Plasma nitriding and nitrocarburising of a supermartensitic stainless steel

F. A. P. Fernandes¹, G. E. Totten², J. Gallego³ and L. C. Casteletti¹

Supermartensitic stainless steels (SMSSs) are a new generation of the classic 13%Cr martensitic steels, lower in carbon and with additional alloying of nickel and molybdenum offering better weldability and low temperature toughness. Several works have shown that plasma nitriding and nitrocarburising 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 nitrocarburised at 400, 450 and 500°C. The plasma treated SMSS samples were characterised by means of optical microscopy, microhardness, X-ray diffraction and dry wear tests. The thickness of the layers produced increases as temperature is raised, for both plasma nitriding and nitrocarburising. X-ray diffraction demonstrates that the chromium nitride content grows with temperature for nitriding and nitrocarburising, which 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 the treatment temperature was raised. The main wear mechanism observed for both treated and untreated samples was grooving abrasion.

Keywords: Nitriding, Nitrocarburising, X-ray diffraction, Wear

Introduction

Supermartensitic stainless steels (SMSSs) are a new generation of the classic 13%Cr martensitic steels, lower in carbon and with additional alloying of nickel and molybdenum offering better weldability 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, nitrocarburising and carburising 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 sufficiently low temperature, 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 steels⁵–⁷ resulting in considerable improvements in wear properties.³ However, the SMSSs 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 nitrocarburised SMSS samples.

Materials and methods

Initially, samples 20 × 30 × 3 mm of UNS S41425 SMSS were cut and then prepared by conventional metallographic techniques to obtain a polished surface. The chemical composition of the steel was: Fe–0.014C–0.93Mn–0.38Si–11.96Cr–7.00Ni–2.05Mo–0.045N–0.39Cu (wt-%).

Prior to the plasma treatments the samples were cleaned by argon sputtering (at the working pressure and a temperature 50°C less than the treatment temperature, for 30 min), inside the plasma chamber. Plasma nitriding (PN) and nitrocarburising (PNC) were performed using the DC method with the following gas mixtures: 80 vol.-%H₂ and 20 vol.-%N₂ for nitriding and 77 vol.-%H₂, 20 vol.-%N₂ and 3 vol.-%CH₄ for nitrocarburising. The treatments were performed at a pressure of 500 Pa for 5 h at temperatures of 400, 450 and 500°C.

Optical microscopy was performed on the cross-sections of the samples using a Zeiss microscope with the interference contrast technique on samples etched with Villela’s reagent. Vickers microhardness measurements
were made on the surface of the treated samples using digital Buehler equipment with a load of 50 gf and a dwell time of 10 s. X-ray diffraction (XRD) patterns were obtained from 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 $K_{\alpha}$) and continuous scanning with a speed of 2° min⁻¹.

Wear tests were performed using a microwear machine with a fixed ball configuration without the use of abrasives. The diameter of the ball was 25 ± 4 mm with a rotational speed of 500 rev min⁻¹ and load of 250 g (2.5 N). Consecutive wear scars with test times of 5, 10, 15 and 20 min 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

Results and discussion

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

It can be seen from Fig. 1 that the layer thickness is greater for nitriding at any given temperature which is due to nitrogen diffusion being faster than carbon in martensite. Thus, the addition of methane as a carbon source in nitrocarburising retards layer growth. Also, layers produced at 500°C (Fig. 1c and e) gave the appearance of a dark surface region under the optical micrograph after the etching process, to which can be ascribed a reduction in 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 nitrocarburised (Fig. 2b). The substrate pattern is shown in both set of lines for comparison purposes and it reveals strong diffraction lines consistent with Fe $\alpha$ and weaker lines related to Fe $\gamma$.

---

1 Optical cross-sections of plasma a–c nitrided and d–f nitrocarburised SMSS samples at a, d 400°C; b, e 450°C; and c, f 500°C

2 X-ray diffraction patterns of plasma a nitrided and b nitrocarburised SMSS samples at 400, 450 and 500°C
PN and PNC of the SMSS yielded distinct diffraction patterns. For nitriding, XRD analyses showed that there was 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 nitrocarburising, 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$_2$N, Fe$_3$N and Fe$_4$N were also found on both nitrided and nitrocarburised surfaces although their amount diminishes as the treatment temperature is increased. Since chromium has a high affinity for nitrogen, it is thought that when the temperature is increased, chromium atoms acquire mobility and become readily bonded with the available nitrogen atoms causing a decrease in the iron nitride content.  

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

Figure 3 provides the results of volumetric wear loss versus running distance for the plasma nitrided (Fig. 3a) and nitrocarburised (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 is less 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 4a–c shows the wear craters of the SMSS samples plasma nitrided at 400, 450 and 500°C respectively. The craters formed after 5 min (200 m) of wear testing were observed by optical microscopy and the black arrow on the figure indicates the direction of movement. Note that the diameter of the wear scars decrease from Fig. 4a to c 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 relating to size.

Calculations of the wear depth for each crater shown in Fig. 4 indicate that the surface layer was penetrated after 200 m for the sample nitrided at 400°C. Therefore, the dark region of the wear scar in Fig. 4a is the substrate. Internally, the wear craters show parallel ridges suggesting that the main active wear mechanism
Table 1 Wear depth (h) after 20 min (800 m) of wear testing, layer thickness (e) and surface microhardness (H) of the plasma nitrided and nitrocarburised SMSS samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>h/µm</th>
<th>e/µm</th>
<th>H/HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMSS-substrate</td>
<td>53±2</td>
<td>...</td>
<td>436±4</td>
</tr>
<tr>
<td>PN 400</td>
<td>38.0±0.3</td>
<td>11.6±0.6</td>
<td>1347±54</td>
</tr>
<tr>
<td>PN 450</td>
<td>30.2±0.5</td>
<td>21±1</td>
<td>1390±37</td>
</tr>
<tr>
<td>PN 500</td>
<td>21±1</td>
<td>28±2</td>
<td>1554±72</td>
</tr>
<tr>
<td>PNC 400</td>
<td>42±1</td>
<td>8±1</td>
<td>1273±34</td>
</tr>
<tr>
<td>PNC 450</td>
<td>26±1</td>
<td>10.0±0.9</td>
<td>1340±29</td>
</tr>
<tr>
<td>PNC 500</td>
<td>21.0±0.4</td>
<td>27±1</td>
<td>1475±39</td>
</tr>
</tbody>
</table>

Conclusions

From this work, it is concluded that plasma nitriding and nitrocarburising treatment of the SMSS produced continuous layers in which the layer thickness increased as the processing temperature increased. X-ray diffraction results indicated that chromium nitride content increases with processing temperature for both treatments as iron nitride content decreases. Moreover, the quantity of carbides increases with processing temperature for nitrocarburising 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 processing temperature for both nitriding and nitrocarburising. The main active wear mechanism during the wear testing of both the treated and untreated SMSS samples was two-body abrasion.

Acknowledgement

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

References