Cavitation erosion resistance of a high temperature gas nitrided duplex stainless steel in substitute ocean water

Carlos Mario Garzón\textsuperscript{a}, Hébert Thomas\textsuperscript{b}, José Francisco dos Santos\textsuperscript{a,\dag}, André Paulo Tschiptschin\textsuperscript{b,∗}

\textsuperscript{a} Metallurgical and Materials Engineering Department, University of São Paulo, Av. Prof. Mello Moraes 2463, CEP-05508-900, São Paulo, Brazil
\textsuperscript{b} Ecole Centrale de Lille, Citè scientifique—BP48, F59651 Villeneuve d’Ascq, Lille, France

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Abstract

The cavitation erosion (CE) resistance of a high temperature gas nitrided (HTGN) UNS S31803 duplex stainless steel (DSS), in substitute ocean water, was evaluated. The CE tests were performed in a vibratory cavitation testing equipment according to ASTM G32-92. For comparison purposes, solution treated samples of the same DSS, as well as of an austenitic UNS S30403 stainless steel (SS), were also studied. After high temperature gas nitriding (HTGN), the duplex stainless steel showed an austenitic surface layer, containing high nitrogen content in solid solution. Five sets of specimens with similar (0.8 wt%) nitrogen contents at the surface, but different grain diameters and increasing texture intensities, were investigated. Three sets of samples with similar grain size and texture but increasing nitrogen contents, between 0.65 and 1.15 wt%, were also studied. The CE mass loss rate of the nitrided samples decreased from 8 to 23 times as compared to the DSS solution treated samples. It was observed that the CE mass loss rate decreased with decreasing grain size, increasing the texture components sharpness or with increasing nitrogen content. The HTGN treatment allowed obtaining samples with CE resistance similar to the cobalt base Inconel and Stellite hard facing alloys. The results of CE tests were analyzed taking into account the major damaging mechanisms, which were examined by scanning electron microscopy observations of eroded surfaces.

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1. Introduction

It has long been recognized that nitrogen alloying of stainless steels improves localized and intercrystalline corrosion resistance, wear resistance, ultimate tensile strength and fatigue strength\cite{1-8}.

High nitrogen austenitic steels have been reported as suitable materials for applications in which erosive damage caused by cavitation, i.e. cavitation erosion (CE)\cite{9-13} is significant, leading to a decrease in the large maintenance costs characteristics of hydraulic systems. The suitability of high nitrogen austenitic steels for these applications is mainly based on both higher CE resistance compared with conventional nitrogen free austenitic steels and lower cost compared with the CE-resistant cobalt-based alloys.

Production routes of high nitrogen stainless steels (HNSS) by alloying, pressure metallurgy, powder metallurgy and solid-state diffusion have been studied\cite{14-17}. Recently, a chemical solid-state nitrogen alloying technique was developed\cite{8,13,14,17-21}, consisting of annealing a SS in a N\textsubscript{2}-containing gas atmosphere in the range 1273–1473 K. In this high temperature gas nitriding (HTGN) treatment, atomic nitrogen is absorbed at the surface of the steel and then diffuses into the near surface region. Case-depths from 0.5 to
HTGN has been successfully used to improve the surface properties of martensitic, austenitic, ferritic-austenitic and martensitic-ferritic SS [1,8,12–14,17–20]. Berns and co-workers [8,13,14,17,18] and dos Santos et al. [12] showed that nitrogen additions to stainless steels by HTGN enhance the CE resistance in distilled water. After nitriding, Berns et al. achieved reduction of the rate of mass-loss during vibratory CE experiments between 2.5 for austenitic SS to 10.5 for duplex SS. The improvement in CE resistance was attributed to the increase in planar dislocation slip and to an increase in metallic characteristics of the interatomic bonding (due to an increase in the concentration of free electrons), leading to a particularly high combination of toughness and yield strength [8]. dos Santos et al. showed that, in an UNS S30403 austenitic SS, the increase in the nitrogen content up to 0.48 wt% in solid solution increases the incubation time (4.5 times) and decreases the wear rate (8.5 times). They pointed out that the excellent CE resistance of high-temperature gas nitrided austenitic SS compared to the conventional SS could be assigned to the strengthening effect of nitrogen without significantly varying the ductility or the work hardening rate. Besides, it was observed that lower amounts of energy were consumed plastically during localized CE impact spots and lower plastic deformation heterogeneities occurred both inside the grains and between them.

