SHORT COMMUNICATION

Effect of plasma nitriding time on the structural and mechanical properties of AISI-O1 steel

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Abstract
In this paper, the effect of plasma nitriding time on the improvement of surface microhardness of AISI O1 steel as a strategy to increase its wear resistance was addressed. The plasma nitriding was carried out in a controlled atmosphere (80% H2(g) and 20% N2(g)), temperature (500°C), and pressure (6 mbar), during the different amount of time (4, 5, and 6 hours). The material was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and microhardness measurements. Moreover, microhardness measurements were carried out to investigate the mechanical properties. From the results, it was verified that the XRD patterns, SEM images, and EDS spectra confirmed the formation of a layer with ε-Fe3N and γ'-Fe4N phases in all nitrided samples. The sample AISI-O1 steel, which was nitrided for 6 hours, exhibited a hardness about 46% higher than the one measured for the untreated sample. This sample also showed the thicker layer, with a mean of 7.22 μm. Therefore, this thermochemical treatment can improve mechanical properties in AISI O1 steel, and suggest its use in compression tools to improve this tools life.

KEYWORDS
AISI-O1 steel, mechanical properties, plasma nitriding, X-ray diffraction

1 | INTRODUCTION

The manufacturing process cost of tools steel is directly associated to the marketing value of the final product. According to Jesus et al.,1 the amount spent on the manufacturing of tools made of steel represents about 40% of the selling price of a product. Salonitis and Kolios,2 estimated that about 50% of this amount is related to resources and materials needed to the manufacturing process. In the pharmaceutical industry, these costs are mainly related to punches and matrixes. The
tools that resist for a long time of use have a more economical manufacturing process, and consequently, the product may become cheaper, as in the case of tablets.

Several surface modification methods have been used as a strategy to increase the tools live of different kinds of steels. Karimbaev et al\textsuperscript{13} used ultrasonic nanocrystal surface modification (UNSM) to increase the surface hardness of AISI 1045 carbon steel layers, and Kim et al,\textsuperscript{4} to AISI M4. Heat treatment and titanium nitride (TiN) coating on AISI-O1 cold work tool steel presented higher mechanical and wear resistance by Kumar et al.\textsuperscript{5} This thermal and thermochemical treatments stand out for increased resistance of tool base material.\textsuperscript{6,7} Among the available methods there are also tempering, nitriding, carbonitriding, cementation, and boriding stand out.\textsuperscript{8-15}

Different studies have demonstrated that plasma nitriding at relatively low temperatures (below 450°C) can allow obtaining a surface layer of nitrides due to diffusion of nitrogen during this process, which results in an increase of the hardness and wear resistance.\textsuperscript{16-19} Zappelino et al,\textsuperscript{20} presented a higher dry sliding wear resistance in samples of cold work tool steel Vanadis 10, with a cryogenic treatment samples followed by plasma nitriding. In addition, this process allows to reduce the treatment time, obtain minimal distortions, low gas consumption, energy and no harm to the environment when compared with other surface modification techniques.\textsuperscript{21,22}

Plasma nitriding process was used in this work to increase the tool live of AISI-O1 steel punches of tablet machines from the Laboratory of Development of Solid Pharmaceutical Forms at Federal University of Piauí (UFPI). For Rosales et al,\textsuperscript{18} the plasma nitriding process is a technic that enhances properties of tools made of AISI-O1 steel, showing a microhardness of 1326 HV and a good result of wear.

Therefore, in this work, we have explained experimental conditions of controlled atmosphere gas (80% H\textsubscript{2}(g) and 20% N\textsubscript{2}(g)), temperature (500°C), and pressure (6 mbar), different times (4, 5, and 6 hours) were used in treatment to available this surface properties of AISI-O1 samples. X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) were used to verify the formation of the nitrides layer after the plasma nitriding process. Moreover, an increase on hardness was measured by microhardness equipment.

## 2 EXPERIMENTAL DETAILS

Three cylindrical samples of AISI-O1 steel with 20 mm of diameter and 8 mm of thickness were used in the assays. The steel also is known as ASTM A 681 type O1, ABNT O1, WNr 1.2510, or DIN 100 MnCrW\textsubscript{4}.\textsuperscript{23} Table 1 shows their chemical composition (wt%) as tempered, rectified, and polished punches obtained from the Laboratory of Development of Solid Pharmaceutical Forms at Federal University of Piauí (UFPI).

