Correlations between microstructure and surface properties
in a high nitrogen martensitic stainless steel

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Abstract

Nitrided and tempered AISI 410S stainless steel was tested under corrosion–erosion conditions and compared to conventional AISI 420 martensitic stainless steel. The corrosion–erosion resistance of the nitrided specimens was higher than that of the AISI 420 steel when tempered at 200 °C, but it decreased with tempering temperature in the range between 200 and 600 °C. The higher corrosion–erosion resistance of the high-nitrogen steel was credited to a more homogeneous distribution of chromium in martensite and a lower number of coarse second-phase particles, especially for tempering temperatures below 550 °C. The hexagonal $\epsilon$-nitride was identified in specimens tempered at 200 °C, while finely distributed cubic CrN nitrides were observed in specimens tempered between 400 and 600 °C. Hexagonal $\text{Cr}_2\text{N}$ nitrides were observed at 550 and 600 °C. These coarse, high-chromium precipitates were responsible for the drop in corrosion resistance of the nitrided specimens.

Keywords: Nitrogen in steels; Surface alloying; Corrosion–erosion; Analytical electron microscopy; Precipitation

1. Introduction

The microstructural changes during tempering of high nitrogen martensitic stainless steels have been recently studied, and sequences of phase transformations in the range 100–700 °C have been proposed based on TEM analyses, dilatometric tests and differential-thermal measurements [1–3]. However, some discrepancies are observed among these studies as a consequence of both variations in the chemical composition of the alloys studied and the application of different experimental techniques.

Although there is agreement concerning precipitation of hexagonal $\epsilon$-nitride $(\text{Fe,Cr})_2\text{N}_{1-x}$ at low temperatures (usually below 200 °C), the sequence of reactions occurring at higher temperatures has not been uniquely established. A classical approach to the problem [4] indicates that the $\epsilon$-nitride can accept higher amounts of nitrogen when the temperature is increased, up to the point when the stable $\text{Cr}_2\text{N}$, also hexagonal, is formed.

On the other hand, the occurrence of a meta-
stable orthorhombic \((\text{Fe},\text{Cr})_2\text{N}\) nitride for tempering temperatures above 300 °C has been reported in Fe–15%Cr–1%Mo–0.6%N alloys [1]. According to Jack and Jack [4], this nitride could be formed as a consequence of the ordering of nitrogen atoms in the octahedral interstices of the \(\varepsilon\)-nitride. In addition, some studies on Fe–Cr–N alloys containing Nb, V or Mn reported the existence of cubic MN-type nitrides in the range of temperatures between 300 and 700 °C [2,3], which could form through a different set of reactions.

It is worth noticing that nitrides with different crystal structure, morphology and chemical composition can coexist over a wide range of temperatures in Fe–Cr–N alloys, and each of them affects the mechanical and corrosion properties of the alloy differently. A fine distribution of coherent nitrides in martensite could be responsible for the superior secondary hardening observed in the range 450–550 °C of Fe–Cr–N and Fe–Cr–Mo–N alloys, when compared to that observed in Fe–Cr–C and Fe–Cr–Mo–C alloys [5]. Conversely, the formation of coarse Cr-rich hexagonal \(\text{Cr}_2\text{N}\) nitrides has been typically associated with reduction in corrosion resistance of austenitic steels, due to chromium depletion in large areas of the matrix around the precipitates [6].

As a consequence of the small size of some of the nitrides and the screening effect caused by the high dislocation density, the microstructure characterization of high-nitrogen martensitic stainless steels demands the use of microdiffraction techniques and high-resolution imaging. Moreover, the chemical characterization of the precipitates is particularly difficult because it is almost impossible to avoid the effect of the matrix when EDX measurements are performed. Despite all these limitations, consistent results can be obtained when data from diffraction, imaging and localized chemical analysis are brought together.

