Effects of hydrogen charging on surface slip band morphology of a type 316L stainless steel

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Abstract

Stress corrosion cracking (SCC) is observed for many metals and alloys whose behavior is ductile in inert environment. Mechanisms occurring during SCC involve strong interactions between the applied stress and the chemical environment. One of the implied processes in the crack propagation is the influence of the anodic dissolution and the hydrogen absorption on dislocation dynamic near the metal surface. At the microscopic scale, the absorption of hydrogen has been reported to increase the velocity of dislocations in different crystal structures and to promote the slip localization and slip planarity. In this study a description of the effects of the hydrogen concentration, grain size and macroscopic deformation level is given and particularly the experimental results of quantitative slip morphology analyses obtained by atomic force microscopy are presented.

The slip morphology of hydrogenated and non-hydrogenated specimens of two grain sizes (140 and 300 µm) are compared after being deformed in tension to 2% and 10% of strain in ambient air (macroscopic strain rates of $10^{-3}$ s$^{-1}$ and $10^{-6}$ s$^{-1}$). Two cathodic hydrogen chargings leading to hydrogen concentrations of 31 wt.ppm and 135 wt.ppm induce a slip localization at $10^{-3}$ s$^{-1}$ at 2% of strain in coarse grained samples. This strain localization is characterized by increases in the mean slip-band spacing value and in the mean slip-band height value of respectively 17% and 40% with 31 wt.ppm and of 100% and 85% with 135 wt.ppm. At 10% of strain and for the two hydrogen concentrations, the hydrogen induces low effects on the slip-band spacings while the slip-band heights increase by 55%. The fine grained specimens show a significant change in the slip morphology at 135 wt.ppm characterized by an increase in the average slip-band height of 60% at 2% of strain and of 56% at 10% of strain in comparison with uncharged samples and present a slip localization at 10% of strain.

Keywords: stainless steel, hydrogen absorption, plasticity

1. Introduction

Stress corrosion cracking (SCC) is characterized by a brittle failure appearing in materials whose behavior in inert environment is ductile. This embrittlement results from strong interactions between corrosion processes and plastic deformation. With regard to austenitic stainless steels in chloride solution, metal anodic dissolution and hydrogen reduction at emerging slip bands (sites of passive film breakdown) may play a key role in the SCC process. Studies on dissolution-plasticity interactions [1] and hydrogen-plasticity interactions [2] show that dissolution and...
hydrogen absorption influence the plasticity by modifying macroscopic mechanical characteristics, like creep rate or yield stress. Although the precise mechanism occurring in SCC process is not yet fully understood, hydrogen-induced plasticity localization is increasingly invoked in many SCC cases (bcc, fcc metals and alloys). Such a strain localization induced by corrosion [3][4] was observed on face-centered cubic metals. In comparison with specimens tested in air, an increase in the slip band spacing (SBS) was measured on brass in conditions of stress corrosion in ammonia solution on flat specimens [3] and ahead of a loaded notch tip [4]. These two studies support a local plasticity enhanced by stress corrosion cracking but with manifestly different demonstrations. Indeed, both authors observed a decrease in the slip band density accompanied by an increase in slip band heights (SBH) for Lian et al. [3] and by a decrease in the SBH for Liang et al. [4]. A reinforced slip localization, characterized by increases in SBS and SBH is also observed by atomic force microscopy (AFM) near nanoscratch on polycrystal metastable 316 steel after a hydrogen charging [5]. However the conditions (hydrogen concentration, local plastic deformation level) of a hydrogen-induced slip localization are not precisely defined. Moreover, the possibility of formation of second phases influencing the slip morphology in this type of steel is invoked. The quantitative results of literature are obtained on a relatively low number of grains and may be not representative of the polycrystalline behavior. The present study, dealing with the effects of hydrogen on the slip morphology, presents a quantification of the SBS and SBH. Measurements are carried out by AFM on a sufficient number of grains to obtain statistical results. The average slip morphology is obtained by slow strain rate tests performed on polycrystalline 316L in precise conditions of macroscopic strain level and absorbed hydrogen concentration.

2. Experimental

2.1 Material

The chemical composition of this type 316L stainless steel used for the study is given in table 1. The relatively high content of nickel promotes the stability of austenite reducing a possible formation of second phases.

