An assessment of the effect of plasma nitriding and nitrocarburizing parameters on the corrosion resistance of sintered steel using the response surface method

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Abstract

The Response Surface Method is an effective means of addressing the combined effect of plasma nitriding parameters on the corrosion resistance of materials. In this work, sintered steel was nitrided under different atmospheres: 75%N₂ - 25%H₂, and 25%N₂ - 75%H₂. In addition, a series of samples was also nitrocarburized by adding CH₄ to the nitrogen-enriched atmosphere. The thickness and composition of the resulting compound layers were determined, along with the resulting microhardness profiles. Finally, the corrosion resistance of the plasma-treated materials was evaluated by potentiodynamic polarization technique. The results indicated that the addition of CH₄ to the plasma atmosphere increased the hardening depth and improved the corrosion rate of the resulting material.

1 Introduction

Powder metallurgy (PM) has been widely used in large scale production of steel components, lowering the final cost of production for mechanical, automotive, and appliance components [1]. In addition, specific parts, such as metallic filters
and self-lubricating bearings can only be manufactured by powder metallurgy. Therefore, increasing efforts have been made towards improving the performance of sintered steels. Residual porosity is particularly deleterious to the mechanical and chemical behavior of powdered materials in applications that demand fatigue, wear and corrosion resistance. Although the recent development of stainless steel powdered alloys has provided a means of producing corrosion-resistant sintered materials [2-7].

The high price of raw materials cancels out the economic benefits of PM processing. Surface-modification techniques can be used to improve the corrosion resistance of sintered steels. Surface-modifying methods include a variety of processes such as surface spraying, surface quenching, and nitrocarburizing, in addition to more sophisticated approaches where surface heating is achieved using laser beams, plasma, electron beams, or ion beams in biased potentials [8-9]. The thickness and properties of the coating or modified layer produced on the surface of the material vary widely as a function of both the technique and corresponding parameters. For instance, the thickness of corrosion-protective barriers may vary from tens of nanometers, as in the case of ion implantation, to a few millimeters, as for laser-generated surface alloys [9-10]. Furthermore, from a mechanical standpoint, the hardness of coating layers range from around 200 Vickers (surface spraying) up to 10,000 Vickers (diamond deposition) [11]. Consequently, each method has its own advantages and disadvantages associated, according to the final application intended for the material. This work addresses the use of plasma nitriding and nitrocarburizing to modify the surface of sintered steel. The set of resulting properties including mechanical (fatigue resistance and hardness), tribological (friction coefficient), and electrochemical (corrosion rate) are determined by the structure and composition of the compound layer that coat the metallic substrate. However, an equally important aspect is the distribution of nitride and carbonitride phases in that layer, which is basically determined by both processing parameters such as plasma atmosphere, temperature, holding time, and cooling rate [12-19], and the nature and contents of alloying elements (especially carbon) in the base steel [20-22]. Although many aspects remain to be investigated, a few trends have been well established in previous studies. Plasma atmospheres containing less than 5% N₂ result in excessively thin compound layers. Thicker compound layers having γ'-Fe₄N as their major phase are usually formed in atmospheres where the N₂ contents vary between 15% and 30% [16-18]. Atmospheres richer in N₂ (more than 60%) and temperatures below 480°C drive the formation of ε-Fe₂,3N. The relative concentration of the ε-phase increases with the addition of carbon to the nitriding atmosphere, resulting, in fact, in a nitrocarburizing process. Similar structures can be formed from conventional methods such as salt bath and gas nitriding [13, 23]. Nevertheless, plasma is an environmentally safe process, in the sense that no salt residues are exuded upon processing. However, recent reports on the superficial treatments, such as plasma nitriding, are not effective in improving the corrosion resistance of materials with residual open porosity, as volume remains exposed to the electrolyte [20–22]. The presence of even a small number of uncoated pores may strengthen the effects of a corrosive action, as the potential difference between substrate and nitride layer represent an effective
galvanic pair [24]. The optimization of plasma processing, as applied to improving the corrosion behavior of sintered steels, is an important tool in broadening the application range of metallurgical powdered components.

