

3. Results and discussion

3.1. Substrate characterization

As shown in Fig. 1, the microstructure of non-nitried API SL X70 microalloyed steel consisted of ferrite, evidenced by the X-ray result, and banded pearlite. The average hardness measured was 240 ± 34 HV. This microstructure is in agreement with the expected one, because the tube material is a controlled-rolled steel [17,18]. Ferrite microstructures are not recommended for nitriding, because this phase promotes the rapid formation of nitrides at the beginning of the process, creating a barrier to the diffusion of the nitrogen atoms, resulting in low depths of nitrided layers [19–22]. Recent works, however, had reported that PN treatment can improve the wear...
Fig. 1 – Microstructure of API-5L X70 microalloyed steel before PN treatments.

Fig. 2 – Microabrasive wear coefficient as a function of the sliding distance for API 5L X70 microalloyed steel before PN treatments.

The wear coefficient as a function of the sliding distance for the API 5L X70 microalloyed steel nitrided at temperature of 410 °C and different pressures is shown in Fig. 3. It is verified that the steady-state wear regime occurs when sliding distances between 250 and 300 m are used.

PN promoted a significant reduction in the wear coefficient of the steel, as inferred in Fig. 3. Increasing pressures led to a decrease in the wear coefficient and the best result was found when a pressure of 4.6 Torr is used. In this case, the value for K is near $6.4 \times 10^{-13}$ m$^3$/N, which is equivalent to a reduction of about 21.5%. This suggests that improvements in wear resistance when PN treatments are performed at 410 °C may be associated with the structure and hardness of the nitrided layer.

Fig. 4 shows the results of XRD and the microstructures of the nitrided layers formed at 410 °C and different PN pressures. All the nitrided layers formed are basically $\gamma'$-Fe$_2$N iron nitride type (Fig. 4a). At lower pressure (2.5 Torr), $\gamma'$ nitride presents diffraction peaks with lower intensity due to smaller thickness of white layer (Fig. 4b). At the pressures of 3.9 and 4.5 Torr, the nitrided layers consist not only of iron nitride type $\gamma'$-Fe$_2$N, but also of iron nitride type $\epsilon$-Fe$_2$$_3$N, which has a higher concentration of nitrogen than the first.

When Fig. 4b is compared with Fig. 4c and d, in addition to the formation of nitride needles, it can be seen that increasing pressures led to the thickening of the white layer.

Grün and Günther [28] reported that the width of the cathodic sheath that is formed around the surface of the sample is strongly affected by the pressure. Low-sheaths have a high atomic nitrogen density than high-sheaths and the first type covers the entire surface of the sample, resulting in nitrided layers with better uniformity and greater thickness [29,30].

Therefore, the less the pressure is, lower and more uniform is the plasma sheath and, consequently, greater is the thickness of white layer.
3.3. Microstructure and wear resistance of the steel plasma nitrided at 440 °C

Fig. 5 shows the wear coefficient as a function of sliding distance for API 5L X70 microalloyed steel nitrided at temperatures of 440 °C and different pressures. Similar to the observed PN treatments at 410 °C, significant reductions in the wear coefficient were obtained and the best result for K (about $5.5 \times 10^{-13}$ m$^2$/N) is obtained when using a pressure of 4.6 Torr.

Fig. 6 shows the results of XRD and the microstructures of the nitrided layers formed at 440 °C and different PN pressures. Fig. 6a suggests that the white layers produced at low pressure (2.5 Torr) are single phased, consisting of γ′-Fe$_2$N type iron nitrides, whereas those produced at 3.9 and 4.6 Torr are dual phased, consisting of iron nitrides type γ′-Fe$_2$N and ε-Fe$_2$N. These results keep a similarity with those reported for PN treatment conducted at 410 °C (Fig. 4a). However, as shown in Fig. 6b–d, the microstructures of the nitrided layers produced at 440 °C are quite different from those produced at 410 °C (Fig. 4b–d).

At 440 °C, no nitride needles were found in the structure of the nitrided layer. Additionally, different from 410 °C, the thicknesses of the white layers, which have a high uniformity, do not grow proportionally with the increase in pressure. The white layer produced at 3.9 Torr is about twice as thick as that produced at 4.6 Torr, which in turn has practically the same thickness as that produced at 2.5 Torr. However, the nitrided layer produced at 3.9 Torr and 440 °C shows the best result of wear resistance, suggesting that the improvement is not associated with the increase in the thickness of the white layer.

