PLASMA NITRIDING AND NITROCARBURIZING OF A SUPERMARTENSITIC STAINLESS STEEL

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Abstract: Supermartensitic stainless steels (SMSS) are a new generation of the classical 13% Cr martensitic steels, lower in carbon and with additional alloying of nickel and molybdenum offering better weldabilty and low temperature toughness. Several works have shown that plasma nitriding and nitrocarburizing of stainless steels at low temperatures produces a hard surface layer which results in increased wear resistance. In this work, SMSS samples were plasma nitrided and nitrocarburized at 400, 450 and 500°C. The plasma treated SMSS samples were characterized by means of optical microscopy, microhardness, X-ray diffraction and dry wear tests. The thickness of the produced layers increases as temperature is raised, for both plasma nitriding and nitrocarburizing. X-ray diffraction demonstrates that chromium nitrides content grow with temperature for nitriding and nitrocarburizing, that also showed increasing content of iron and chromium carbides with temperature. After plasma treating, it was found that the wear volume decreases for all temperatures and the wear resistance increased as treatment temperature was raised. The main wear mechanism observed for both treated and untreated samples was grooving abrasion.

Key words: Nitriding; Nitrocarburizing; X-ray diffraction; Wear.

1 INTRODUCTION

Supermartensitic stainless steels (SMSS) are a new generation of the classical 13% Cr martensitic steels, lower in carbon and with additional alloying of nickel and molybdenum offering better weldabilty and low temperature toughness. Martensitic stainless steels are often hardened by bulk heat treatment (quenching and tempering) however, further increases in surface hardness and wear resistance by surface engineering can improve the performance and extend the service life of a part[1,2].

Surface coatings are one of the most versatile ways to improve the performance of components with respect to wear and/or corrosion. Thermochemical surface engineering processes including nitriding, nitrocarburizing and carburizing have long been used to improve the surface properties stainless steels[3,4].

It is well known that when such treatments are performed in austenitic stainless steel at a temperature sufficiently low, a nitrogen expanded austenite, or S-phase can be produced[3,4]. Several attempts have been made to produce expanded phases on ferritic and martensitic stainless steels. Some studies have demonstrated the possibility of producing the "expanded martensite" on martensitic and precipitation hardening stainless steels[5-7] resulting in considerable improvements of wear properties[5]. However the SMSS's have not been systematically investigated so far. The purpose of this study is to evaluate the influence of treatment temperature on the morphology, microstructure, microhardness and wear resistance of a plasma nitrided and nitrocarburized SMSS samples.

2 MATERIALS AND METHODS

Initially samples with 20x30x3mm of UNS S41425 supermartensitic stainless steel (SMSS) were cut and then prepared by conventional metallographic techniques to obtain a polished surface. The chemical composition of the steel was (in wt%): C, 0.014; Mn, 0.93; Si, 0.38; Cr, 11.96; Ni, 7.00, Mo, 2.05; N, 0.045; Cu, 0.39; and Fe, balance.

Prior to the plasma treatments the samples were cleaned by argon sputtering (on work pressure and temperature of 50ºC less than the treatment temperature, for 30 min), inside the plasma chamber. Plasma nitriding (PN) and nitrocarburizing (PNC) were performed using the DC method with the following gas mixtures: 80 vol. % H_2 and 20 vol. % N_2, for nitriding and 77 vol. % H_2, 20 vol. % N_2 and 3 vol. % CH_4 for nitrocarburizing. The treatments were performed at a pressure of 500Pa during 5h at temperatures of 400, 450 and 500ºC.

Optical microscopy analyses were performed on the cross-section of the samples using a *Zeiss* microscope with the interference contrast technique on samples etched with *Villela* reagent. *Vickers* microhardness measurements were made on the surface of the treated samples using digital *Buehler* equipment with a load of 50gf and a dwell time of 10s. X-ray diffraction (XRD) patterns were obtained on the surface of the samples in a *Geigerflex Rigaku* equipment with a scanning angle from 30 to 100°. The tests were performed using copper radiation (Cu-Kα) and continuous scanning with a speed of $2°.min^{-1}$.

The wear tests were performed on a micro-wear machine with a fixed-ball configuration without the use of abrasives. The diameter of the ball was 25.4mm with rotational speed of 500rpm and load of 250g (2.5N). Consecutive wear scars with test times of 5, 10, 15 and 20min were produced to obtain the volume-loss curve. The removed volume (V) of each wear crater and its depth (h) were calculated according to the literature[8].

3 RESULTS AND DISCUSSION

Figure 1 shows optical micrographs from the cross-sections of plasma nitrided (Fig. 1a-1c) and nitrocarburized (Fig. 1d-1f) SMSS samples. The micrographs reveal continuous layers showing the martensitic matrix beneath each layer. The average thickness (e) of the produced layers for each condition of treatment was measured directly from the optical micrographs.