In this scenario, the aim of the present study is to compile basic information as to the combined effect of plasma processing parameters on the microstructure of nitrided layers as well as on the mechanical and chemical behavior of the surface-modified materials.

2 Materials and methods

2.1 Material sintering

The chemical composition of the powders used to produce sintered 3.8 wt.% Mn - 0.4 wt.% C - bal. Fe alloys is described on Table 1. The alloying elements were added to the ferrous matrix in the form of a FeMnC master alloy, whose particles were all finer than 45 μm. The final carbon content was adjusted adding 0.08 wt.% graphite to the powder mixture. Finally, 0.6 wt.% zinc stearate was added, and the final composition was mixed in a Y-mixer for 90 min at 45 rpm.

<table>
<thead>
<tr>
<th>Powder</th>
<th>C</th>
<th>O</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe Ancorsteel 1000 B</td>
<td>&lt;0.01</td>
<td>0.09</td>
<td>&lt;0.01</td>
<td>0.1</td>
<td>0.005</td>
<td>0.009</td>
<td>bal.</td>
</tr>
<tr>
<td>Master alloy</td>
<td>6.5</td>
<td>-</td>
<td>0.22</td>
<td>76.05</td>
<td>0.25</td>
<td>0.01</td>
<td>bal.</td>
</tr>
</tbody>
</table>

The powder mixture was then uniaxially pressed under 600 MPa into 9.5 mm pellets using a double acting press equipped with a moving die body. Subsequently, the green pellets were pre-sintered at 600°C in 90% H₂ + 10% CH₄. The furnace was heated up to the pre-sintering temperature at a rate of 30°C/min, and the holding time was set to 1 hour. The specimens were then pressed once more under 600 MPa using a 10-mm die, and the resulting pellets were sintered at 1220°C under the same atmosphere employed in the pre-sintering stage. Finally, the material was either nitrided or nitrocarburized in a plasma reactor, as described in early report [25]. A series of samples were not plasma treated in order to establish grounds for a comparative analysis on the efficiency of the surface treatment.

2.2 Plasma nitriding

Prior to plasma surface treatment, the pellets were cleaned with acetone in ultrasound bath for 2 minutes. The cleaning step was completed inside the plasma reactor, where the material was exposed to a discharge in H₂ flow (2.0 cm³/s) at 300°C for 15 minutes. At that point, the pressure in the chamber was set to 200 Pa, and the applied potential ranged from 400 to 450 V. Table 2 presents a full description of the processing parameters used in the final plasma treatment.
Table 2: Set of plasma processing parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>510°C (783 K); 540°C (813 K), 570°C (843 K)</td>
</tr>
<tr>
<td>Holding time</td>
<td>2, 4, and 6 h</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>75% N₂ + 23,75% H₂ + 1.25% CH₄; (atm 1)</td>
</tr>
<tr>
<td></td>
<td>75% N₂ + 25% H₂ (atm 2)</td>
</tr>
<tr>
<td></td>
<td>25% N₂ + 75% H₂ (atm 3)</td>
</tr>
<tr>
<td>Flow</td>
<td>4 cm³/s (4 x 10⁻⁶ m/s)</td>
</tr>
<tr>
<td>Pressure</td>
<td>400 Pa</td>
</tr>
<tr>
<td>Voltage</td>
<td>400 to 610 V</td>
</tr>
<tr>
<td>Cooling atmosphere</td>
<td>N₂</td>
</tr>
<tr>
<td>Pulse time on</td>
<td>80 to 120 ms</td>
</tr>
<tr>
<td>Pulse time off</td>
<td>80 to 120 ms</td>
</tr>
</tbody>
</table>

2.3 Microstructural and mechanical characterization

Both optical and electronic microscopy were employed in the microstructural analysis of the compound layers. A Zeiss Neophot 30 optical microscope and a Philips XL3O scanning electron microscope were used to inspect polished and etched cross sections of the plasma-treated surfaces. Phase identification took place by X-ray diffraction using Cu-kα radiation (λ = 0.154060 nm). Diffraction patterns were gathered in a Philips X’Pert equipment set to 30 mA and 40 kV. The angular range 30° < 2θ < 100° was scanned at a goniometer speed of 0.01°/s.