The comprehensive study of the microstructure of Fe–Cr–N alloys has become increasingly important due to their potential engineering applications [7–9]. In contrast to the conventional martensitic stainless steels, these materials can combine elevated hardness and wear resistance with good corrosion properties in several environments [10,11]. In previous works [12,13], the corrosion–erosion behavior and polarization response of Fe–Cr–N alloys were compared to those of conventional martensitic stainless steels (Fe–Cr–C alloys), and it was found that substitution of carbon by nitrogen effectively improved the resistance of the surface to the synergistic action of corrosion and wear.

In this work, a detailed study of the microstructure of a wide range of composition nitrided and tempered AISI 410S stainless steel samples was carried out with the aim of understanding their behavior under corrosion–erosion conditions. Conventional AISI 420 stainless steel samples were also analyzed for comparison purposes.

### 2. Experimental

High-nitrogen martensitic stainless steels were produced through gas nitriding of AISI 410S samples at temperatures between 1273 and 1473 K (high-temperature nitriding) and \(\text{N}_2\) pressures between 0.1 and 0.25 MPa for 6 h, according to a procedure described in previous work [14]. The nitriding conditions were selected to obtain precipitate-free martensitic cases with interstitial content at the surface comparable to that of the conventional AISI 420 stainless steel. The chemical composition at the surface of the studied materials is given in Table 1.

After nitriding, the specimens were direct-quenched in oil and tempered at temperatures between 200 and 600 °C for 1 h. Quenched and tempered AISI 420 specimens were used for comparison purposes. A temperature of 1273 K was selected for austenitizing these samples, and the tempering conditions were similar to those used for the high nitrogen specimens.

<table>
<thead>
<tr>
<th>Material</th>
<th>Cr</th>
<th>N</th>
<th>C</th>
<th>Si</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrided AISI 410S</td>
<td>13.00</td>
<td>0.42</td>
<td>0.03</td>
<td>0.36</td>
<td>Balance</td>
</tr>
<tr>
<td>AISI 420</td>
<td>12.30</td>
<td>–</td>
<td>0.37</td>
<td>0.24</td>
<td>Balance</td>
</tr>
</tbody>
</table>
2.1. Corrosion–erosion tests

Corrosion–erosion tests were performed with a test machine described in previous works [12,13]. Substitute ocean water (ASTM D 1141-90 Standard) and quartz particles with mean diameter between 0.3 and 0.5 mm constituted the slurry used in the tests. The pH of the slurry was controlled by NaOH addition to a value of 8.2 ± 0.1 in all experiments. The setup allowed the adjustment of mean impact angles of 45 or 90° over the surface of the specimens, with an approximate impingement velocity of 3.5 m/s.

Mass loss was periodically measured during the 96 h testing period. The wear results were normalized in terms of specific mass loss, \( \Phi \), as defined in Eq. (1):

\[
\Phi = \frac{\Delta W}{S}
\]

where \( \Delta W \) is the cumulative mass loss expressed in gram (g) and \( S \) is the geometrical exposed surface, in square meters (m²). The temperature of the slurry was periodically measured during the experiments, and after each cycle of the 96-h test, the container was emptied and refilled with fresh slurry. In order to evaluate the individual effects of corrosion and erosion, non-corrosive erosion tests were carried out replacing substitute ocean water by tap water, while solid-free impingement tests were performed in quartz-free substitute ocean water. These two tests were performed only with specimens tempered at 200 °C.

2.2. Microstructure and localized chemical composition

Both thin foils and carbon extraction replicas were prepared for TEM/STEM analysis. Slices 250–300 µm in thickness were cut from the surface of the specimens by using a precision diamond saw, then mechanically ground to 60–80 µm and polished with 3 µm-diamond and 1 µm-Al₂O₃ water-based slurries. Discs 3 mm in diameter were cut from these slices using a mechanical punch and dimpled to 10–15 µm thickness. The final thinning of the specimens was carried out mostly by electro polishing in (10% perchloric acid + 90% acetic acid) solution at 25 °C. Nevertheless, all the samples used for EDX analysis were ion milled (instead of electro polished) using a double-gun precision ion polishing system (PIPS), operating at 4 keV with impact angles of 4°. Carbon extraction replicas were obtained from bulk specimens after chemical etching with Kalling’s reagent for 3–5 min. Copper–palladium 100-mesh grids were used for supporting the carbon films.