As presented in Table 1, this AISI-O1 steel presents in its chemical composition a small amount of some metals as tungsten (W), manganese (Mn), and vanadium (V). During the heat treatment process of quenching and tempering, this oil-quenched steel has a transformation of Austenite phase with a face-centered cubic structure to Martensite phase with body-centered tetragonal (BCT) structure,\textsuperscript{24} which is obtained by the rapid cooling in at its melting temperature. Finally, the cylindrical steel AIS-O1 samples were sanded, polished according to ASTM E311, and washed with a solution of 70% isopropyl alcohol and 30% deionized water, in following was dried and stored. The plasma nitriding reaction was carried out at the Plasma Laboratory (LABPLASMA) at the Industry and Cultural Production Department of the Federal Institute of Education, Science, and Technology of Piauí (IFPI). Before starting the process, all samples were cleaned by ultrasonic immersion in acetone for 10 min. The parameters such as pressure, temperature, and gas concentration were established for the pre-sputtering processes and the plasma nitriding process, respectively (Tables 2 and 3). The treatments were performed in triplicate.

### Table 1 Steel AISI-O1 chemical composition (wt%)

| Chemical elements | C  | Si | Mn  | Cr | W  | V  |
|-------------------|----|----|-----|----|----|----|
| Weight percent (%)| 0.90 | 0.30 | 1.15 | 0.50 | 0.50 | 0.20 |

### Table 2 Pre-sputtering parameters used for treatment of plasma nitriding in AISI-O1 steel samples

| Time (h) | Pressure (mBar) | Temperature (°C) | Voltage (V) | Current (A) | Gas concentration |
|----------|-----------------|------------------|-------------|-------------|------------------|
| Pre-sputtering | 1 | 1.6 | 400 | 250 | 0.20 | 30 sccm de H\textsubscript{2}(g) |
According to Table 2, before starting the plasma nitriding process, samples were submitted to plasma with H$_2$(g) for 1 hour at low pressure in order to start the formation of ions and facilitate the nitrogen diffusion in the process with (80% H$_2$(g) and 20% N$_2$(g)), as presented in Table 3. After several tests with different pressures for the nitriding process, it was determined that only at low pressure, it was observed an increase in the surface hardness.

The structural analysis of the materials was obtained from the XRD patterns, using a LabX XRD-6000 diffractometer (Shimadzu, Japan), with Cu-Kα radiation ($\lambda = 0.15406$ nm), in the $2\theta$ range from 30° to 90°, and with a scanning velocity of 2°/min. The microstructure of the material and the formation of the nitride layer in the samples were examined by scanning electron microscope (SEM) with emission field canon, FEI mark, Quanta FEG 250 model, and an acceleration voltage of 1 to 30 kV. This equipment has a Silicon drift detector, Ametek brand, HX-1001 model, with 126 eV of resolution, and an Apollo X-SDD detector; it was used to confirm the chemical composition of the material. Images were recorded with a backscattered electron detector, with an acceleration voltage of 20 kV, and an increase of 10 000 times. In order to carry out this characterization electron assay, the samples were cut transversely in a metallographic slicer under Teclago CM 60. The cooling and the hot inlay were obtained with a bakelite in the Arotec PRE 30Mi equipment. Finally, the microhardness measurements of the samples’ surface, according to the Vickers standard, were carried out on the INSIZE HV 1000 equipment from the UFPI Metallurgy Laboratory, using 25 gf and 15 seconds print loads, with a square base pyramidal diamond penetrator. Twelve impressions and the mean value were obtained for each sample.

### RESULTS AND DISCUSSION

#### 3.1 XRD analysis

XRD pattern of as-O1 steel, Figure 1, confirms the Martensite phase from the structural transformation during tempering step of the material.\textsuperscript{[5,18,24-26]}

The Martensite is a solid phase at a very hard form of the steel crystalline structure formed by an interstitial supersaturated solution of carbon (C) in alpha (α’) iron, with a BCT structure,\textsuperscript{[24]} in which iron (Fe) atoms are at the vertices, and C atoms at faces and at edges. Thus, it was determined that the materials have a highly distorted lattice.

![XRD patterns of as-O1 steel](image)
Figure 2A-C shows XRD patterns of AISI-O1 steel treated through plasma nitriding at different times (6, 5, and 4 hours), respectively. All XRD patterns presented different phases from as-O1 steel, and were identified from the Inorganic Crystal Structure Database (ICSD).

