Improvement of the cavitation erosion resistance of an AISI 304L austenitic stainless steel by high temperature gas nitriding

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Abstract

An AISI 304L austenitic stainless steel was high temperature gas nitrided in N$_2$+Ar atmospheres under N$_2$ partial pressures up to 0.10 MPa at 1423 K for 21.6 ks. Nitrogen contents at the surface up to 0.48 wt.% and case depths up to 1 mm were obtained. All the samples showed fully austenitic microstructures free of precipitates. Solution treated AISI 304L as well as nitrided samples were tested in distilled water in a vibratory cavitation erosion (CE) equipment. Characterization of the test specimens was made by optical microscopy, electron back scattering diffraction coupled to a scanning electron microscope (EBSD–SEM), X-ray diffraction (XRD), wavelength dispersive spectroscopy (WDS) microanalysis and depth-sensing indentation tests. All the samples had almost the same mean grain diameter, $\sim$80 $\mu$m, similar mesotexture and macrotexture, though the nitrogen contents differed. The nitrided samples exhibited much better cavitation erosion resistance and the erosion rate was reduced by almost 8.5 times. Increasing the N$_2$ partial pressure increased the nitrogen content at the surface, leading to an increase in the incubation period for damage and a decrease in the erosion rate.

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1. Introduction

When compared to nitrogen-free stainless steels, nitrogen-bearing stainless steels exhibit much better surface properties—corrosion (localized and intergranular), wear resistance [1–6] and bulk properties such as very high strength, with good ductility and toughness [1,3]. Considerable emphasis has been placed on both liquid- and solid-state routes to produce high performance low cost nitrogen-alloyed stainless steels. In the solid-state production routes, the steel surface and near surface regions are nitrogen alloyed through chemical, implantation, plasma or laser techniques [7]. A new high temperature gas nitriding (HTGN) treatment that allows obtaining high nitrogen cases, about 1 mm in depth, on stainless steels was developed [8–12]. In this treatment, high nitrogen contents, $\sim$0.5–1.0 wt.%, are dissolved in austenite, in the 1273–1473 K temperature range. Berns et al. [11] showed that when HTGN is applied to austenitic–ferritic, martensitic and austenitic stainless steels, their cavitation erosion (CE) resistance is considerably increased [9–11]. This new HTGN treatment is different from conventional nitriding, usually performed between $\sim$750 and 850 K, in which intense chromium nitride precipitation occurs, greatly increasing the hardness, but impairing the corrosion resistance of stainless steels. Additionally, quite different from conventional gas nitriding, where ammonia–hydrogen (NH$_3$–H$_2$) gas mixtures are used, the HTGN treatment is performed in still (N$_2$) gas atmosphere which is neither explosive nor toxic. As gas flux and gas control equipments are not necessary, energy losses and costs are diminished [1]. Fu et al. [13] compared the CE resistance of a (18 Mn–18 Cr–0.5 N) wt.% steel with that of a (15 Cr–5 Ni–0.6 Mo) wt.% and a (12 Cr–6 Ni–0.6 Mo) wt.% steels, and showed that the high nitrogen steel exhibited three times and two times higher CE resistance, respectively. Mills and Knutsen [14] compared the CE resistance of a (19 Cr–10 Mn–0.6 N) wt.% steel, an AISI 304 stainless steel and a Hadfield steel, and showed that the high nitrogen steel exhibited better CE resistance.
Berns et al. [11] attributed the better CE performance of high nitrogen stainless steels to the effect of nitrogen in lowering the stacking fault energy (SFE), leading to an increase in plasticity and work hardening [10,11]. According to Fu et al. [13], the high CE resistance of a (18 Mn–18 Cr–0.5 N) wt.% steel is related to its good mechanical properties induced by changes in the dislocation configurations, CE-induced mechanical twinning or formation of stacking faults and CE-induced phase transformation.

Mills and Knutson [14] reported that three main events occur at the initial stages of CE in CrMnN and AISI 304L austenitic stainless steels, namely, plastic deformation of individual grains, discontinuous plastic extruding effects at grain boundaries and fatigue damage initiated at high extruded grain boundaries. They pointed out that one of the key features controlling the performance of austenitic stainless steels during CE is the resistance to plastic flow. In a CrMnN steel, they observed that the CE rate decreased with increasing amount of cold work. They stressed the importance of the increase in yield strength leading to a decrease of plastic deformation in individual grains during the early CE stages, to a strength leading to a decrease of plastic deformation in ing. They stressed the importance of the increase in yield strength leading to a decrease of plastic deformation in individual grains during the early CE stages, to a strength leading to a decrease of plastic deformation in

In a review paper, Hänninen et al. [3] concluded that the main reason for the increase in CE resistance of nitrogen-bearing austenitic stainless steels is the solid solution hardening effect of nitrogen, while the effects of martensitic transformation and change in SFE are less important.

