Morphology of the DIN 100Cr6 Case Hardened Steel after Plasma Nitrocarburizing Process

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Nitrocarburizing is considered one of the most important thermochemical treatments for surface modification of metallic materials and involves the simultaneous diffusion of nitrogen and carbon onto the surface. Understanding and controlling the formation of the nitrocarburized layer have considerable industrial interest due to the improvements regarding wear, fatigue, and corrosion resistances. DIN 100Cr6 steel samples were treated by plasma nitrocarburizing for two hours, with two treatment temperatures (550 and 600°C) and four methane concentrations in the gas mixture composition (0, 1.0, 1.5, and 2.0%). SEM and XRD analyses, and wear resistance tests were used to characterize the samples. Results showed that the treatment temperature and atmosphere composition had considerable influence on the compound layer morphology. For nitrided samples the compound layer consists of γ'-Fe₄N phase, and the presence of carbon in the gas mixture helps stabilize the ε-Fe₂₋₃N phase. Higher CH₄ concentration in the treatment atmosphere improve the sample superficial wear resistance.

Keywords: Surface modification, plasma nitrocarburizing, wear resistance.

1. Introduction

The plasma nitrocarburizing is a thermochemical process of surface hardening that uses a glow discharge to introduce nitrogen and carbon simultaneously onto the material surfaces 1,2. This process is usually recommended for carbon steels, as they do not have enough constituents to form nitrides such as other medium alloy steels 3. The process modifies the alloy surface proprieties due to the formation of crystalline phases such as iron nitrides and/or carbonitrides 4, improving considerably the corrosion 5 and wear resistances 6-12. Recently there have been a number of reports dealing with the nitrocarburizing of steels 6,7,13-15.

The nitrocarburizing process can be carried out at temperatures above or below the temperature of the transformation of the α phase (ferrite) to the γ phase (austenite) of Fe-N diagram (temperature of 590°C). The process is termed ferritic nitrocarburizing if it occurs bellow the eutectoid temperature, and a compound layer is formed over a diffusion zone enriched in nitrogen. If the process occurs above the eutectoid temperature, it is termed austenitic nitrocarburizing, and there is a partial transformation of the ferritic matrix into the austenite phase, with the formation of three layers: the compound layer, the diffusion zone, and between these two layers, the so called transformed austenite layer. This austenite layer can transform into martensite during rapid cooling of the sample, thereby increasing the hardness in the region below the compound layer 1.

The most desirable phase to comprise the microstructure of the compound layer is the single ε-Fe₂₋₃N phase. However, it has been found that the compound layer formed by plasma nitrocarburizing usually consists of a heterogeneous mixture of ε-Fe₂₋₃N and γ'-Fe₄N phases 16,17,19. The compound layer composition is quite sensitive to the chemical composition of the treatment atmosphere. According to the Fe-C-N phase diagram, the presence of carbon in the gas mixture contributes to the formation of the ε-Fe₂₋₃N phase 20,21. A plasma nitriding without carbon in its treatment atmosphere is able to produce a microstructure in the compound layer composed by only the γ'-Fe₄N phase 22,23, with the formation of no ε-Fe₂₋₃N phase, or only a small amount of it 24. The stabilization of the ε-Fe₂₋₃N phase is possible by using, for instance, methane as a carbon source in the nitrocarburizing atmosphere 25,26.

The high solubility of nitrogen on the steel, leads to the high nitrogen level in the near surface and greatly contributes to the penetration of carbon atoms towards the substrate, as if the carbon atoms are pushed into the lower part of the hardened layer by the nitrogen atoms, resulting in a low carbon level in the N-enriched layer. 27.

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The purpose of this study is to investigate the influence of the temperature and the methane concentration on the wear resistance and microstructure of DIN 100Cr6 steel submitted to the plasma nitrocarburizing process.

2. Experimental Procedure

The DIN 100Cr6 steel substrates, with chemical composition presented in Table 1, were plasma nitrocarburized by a pulsed d.c. glow discharge under a pressure of 300 Pa, using a MP-250 industrial equipment. The applied current and voltage (range of 300 to 500 V) were controlled to achieve and assure the desirable processes temperatures.

The following conditions were used as parameters: two different treatment temperatures, 550±5°C and 600±5°C; nitrocarburizing treatment time fixed in 2 hours; and atmospheres with 74% N2 and concentrations of 1, 1.5, and 2.0% of CH4 with H2 as balance. A single steel substrate was nitried under an atmosphere of 25% H2-75% N2. The samples were slow cooled in the plasma chamber using an inert atmosphere. The Table 2 summarizes the experimental data for the nitrocarburizing process.

