Improvement of Corrosion-Erosion Resistance of Martensitic Stainless Steels by Nitrogen Addition at High Temperature

A. Toroa, D. K. Tanakab, A. Sinitorab, A. P. Tschiptschina

aMetallurgical and Materials Engineering Department – University of São Paulo
bMechanical Engineering Department – University of São Paulo
Av. Prof. Mello Moraes 2463, CEP 05508-900, São Paulo / Brazil

Abstract

AISI 410S (13%Cr-0.08%C max.) stainless steel specimens were nitrided at 1473 K under 0.25 MPa high purity nitrogen atmosphere, and then oil quenched and tempered at 473 K. After this treatment, 2 mm-depth martensitic cases with 0.52 wt% N at the surface were obtained, the nitrogen content at the core being 0.035 wt%. Slurry wear tests were performed by placing the specimens in a stainless steel vessel containing substitute ocean water (ASTM D1141 Standard) and quartz particles with 0.3-0.5 mm diameter. The particle impact velocity, pH of solution, impact angles and solid content of the slurry were controlled. The slurry temperature, mass losses, surface damages and microstructure changes were periodically monitored during the 96 hours tests. Quenched and tempered AISI 410 and AISI 420 stainless steels were used as comparison materials.

The erosion-corrosion resistance of the nitrided and 473 K tempered AISI 410S steel was better than that of the AISI 410 and AISI 420 steels. This behavior was primarily due to the better corrosion resistance of the nitrided alloy, measured by potentiodynamic method. Scanning Electron Microscopy showed that intergranular corrosion of the AISI 410 and AISI 420 alloys was an important cause of mass loss, while it was not observed in the nitrided specimens.

Keywords: Nitrogen addition to steels; Corrosion-erosion resistance; Slurry wear

1. Introduction

A wide variety of techniques including alloying, coating deposition and thermo-chemical treating have been used to improve stainless steels' corrosion-wear resistance. Guenbour et al1 studied the influence of alloying elements in corrosion-abrasion of stainless steels in phosphoric acids containing chloride ions and SiC particles. Hodgkiess et al2 used a cermet coating material thermally sprayed onto stainless steel discs to enhance the resistance to corrosion-erosion in saline solution with silica particles. Berns et al3 improved the corrosion resistance of near net shape components for petrochemical industry by nitrogen addition in solid state. Synergism between corrosion and wear is extremely important for a wide range of applications regarding the use of stainless steels.

It has been established that nitrogen improves the pitting corrosion resistance of stainless steels4,5,6, although the chemical and/or electrochemical mechanisms that explain this effect are not clearly established. Conversely, experimental results concerning the effect of nitrogen alloying on generalized corrosion resistance are, in many cases, contradictory5,7. The beneficial effect of nitrogen on erosion resistance is commonly associated to solid solution hardening and second phase precipitation; hard chromium nitrides and carbonitrides provide good abrasion wear
resistance, but in some cases the corrosion resistance is seriously reduced due to chromium depletion of metallic matrix. Three main routes are commonly used for obtaining high nitrogen steels: high-pressure melting, powder metallurgy and solid-state alloying. Melting under pressure is recommended for large-scale fabrication but it requires complex and costly equipment; powder metallurgy requires a hot isostatic pressing stage to obtain full-density components. Solid-state alloying allows changing the surface properties of several materials with minor modification of bulk properties. When dealing with wear and corrosion, solid state alloying is one of the most suitable processes due to reduced costs and simplicity.

The aim of this work is to study the effect of nitrogen solid state alloying on the corrosion-erosion resistance of a martensitic stainless steel tested in seawater-quartz slurry.

2. Experimental Procedure

The chemical composition of the stainless steels used in this investigation is shown in Table 1.

<table>
<thead>
<tr>
<th>Steel</th>
<th>Cr</th>
<th>C</th>
<th>Ni</th>
<th>Mn</th>
<th>Si</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 410S</td>
<td>13.0</td>
<td>0.07</td>
<td>0.20</td>
<td>0.38</td>
<td>0.36</td>
<td>0.035</td>
</tr>
<tr>
<td>AISI 410</td>
<td>11.5</td>
<td>0.13</td>
<td>0.20</td>
<td>0.60</td>
<td>0.36</td>
<td>0.015</td>
</tr>
<tr>
<td>AISI 420</td>
<td>12.4</td>
<td>0.37</td>
<td>0.75</td>
<td>0.50</td>
<td>0.24</td>
<td>0.018</td>
</tr>
</tbody>
</table>

2.1. High temperature nitriding of AISI 410S steel and heat treatments

AISI 410S steel was gas nitrided in an experimental setup described in a previous work. The specimens were placed in a tubular furnace and heated up to 1,473 K under 10⁻³ Torr vacuum during 1 hour. High purity nitrogen was introduced in the furnace and the system was maintained at 0.25 MPa during 6 hours. At the end of the treatment the specimens were oil quenched and tempered at 473 K during 1 hour under 0.15 MPa argon atmosphere. AISI 410 and AISI 420 steels were austenitized at 1,273 K during 1 hour under argon atmosphere, oil quenched and tempered at the same conditions used for the nitrided AISI 410S specimens. After the treatments, all the specimens were polished to 0.03±0.02 μm to standardize the surface finishing conditions for corrosion-erosion tests.