The mechanism by which nitrogen improves the CE resistance of stainless steels is still not clear, and no systematic studies of the effect of increasing nitrogen contents on the CE resistance of austenitic stainless steels were performed. The aim of this work is to study the effect of increasing nitrogen contents, through high temperature gas nitriding, on CE resistance of an AISI 304L austenitic stainless steel. Five sets of samples with similar microstructure, microtexture and mesotexture, but with different nitrogen contents at the surface were studied. The results of the CE vibratory tests in distilled water were analyzed taking into account microstructural changes during CE tests and the effect of the nitrogen content on stress–strain properties measured by depth sensing indentation tests.

2. Experimental

2.1. High temperature gas nitriding treatments

Cylindrical specimens (19 mm in diameter × 6 mm in thickness) of an AISI 304L (18.7 Cr–9.6 Ni–1.9 Mn–0.95 Si–0.03 C–0.04 P–0.02 S) wt.% austenitic stainless steel were high temperature gas nitrided in high purity N2 + Ar atmospheres for 21.6 ks, and then direct quenched in water. The thermochemical treatments were performed at 1423 K under 0.02, 0.04, 0.07 and 0.10 MPa N2 partial pressures. For comparison purposes, a set of as received samples were solution treated under Ar atmosphere using the same set of temperature and time parameters.

2.2. CE tests

Vibratory CE experiments were carried out according to ASTM G12-92 standard, although a slight modification was introduced by using an unattachment arrangement. The test specimen was placed below the vibrating horn. The separation between the samples and the vibrating horn was 1.0 mm. The tests were performed in a Telsonic SG 1000 equipment operating at a vibratory frequency of 20 kHz and a peak to peak amplitude of 40 μm. The cavitation medium was distilled water at 293 K and the cavitated area was 198.6 mm2. Mass-loss measurements to the nearest 0.0001 g were made intermittently in interrupted tests up to a maximum exposure period of 108 ks.

2.3. Test specimens characterization

The microstructure of the specimens was examined by optical and scanning electron microscopy (OM and SEM) and by X-ray diffraction (XRD). Nitrogen contents at the surface of the samples and nitrogen profiles in the transverse section were measured through wavelength dispersive spectrometry (WDS) microanalysis by using an Oxford WDX600 spectrometer coupled to a Cambridge Stereoscan 440 scanning electron microscope operating at 10 kV.

The microtexture and the mesotexture of the samples were determined by electron backscatter diffraction (EBSD), using a TSL–EBSD instrument interfaced to a Philips XL30 scanning electron microscope. Three microregions between 1 and 3 mm2 were analyzed at the surface of the samples. The orientation distribution function (ODF) was calculated according to Bunge notation. The grain boundaries were classified as coincidence-site lattice (CSL) and non-CSL in terms of the relative misorientation between adjacent grains, according to Brandon’s criterion. The boundaries with a degree of coincidence (Σ number) lower than 29 were considered as CSL.

Depth-sensing indentation tests were carried out in a Fisherscope H100 apparatus, using a Vickers indenter tip. The indentation conditions for testing were: pre-load of 0.4 mN, peak load of 250 mN, loading time of 90 s, dwell time at peak load of 20 s and unloading time of 90 s. The force-depth (P-h) indentation data (Fig. 1) were analyzed using the method proposed by Oliver and Pharr [14], determining the hardness (H), the total indentation work (Wt), the irreversible indentation work (Wf), the reversible indentation work (Wr), the loading slope (S1) and the unloading slope (S2). The strain-hardening coefficient (σr) during indentation was calculated introducing a correction function f(x) [16], to the Oliver and Pharr procedure expressed by equation 1, for a
Vickers indenter:
\[ f(n) = 1.202 - 0.857n + 0.302n^2 = \frac{S_1 W_t}{S W_e} \] (1)

3. Results

3.1. Characterization of as treated samples

The solution treated and the nitrided samples had austenitic microstructures free of precipitates. Fig. 2 shows the WDS measured nitrogen contents and the grain size at the surface of the samples. As expected, Sieverts’ law was obeyed: the nitrogen content varied with the square root of the nitriding pressure. On the other hand, the nitriding pressure did not have any important effect over the grain size (∼80 µm) of the samples.

Fig. 2. Nitrogen content (a) and average grain diameter (b), at surface of the samples as a function of the square root of N2 partial pressure.

Both hardness and nitrogen content decrease monotonically with the distance from the surface, as shown in Fig. 3 for a sample nitrided under 0.07 MPa.