It is established that nitrogen reacts with the elements present in steel, generating new nitrides with the alloying elements. This way, \( \varepsilon \)-Fe\(_3\)N, \( \gamma' \)-Fe\(_4\)N, Fe\(_{24}\)N\(_{10}\) and NW phases were identified, according to ICSD\#163929, ICSD\#79980, ICSD\#24652 and ICSD\#257079, respectively. The last one start to appear just in N6h-O1, at peak at 35.6°. With the increase in plasma nitriding time, N atoms are diffused and react with metals of greater affinity, in this case tungsten (W). (Muñoz Riofano, R.M.; Casteletti, L.C.; Nascente, P.A.P. Surf. Coat. Technol. 200 (2006) 6101.)

The reactions occurred between N and Fe (in higher percentage in substrate) formed iron nitrides, and these compounds can be considered responsible to improve the mechanical properties, as high hardness, good wear resistance, and excellent corrosion resistance. 7,27

The martensitic phase (\( \alpha' \)), which composes the untreated sample, remained in all nitrided samples at peaks of 44.5° and 64.8°, showing that martensitic matrix formed during tempering is still there and the plasma nitriding does not modify the material base.

### 3.2 SEM image analysis

The SEM images were used to monitor the thickness, surface, and morphology of the samples after the plasma nitriding modification. Figure 3A-C illustrates the FE-SEM images from the AISI-O1 steel sample treated with plasma nitriding at different times (4, 5, and 6 hours), respectively.
The FE-SEM images in Figure 3A-C showed an increase in thickness, at order of micrometers (μm), with time of plasma nitriding process (from 4 to 6 hours). The compound layer is formed by nitrogen (N) atoms that take interstitial sites in iron structure. Diffusion mechanism is a time-dependent process, and it became clear with the increase in thicknesses of the layers. Therefore, it was observed that the sample obtained after 6 hours in plasma nitriding process (Figure 3C) showed a layer larger than the one obtained after 5 hours, which was higher than 4 hours. These were measurement in $7.22 \pm 0.91$, $6.78 \pm 0.84$, and $6.29 \pm 0.62$ μm, respectively.

The increase in layer thickness occurs due to the ionic beams in the substrate become more intense, raising the rate of nitrogen atoms diffusion with fast movement. This nitrogen diffusion can be observed in XRD pattern (as shown in Figure 2) with the increase in intensity of Fe$_4$N peaks. N6h-O1 is more intense than N4h-O1, and N5h-O1. However, it is not possible to verify through the FE-SEM images in the diffusion zone, as presented in other studies. Reis et al suggest that this may occur due to the fact that at the usual plasma processing temperatures (350°C-550°C), both the nitrogen solubility in the alloy and the diffusion coefficient of nitrogen are smaller and a layer of nitrides (compounds layer) is formed. Thus, this layer acts as a barrier that prevents the continuous growth of the compound layer, or the diffusion zone. In addition, the martensite phase with tetragonal structure is very hard and can prevent the diffusion of nitrogen in the network due to its distorted structure.

Small carbides, presumably Fe$_3$C, can be seen in the inner of samples in FE-SEM images, Figures 3A-C. These carbides are formed from the martensitic matrix during tempering and they are evenly distributed within it.

Figure 4 displays the SEM image from the surface, elementary composition percentage (%), and EDS spectrum for as-O1 sample.

From the EDS spectrum data, it was confirmed the presence of chemical elements from the material in accordance with the literature, even with some divergent percentages, such as for the carbon (C). This result shows that the material has a greater quantity of iron (Fe), followed by carbon (C), manganese (Mn), chromium (Cr), also tungsten (W), vanadium (V), and silicon (Si). These percentages may justify the formation of the compounds, which were shown and identified.
though the XRD patterns (Figure 2A-C). Moreover, some of the chemical elements with higher percentages allowed forming the new compounds as nitrides.

Figure 5A-L displays the SEM images of the surface area, chemical elemental composition, and EDS spectra (surface and internal point) for AISI-O1 steel treated by plasma nitriding at 4, 5, and 6 hours, respectively.