XRD analyses were performed using a Rigaku X-ray Equipment, model Geiger-Flex, under the following conditions: Cu-Kα radiation (λ = 1.54056 Å), scan angle (θ-2θ) from 5° to 90°, advance angle: 0.032°/second. The Diffrac EVA software was used for spectral analysis.

SEM analyses were performed using a Philips XL-30 FEG microscope equipped with an energy dispersive spectrometer (EDS).

For the tribological analysis, it was employed a ball-on-disk test, with a 25.4mm diameter and hardened chromium-steel ball material. A load of 1.21 N, speed of 400 rpm, without lubricants or abrasives, and test times of 5, 10, 15, and 20 minutes were the parameters used in the tests (the test time is proportional to the sliding distance, so the results show the sliding distance variable instead of test time). The wear parameters were chosen to produce a wear crater diameter proportional to the sample size, and this way, to compare the values between the different tests times chosen.

The wear crater diameters were measured using a Carl Zeiss reflective light microscope, model Axio Lab.A1, with integrated camera. The wear volumes and the wear crater depth of the samples were calculated according to Eq. (1), given in mm3 and Eq. (2), given in mm2 respectively.

\[ V = \frac{\pi \cdot h^4}{64 \cdot r} \] (1)

Where \( r \) represents the radius of the sphere [mm], \( h \) is the wear crater diameter [mm], \( V \) is the wear volume [mm3].

\[ V = \frac{\pi \cdot h^2}{3} \cdot (3 \cdot R - h) \] (2)

Where \( r \) is the radius of the sphere [mm], \( h \) is the crater depth [mm], and \( V \) is the wear volume [mm3].

3. Results and Discussion

Figs. 1 and 2 display the XRD diffractograms for the hardened layers produced at 550°C and 600°C respectively, under four different CH4 concentrations in the gas mixture.

The nitrided sample presents intense peaks associated to the \( \gamma' \)-Fe4N phase and only very minor peaks of the \( \varepsilon \)-Fe2-3N phase, as reported by Nobuki et al.30. The compound layers formed under higher amount of CH4 consists mainly of the \( \varepsilon \)-Fe2-3N phase with trace amounts of the \( \gamma' \)-Fe4N phase. The addition of methane in the gas mixture increased the amount of carbon in the nitrocarburized atmosphere, and consequently increased the \( \varepsilon \)-Fe2-3N phase amount in the modified surface layer, as reported in the literature 22,23,26.

The nitrogen and carbon mean concentration profiles of the nitrocarburized layer produced on DIN 100Cr6 steel at 550°C and 600°C are shown in Figs. 3 and 4, respectively. It can be observed that a dual-layer structure was produced,

Table 1. Chemical composition of the samples.

| Chemical composition (wt.%) | C | Cr | Mn | Si |
|---------------------------|---|----|----|----|
|                           | 0.98 – 1.10 | 1.30 – 1.60 | 0.25 – 0.45 | 0.15 – 0.35 |

Table 2. Experimental data for the nitrocarburizing process.

| Condition | Pressure (Pa) | Voltage (V) | Time (h) | Temperature (°C) | Gas Mixture (Concentration in cm³/min) |
|-----------|---------------|-------------|----------|------------------|--------------------------------------|
|           |               |             |          |                  | CH4 | N2 | H2 |
| 1         | 300           | 300 to 500  | 2        | 550±5            | 0%  | 75%| 25% |
| 2         | 300           | 300 to 500  | 2        | 600±5            | 0%  | 75%| 25% |
| 3         | 1%            | 74%         |          | 550±5            | 1%  | 74% | Balance |
| 4         | 1.5%          | 74%         |          | 550±5            | 2%  | 74% | Balance |
| 5         | 1%            | 74%         |          | 600±5            | 0%  | 75%| 25% |
| 6         | 1%            | 74%         |          | 600±5            | 1%  | 74%| Balance |
| 7         | 1.5%          | 74%         |          | 600±5            | 2%  | 74%| Balance |
| 8         | 2%            | 74%         |          | 600±5            | 2%  | 74%| Balance |
Morphology of the DIN 100Cr6 Case Hardened Steel after Plasma Nitrocarburizing Process

comprising of a N-enriched layer with a high nitrogen content on top of a C-enriched layer with a high carbon content. This is explained by the presence of the $\varepsilon$-Fe$_3$N and $\gamma'$-Fe$_4$N phases found in the compound layer for all nitrocarburized samples treated at both temperatures. The low amount of carbon in the compound layer is a consequence of the high nitrogen concentration, due to the higher thermodynamic stability of the nitrides in relation to the carbides. The high solubility of nitrogen leads to the high nitrogen level in the near surface region and greatly contributes to the penetration of carbon atoms towards the interior of the steel. This can be pictured as follows: the carbon atoms are pushed into the lower part of the hardened layer by the nitrogen atoms, resulting in a low carbon level in the N-enriched layer.