The results of EBSD analysis on the sample surface are summarized in Table 1. The texture of the samples was weak, the main texture components being (1 1 1)⟨uvw⟩ and (1 1 0)⟨uvw⟩. No significant difference in microtexture and the grain boundary character distribution were observed for the different nitriding pressures. The fraction of Σ3 twin boundaries was ∼0.45, and the fraction of Σ1 low angle boundaries was ∼0.06. These CSL fractions were calculated on a length basis.

The results of depth-sensing indentation tests made on surface of the samples are summarized in Table 2 (each value is an average of 20 measurements), and Fig. 4 shows a representative force-depth indentation curve for each studied condition. It was observed that the increase in nitrogen content led to an increase of \( H \) and \( W_e \) and to a decrease of \( W_t \) and \( W_{ir} \), while \( n \) did not change significantly.

Fig. 5 shows \( W_{ir}/W_t \) (ductility index) and \( H \) as a function of the nitrogen content. The \( W_{ir}/W_t \) ratio is the fraction of the total indentation work used for plastically strain the
Table 1
Grain boundary character distribution and microtexture components measured by EBSD at surface of the samples

<table>
<thead>
<tr>
<th>P \textsubscript{N\textsubscript{2}} (MPa)</th>
<th>Fraction of CSL boundaries</th>
<th>Intensity of microtexture components (times random)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X1</td>
<td>X3</td>
</tr>
<tr>
<td>0.00</td>
<td>0.055</td>
<td>0.535</td>
</tr>
<tr>
<td>0.02</td>
<td>0.055</td>
<td>0.435</td>
</tr>
<tr>
<td>0.04</td>
<td>0.095</td>
<td>0.425</td>
</tr>
<tr>
<td>0.07</td>
<td>0.050</td>
<td>0.430</td>
</tr>
<tr>
<td>0.10</td>
<td>0.030</td>
<td>0.515</td>
</tr>
</tbody>
</table>

Fig. 3. Nitrogen content and hardness profiles of the AISI 304L steel nitrided under 0.07 MPa N\textsubscript{2} partial pressure.

Material. It was observed that while hardness increased roughly linearly with the nitrogen content, W\textsubscript{ir}/W\textsubscript{t} remained almost constant.

3.2. CE resistance

Fig. 6 shows the cumulative mass loss as a function of CE exposure time. These curves can be divided into two stages, namely, an incubation period, in which the mass loss is very small, and a damage period, in which the cumulative mass loss increases with exposure time. This two stage behavior is in accordance with reported results for austenitic stainless steels [11,14]. In Fig. 6, one can clearly see that increasing the nitrogen content extends the incubation period to longer times and decreases the mass-loss curve slope.

Table 2
Results of depth-sensing indentation tests at surface of the samples

<table>
<thead>
<tr>
<th>P \textsubscript{N\textsubscript{2}} (MPa)</th>
<th>Nitrogen content (wt.%)</th>
<th>W\textsubscript{t} (mJ)</th>
<th>W\textsubscript{e} (mJ)</th>
<th>W\textsubscript{ir} (mJ)</th>
<th>nH (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.00</td>
<td>196.1</td>
<td>17.7</td>
<td>184.4</td>
<td>0.16</td>
</tr>
<tr>
<td>0.02</td>
<td>0.18</td>
<td>184.3</td>
<td>18.0</td>
<td>166.6</td>
<td>0.19</td>
</tr>
<tr>
<td>0.04</td>
<td>0.26</td>
<td>172.7</td>
<td>18.7</td>
<td>154.6</td>
<td>0.15</td>
</tr>
<tr>
<td>0.07</td>
<td>0.33</td>
<td>172.8</td>
<td>19.1</td>
<td>153.2</td>
<td>0.16</td>
</tr>
<tr>
<td>0.10</td>
<td>0.48</td>
<td>155.2</td>
<td>20.8</td>
<td>134.7</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Fig. 4. Force-depth indentation curves measured on the samples surface.

Fig. 5. W\textsubscript{ir}/W\textsubscript{t} and H as a function of the nitrogen content.
Table 3 shows the incubation time, $t_i$, and the maximum mass-loss rate as a function of the nitrogen content. One can see that as the nitrogen content at the surface increases, there is a significant increase of $t_i$ and a decrease of the erosion rate. Increasing the nitrogen content up to 0.48 wt.%
increases 4.6 times the incubation time and decreases 8.6 times the mass-loss rate.

3.3. Characterization of CE-tested samples

Fig. 7 shows the appearance of the surface at the initial stages of CE tests for solution treated and for nitried samples. At the beginning of the CE tests, plastic deformation occurs and slip lines can be observed inside individual grains. In each grain, heterogeneous deformation occurs by localized impact spots, leading to a microrelief at the surface. The higher the nitrogen content, the fewer slip lines and microreliefs are observed. The plastic deformation intensity in each grain is different due to differences in spatial orientation of their lattices, leading to protrusions at grain boundaries. Especially large protrusions can be formed when one grain suffers intense plastic deformation, while its neighbor deforms very little. The higher the nitrogen content, the lower are both the grain deformation and the level of protrusion at grain boundaries.