Fu et al. [10] pointed out that the higher CE resistance of a 18Mn–18Cr–0.5N HNSS when compared with the 0Cr–13Ni–6Mo and 0Cr–16Ni–5Mo SS is related to its high strength, its high work hardening rate and consumption of impact energy during CE. Tschiptchin and Toro [6] reported that the increasing resistance to plastic flow is one of the key features controlling the performance of high nitrogen austenitic stainless steels during CE. Hänninen et al. [9] concluded that the main reason for the increase in CE resistance of nitrogen bearing austenitic stainless steels is the solid solution hardening effect of interstitial atoms, the strain induced martensite transformation and the low SFE of these alloys being less important.

The aim of this work is to evaluate the effect of high temperature gas nitriding on the CE resistance, in substitute ocean water, of an UNS S31803 DSS.

2. Experimental

2.1. Materials

UNS S31803 ferritic-austenitic duplex stainless hot rolled sheets 9 mm in thick and UNS S30403 austenitic SS bars with 19 mm in diameter (used as comparison material) were studied. Table 1 gives the chemical composition of these steels.

<table>
<thead>
<tr>
<th>Material</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
<th>Cu</th>
<th>C</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>UNS S31803</td>
<td>22.5</td>
<td>5.4</td>
<td>3.0</td>
<td>1.9</td>
<td>0.14</td>
<td>0.019</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>UNS S30403</td>
<td>18.7</td>
<td>9.6</td>
<td>–</td>
<td>1.9</td>
<td>0.05</td>
<td>0.005</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>

2.2. Nitriding treatments

UNS S31803 DSS samples were high temperature gas nitrided and then direct quenched in water. The specimens were heated up to the nitriding temperature, between 1398 and 1473 K, under 0.13 Pa, in a vacuum chamber, and then exposed to a high purity Ar + N2 atmosphere. Seven different nitriding treatments were studied as shown in Table 2. Part of the samples was nitrided using isobaric HTGN treatments; the other part was nitrided using a recently developed [22] non-isobaric HTGN treatment cycle. The isobaric HTGN treatments were carried out between 1423 and 1473 K for times varying between 18 and 72 ks under N2 partial pressures varying between 0.06 and 0.09 MPa. The non-isobaric HTGN treatments were carried out between 1398 and 1421 K for times varying between 10.8 and 18 ks, being the N2 partial pressure varied according to the scheme shown in Fig. 1. They consist of cycling the specimen between two different N2 partial pressures: a high pressure stage (sorption stage) and a vacuum one (desorption stage). During the nitrogen desorption stages (P N2 ∼ 0) ferrite grains precipitation is induced; during subsequent nitrogen sorption stages these ferritic grains dissolved. Thus, the sequence of reactions, γ → (α + γ) → γ inhibits austenitic grain growth in the nitrided case. A complete description of the nitriding treatments carried out under variable N2 partial pressures was made elsewhere [22].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (K)</th>
<th>Time (ks)</th>
<th>N2 partial pressure (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S11803-20h</td>
<td>1473</td>
<td>72.0</td>
<td>0.09</td>
</tr>
<tr>
<td>S31803-5h</td>
<td>1823</td>
<td>28.8</td>
<td>0.06</td>
</tr>
<tr>
<td>S31803-3h</td>
<td>1423</td>
<td>18.0</td>
<td>0.06</td>
</tr>
<tr>
<td>S31803-3h-B1</td>
<td>1423</td>
<td>18.0</td>
<td>Non-isobaric</td>
</tr>
<tr>
<td>S31803-3h-B2</td>
<td>1398</td>
<td>10.8</td>
<td>Non-isobaric</td>
</tr>
<tr>
<td>S31803-3h-B3</td>
<td>1423</td>
<td>10.8</td>
<td>Non-isobaric</td>
</tr>
</tbody>
</table>
The nitriding parameters were selected after prior nitriding tests, aiming to obtain five sets of samples with similar nitrogen content at the surface, but different grain sizes and microtextures and three sets of samples with similar grain size and microtexture but increasing nitrogen content at the surface.