Table 1
Chemical composition of 316L

<table>
<thead>
<tr>
<th>Elements</th>
<th>Fe</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>S</th>
<th>P</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Cu</th>
<th>N2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt.pct</td>
<td>62.43</td>
<td>0.012</td>
<td>0.41</td>
<td>1.82</td>
<td>0.002</td>
<td>0.016</td>
<td>14.85</td>
<td>17.51</td>
<td>2.75</td>
<td>0.12</td>
<td>0.077</td>
</tr>
</tbody>
</table>

Flat samples were cut from a 2 mm thickness sheet by spark machining. The geometry of the flat tensile specimens are 8 mm gauge length, 2 mm width and 0.5 mm thickness. All the specimens were electropolished. Two heat treatments have been realized to homogenize the grain size of the specimens: 30 min at 1150°C followed by ice-cold quenching; 5 hours at 1200°C followed by ice-cold quenching. It displays two equiaxed microstructures with an average grain size (d) of 140 µm after treatment at 1150°C and of 300 µm at 1200°C.
2.2 Hydrogen charging and plastic deformation

Hydrogen was introduced in the tensile samples by galvanostatic cathodic charging in 0.1N NaOH at 95°C either at 50 mA/cm$^2$ for 72 hours or at 100 mA/cm$^2$ for 6 days in order to increase the hydrogen concentration in the samples. Due to the small hydrogen diffusivity in austenitic stainless steels [6], the hydrogen concentration profile throughout the thickness of the samples can be considered to be homogeneous only for the larger charging time.

The total hydrogen content was quantified by charging small coupons (10 x 6 x 0.5 mm) in the same conditions. The samples were repolished after charging and then melted at 1500°C in a hydrogen analyzer (H-Mat 2500) in order to measure, with the nitrogen carrier fusion thermal conductivity method, the total hydrogen content introduced by cathodic charging. The average hydrogen concentration in the uncharged samples is equal to 3.5 ± 0.3 wt.ppm. Cathodic charging at 50mA/cm$^2$ for 72 hours leads to a hydrogen concentration of 31 ± 8 wt.ppm whereas the hydrogen concentration is equal to 135 ± 5 wt.ppm after charging at 100 mA/cm$^2$.

Just after cathodic charging, the tensile specimens were deformed by uniaxial tensile straining in air at room temperature at a constant strain rate of $10^{-3}$ s$^{-1}$ up to a strain of 2% or 10%, and at $10^{-6}$ s$^{-1}$ up to a 2% plastic strain.

2.3 AFM observations

The characterization of the strained specimen surfaces is carried out by AFM (VEECO type Dimension 3100) by high resolution topography measurements by considering parameters, such as grain size, deformation level and hydrogen concentration. The AFM equipped with an optical microscope allows a preliminary investigation of the polycrystal aggregate in order to focus the AFM observations in the most interesting grains (Figure 1a). Commonly the AFM scan has a size of 50 µm × 50 µm, with 512 pixels per scan line. Two types of images were taken in contact mode: topographic mode and signal error mode. The first mode provides topographic information, like the slip-band spacings and the slip-band heights whereas the second mode instantaneously reflects the variations in lateral forces and allows a clear visualization of the slip line features.

Measurements of all slip-band heights (SBH) and slip-band spacings (SBS) of each analyzed grain were performed with the sections perpendicular to the slip lines extracted from the topographical AFM images (Figures 1b,1c). A software was especially written for the analysis of these sections and allows the automatic or semi-automatic determination of the surface morphological characteristics. The automatic procedure calculates the SBS and the SBH values from the location of slip steps. This mode was seldom used except on perfectly clear surfaces. Indeed the presence of impurities can create extrema which will be considered as slip steps. The semi-automatic version allows to avoid this type of errors. In this case, the location of slip steps is carried out by the user. This one indicates the position of each slip step by using the topographic image of the grain surface (Figure 1b).

Table 2 and figures 3, 4 present the results of the observations of hydrogenated and non-hydrogenated specimens, with a grain size of 140 µm or of 300 µm, plastically strained up to 2% and 10% of strain.
3. Results

The number of analysed grains and of slip bands is given in Table 2 together with the mean values of SBH and SBS. The statistical uncertainties on the mean values are given with a 95% confidence level.

The change in SBS and SBH with the plastic deformation and the hydrogen concentration are illustrated in figures 3 and 4.