Microhardness profiles were obtained from a Shimadzu equipment. Three identical samples were used for each set of plasma-processing parameters. Each hardness value reported corresponded to an average of 5 indentations caused by a load of 0.025 kg applied onto the sample for 15 s. Marks were 30 μm apart.

2.4 Electrochemical analysis

Electrochemical analyses were carried out at ambient temperature (22 ± 2°C) using a EG&G-Princeton Applied Research Potentiostat/Galvanostat 273 A connected to a personal computer. The electrochemical cell was formed by a three electrode cell system. The working electrode consisted of the sample itself having a total area of 0.283 cm². Saturated Calomel Electrode coupled to a Luggin capillary functioned as the reference electrode. Finally, the counter-electrode consisted of two inert graphite bars. The measured voltage was later normalized to a Hydrogen Normal Electrode (HNE) [26]. The electrolyte consisted in a KNO₃ 0.5 M solution (pH = 6) prepared from highly pure KNO₃ and pure water, obtained from a MILLIPORE system. Each scan lasted 3600 s. The bias potential of the working electrode ranged from -250 mV x E₀C to 1.6 V, and the scan rate was set to 0.8 mV/s.
2.6 Statistical analysis

The influence of raw materials and sample preparation, as possible sources of discrepancies, was ruled out as the starting powders came from single batches, and the preparation methodology was rigorously the same for all samples. The statistical analysis was designed based on a factorial model with a central point, such as

\[ y = a_0 + a_1 x_1 + a_2 x_2 + a_{12} x_1 x_2 \]  \hspace{1cm} (1)

The method of minimum squares was then used to plot the response surface for the thickness of the compound layer and corrosion rate [27].

Automated variance analysis and surface fitting was carried out using an appropriate software.

3 Results and discussion

3.1 Thickness of the compound layer and hardening depth

The response surfaces corresponding to the thickness of the compound layer (Figure 1) are inclined with respect to their reference axes. Under CH₄-free atmospheres (Figure 1b and c), increasing the nitriding holding time from 2 to 6 hours at 570°C did not result in significantly thicker compound layers. Conversely, a similar increase of the holding time at 510°C, resulted in reasonably thicker layers for both atmospheres. The saturation of the growth rate of the compound layer for shorter times at higher temperatures is possibly related to an increase of the diffusion coefficient of nitrogen in iron, as the temperature increases. Further evidence confirming this hypothesis has been reported in the literature [14,25]. In addition, Figure 1 also shows that thick compound layers can alternatively be obtained increasing the relative amount of N₂ in the atmosphere. Other than that, all response surfaces depicted in Figure 1 are quite similar.

An analysis of the response surface obtained from nitrocarburized specimens (Figure 1a) indicated the growth of the compound layer as both temperature and holding time increased. Figure 1a and b also suggested that the addition of CH₄ to the atmosphere prompted the formation of reasonably thick compound layers. In addition, the presence of CH₄ in the atmosphere changes the holding time into an important process parameter, significantly affecting the final characteristics of the nitrocarburized surface. This can be rationalized considering that the diffusion coefficient of carbon in iron is higher than that of nitrogen for the temperature range investigated. Therefore, the diffusion of nitrogen was enhanced adding carbon to the atmosphere, via a mechanism of mutual diffusion.
Figure 1: Response surface for thickness of the compound layer as a function of
the nitriding temperature and holding time. (a) atm 1: 75%N\textsubscript{2}-23.75%H\textsubscript{2}-1.25%
CH\textsubscript{4}; (b) atm 2: 75%N\textsubscript{2}-25%H\textsubscript{2}; (c) atm 3: 25%N\textsubscript{2}-75%H\textsubscript{2}.
3.2 Microhardness profile

Figure 2 depicts microhardness profiles that illustrate the effects of the processing parameters on such property. Increasing the nitriding holding time increased both the absolute hardness and the hardening depth of the material (Figure 2a). This was expected, since longer times imply in higher contents of nitrogen in the diffusion zone. On the other hand, increasing the nitriding temperature softened the material (Figure 2b). As the temperature decreased, so did the diffusion coefficient of nitrogen in iron, and, consequently, the concentration of nitrogen in the diffusion zone. Nevertheless, the average size of nitride precipitates also decreased, at the same time that the number of sites increased. As a result, the precipitate particles packed together, thus inhibiting the movement of dislocations which, in turn, hardened the material. Adding CH₄ to the plasma atmosphere also increased both the hardness and hardening depth of the material. Finally, the effect of increasing the relative amount of nitrogen in the atmosphere was also towards hardening the material, as a result of an increase in concentration and chemical potential of nitrogen.