The results showed in Figure 5A,B confirmed the presence of nitrogen (N) in the formed layer for N4h-O1, supporting XRD pattern, shown in Figure 2, which confirms the modified surface by plasma nitriding process by reactions between nitrogen and the base elements of the substrate. The same is verified for N5h-O1 and N6h-O1. Figure 5B shows the mean values of weight percentages from each element detected in the layer. It was determined a percentage of 10.9% of nitrogen into the surface of the material. Thus, it was confirmed that the nitrogen was diffused only in the formed layer, prevailing on the bottom of the material, as shown through the elemental chemical composition of as-O1 steel in the EDS spectrum (Figure 5C,D). The results for N5h-O1 and N6h-O1 were similar, as shown in Figure 5E-L.

![Figure 5](image-url)

**Figure 5**  (A,E,I) SEM images at the local area surface, (B,F,J) elemental chemical composition, and (C,D,G,H,K,L) EDS spectra at surface and internal for AISI-O1 steel treated by plasma nitriding at 4, 5 and 6 hours, respectively
3.3 | Microhardness analysis

Figure 6A presents the comparison of microhardness values measured in the samples before the plasma treatment (as-O1) and post-treatment (N4h-O1, N5h-O1, and N6h-O1). Moreover, Figure 6B also shows the evolution of hardness on surface for the annealed state of AISI-O1 steel, which had a value of 220 HV, according to the literature.19 For the as-O1 sample, the value was measured in 655 HV, confirming the reference values.20 The maximum values after the thermal treatment by tempering was 700 HV.

Figure 6A shows that, after plasma nitriding treatment, the microhardness of the surface increase 36% for the sample treated during 4 hours of plasma nitriding (890 HV) and 45% for the one treated during 5 hours (951 HV). However, in 6 hours of treatment, the mean of the microhardness was not expressive (958 HV) to justify 1 hour more in the treatment. The surface hardening is caused by the interstitial diffusion of atomic nitrogen on the surface of iron alloys,31 confirmed by XRD and EDS results. Thus, phase formation Fe$_3$N may be responsible for generating an improved hardened layer, attributed not only to the intrinsic hardness of the new precipitated phases but also to the diminished plastic deformation on the matrix produced for the formation of the new precipitates in the steel.18,28 In addition, it was verified progresses increases of the formed thickness (SEM images, as displayed previously in Figure 3). Therefore, the employment of plasma nitriding increases the surface microhardness $\sim$335% of the material in comparison to the annealed steel.

The hardness profile in Figure 6B shows the microhardness decrease from surface to the inner of all samples, and for N4h-O1 sample occurs more quickly, revealing thickness smaller then N6h-O1 layer. N5h-O1 sample had an intermediate result. These profile results are in agreement with SEM images. In approximately 25 μm the N6h-O1 sample is the only one that has microhardness equal to the As-O1 sample. This suggest that the longer treatment time, greater the microhardness in deeper layers.18,30,32
4 | CONCLUSIONS

In summary, the structural, morphological, and mechanical properties of untreated and treated AISI-O1 steel through plasma nitriding at different times (4, 5, and 6 hours) has been explored in detail in this study, using different characterization techniques. Moreover, it was determined that plasma nitriding is an efficient and relatively inexpensive technique to improve mechanical properties of AISI-O1 steel. The treatment time showed to be a parameter that influences, mainly, on the nitrogen diffusion through the material structure, resulting in the formation of a nitride layer, thicker over time, which was responsible for the increase in the samples surface microhardness. The XRD patterns showed that the treated AISI-O1 steel was formed mainly from iron nitrides in ε-Fe₃N and γ'-Fe₄N phases, as well as NW tungsten nitride compound in sample with 6 hours of treatment, justifying the increase in the surface hardness of AISI-O1 steel samples. The SEM images indicated that the layer thickness increased as the treatment time increased, corroborating with literature, and justifying the microhardness increase in the surfaces with the longest duration of treatment. Finally, it was found that after 6 hours of treatment, a significant improvement of the AISI-O1 steel hardness was achieved, about 335% compared to commercial annealed steel, and 46% compared to tempered steel. This may increase the punches life for drug compression.

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CONFLICT OF INTEREST
The authors declare no potential conflict of interest.

AUTHOR CONTRIBUTIONS
Luciane Norberto de Araújo: Formal analysis; investigation; methodology; validation; writing-original draft. Armystron Gonçalves de Araújo: Data curation; formal analysis; methodology; visualization; writing-original draft. Maria Onaira Ferreira: Formal analysis; methodology; resources; visualization. Rômulo Ribeiro de Sousa: Conceptualization; funding acquisition; project administration; supervision; writing-original draft; writing-review and editing. Lívio César Nunes: Supervision; validation; visualization; writing-original draft.

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