The majority of the tests were conducted at $10^{-3}$ s$^{-1}$ (table 2a). A few tests were performed at $10^{-6}$ s$^{-1}$ on fine grained specimens (table 2b).
Table 2
Parameters of the studied populations of SBH and SBS ("-" symbol indicates non-hydrogenated specimens).

a) Mechanical test conditions: $\varepsilon=10^{-3}$ s$^{-1}$- ambient air

<table>
<thead>
<tr>
<th>Grain size (µm)</th>
<th>Hydrogen concentration (ppm)</th>
<th>Macroscopic strain</th>
<th>Number of analysed grains</th>
<th>Number of analysed slip bands (µm)</th>
<th>SBS (µm)</th>
<th>SBH (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d = 300 µm</td>
<td>-</td>
<td>-</td>
<td>11</td>
<td>326</td>
<td>1.57±0.15</td>
<td>20±3</td>
</tr>
<tr>
<td></td>
<td>31 ppm</td>
<td>2%</td>
<td>10</td>
<td>267</td>
<td>1.84±0.23</td>
<td>28±3</td>
</tr>
<tr>
<td></td>
<td>135 ppm</td>
<td>14</td>
<td>181</td>
<td></td>
<td>3.15±0.46</td>
<td>37±4</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>10</td>
<td>499</td>
<td></td>
<td>0.94±0.06</td>
<td>28±3</td>
</tr>
<tr>
<td></td>
<td>31 ppm</td>
<td>12</td>
<td>587</td>
<td></td>
<td>0.90±0.04</td>
<td>45±4</td>
</tr>
<tr>
<td></td>
<td>135 ppm</td>
<td>11</td>
<td>444</td>
<td></td>
<td>1.06±0.08</td>
<td>43±3</td>
</tr>
<tr>
<td>d = 140 µm</td>
<td>-</td>
<td>2%</td>
<td>17</td>
<td>959</td>
<td>0.85±0.04</td>
<td>10±1</td>
</tr>
<tr>
<td></td>
<td>31 ppm</td>
<td>16</td>
<td>1103</td>
<td></td>
<td>0.72±0.03</td>
<td>10±1</td>
</tr>
<tr>
<td></td>
<td>130 ppm</td>
<td>15</td>
<td>751</td>
<td></td>
<td>0.76±0.03</td>
<td>16±1</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>12</td>
<td>772</td>
<td></td>
<td>0.66±0.02</td>
<td>16±1</td>
</tr>
<tr>
<td></td>
<td>31 ppm</td>
<td>12</td>
<td>932</td>
<td></td>
<td>0.60±0.02</td>
<td>15±1</td>
</tr>
<tr>
<td></td>
<td>135 ppm</td>
<td>11</td>
<td>586</td>
<td></td>
<td>0.77±0.04</td>
<td>25±2</td>
</tr>
</tbody>
</table>

b) $\varepsilon=10^{-6}$ s$^{-1}$- ambient air

<table>
<thead>
<tr>
<th>Grain size (µm)</th>
<th>Hydrogen concentration (ppm)</th>
<th>Macroscopic strain</th>
<th>Number of analysed grains</th>
<th>Number of analysed slip bands (µm)</th>
<th>SBS (µm)</th>
<th>SBH (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d = 140 µm</td>
<td>-</td>
<td>2%</td>
<td>8</td>
<td>305</td>
<td>1.00±0.06</td>
<td>12±1</td>
</tr>
<tr>
<td></td>
<td>135 ppm</td>
<td>3</td>
<td>131</td>
<td></td>
<td>0.56±0.06</td>
<td>3±1</td>
</tr>
</tbody>
</table>

Figure 3
Mean slip-band spacing (SBS) as a function of macroscopic strain for fine grained specimens (d=140 µm) and coarse grained specimens (d=300 µm), $\varepsilon=10^{-3}$ s$^{-1}$. 
3.1 Influence of grain size, hydrogen concentration and plastic deformation on the SBH and SBS values after straining at $10^{-3}$ s$^{-1}$

3.1.1 Small grained specimen (d = 140 µm)

In comparison with the uncharged specimens, the stability of the mean SBS value in the samples deformed up to 2 and 10% charged with 135 wt ppm hydrogen and the large increase in the SBH (60% at 2% of strain and 56% at 10% of strain) is a clear demonstration of an increase in the slip localization. In this deformation range, for the samples charged with 135 wt ppm hydrogen, the plastic deformation is localized at the slip bands which appeared before 2% of strain. More precisely, the increase in the mean SBS value is equal to 17% in sample deformed up to 10% charged with 135 wt ppm hydrogen in comparison with the uncharged specimen.

In specimens charged with a hydrogen concentration of 31 wt.ppm, a slight reduction of the mean SBS is observed (figure 3, table 2) in comparison with uncharged specimens. This decrease yields 15% in the 2% deformed samples and 9% in the 10% deformed samples.