3.4. Surface hardness and hardness profiles of the nitrided layers

Fig. 7 shows the hardness profiles for nitrided layers produced at 410 °C and 440 °C, and different nitriding pressures. From these hardness profiles, one can verify that nitrided layers produced at 440 °C and pressures of 3.9 and 4.6 Torr have not only higher surface hardness but also are deeper or thicker than those produced at 410 °C.

Higher values for diffusion coefficient of nitrogen at 440 °C than at 410 °C can explain the greater depths found for nitrided layers obtained at 440 °C.

The best wear resistance ($5.5 \times 10^{-13}$ m$^2$/N) is presented by the layer produced at 440 °C and 4.6 Torr. Although the layer produced at 440 °C and 3.9 Torr is as hard and deep as that produced at 4.6 Torr, it exhibits a low wear resistance. This indicates that the wear resistance behaviour is associated not only with the surface hardness and thickness of the nitrided layers.
layer, but also with the presence of the white layer in the nitrided layer structure.

As shown in Fig. 6c, the white layer on the sample nitrided at 440 °C and 3.9 Torr is about twice as thick as that produced at 440 °C and 2.5 Torr (Fig. 6b), or at 440 °C and 4.6 Torr (Fig. 6d). Therefore, the layer produced at 440 °C and 3.9 Torr has low wear resistance due to a high thickness of white layer. The behaviour fairly agrees with what has been reported by several works in the literature; on the one hand showed that wear resistance is increased with thickening of the nitrided layer (diffusion zone) and, on the other hand, is decreased with thickening of the white layer [19–23]. Generally, these papers argue that the white layers are hard, but brittle, and are more easily detached when they are dual or polyphased. During the formation of these layers, tensile stresses are generated, resulting in cracks and increased worn volume.

3.5. Uniformity and width of the plasma sheath

Built based on visual observations during the PN treatments carried out in this work, Fig. 8 shows schematically the effect of pressure on the width and the uniformity of the cathodic sheaths formed around the samples during the PN treatments.

As one can see, for both temperatures, pressure can affect the characteristics of the plasma sheath that forms around the samples. The use of high pressures led to the generation of
cathodic sheaths that have low width and dark purple colouration, while low pressures allow to form high width sheaths but with light purple colouration. According to Collins and Tendys [29], the low width sheaths are characterized by high density of atomic nitrogen and, consequently, the resulting nitrided layers are thicker.

Grün and Günther [28] demonstrated the importance of pressure in controlling the PN process. Very low pressures have allowed the formation of a wide width and wide-spread plasma sheath. As a result, the process temperature is not reached and the growth of the nitrided layer is impaired. Likewise, very high pressures can hinder the development of the nitrided layer due to covered problems, since the plasma sheath becomes very thin.

Fig. 8 also shows that the effect of pressure is more significant at 440 °C than 410 °C. At 4.6 Torr, the plasma sheath is very thin and in some regions of the sample surface, coating becomes so poor that the plasma can be extinguished (switched off). As a result, PN treatments are impossible to execute when trying to use high pressures.

The non-uniformity of the plasma sheath, therefore, justifies a low thickness of the white layer obtained at 4.6 Torr and 440 °C which is practically the same as that produced at 2.5 Torr and 440 °C.

4. Conclusions

The following conclusions can be drawn after the PN treatments of API SL X70 steel performed at different working pressures:

- All PN conditions used in this work improved wear resistance compared with non-nitrided steel.
- The uniformity and width of the plasma sheath have a primary effect on the structure and thickness of the formed nitrided layers and, consequently, the wear resistance of the steel.
- Treatments performed at high pressures led to the generation of plasma sheaths characterized by low width and a dark purple staining, whilst low pressures produce high width plasma sheaths and light purple staining.
- The treatments performed with higher pressures and temperatures, consequently with more uniform plasma sheath and smaller width, offer the best wear resistance result. In this case, the nitrided layer formed has a thinner white layer, is more uniform and deeper, although it consists of dual phase nitrides.

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REFERENCES


Conflicts of interest

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