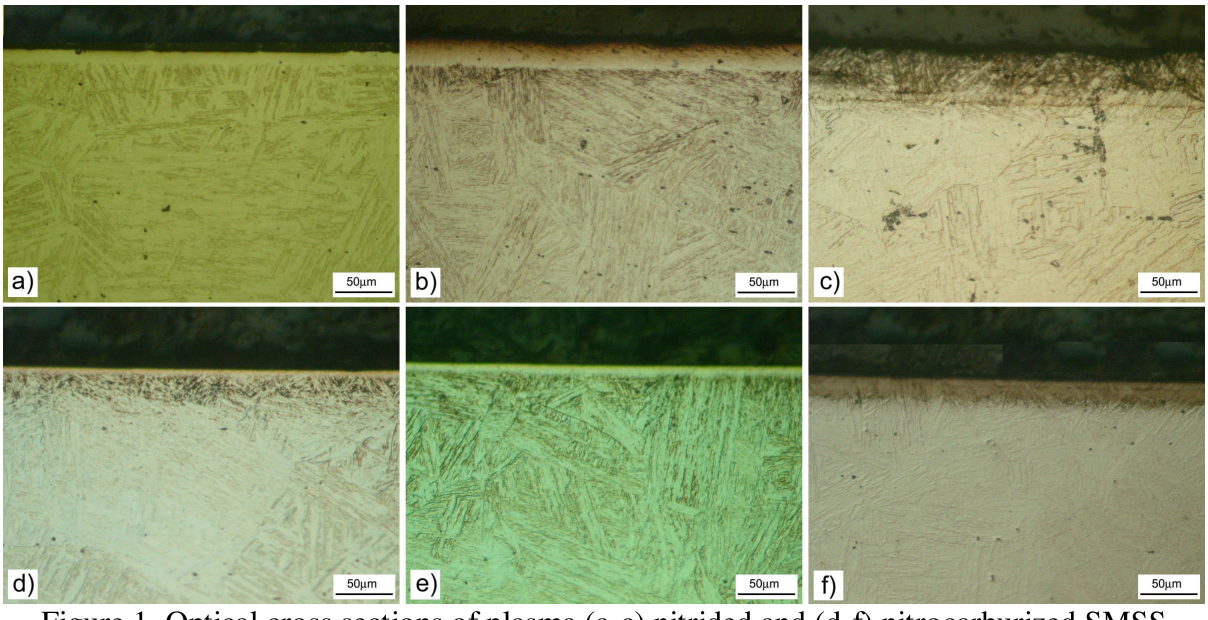

Figure 1, Optical cross sections of plasma (a-c) nitrided and (d-f) nitrocarburized SMSS samples at (a, d) 400ºC, (b, e) 450ºC and (c, f) 500ºC.

It can be seen from Fig. 1 that layer thickness is larger for nitriding at a given temperature which is due to nitrogen diffusion being faster than carbon in martensite. Thus, the addition of methane as a carbon source in nitrocaburizing retards layer growth. Also, layers produced at 500°C (Fig. 1c and 1e) yielded the appearance of a dark region on the optical micrograph after the etching process which can be ascribed to a reduction of the corrosion resistance of these layers.

Figure 2 depicts the XRD patterns of the untreated SMSS and the samples that were plasma nitrided (Fig. 2a) and nitrocrburized (Fig. 2b). The substrate pattern is shown in both set of lines for comparison purposes and it reveals strong diffraction lines consistent with Fe α and weaker lines related to Fe γ.

PN and PNC of the SMSS yielded distinct diffraction patterns. For nitriding, XRD analyses showed that there were no chromium nitride precipitation in the sample nitrided at 400°C, while chromium nitrides were formed during nitriding at 450°C, and the amount increased with increasing nitriding temperature to 500°C. For nitrocarburizing, the same tendency related to the presence of chromium nitrides was observed. However, an increasing amount of iron and chromium carbides due to the presence of the carbon in addition to the chromium nitrides was also observed.

Iron nitrides such as Fe_2N, Fe_3N and Fe_4N were also found on both nitrided and nitrocarburized surfaces although their amount diminishes as treatment temperature is increased. Since chromium has a high affinity with nitrogen, it is estimated that when the temperature is increased, chromium atoms acquire mobility and become readily bonded with the available nitrogen atoms causing a decrease on the iron nitrides content[4].