Generally speaking, in the samples with lower nitrogen contents (up to 0.26 wt.%), the CE damage starts at protruded grain boundaries and at slip lines as well. On the other hand, in the samples with higher nitrogen contents, the damage starts preferentially at protruded grain boundaries. However, cleavage fracture and pits formed at deformation heterogeneities inside the grains (DHIG) and at sharp grain boundary corners (SBC) can start the damage, as shown in Fig. 8.

Fig. 8. Start of CE damage at deformation heterogeneities inside the grains (DHIG) and at sharp boundary corners (SBC) for a sample with 0.48 N (wt.%) at surface.

Fig. 9. Flaking of material during CE after 5.4 ks in a sample without nitrogen addition (solution treated).
Three mechanisms of mass removal were observed: (i) flaking of the material from slip lines or grain boundaries (Fig. 9); (ii) formation of deep microcavities due to microjet action, by a fatigue mechanism (Fig. 10); (iii) fracture of debris circa 5–20 μm in diameter by a combined effect of microfatigue and microcrack formation (Fig. 10).

In the higher nitrogen content samples, flaking and formation of deep microcavities are negligible, and mass is removed predominantly by debris fracture, as shown in Fig. 11 for a sample with 0.48 wt.% nitrogen at the surface, tested in CE after 108 ks.

Fig. 12 shows the fraction of CSL and non-CSL boundaries in which damage started after 7.2 ks exposure to CE, for a sample with 0.48 wt.% N at the surface. The CSL fractions were calculated on a number basis and correspond to...
Fig. 12. Fraction of CSL and non-CSL boundaries damaged in a sample with 0.48 N (wt.%) at surface after a CE exposure time of 7.2 ks.

The ratio between damaged and total grain boundaries of a specific \( \Sigma \) number. In total 350 boundaries were analyzed. It was observed that \( \Sigma 3 \) (twins) boundaries are almost twice more susceptible than any other high angle grain boundary. Future works should be made studying the relation between 3D grain boundary crystallography and the onset of CE damage.

3.4. Correlation between indentation parameters and CE resistance

Fig. 13 shows the incubation time and the maximum erosion rate as a function of the indentation work and hardness. The incubation time increases with reversible indentation work and with hardness, and the maximum mass-loss rate increases with the total indentation work and decreases with hardness.

The observed behavior is in agreement with several reported works [17,18] that correlate the CE resistance with various forms of strain energy derived from tension tests, e.g., the ultimate resilience (UR):

\[
UR = \frac{(UTS)^2}{2E}
\]

where UTS is the ultimate tensile strength and \( E \) is the modulus of elasticity.

4. Discussion

The results showed that increasing the nitrogen content in solid solution, up to 0.48 wt.%, increased the hardness, the reversible indentation work \( W_r \) and decreased the irreversible indentation work \( W_i \), without significantly changing the work hardening rate. The increase in nitrogen
content increases the elastic energy returned to the environment and decreases the amount of plastic energy absorbed by the alloy, at cavitation impact spots. 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 less deformed grains.

As shown earlier, the mass loss inside microcavities occurs by a fatigue mechanism. Mills and Knutsen [14] reported the occurrence of grain boundary extrusion during cavitation erosion of austenitic stainless steels and that these areas are submitted to higher stress levels than the flat ones, leading to fatigue crack nucleation and growth at these regions. The increase in nitrogen content leads to a more even deformation, to less extruded grain boundaries and to smaller amounts of microcavities. In the high nitrogen specimens, mass loss occurred mainly by microcrack formation at the first stages of damage and by a synergistic effect of microfatigue and microcrack formation at the latter stages of damage. On the other hand, in the low nitrogen specimens, mass loss occurred by microfatigue associated with microcrack formation in all stages of damage.

5. Conclusions

1. High temperature gas nitriding treatment significantly improves the CE resistance of austenitic AISI 304L stainless steels. Increasing the nitrogen content in solid solution (up to 0.48 wt.%) through HTGN increases 4.6 times the incubation time and decreases 8.6 times the erosion rate.

2. The onset of CE damage on the non-nitrided samples occurred preferentially at both high angle grain boundaries and slip lines. On the other hand, in the higher nitrogen content samples, the CE damage started preferentially at high angle grain boundaries. In those samples, Σ3 (twins) boundaries were almost twice more susceptible than any other high angle grain boundary.

3. The incubation time increases linearly with the reversible indentation work, and the maximum mass-loss rate increases roughly linearly with the total indentation work.

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