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# Scratch resistance of low-temperature plasma nitrided and carburized martensitic stainless steel

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ABSTRACT

Martensitic stainless steel is a potential material class for selection in some tribological systems, particularly those subjected to wear by hard particles and corrosion. To improve its mechanical resistance, without loss of corrosion performance, surface treatments such as low-temperature nitriding and carburizing have been systematically employed. In this context, this paper studied martensitic stainless steel samples subjected to different plasma-assisted treatments, in the case the plasma nitriding and plasma carburizing. The treatments were carried out at temperatures of 300, 350 or 400 °C, for different times, aiming to compare the scratch resistance of the treated surfaces. Specimens were initially characterized using X-Ray diffractometry, micro and nanohardness measurements. Scratch resistance was performed using the constant load mode for two levels, 8 and 15 N. All worn tracks were evaluated using optical interferometry, to get information about the widths and depths of track profiles. Worn surfaces were analysed using scanning electron microscope, revealing tensile cracks on the surface of nitrided samples. The friction coefficient and the wear resistance were analysed and related to the geometry of scratches, which was associated to the micro-mechanism of wear. Despite the high hardness and low friction coefficient achieved using nitriding treatment, the global performance of carburized samples could be considered as more suitable, because the carburized case significantly minimized the cracks formation. Therefore, plasma carburized martensitic stainless steel can be considered an adequate combination for corrosion environments subjected to wear.



## 1. Introduction

Martensitic stainless steels that present low-carbon contents are widely used in manufacturing machinery and hydraulic components such as turbines, pumps, valves and pipes [1,2]. For most applications, these parts are submitted to conditions where mechanical properties, beyond the wear resistance are essentials. Different surface modification techniques, such as carburizing, carbonitriding, nitriding, among others, have been employed to improve the tribological properties and mechanical resistance of stainless steels [3,4].

The treatments carried out at low temperatures, typically below 500 °C, in the case of martensitic steels, result in surface layers with the presence of metastable phases, where the introduction of a chemical element such as nitrogen or carbon by diffusion leads to formation of expanded phases in martensite and austenite [5,6]. Moreover, low temperatures treatments in stainless steels have been used to avoid any kind of second-phase precipitation, such as chromium nitride and/or carbide, avoiding losses in the corrosion resistance [7,8].

Despite the variety and particularities of investigations concerning the wear resistance of plasma nitrided [6,9] and carburized [10] of martensitic stainless steels, the use of similar conditions of treatment is relatively scarce [3,4], giving rise a difficult to perform a direct comparison among the performances of them.

In present work, the surface of a Fe–13%Cr–3%Ni–Mo alloy, comprising a martensitic stainless steel, was investigated aiming to determine its scratch resistance after different low-temperature plasma nitriding and carburizing have been applied.

## 2. Experimental procedure

### 2.1. Material and plasma treatments

Samples of Fe–13%Cr–3%Ni–Mo martensitic stainless steel were cut in dimensions of $20 \times 20 \times 10\ mm^3$. The average chemical

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**Table 1**
Typical chemical composition of the studied steel substrate for Fe–13%Cr–3%Ni–Mo alloy.

| Chemical composition (% in weight) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| % C | % Mn | % Si | % Cr | % Ni | % Mo | % P | % S | % Fe |
| 0.013 | 0.94 | 0.52 | 12.25 | 3.32 | 0.38 | 0.024 | 0.015 | Balance |

composition of the substrate is shown in Table 1 [11].

After cutting, the samples were ultrasonically cleaned in bath for 10 min using ether, followed by plasma cleaning.

The samples were plasma treated at the cathode, which was negatively biased at the voltage of 675 ± 15 V, using square waveform pulsed power supply. The power transferred to the plasma, and thus the sample treatment temperature control, was adjusted by varying the switched-on time, being the pulse period 240 μs. The sample temperature was measured by means of a chromel–alumel thermocouple (type K of 1.5 mm diameter), placed inside the sample support, which is inserted to a depth of 15 mm into the sample, in similar mode and plasma apparatus to those previously presented in [12]. The plasma nitriding treatment was performed at 300, 350 and 400 °C, for a time of 24 h (86.4 ks), and at the treatment temperature of 400 °C for times of 6, 12, and 24 h (21.6, 43.2, and 86.4 ks, respectively), at pressure of $4 \times 10^2$ Pa (3 Torr), with gas flow rate of $5.0 \times 10^{-6}$ $m^3$ $s^{-1}$ (300 sccm), for the gas mixture of 5 vol% $N_2$ + 95 vol% $H_2$). Before treatment, sample was plasma cleaned under $H_2$ electrical discharge at 200 °C, for 0.6 ks, at the same pressure specified for the treatment. On the other hand, the same nitriding parameters were used to the plasma carburizing treatment, except the gas flow rate, which was $6.7 \times 10^{-6}$ $m^3$ $s^{-1}$ (400 sccm), and the gas mixture flow, which was 0.995 (20 vol% Ar + 80 vol% $H_2$) + 0.005 (100 vol% $CH_4$).