It is possible to observe the presence of a small amount of nitrogen and a large amount of carbon in the diffusion zone, but both amounts decrease along the chemical composition line until they reach the chemical composition of the sample core. The compound layer morphology for almost all samples is illustrated in Fig. 5. In the upper part of the compound layer, which contains the porous layer, the predominant phase is the $\varepsilon$ phase. In the lower part of the compound layer, which presents a columnar pattern structure, $\varepsilon$ and $\gamma'$ are the predominant phases.

Figs. 6 and 7 show the images of the wear craters obtained after the fixed ball wear test for the eight nitrocarburized samples under the eight different treatment conditions at 550°C and 600°C, respectively. Each row in Figs. 6 and 7 are associated to the wear crater images of the nitrocarburized samples at different CH$_4$ concentrations, where the first row shows the results with 0% CH$_4$ concentration, the second with 1%, the third

Figure 1. XRD diffractograms for samples treated at 550°C.

Figure 2. XRD diffractograms for samples treated at 600°C.

Figure 3. Chemical composition profiles for the samples nitrocarburized at 550°C.

Figure 4. Chemical composition profiles for the samples nitrocarburized at 600°C.
1.5%, and the fourth row with 2%. The columns represent the wear crater images for the four different test times. The first column for the test time of 5 minutes (sliding distance of 160m), the second column, for 10 minutes (sliding distance of 320m), the third, for 15 minutes (sliding distance of 480m), and the fourth, for 20 minutes (sliding distance of 640m).

From Figs. 6 and 7, it is possible to verify that the wear mechanism presented in all nitrocarburized samples is the abrasive wear. The damaged zone for all samples, presented scratches and groove appearance caused by the removal of material from the surface.

Once the values of the wear crater diameters were determined, the Eq. (1) was used to calculate the wear volume, and the results are presented in Figs. 8 and 9, for 550°C and 600°C respectively.

The results show that the nitrocarburized samples with richer CH₄ concentrations, regardless of the process temperature, present the best wear resistances. These results can be attributed to the distinct phases formed in the compound layer for different nitrocarburizing parameters. The higher wear resistance values are associated to the samples that were nitrocarburized with 1.5% and 2% of CH₄, at both temperatures, and the reason for this, is the presence, in the microstructures of the modified layers, of a large quantity of the ε-Fe₂₋₃N phase with only traces of the γ'-Fe₄N phase. The high concentration of methane in the gas mixture promotes the formation of the ε-Fe₂₋₃N phase, which has a higher hardness and a higher wear resistance than the γ'-Fe₄N phase.

The wear crater depth was calculated using Eq. (2). For all nitrocarburizing samples, the wear craters depth were not enough to exceed the superficial layer produced, as shown in Figs. 10 and 11, for 550°C and 600°C respectively.

For samples nitrocarburized with 1.5 and 2% of CH₄, the presence of ε phase with high thickness, was essential to provide low material removal at wear testing, and consequently, reduction of wear crater depth.
Morphology of the DIN 100Cr6 Case Hardened Steel after Plasma Nitrocarburizing Process

4. Conclusions

From the present study of the microstructure and tribological behavior of plasma nitrocarburized DIN 100Cr6 steel, the following can be concluded:

- The parameters studied in this thermochemical treatment, such as temperature and chemical composition of the gas mixture, affect the surface layer tribological properties and morphology.
- The nitrided samples have a compound layer which was composed only by the $\gamma'$-Fe$_4$N phase. For the nitrocarburized samples, the compound layer is a mixture of $\varepsilon$-Fe$_{2-3}$N and $\gamma'$-Fe$_4$N phases.
- The amount of each one of these phases is a function of the CH$_4$ concentration present in the nitrocarburizing atmosphere.
- The lowest wear rate was achieved for the samples that had been nitrocarburized using a gas mixture richer in CH$_4$, regardless of the process temperature.
- The wear mechanism presented in all nitrocarburized samples is the abrasive wear.

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