All the specimens were analyzed in a JEOL 2000FX TEM, with a LaB₆ filament operating at 200 kV. SAD diffraction patterns were obtained using an aperture that covered an area of 40 nm in the specimen when observed at a 200 000× magnification. The camera length of the microscope was calibrated using the ring patterns produced by a pure gold powder standard. Qualitative EDX microanalyses were carried out by using an ultrathin window Si (Li) detector attached to the column of the microscope at an angle of 40°.

High-resolution imaging and quantitative EDX microanalyses were performed in a VG HB603 FEG-STEM, operating at 300 kV. A windowless Si (Li) detector was used, with angular aperture of 0.30 sr and takeoff angle of 40°. The beam current was between 0.45 and 0.55 nA for all the measurements. The acquisition rate for compositional mapping was 200 ms/pixel, and the spatial resolution was estimated at 1.5 nm [15].

3. Results and discussion

3.1. Corrosion–erosion tests

Fig. 1 shows the specific mass loss \( \Phi \) for AISI 420 and nitrided AISI 410S samples after corrosion–erosion tests in substitute ocean water containing quartz particles, as a function of testing time, impact angle and tempering temperature. The total specific mass loss for the nitrided steel increased with tempering temperature in the 200–600 °C range, although the shape of the time-variation curves was very similar for all the conditions studied. The reduction in the slope of the curves for longer times was mainly associated with deterioration of the quartz particles, since they can break or get smoothened as a consequence of repeated impacts against the specimen surface or...
Each other. This effect has been shown previously for similar erosion conditions [16]. The mass losses of the nitrided samples were higher under normal impact than in oblique incidence, but the maximum values measured in each case were considerably lower than those of the AISI 420 specimens.

Fig. 2 shows the effect of synergism between corrosion and erosion on the total specific mass loss after 96-h tests, for nitrided AISI 410S and conventional AISI 420 specimens tempered at 200 °C. It can be seen that the synergistic effects were considerably greater in the Fe–Cr–C alloy (AISI 420) than in the Fe–Cr–N alloy. Analysis of the worn surfaces indicated intergranular corrosion and spalling of hard particles in the microstructure as the most important mechanisms of mass removal in the 420 stainless steel. In the nitrided AISI 410S steel, on the other hand, no evidences of these mechanisms were observed [12].

The large differences observed between the nitrided and conventional steels tempered at 200 °C can be related to the mechanical properties, chemical composition and microstructure of the specimens. In particular, the hardness of the surface is commonly used as a first-approach parameter to understand the results observed in standard wear tests. Nevertheless, since in the experiments carried out in this work the materials tempered at 200 °C had comparable surface hardness at the beginning of the tests (AISI 420 = 47 HRC, nitrided AISI 410S = 50 HRC) this was not considered a substantial factor.

Regarding the mean chemical composition of the specimens, the difference in chromium content of the steels (13 wt% in AISI 410S vs. 12.3 wt% in AISI 420) also does not appear to be significant for explaining the huge differences in corrosion—
erosion resistance in the tests. Furthermore, what could be really considered a crucial factor affecting corrosion resistance is the presence of sharp gradients in chromium concentration in the matrix, which have been observed before in sensitized austenitic stainless steels [17].

At this point, detailed analysis of the microstructure becomes a decisive task to understand the differences observed in corrosion–erosion tests, not only between the nitried and conventional steels, but also among the nitried steels tempered at different temperatures.