### 2.2. Characterization of samples

Phases of the treated surfaces were determined by X-ray diffractometry (XRD), using Shimadzu XRD-6100 equipment and CuKα (l = 1.5418 A) radiation, for Bragg-Brentano (θ–2θ) configuration, current of 20 mA, voltage of 40 kV, with step of 0.02°$s^{-1}$, and for angle θ varying between 30 and 120°.

Thicknesses of nitrided and carburized layers were determined in a cross sectional view of samples, etched with Marble. They were measured using an optical microscope.

Superficial Vickers hardness was determined to evaluate the load bearing effect, conducted in a Mitutoyo HM 100 equipment, using loads of 50, 100, 200 e 300 gf and a dwell time of 15 s. Each average value of hardness corresponds to a series of 3 measurements.

The XP-MTS nanoindenter equipment was used to determine hardness of the treated surface. The nanoindentation technique carried out using loads up to 4 g (40 mN) and loading time of 10 s. Polished cross sections, with Ra of 0.05 μm, were exposed to indentation cycles, varying the positions at each 10 μm, up to 80 μm depth.

### 2.3. Scratch tests and worn surface analyses

Scratch tests were conducted using a tribometer UMT – 2 Multi-Specimen Test System, CETR. The applied loads were 8 and 15 N, corresponding to a contact pressure of 254.7 and 477.7 MPa, respectively. The selection of these loads followed a result obtained in preliminary tests using variable test mode, from 2 to 30 N, the same range used by Farokhzaded et al. [13] for plasma nitrided Ti-4Al-6V alloy. After that, a range of probable critical loads was identified for both set of samples, resulting in the choice of two levels. The tests were conducted with a Rockwell type diamond indenter with a radius of 0.2 mm without lubrication and a displacement speed of 0.017 mm/min. Average values of friction coefficient correspond to a series of three repetitions, being each scratch distant 2 mm from each other.

The geometry of scratches was analyzed using an optical interferometer - Talysurf CCI Lite. The sampling dimensions of each measurement were $0.8 \times 0.8$ $mm^2$ with a resolution of $1024 \times 1024$ points. The depths, widths and the pile-ups of scratches were calculated from the cross sections, according to Fig. 1. The average values correspond to a series of three measurements. To analyze the geometry of scratches the procedures suggested by ASTM G171 standard were followed [14]. Based on these measurements, the calculation of scratch hardness number ($H_S$) and abrasion factor (Fab) was possible, following the Eqs. (1) and (2), respectively:

$$H_S = 8P/\pi w^2 \quad (1)$$

$$F_{ab} = (area\ of\ groove - area\ of\ pile\text{-}ups / area\ of\ groove), \quad (2)$$

where $P$ is the normal force and $w$ is the scratch width. Further, a scanning electron microscope was used to observe the worn surfaces.

## 3. Results and discussion

### 3.1. Phases characterization

Fig. 2 shows XRD patterns of the studied surfaces subjected to the nitriding, and carburizing treatments. For all nitrided surfaces (Fig. 2a), results confirm the formation of nitrogen-expanded martensite and iron nitride phases. In addition, results also suggest that chromium nitride phase is present only in the sample nitrided at 400 °C-24 h, which is confirmed by the reflections of the CrN (311) peak. This result is worth to be emphasized, since chromium nitride formation is always related to the sensitization phenomena in stainless steels, thus decreasing the corrosion resistance of the treated surface. Similarly, for all carburized surfaces (Fig. 2b),

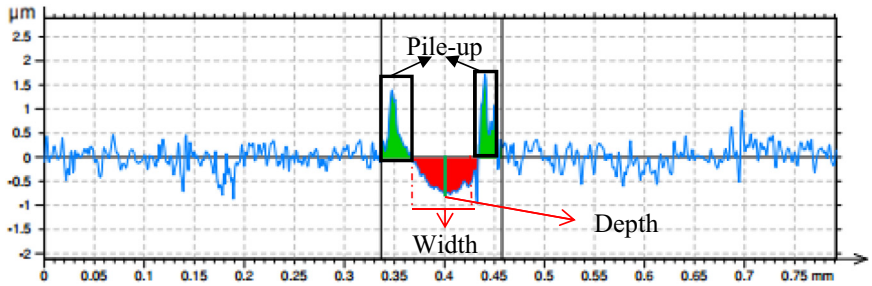


**Fig. 1.** Cross section illustration of a scratched sample, indicating the measurements of depth, width and pile-up of scratch.