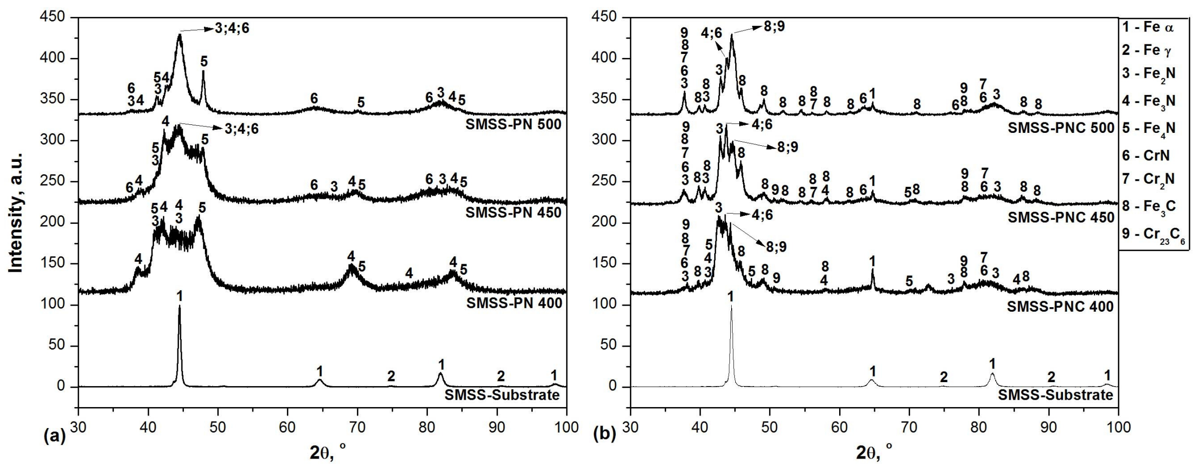

Figure 2, X-ray diffraction patterns of plasma (a) nitrided and (b) nitrocarburized SMSS samples at 400, 450 and 500ºC.

Thus, the differences in the XRD patterns of the nitrided and nitrocarburized SMSS samples can be mainly attributed to the presence of methane in the nitrocarburizing gas mixture which leads to carbide formation. The dark region observed in the micrographs of the layers produced at 500ºC (Fig. 1c and 1e) is probably related to the massive precipitation of carbides and/or nitrides, depending on the treatment, which can lead to a decrease of the corrosion resistance.

Figure 3 provides the results of volumetric wear loss versus running distance for the plasma nitrided (Fig. 3a) and nitrocarburized (Fig. 3b) SMSS samples; and the substrate itself. Both the plasma treated samples and the substrate showed a gradual volumetric wear with increasing running distance. The wear curves reveal that the wear volume decreased for all plasma treated samples relative to the wear of the substrate. The curve shapes for both PN and PNC treatments were similar showing that wear volume decreases with treatment temperature. Consequently, wear resistance increases with temperature.

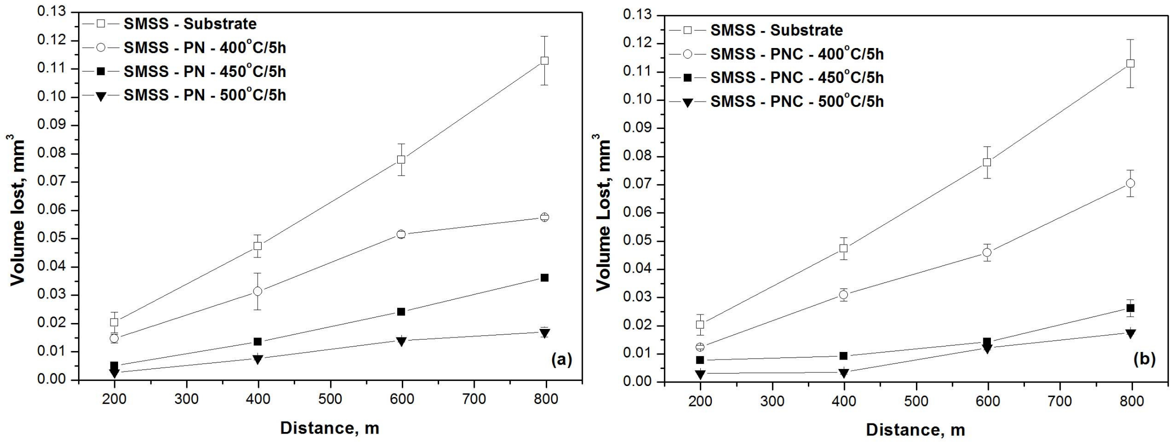

Figure 3, Wear volume loss curves of plasma (a) nitrided and (b) nitrocarburized SMSS samples.

Figure 4 shows the wear craters of the SMSS samples plasma nitrided at 400ºC (Fig. 4a), 450ºC (Fig. 4b) and 500ºC (Fig. 4c). The craters formed after 5min (200m) of wear testing were observed by optical microscopy and the black arrow on the figure indicates the direction of movement. Note that the width of the wear scars decrease from Fig. 4a to 4c as treatment temperature increases which shows the influence of the plasma treatment temperature on the wear process. The PNC treatment yielded similar craters and the same trend related to size.