3.2. Microstructure and localized chemical composition

Fig. 3 shows the typical microstructure of the AISI 410S after high-temperature nitriding followed by oil quenching. The nitriding conditions (temperature and N₂ pressure) were such that the microstructure of the as-quenched specimen was composed only of martensite and retained austenite. It can be seen in Fig. 3(b) that some regions have a high dislocation density while in some other areas twins were formed. This configuration has been observed previously in several Fe–Cr–N and Fe–Cr–Mo–N alloys [18]. The analysis of a number of diffraction patterns led to the following lattice parameters for martensite: \( a = 0.286 \, \text{nm} \), \( b = 0.289 \, \text{nm} \) (\( c/a = 1.013 \)), which are very close to the expected values for Fe–N martensite containing 0.4 wt% N (\( c/a = 1.0139 \)) [4].

Depending on the tempering temperature, three different nitrides were identified in the nitried steel: hexagonal \( \varepsilon-(\text{Fe,Cr})_2\text{N}_{1-x} \), face-centered cubic CrN, and hexagonal \( \text{Cr}_2\text{N} \). Fig. 4 shows the experimental and calculated diffraction patterns from a small region inside a martensite lath in a specimen tempered at 200 °C. The aspect of martensite in this specimen is shown in Fig. 4(c). Two arrays of points can be identified in the diffraction pattern: the brighter spots correspond to the reflections from the martensitic matrix in a direction close to the \( B_M = [0 1 2] \) zone axis, while the fainter spots (closer to the transmitted beam) correspond to a direction close to \( B_\varepsilon = [0 0 0 1] \) in the \( \varepsilon \) nitride.

Calculations made on the diffraction patterns provided the values of the lattice parameters for the \( \varepsilon-(\text{Fe,Cr})_2\text{N}_{1-x} \) nitride shown in Table 2, which are consistent with those reported in the literature [1,4]. The differences between the calculated values and those from the literature arise mainly from the difficulty in obtaining the diffraction pat-

Fig. 3. Microstructure of high-temperature nitried AISI 410S steel. a) SEM micrograph showing the general aspect of martensite, b) Bright-Field TEM image showing regions with high density of dislocations (1) and twinned areas (2). The diffraction pattern shown was taken from one of the regions marked 1.
Fig. 4. a) Experimental and b) calculated diffraction patterns including the reflections from the martensitic matrix and from the precipitated ε-nitride; c) Bright-Field TEM micrograph of martensite, showing twins and areas with a high density of dislocations; d) Combined stereographic projection showing the Jack orientation relationship $^4 [011]_M // [0001]_N$, Nitrided AISI 410S stainless steel tempered at 200 °C.

Table 2
Lattice parameters and relative concentrations of Cr and Fe of nitrides identified in nitrided AISI 410S steel after tempering at temperatures between 200 and 600 °C. The chemical analyses were performed on carbon extraction replicas.

<table>
<thead>
<tr>
<th>Nitride type</th>
<th>Lattice parameters (nm)</th>
<th>Tempering temperature (°C)</th>
<th>Mean $C_{Cr}/C_{Fe}$ from EDX data*</th>
</tr>
</thead>
<tbody>
<tr>
<td>ε-(Fe,Cr)$<em>2$N$</em>{1-x}$</td>
<td>$a = 0.260 \pm 0.03$</td>
<td>200</td>
<td>N.A.</td>
</tr>
<tr>
<td></td>
<td>$c = 0.446 \pm 0.03$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CrN</td>
<td>$a = 0.409 \pm 0.01$</td>
<td>400</td>
<td>2.5–3.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500, 550, 600</td>
<td>16–22</td>
</tr>
<tr>
<td>Cr$_2$N</td>
<td>$a = 0.4685 \pm 0.01$</td>
<td>550, 600</td>
<td>40–50</td>
</tr>
<tr>
<td></td>
<td>$c = 0.4306 \pm 0.01$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

N.A. = Not analyzed.

* Calculated according to the Cliff–Lorimer equation, with $K_{CrFe} = 0.89 \pm 0.04$. 
tern under the exact orientation relationship established by Jack and Jack [4], namely \([0 1 1]_M// [0 0 0 1]_e\), which is represented in the stereographic projection of Fig. 4(d). In fact, the diffraction pattern shown in Fig. 4(a) was obtained with the electron beam in a direction between \([0 1 1]_M\) and \([0 1 2]_M\).