Figure 2: Microhardness profiles showing the effect of (a) nitriding time; (b) nitriding temperature, (c) addition of CH₄ to the nitriding atmosphere, and (d) N₂:H₂ ratio.
3.3 Composition of the compound layer

The composition of the compound layer was assessed by X-ray diffraction (XRD). Prior to surface treatment, the pattern corresponding to the sintered substrate depicted only the presence of the BCC Fe-α structure. Although areas resembling cementite (θ-Fe₃C) had been previously observed by optical microscopy, the presence of that phase was not confirmed by X-ray diffraction. Figure 3 illustrates the XRD patterns that followed plasma treatments. In addition to Fe-α, resulting from the interaction of the incident beam with the metallic substrate, peaks corresponding to nitride phases of composition γ'-Fe₄N and ε-Fe₂₃N were also identified. Samples nitrided under atm 1 (containing CH₄) revealed the presence of a mixture of ε-Fe₂₃N and γ'-Fe₄N (Figure 3a), except for the sample treated at 570°C/2 h (PD), whose compound phase consisted exclusively of ε-Fe₂₃N. The relative intensity of the diffraction lines corresponding to ε-Fe₂₃N and γ'-Fe₄N revealed that the former was the major phase resulted from the nitrocarburizing process. Samples labeled PF to PH, nitrided under atm 2, at relatively low temperatures (510°C and 540°C), also depicted high contents of ε-Fe₂₃N (Figure 3b). However, in this case, increasing the nitriding temperature to 570°C enhanced the precipitation of γ'-Fe₄N. This result is in good agreement with previous studies that pointed out an increase of the relative amount of γ' as the nitriding temperature increased [13-19]. Figure 3c shows the XRD patterns obtained from samples nitrided under atm 3 (labeled PK to PO). Reducing the relative amount of nitrogen in the atmosphere stabilized γ'-Fe₄N. As a matter of fact, γ' - Fe₄N was the major phase observed for all samples nitrided under atm 3, except sample PL (510°C/6 h). In that case, the higher content of ε-Fe₂₃N was most likely related to the excessively long nitriding time, responsible for depleting the substrate of carbon, which diffused towards the compound layer (Figure not shown here).

3.4 Corrosion resistance

In addition to the corrosion rate, estimated at the Tafel region of the curve, potentiodynamic plots also offered information on active dissolution, active-passive transition, passivation, and transpassivation.

$E_{corr}$ vs. time scans revealed that the plasma treatment shifted $E_{corr}$ to nobler values. Nevertheless, the rapid decrease of the potential as the nitriding holding time increased is an indicative of the beginning of the corrosion process and the tendency of the material not to passivate. Samples nitrocarburized in the presence of CH₄ displayed a rather distinct behavior, with a slightly increase on the potential, such as it was the case of sample PA.

Potentiodynamic polarization scans were performed on both sintered and sintered/plasma-treated specimens (Figure 4). Although nitrocarburizing reduced the anodic dissolution current of the material (Figure 4a), an increase in the passivation current of the plasma-treated material with respect to the plain sintered material could also be noticed. This indicated that, in the range of high potentials, the oxide layer was more resistant to corrosion than the compound.
Surface Treatment

layer. At the vicinity of the active-passive region, the performance of the compound layer improved. A reasonable explanation to this fact is the breakdown of the thinnest areas of the compound layer, resulting in the formation of a galvanic cell between substrate and nitride layer. The results obtained for the material nitrided under atm 2 and 3 are shown in Figure 4b and c, respectively. As a result of the nitriding process, the passivation region between 0.7 and 1.6 V could no longer be observed. However, the region of anodic dissolution of the nitrided material extended all the way to the transpassivation region. Moreover, the current values were lower than those obtained for the passivation region of the sintered material (samples labeled P).