2.3. Solution-annealing treatments

UNS S31803 DSS and UNS S30403 austenitic SS (comparison purposes) samples were solution-annealed at 1373 K (S31803) and 1423 K (S30403) for 21.6 ks and then quenched in water. The samples were heated up to the treatment temper-
Vibratory CE experiments were carried out using a Telasonic SG 1000 device, operating at a vibratory frequency of 20 kHz and a peak to peak amplitude of 40 \mu m. CE experiments were carried out according ASTM G32-92 standard. A slight modification was introduced, by using an indirect test arrangement, which consists of placing the test specimen below the vibrating horn. Fig. 2 shows the experimental setup. By using a metallic support with an articulated arm and a height measuring device (readability of 0.01 mm) the separation between the sample and the vibrating horn was 0.5±0.01 mm. The tests were carried out in substitute ocean water at 293 K, prepared according to ASTM D 1141-90 standard. The pH of the test medium was controlled, by NaOH addition, to a value of 8.2±0.1 in all experiments. Mass loss measurements were made intermittently after interrupting the test, using a Scientech SA120 scale with a readability of 0.1 mg.

2.5. Test specimens characterization

The microstructure of the specimens was examined by optical and scanning electron microscopy (OM and SEM). Nitrogen contents at the surface of the samples were measured through X-ray wavelength-dispersive spectrometry (WDS) microanalysis by using an Oxford WDX600 spectrometer coupled to a Cambridge Stereoscan 440 scanning electron microscope.

The microtexture at the surface of the samples was studied by scanning orientation microscopy, using an electron back scattering diffraction TSL-EBSD instrument interfaced to a Philips XL30TM scanning electron microscope. Both, grain boundary character distribution and crystallographic orientation distribution were analyzed. Metallographic preparation consisted of emery paper grinding followed by diamond paste polishing and a final 1.8 ks stage of 0.05 \mu m colloidal silica polishing.

The crystallographic orientation distribution functions (ODF) were calculated according to the Bunge notation. The grain boundaries were classified as low-\Sigma coincidence-site lattice (CSL) and non-CSL, in terms of the relative misorientation between adjacent grains, according Brandon’s criterion. Grain boundaries with a degree of coincidence (\Sigma number) lower than 29 were considered as low-\Sigma CSL boundaries.

Depth-sensing indentation tests were carried out in a Fishescopes H100 apparatus, using a Vickers indenter tip. The maximum load was 250 mN, the loading and unloading times were 90 s and the dwell time at peak load was 20 s. The indentation data were analyzed using the method proposed by Oliver and Pharr \cite{23}. Each data point is an average of 20 measurements. The indentation data analyzed were: hardness (H), total indentation work (Wt), irreversible indentation work (Wir), reversible indentation work (We), loading slope (S1), unloading slope (S2), and strain-hardening coefficient during indentation (n). The n coefficient was calculated.
introducing a correction function, \( f(t) \) [24], to the Oliver and Pharr procedure, expressed by Eq. (1) for a Vickers indentor:

\[
f(t) = 1.202 - 0.857e + 0.302e^2 \frac{\Sigma_1 W_1}{\Sigma_2 W_e} \tag{1}
\]

3. Results

3.1. Test specimens characterization

Fig. 3 shows a micrograph taken in the transverse section of a sample nitrided at 1423 K for 28.8 ks, and Fig. 4 shows EBSD grain map and ODF sections at \( \phi_2 = 0^\circ \) and \( \phi_2 = 45^\circ \) (Bunge notation) at the surface of the same sample. From the surface to the core (from left to right) three regions with different microstructures are observed: an austenitic surface layer, a transition region and a ferritic-austenitic duplex core.

No nitrides were observed in the high nitrogen austenitic layer, a transition region and a ferritic-austenitic duplex core. Different microstructures are observed: an austenitic surface to the core (from left to right) three regions with (Bunge notation) at the surface of the same sample. From

Table 4 gives the results of depth-sensing indentation tests, \( H, W_e, W_m, W_t \) and \( N \), made on top of the samples. One can see a strong hardening effect of nitrogen alloying without meaningful variations on the work hardening rate during indentation. In samples with ca. 40 μm in grain diameter, increasing the nitrogen content from 0.65 to 1.15 wt% increases hardness from 3.75 to 4.1 GPa (9%), \( W_t \) varied between 23.54 and 23.0 mJ (−2.3%), \( W_e \) varied between 145.2 and 136.5 (−6%) and \( W_a \) varied between 121.4 and 113.1 mJ (−6.8%).