3.1.2 Large grained specimen (d = 300 µm)

The SBH increases after hydrogen charging up to 31 wt.ppm and 135 wt.ppm (+40% and +85% respectively) for a 2% strain. These increases in the SBH values are accompanied by the increase in the SBS of 17% with 31 wt.ppm of hydrogen and of 100% with 135 wt.ppm of hydrogen. This is another evidence of a hydrogen-induced slip localization. On the other hand, in the samples deformed up to 2% and 10%, the mean SBH increases regardless of the initial hydrogen concentration (figure 4), suggesting an increased dislocation mobility. The slip localization which occurs at 2% of strain seems to decline at 10% strain especially for the samples charged with 135 wt.ppm of hydrogen. In these samples, the mean values step height are close to those in 31 wt.ppm and the mean slip-band spacing does not change with the hydrogen content.
A few cross-slip events were observed in this 316L steel for the low strain levels. However, a decrease in the cross-slip events is observed in the hydrogenated coarse-grain sample deformed at 10% (Figures 5) in comparison with the non-hydrogenated coarse-grained samples deformed up to 10% at $10^{-3}$ s$^{-1}$. In non-hydrogenated coarse-grained samples, the slip lines are clearly wider and less straight with many cross-slip events (Figure 5a). An increase in the slip planarity is observed at 10% of strain in pre-charged coarse-grained polycrystals.

Figure 5
AFM images (signal error mode) of the slip traces on large grained (d=300 µm) samples strained up to 10% at $10^{-3}$ s$^{-1}$. a) uncharged samples, b) samples pre-charged with 135 wt.ppm. Cross-slip is marked with arrows.

3.2 Influence of hydrogen on the SBS and SBH values after straining of small grained samples at $10^{-6}$ s$^{-1}$

Although only a few AFM measurements were carried out with specimens strained at $10^{-6}$s$^{-1}$ after hydrogen pre-charging, the mean values of SBS and SBH for samples pre-charged with 135 wt ppm, give evidence of a significant slip band density (table 2) with a low SBH value. These experimental conditions lead to a very homogeneous plastic deformation.

4. Discussion

4.1 Influence of the hydrogen content on the slip morphology

The most remarkable effect of hydrogen pre-introduced in the samples before plastic deformation is observed with the fine-grained specimens pre-charged with 135 wt.ppm of hydrogen and strained up to 10% of strain. For these conditions, a localization of the slip is observed. This phenomenon seems to operate well before 10% of strain since SBS do not change between 2% and 10% of strain. A pronounced effect of hydrogen is also observed with coarse-grained specimens containing 31 and 135 wt.ppm hydrogen, at 2% of strain. In this case, the large increase in the SBS and SBH correlated with the increase of the hydrogen concentration, suggests an reinforced slip localization. Since this effect is not observed anymore for the 10%
deformed samples, one can infer that in coarse-grain samples, the hydrogen-induced slip localization occurs in the first stages of deformation.

Katz et al. [5] observed a more significant effect of hydrogen absorption on the slip morphology whereas the conditions of hydrogen charging are less severe due to lower charging time and temperature than in the present work. SBH increases by a factor three and SBS by a factor six along the pile-up produced by nanoscratch tests. The differences may be due to an extremely localized hydrogen concentration in the near-surface region and high uncontrolled localized deformation level inherent in the nanoscratch tests.

The increase in the SBH confirms observations reported for stainless steels [3-6] and supports previous experimental observations [8-10] which consider that mobile dislocations induce an accelerated hydrogen transport into the bulk as first suggested by Bastien and Azou [10]. The hydrogen transport may be in the form of Cottrell atmosphere on moving dislocations leading to high and localized hydrogen concentration. Experimental observations and theoretical calculations suggest that the presence of hydrogen atmospheres in solid solution decreases the barriers (elastic interactions between dislocations) to dislocation motion and therefore increases the dislocation mobility [12][13].

At $10^{-3}$ s$^{-1}$, the hydrogen-induced slip localization can be related with an increase in the planar slip, as it is observed in the coarse-grain samples with a macroscopic strain of 10% (figure 5). Such an increase in planar slip was previously reported [7,14-17]. A decrease of the stacking-fault energy of about 20% was measured for 310s stainless steel [14] whereas a 40% reduction of the stacking-fault energy was reported for AISI 304 steel [16] inducing a lower propensity to cross-slip.