The values of the corrosion rate were interpreted from a statistical standpoint, resulting in the response surface depicted in Figure 5. As it can be seen, all surfaces are at an angle with respect to their reference axes. The lowest corrosion rates obtained for each atmosphere investigated corresponded to samples labeled PD, PI, and PL, respectively (Table 3). The corrosion rates for samples PD and PI showed an improvement with respect to the plain sintered material. Comparing the response surface for the corrosion rate (Figure 5) to those for the thickness of the compound layer (Figure 1), it can be suggested that below a critical value, plasma nitriding actually deteriorates the corrosion behavior of the material. Apparently, the composition of the compound layer also determines the corrosion rate of nitrided materials. The improvement observed for the corrosion resistance of nitrocarburized specimens was generally linked to the thickening of the compound layer. Nevertheless, the best corrosion rates were obtained for samples nitrocarburized at 570°C/2 h (label PD), although the corresponding compound zones were thinner than those of samples PE. This can be explained based on the XRD patterns, which revealed that whereas the compound layer of sample PD consisted exclusively of ε-Fe2.3N, that of sample PE contained a mixture of ε-Fe2.3N and γ'-Fe4N. Another important aspect is the substantial presence of pores in the compound layer of samples PE. Porosity is generally a result of the decomposition of ε-Fe2.3C4N into Fe3C and nitrogen [28-29]. Comparing Figure 6a and b indicated that the effective action of the corrosion barrier is related to a uniform coating rather than the thickness of the compound layer itself. Consequently, lower corrosion rates were obtained from samples nitrided under atm 3, regardless of their relatively thinner compound layers. The variance analysis of the overall results suggested that for CH4-free atmospheres none of the processing parameters or their combination were determinant on the final characteristics of the compound layer. On the other hand, adding CH4 to the atmosphere drastically changed the relative importance of all parameters investigated (Figure 5), and they all became meaningful. Furthermore, the atmosphere also affected the curvature of the response surface, suggesting that the response surface for nitrocarburized specimens would be better fitted by a quadratic model, such as

\[ y = b_0 + b_1x_1 + b_2x_2 + b_{11}x_1^2 + b_{22}x_2^2 + b_{12}x_1x_2 \]  \( (2) \)
However, the increase in the number of constants to be adjusted, as compared to equation (1) would require a great number of experiments, which would prevent the conclusion of the present study in a timely fashion.