It is important to consider that hardening due to grain refinement did not lead to an increase in the amount of elastic indentation work (\( W_t \)), as observed in the case of nitrogen solid solution hardening, probably due to the sharp variation in texture associated to grain refinement.
3.2 CE tests

Fig. 5 shows the cumulative mass loss as a function of exposure time. The curves can be divided into two stages, namely, an incubation period, where the mass loss is very small—not detectable with the scale—and a damage period, where the cumulative mass loss increases with exposure time. The behavior of both UNS S31803 DSS and UNS S30403 austenitic SS solution treated is similar. In contrast, it can be seen that nitrided samples have much higher CE resistance than non-nitrided ones.

Fig. 6 shows the mass loss rate as a function of exposure time for nitrided samples. Mass loss rate values were calculated by the derivative of the cumulative mass loss data with respect to time. One can see that in the damage period the mass loss rate increases with exposure time, tending to a stationary value, i.e. the maximum mass loss rate. Fig. 7 shows the effect of nitrogen content and of grain refinement (and simultaneous increase in texture intensity) on the hardness, the incubation time and the maximum mass loss rate of nitrided samples. It can be seen that the higher the nitrogen content, the higher are the hardness and the incubation time for starting scale-detectable damaging and the lower is the maximum mass loss rate. Additionally, the finer the microstructure (and sharper the texture) the harder are the samples and the lower is the maximum mass loss rate, although a monotonous relationship between grain size or texture intensity and incubation time was not observed.

In samples with ca. 40 µm in grain diameter, increasing the nitrogen content from 0.65 to 1.15 wt% increases the incubation time 1.4 times and decreases the mass loss rate 3.0 times. In samples with ca. 0.8 wt% N, the mass loss rate of the most resistant sample is 2.4 times lower than the mass loss rate of the less resistant one. This 2.4 times variation in mass loss rate, observed in the 0.8 wt% N is especially significant considering the already high CE resistance of the nitrided samples.

The mass loss rates and incubation times of the solution treated samples were 0.42 mg/ks—5.1 ks (UNS S31803), 0.44 mg/ks—10.8 ks (UNS S30403). Thus, the HTGN nitriding treatment of UNS S31803 DSS decreased the mass loss rate between 7.6 and 23.3 times and increased the incubation time between 14 and 20 times, leading to steels with mass loss rates up to 2.4.5 lower than the UNS S30403 austenitic SS.

3.3 Scanning electron microscopy of eroded surfaces

Fig. 8 shows the appearance of the surface at the initial stages of CE damage—incubation period—for a nitrided sample with 0.77 wt% N at the surface and a grain diameter of 92 µm. The appearance of the eroded surfaces of all nitrided samples is similar to the one shown in Fig. 8. At the earliest stages of CE tests, plastic deformation occurs and slip lines can be observed inside individual grains, which display a micro-relief formed by cavitation impact waves. The plastic deformation intensity in each grain is different due to both their own lattice spatial orientation and their neighbors’ lattice spatial orientation. Due to restrictions to deformation (sliding and rotation) imposed by the polycrystalline struc-
Fig. 7. Hardness, incubation time and maximum mass loss rate as a function of nitrogen content and grain size. TR: times random texture intensity of the component (100)[001].

Fig. 8. Surface of an UNS S31803 nitrided sample with 0.77 wt% N at the surface and 92 μm grain diameter. Earliest stages of CE damage (the incubation time according mass loss measurements was 57.6 ks).
ture, grain boundaries become regions of stress concentration, initiating the process of mass removal. As a general rule, it was observed that grain boundary damaging starts preferentially at grain boundaries of grains displaying intense formation of slip lines and micro-relief. In Fig. 8 one can see that grain boundary damaging is restricted to the boundary region and growth towards the inner region of the grains is inhibited. During the incubation period mass removal inside the grains starts at weak pits formed in slip lines, and specially at slip line intersections. SEM observation of the eroded surfaces did not allow concluding if the pits were formed by cavitation impact waves, by localized corrosion or by a combined impact/corrosion mechanism. However, it is known that this kind of high nitrogen stainless steel has extremely high resistance to localized corrosion [1,13,14,18].