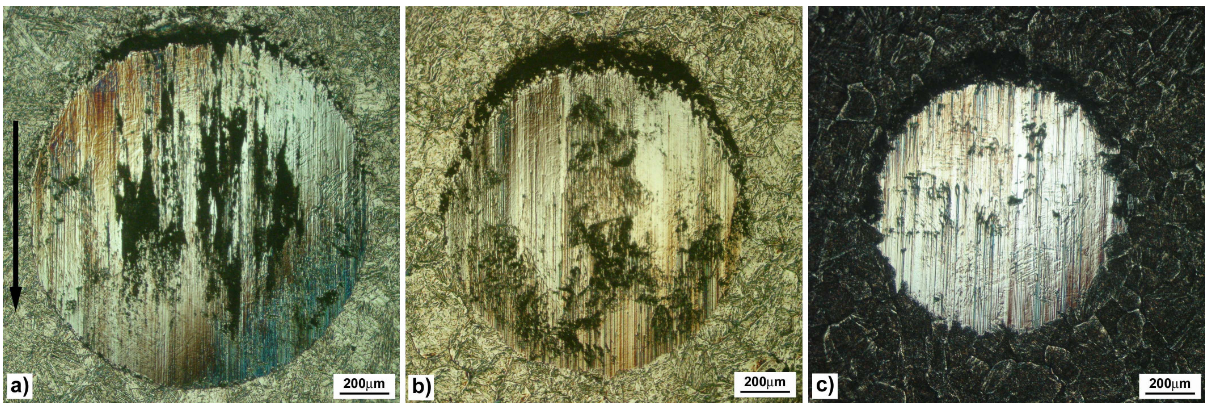

Figure 4, Wear craters of plasma nitrided SMSS samples at (a) 400ºC, (b) 450ºC and (b) 500ºC after 5min (200m) of testing.

Calculations of the of the wear depth for each crater shown in Fig. 4 indicates that the layer was perforated after 200m for the sample nitrided at 400°C. Therefore, the dark region of the wear scar in Fig. 4a is indeed the substrate. Internally, the wear craters show parallel ridges suggesting that the main active wear mechanism during wear testing of the treated and untreated SMSS samples was a grooving process (two-body abrasion).

Table 1 shows a compilation of the wear depths (h) after 800m, layer thickness (e) and surface hardness (H) of all PN and PNC layers. The wear processes for all plasma treated samples resulted in shallow wear depths for all treated samples when compared to the substrate. Tab. 1 shows that microhardness increases as temperature was increased for both nitriding and nitrocarburizing treatments. The hardness values probably increase due to a combined effect of layer thickness and massive nitride and/or carbide precipitation providing the layer with high penetration resistance.

Table 1 - Scar depth (h) after 20min (800m) of wear testing, layer thickness (e) and surface microhardness (H) of the plasma nitrided and nitrocarburized SMSS samples.

Sample	h, µm	e, µm	H, Hv
SMSS-Substrate	53±2	---	436±4
PN 400	38.0±0.3	11.6±0.6	1347±54
PN 450	30.2±0.5	21±1	1390±37
PN 500	21±1	38±2	1554±72
PNC 400	42±1	8±1	1273±34
PNC 450	26±1	10.0±0.9	1340±29
PNC 500	21.0±0.4	27±1	1475±39

Comparing the shape of the wear curves (Fig. 3) with the crater depth results of Tab. 1 shows that in the case of the samples treated at 400 and 450°C, the perforation of the layer occurred after 800m. Nevertheless, these samples supported the applied load resulting in low wear volume compared to the base material. The samples subjected to PN and PNC at 500°C did not undergo layer perforation resulting in greater wear resistance. Thus the results and observations above suggest that a harder layer results in a better wear performance.

4 CONCLUSIONS

From this work, it is concluded that plasma nitriding and nitrocarburizing treatment of the SMSS produced continuous layers in which the layer thickness increased as temperature increased. XRD experiments indicated that chromium nitride content increases with temperature for both treatments as iron nitride content decreases. Moreover the quantity of carbides increased with temperature for nitrocarburizing due to the presence of carbon.

The fixed-ball wear tests revealed that wear volume decreased for all plasma treated samples relative to the substrate and the wear resistance among the plasma treated samples increases with temperature for both nitriding and nitrocarburizing. The main active wear mechanism during the wear testing of the treated and untreated SMSS samples was two-body abrasion.

Acknowledgements

The authors acknowledge CAPES for the scholarship granted to F.A.P. Fernandes.

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