The decrease in the SBS observed at $10^{-3}$ s$^{-1}$ on small grained samples hydrogenated with 31 wt.ppm at 2% and 10% strain and at $10^{-6}$ s$^{-1}$ may indicate a decrease in the dislocation mobility. Thus the slip localization observed in 316L steel depends on the hydrogen concentration and on strain rate. In samples with grain size of 140 µm, the decrease in the hydrogen concentration and in the strain rate tend to homogenize the slip distribution at the surface. In fine grained samples, for the strain rate of $10^{-3}$ s$^{-1}$ and the higher deformation level (10%), the stability of mean SBS values linked with the increase in the SBH in the samples pre-charged with 135 wt ppm hydrogen could be due to the segregation of hydrogen on dislocations tending to localize the slip. This hydrogen segregation and the resulting heterogeneity of hydrogen concentration, which would be more pronounced for large hydrogen concentrations, lead to a strain localization.

4.2 Grain size effects on the slip morphology

The change in SBS between 2 and 10% of strain (Figure 3) indicates a higher increase in the slip band density in this deformation range in the coarse grained samples in comparison with the small grained samples, regardless of the hydrogen concentration. This observation suggests a more relatively significant accommodation of the plastic strain by intensification of the primary slip system in the coarse grained samples. Indeed, more multiple slip, mainly initiated at grain boundaries, is observed in fine grained polycrystals (Figure 6). This process of intergranular accommodation results from incompatibilities of plastic deformation between adjacent grains. These observations reflect that, if the grain plastic deformation is described as the sum of the contributions of the grain boundary regions and the grain core, the contribution of the grain core, characterized by a development of the primary slip system, is much more important in the coarse grains. As for the small grains, they show a more significant intergranular deformation,
characterized by multiple slip at grain boundaries, in particular for 2% of strain. This difference in the plastic deformation processes may explain the relatively high effect of hydrogen on coarse-grain primary slip at 2% of plastic deformation, especially on the slip-band spacing distributions (Table 2). More precisely, in the first steps of fine-grain polycrystal plastic deformation, the grain boundary slip system activation tends to occult the core primary one. In previous studies on the stages of deformation in terms of hardening rate and dislocation structures of 316L steel [18,19] it was shown that intergranular long-range internal stresses decrease with the grain size at the stage I of deformation with the appearance of multiple slip and cross-slip at the stages II and III [190]. Consequently, the stresses related to the grain boundaries and the subsequent mechanisms may delay the effect of hydrogen on the primary slip system, subject of the present study, in the small grains.

One can thus infer that the effects of absorbed hydrogen on slip morphology are less pronounced at 2% of strain on fine grained samples because of the relatively low contribution of the intragranular slip at the considered deformation levels. In this case, a high hydrogen concentration (135 wt.ppm) is necessary to significantly modify the slip morphology by increasing the mean slip-band height. Combined with a high macroscopic strain (10%), a high hydrogen concentration induces a slip localization in fine grained polycrystals.

Figure 6  
Optical images of the deformed grain surface illustrating a higher occurrence of the multiple slip in fine grained (a) than in large grained (b) samples ($\varepsilon=2\%$, $10^{-3}$ s$^{-1}$).

a-  d = 140 µm                                      b-  d = 300 µm

5. Conclusion

This study provides a statistical quantification of the effects of hydrogen concentration, grain size and macroscopic deformation on the slip morphology of a polycrystalline stainless 316L steel. The surface observations performed by atomic force microscopy after hydrogen charging and plastic deformation by tensile straining evidence a modification of surface slip morphology in the presence of internal hydrogen.

Hydrogen induces a slip localization in coarse grained specimens (d=300 µm) strained up to 2% of macroscopic strain at $10^{-3}$ s$^{-1}$. This effect is characterized by an increase in the mean values of
the slip band spacing (+17% with 31 wt.ppm hydrogen and +100% with 135 wt.ppm hydrogen) and an increase in the slip band height (+40% with 31 wt.ppm and 85% with 135 wt.ppm hydrogen). At 10% of macroscopic strain, hydrogen significantly affects the slip-band height distributions (+55%) and decreases the propensity to the cross-slip. In fine grained samples (d=140 µm), a slip localization at 10% of strain with increases of 17% in the average slip-band spacing and of 56% in the average slip-band height was observed for samples pre-charged with 135 wt.ppm of hydrogen. A decrease in the SBS observed at 10⁻³ s⁻¹ on samples hydrogenated with 31 wt.ppm at 2% and 10% strain and at 10⁻⁶ s⁻¹ is observed. The influence of the grain size on the slip morphologies are discussed in terms of internal stresses.

References

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