In Fig. 8 one can see that CE damage of neighboring grains is highly heterogeneous: a lot of grains, in which the mass removal is extensive, appear beside other almost not damaged. As a general rule, it was observed that grains displaying intense slip lines formation at the earliest CE stages are the same grains in which mass removal is extensive. Therefore, it is probable that the grains more resistant to CE are those with lattices spatially oriented parallel to directions of high energy consumption during plastic deformation.

Fig. 9 shows the appearance of the surface at the later stages of CE tests—in the damaged period—of two nitrided samples with ca. 0.8 wt% N and 20 and 125 μm mean grain diameters. It can be seen that mass removal occurs due to fracture of debris, ca. 5–20 μm in diameter, by a combined effect of microfatigue and microcrack formation.

4. Discussion

The results showed that increasing the nitrogen content from 0.65 to 1.15 wt% increases the hardness and the elastic indentation work and decreases the total and irreversible indentation works, without significantly varying the strain-hardening coefficient during indentation. Thus, it can be reasonably supposed that due to increase in nitrogen content there is an increase in the elastic energy returned to the environment and a decrease in the amount of plastic energy absorbed by the sample. Therefore, the specimen is plastically loaded to a lesser extent and at the same time shows a greater resistance to plastic deformation, due to hardening, leading to an increase in the incubation time and to a decrease in mass loss rate.

On the other hand, in the range of the grain diameters studied, grain refining was not a strong hardening mechanism. Refining the microstructure led to a hardness increase of only 9%, while all the indentation works (W_t, W_e and W_ir) decreased. Thus, it can be supposed that due to grain refining the specimen is plastically loaded to a greater extent beneath the cavitation impact waves, but at the same time the resistance to plastic deformation is greater, leading to a decrease in mass loss rate. However, the slight increase in hardness is not big enough to explain the steep variation in mass loss rate (up to 240%). SEM observations of eroded surfaces suggest that the simultaneous increase in texture intensity, related to grain refining is also responsible for the observed decrease in mass loss rate.

The non-monotonous relationship observed between grain refining and incubation time can be related to the opposing effects of grain refining in the amount of weak points suitable to start CE damage and in the resistance to plastic deformation. Grain boundaries are weak regions where CE damage can start as they act as stress concentrators under cavitation impact waves; on the other hand their presence increase the overall plastic deformation resistance, impairing the onset of the damage.

It is also worth noting that UNS S31803 nitried specimens showed mass loss rates 24.5 times lower than the mass loss rate shown by UNS 30403 solution treated specimens. This mass loss rate can be compared to those, characteristics of much more expensive Co-based alloys, in the range 3 to 32 times lower than UNS S30403 SS [25].

5. Conclusions

1. High temperature gas nitriding strongly improves the CE resistance in substitute ocean water of UNS S31803 du-
plex SS. Nitrided samples with nitrogen contents between 0.65 and 1.15 wt%, mean grain diameters between 20 and 125 μm and maximum (g) texture intensities between 2 and 11 times random, displayed incubation times between 14 and 20 times higher and mass loss rates between 7.6 and 23.3 times lower than solution treated samples of the same steel.  

2. In samples with ca. 40 μm in grain diameter, increasing the nitrogen content from 0.65 to 1.15 wt% increases the incubation time 1.4 times and decreases the mass loss rate three times. This can be attributed to: (i) an increase of the resistance to plastic deformation without significant variation of the work hardening rate and (ii) a decrease of the plastic loading by cavitation impact waves.

3. Simultaneous grain refinement and increase in texture intensity in samples with ca. 0.8 wt% N led to a decrease in the mass loss rate of 2.4 times.

4. The mass loss rate of the less CE resistant and the most CE resistant UNS S31803 nitrided samples were eight times and 24.5 times lower than the mass loss rate of an UNS S30403 SS solution treated. Therefore, it can be concluded that (22.5Cr−5.4Ni−3.0Mo−1.1N) wt% austenitic stainless steel is a suitable material for structural applications, where cavitation erosion resistance, especially in corrosive environments, is an important requisite.

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References