2.2. Corrosion – Erosion tests

Corrosion-erosion experiments were performed in the test machine shown in Figure 1. It consists of a stainless steel vessel containing slurry made of substitute ocean water and 20% quartz particles (0.3-0.5 mm diameter). The specimens were fixed to electrically insulated metallic holders. The setup allowed the adjustment of impact angles to 45° or 90°. The slurry was impinged against the specimens’ surface by a polypropylene disk driven by an electronically controlled electric motor. The temperature of the slurry, as well as specimens’ mass losses and roughness changes were periodically measured. The slurry was renewed after every 96 hours test cycle. Specific mass loss Φ, defined as the quotient between the cumulative mass loss ΔW (in gram) and the geometrical exposed surface S (in m²) was used to normalize the mass loss results.
In order to study the synergism between corrosion and wear, non-corrosive erosion tests were carried out replacing substitute ocean water by tap water, while solids-free impingement tests were performed in solids-free substitute ocean water.

2.3. Evaluation methods

The nitrogen contents in the gas nitrided specimens were analyzed by Fusion Under Inert Gas and Glow Discharge Optical Spectrometry (GD-OS) techniques. Changes in surface finishing were analyzed with Scanning Electron Microscope and stylus profile roughness tester. Mass losses were measured with a precision analytical scale with 0.1 mg sensitivity.

3. Results and discussion

3.1. Specific mass loss

Figure 2 shows the typical variation of specific mass loss as a function of the testing time for AISI 410/420 and nitrided AISI 410S steels. Figure 3 shows the effect of synergism between corrosion and wear for AISI 420 and nitrided AISI 410S specimens, calculated from the specific mass losses obtained after 96 hours tests. The nitrided AISI 410S specimens showed the better resistance to corrosion-erosion, both under 45° and 90° impingement angle, when compared to those of AISI 410/420.

Figure 2. Variation of specific mass loss of specimens as a function of testing time.
Under oblique incidence cutting would be the dominant wear mechanism; the better resistance of the nitrided steel under these conditions can be associated to its high hardness. Under normal incidence, martensite brittle fracture and spalling of second phase particles are expected; the absence of coarse precipitates in the nitrided AISI 410S prevents its spalling.

Figure 3. Synergism between erosion and corrosion in AISI 420 and nitrided AISI 410S steels.

Synergism between corrosion and wear was greater in the AISI 420 specimens than in the nitrided ones. This result can be associated to the better corrosion resistance of the nitrided AISI 410S steel in saline environments, which was confirmed by electrochemical tests accomplished in 0.5M H_2SO_4 + 3.5%NaCl solution.

3.2. Effect of microstructure and chemical composition

Figure 4 shows the measured and calculated nitrogen profiles for the AISI 410S steel after gas nitriding at 1,473 K under 0.25 MPa N_2 atmosphere. The nitrogen content at the surface was 0.52% before and 0.45% after final polishing, due to material removal from the surface. The nitrogen-enriched case was composed by a martensitic region with 1.1 mm thick, followed by a duplex ferrite/martensite region with ca 1 mm. No precipitates were detected by SEM analysis (Figure 5) allowing the assumption that all nitrogen is in solid solution in martensite and ferrite. This is supported by Thermocalc® simulation, which showed that the N_2 ⇄ 2[N]_2 reaction is the only one occurring at 1,473 K under 0.25 MPa N_2 pressure^15. All the nitride-forming reactions are inhibited at these conditions. Figure 6 shows a calculated phase diagram illustrating several solid-gas equilibrium conditions as a function of nitriding temperature under 0.25 MPa N_2 pressure.

Figure 4. Micro-hardness and measured and calculated nitrogen profiles of gas nitrided AISI 410S stainless steel. Nitriding conditions: 1473 K, 0.25 MPa N_2 pressure, oil quench.
The microstructure of quenched and tempered AISI 410/420 stainless steels was composed by martensite with precipitated carbides, which were localized preferentially at prior austenite grain boundaries.

Figure 5. Microstructure of martensitic case (a) and duplex martensite/ferrite region (b) of nitrided and tempered AISI 410S; and c) microstructure of quenched and tempered AISI 420.

Figure 6. Calculated phase diagram for Fe-13%Cr-N alloys in equilibrium with gaseous nitrogen at 0.25 MPa pressure. Some experimental results obtained after 6 hours-nitriding are shown.

The higher corrosion resistance of nitrided AISI 410S specimens can be attributed to a high nitrogen content in solid solution, leading to a lower chromium depletion in the matrix after 473 K tempering. It is known that these two characteristics promote the increase in pitting and intergranular corrosion resistance of stainless steels\(^5\), and the results of this work suggest that a reduction in synergistic effects could also be expected.

3.3. Effect of impingement velocity

Figure 7. Effect of impact velocity on specific mass loss under erosion and corrosion-erosion of the AISI 420 and nitrided AISI 410S steels. Substitute Ocean Water + 20% quartz particles.
Figure 7 shows the variation of specific mass loss $\Phi$ of AISI 420 and nitrided AISI 410S specimens as a function of impingement velocity $V$, under corrosion and corrosion-erosion conditions. The accepted relationship\textsuperscript{8,10} $\Phi = k V^n$ (where $k$ and $n$ are constant) is observed, being the velocity exponent $n$ greater when corrosion is present. The increase in the value of $n$, due to corrosion, is more accentuated in the carbon-alloyed than in the nitrided steels, which indicates a better resistance of the nitrogen bearing alloy to the synergistic effects discussed above.

4.Conclusions

4.1. Nitrided, direct quenched and 473 K tempered AISI 410S steel was more resistant to corrosion-erosion than AISI 410 and AISI 420 quenched and tempered at the same temperature, when tested in a slurry composed by quartz particles in substitute ocean water.

4.2. The synergistic effects between corrosion and erosion mechanisms were more accentuated in AISI 410/420 stainless steels than in the nitrided AISI 410S. Better intergranular corrosion and reduced spalling of second phase particles of the nitrided low carbon martensitic stainless steel strongly contribute to this performance.

References