Abundant precipitation of cubic CrN nitrides was observed in specimens tempered between 500 and 600 °C, and smaller amounts were also present in specimens tempered at 400 °C. These nitrides were found at the martensite lath interfaces and also formed a very fine structure inside the laths.

In the specimens tempered at 550 and 600 °C, hexagonal Cr\(_2\)N nitrides precipitated together with the cubic CrN. The lattice parameters of the CrN and Cr\(_2\)N-type nitrides were computed from diffraction patterns of extraction replica, and the results are given in Table 2.

Fig. 5 shows a typical ring diffraction pattern obtained from extraction replica of samples tempered at 500 and 600 °C. Only small cubic CrN nitrides were detected in the specimens tempered at 500 °C, with a mean size between 5 and 20 nm (Fig. 5(a,b)). On the other hand, a high volume fraction of both cubic and hexagonal nitrides was

![Fig. 5. Typical diffraction patterns and bright-field TEM images of extraction replicas from nitried AISI 410S specimens tempered at 500°C (a, b) and 600 °C (c, d).](image-url)
observed in the specimens tempered at 600 °C, as shown in Fig. 5(c,d). Most of the plate-like precipitates in Fig. 5(d) are CrN nitrides, while the Cr₂N precipitates are rounded and located preferentially at the grain boundaries. In the specimens tempered at 400 °C, some of the rings matched the fcc structure mentioned above, but some additional rings seemed to correspond to an orthorhombic structure. The calculated lattice parameters, however, were different from those reported by Berns et al. [1] in Fe–15%Cr–1%Mo–N alloys. As a complete sequence of rings was not observed for this structure, only the fcc-type precipitates were included in Table 2 for the tempering temperature of 400 °C.

Fig. 6 shows typical TEM and STEM micrographs from a nitrided AISI 410S specimen tempered at 550 °C, in which both CrN and Cr₂N precipitates were identified. They form preferentially at the interface between martensite laths. Fig. 7 shows the Cr and Fe distributions in the same specimen, in a region containing CrN nitrides. A fine dispersion of small precipitates inside the grain and coarse particles at the boundaries between martensite laths can be seen.

EDX point measurements for CrN and Cr₂N nitrides are shown in Fig. 8, together with typical EDX spectra from the matrix in a region far from the nitrides. The effect of the matrix in the EDX spectra of the nitrides can be confirmed by comparing the spectra of Fig. 8 with those of Fig. 9, which were obtained from carbon extraction replicas. The results from the replicas showed that, although the chromium content of the CrN nitrides is effectively higher than that of the Cr₂N particles, the actual \( \frac{C_{Cr}}{C_{Fe}} \) relationship was not obtained when the spectra were taken from thin foils.

3.3. AISI 420 stainless steel

Coarse M₂₃C₆-type carbides were observed in the AISI 420 specimens quenched and tempered at 200 °C, as can be seen in Fig. 10. These precipitates are responsible for large chromium depletion in the metallic matrix, as shown in the compositional STEM maps of Fig. 11. The size of the chromium-depleted areas was circa 250 nm, which is about 10 times greater than that measured in the nitrided AISI 410S stainless steel. A lattice parameter of 0.99 ± 0.01 nm was calculated from diffraction patterns taken both from extraction replicas and thin foils.

The amount of undissolved carbides in the AISI 420 stainless steel could be reduced by increasing the austenitizing temperature, but this procedure usually leads to undesirable grain growth and nega-
Fig. 7. Cr and Fe distribution in nitrided AISI 410S, tempered at 550 °C for 1 h. EDX windowless Si (Li) detector, STEM-300 kV, probe size 1.5 nm, beam current 0.5 nA. The profiles were taken along the line indicated in the $C_{\text{Cr}}/C_{\text{Fe}}$ map.