Table 3: Results from potentiodynamic polarization and material ranking

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_{corr}$ (mV)</th>
<th>$E(i=0)$ (mV)</th>
<th>$I_{corr}$ ($\mu$A/cm$^2$)</th>
<th>Corrosion rate (mm/year)</th>
<th>Rank</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>-0.50</td>
<td>-0.67</td>
<td>41.51</td>
<td>0.48 + 0.08</td>
<td>Good</td>
</tr>
<tr>
<td>PA</td>
<td>-0.45</td>
<td>-0.68</td>
<td>95.70</td>
<td>1.11 + 0.15</td>
<td>Poor</td>
</tr>
<tr>
<td>PB</td>
<td>-0.42</td>
<td>-0.53</td>
<td>14.57</td>
<td>0.18 + 0.05</td>
<td>Good</td>
</tr>
<tr>
<td>PC</td>
<td>-0.44</td>
<td>-0.46</td>
<td>16.74</td>
<td>0.20 + 0.04</td>
<td>Good</td>
</tr>
<tr>
<td>PD</td>
<td>-0.39</td>
<td>-0.57</td>
<td>5.56</td>
<td>0.06 + 0.03</td>
<td>$\text{Excellent}$</td>
</tr>
<tr>
<td>PE</td>
<td>-0.40</td>
<td>-0.53</td>
<td>10.87</td>
<td>0.13 + 0.02</td>
<td>Good</td>
</tr>
<tr>
<td>PF</td>
<td>-0.52</td>
<td>-0.66</td>
<td>67.50</td>
<td>0.78 + 0.35</td>
<td>Regular</td>
</tr>
<tr>
<td>PG</td>
<td>-0.46</td>
<td>-0.66</td>
<td>85.20</td>
<td>0.99 + 0.24</td>
<td>Regular</td>
</tr>
<tr>
<td>PH</td>
<td>-0.39</td>
<td>-0.54</td>
<td>62.00</td>
<td>0.72 + 0.08</td>
<td>Regular</td>
</tr>
<tr>
<td>PI</td>
<td>-0.40</td>
<td>-0.63</td>
<td>50.30</td>
<td>0.58 + 0.17</td>
<td>Regular</td>
</tr>
<tr>
<td>PJ</td>
<td>-0.44</td>
<td>-0.64</td>
<td>77.09</td>
<td>0.89 + 0.26</td>
<td>Regular</td>
</tr>
<tr>
<td>PK</td>
<td>-0.29</td>
<td>-0.45</td>
<td>18.36</td>
<td>0.21 + 0.24</td>
<td>Good</td>
</tr>
<tr>
<td>PL</td>
<td>-0.41</td>
<td>-0.52</td>
<td>15.10</td>
<td>0.18 + 0.06</td>
<td>Good</td>
</tr>
<tr>
<td>PM</td>
<td>-0.43</td>
<td>-0.61</td>
<td>44.97</td>
<td>0.52 + 0.45</td>
<td>Good</td>
</tr>
<tr>
<td>PN</td>
<td>-0.28</td>
<td>-0.46</td>
<td>17.53</td>
<td>0.20 + 0.08</td>
<td>Good</td>
</tr>
<tr>
<td>PO</td>
<td>-0.35</td>
<td>-0.52</td>
<td>34.49</td>
<td>0.40 + 0.34</td>
<td>Good</td>
</tr>
</tbody>
</table>

* average + 1.96 x sample standard deviation

Table 3 also summarizes the average values of $I_{corr}$, $E_{corr}$, $E(i=0)$, and corrosion rate. Along with a qualitative rank on the performance of the different materials in the corrosive environment investigated ($\text{KNO}_3$ 0.5 M solution). The results showed that, under specific plasma conditions it was possible to improve the corrosion resistance of the original sintered material. The best results were obtained from nitrocarburized specimens, as the presence of CH$_3$ in the plasma atmosphere generally resulted in uniform and relatively thick compound layers, that extended to the innermost regions of open pores (Figure 6), thus improved even further the corrosion resistance of the material.
Figure 3: X-ray diffraction patterns of specimens treated under different times and atmospheres. (a) atm 1: 75%N₂-23,75%H₂-1,25% CH₄; (b) atm 2: 75%N₂-25%H₂; and (c) atm 3: 25%N₂-75%H₂.
Figure 4: Potentiodynamic polarization curves of plain sintered specimens (P), and samples nitrided under atm. 1 at 510°C/2 h (PA), atm. 2 at 570°C/2 h (PI), and atm. 3 at 510°C/2 h (PK).
Figure 5: Response surface for the corrosion rate as a function of the temperature and nitriding holding time, along with corresponding variance analyses. (a) atm. 1; (b) atm. 2, (c) atm. 3.
4 Conclusions

- The thickness of the compound layer is generally determined by the nitriding temperature. The holding time becomes an important parameter when the plasma atmosphere contains CH₄;
- The hardening depth is significantly affected by the holding time, particularly at low temperatures. Temperature affected the hardening depth only upon nitrocarburizing;
- Nitrocarburizing atmospheres are more efficient in increasing the thickness of the compound layer and hardening depth;
- In N₂-rich atmospheres, the relative amount of γ'‐Fe₄N increased with the nitriding temperature. Reducing the relative amount of N₂ assisted in the formation of γ'-Fe₄N, whereas CH₄ drove the precipitation of ε-Fe₂₃N;
- Nitriding and nitrocarburizing resulted in a decrease of the anodic dissolution current which indicated an improvement of the corrosion resistance of the material in that potential range. At higher potentials, the compound layers ruptured at their thinnest areas, thus exposing the substrate. Corrosion in the interface-to-substrate direction was observed;
- The presence of CH₄ in the atmosphere resulted in uniform coatings that worked as effective corrosion barriers on sintered substrates.

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References