Fig. 8. EDX spectra of hexagonal and cubic nitrides, taken from a thin foil prepared by Ion milling. Nitrided AISI 410S, tempered at 550 °C for 1 h.
3.4. Relation between surface properties and microstructure

The variation of the total mass loss after 96-h tests as a function of tempering temperature is shown in Fig. 12 for the nitried AISI 410S and conventional AISI 420 stainless steels. The nitried steel is considerably better than the AISI 420 when tempered at 200 or 400 °C, and both steels are roughly equivalent tempered at 600 °C.

As chromium is evenly distributed in the matrix of the nitried specimens tempered at 200 °C, the microstructure does not present preferential points for pitting or intergranular corrosion. Additionally, extensive mechanical damage is prevented because the hardness of the matrix is high enough to reduce cutting by the action of quartz particles. When the tempering temperature is increased to 400 °C, precipitation of cubic CrN nitrides promotes some chromium depletion in the matrix, but the effect is not significant due to the small size of the precipitates. This fact is also responsible for preventing wear by brittle fracture mechanisms (spalling), since the precipitates are too small to be broken as a result of the impact of the quartz particles. Furthermore, an increase in hardness is observed as a consequence of the fine dispersion of nitrides,
Fig. 11. Cr and Fe distribution around $\text{M}_2\text{C}_6$ precipitates in quenched and 200 °C-tempered AISI 420 martensitic stainless steel.

Fig. 12. Specific mass loss $\Phi$ as a function of the tempering temperature. Corrosion-erosion tests in slurry composed of substitute ocean water and quartz particles.

and this effect is more pronounced for tempering temperatures between 450 and 550 °C [5].

The specimens tempered at 600 °C, on the other hand, showed larger Cr-depleted areas (although not as large as those observed in the AISI 420 steel) and relatively low hardness (32 HRC) as a result of profuse precipitation and coarsening of $\text{Cr}_2\text{N}$ nitrides, as well as of recovery effects in the matrix. Nevertheless, polarization tests have shown that the prejudicial effects of this precipitation behavior are more accentuated on generalized than in localized corrosion [13], which can be an indication that the Cr gradients in the matrix are not too pronounced.

Regarding the AISI 420 stainless steel, synergetic effects between brittle fracture of $\text{M}_2\text{C}_6$ precipitates and intergranular corrosion caused high mass losses, specially for tempering temperatures of 200 and 400 °C. Increasing tempering temperature had a beneficial effect on corrosion resistance due to some homogenization of the chromium distribution in the matrix, even though new Fe$_3$C precipitates are expected to be formed above 250 °C [19]. On the other hand, wear marks associated with spalling were observed in all the AISI 420 specimens, which indicates that the incidence of this mechanism was not affected by the tempering temperature.

4. Conclusions

- The corrosion–erosion resistance of nitrided AISI 410S stainless steel containing 0.42 wt%
N at the surface decreased with tempering temperature in the range 200–600 °C, mainly as a consequence of precipitation of cubic CrN nitrides between 400 and 600 °C and hexagonal Cr$_2$N nitrides at 550 and 600 °C. Precipitation of hexagonal ε-nitrides at 200 °C did not affect the surface properties significantly.

- Finely dispersed cubic CrN nitrides were observed in nitrided specimens tempered between 500 and 600 °C, with a mean size between 5 and 20 nm. These precipitates were located both inside the grains and at the interfaces between martensite laths.
- Coarse, hexagonal Cr$_2$N nitrides were observed in specimens tempered at 550 and 600 °C preferentially at the lath boundaries. The substitution of chromium by iron in these precipitates was not significant.
- The corrosion–erosion resistance of the nitrided steel was superior to that of conventional AISI 420 for tempering temperatures of 200 and 400 °C. The main reason for this difference was attributed to the occurrence of large Cr-depleted areas around M$_{23}$C$_6$-type precipitates in the conventional steel. After tempering at 600 °C, both steels showed similar surface properties.

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