New super martensitic stainless steels for oil & gas industry: correlation between molybdenum content and hydrogen embrittlement

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Abstract

Today, requirements for super martensitic stainless steels in terms of mechanical and corrosion resistance properties increase continuously. Effects of several alloying elements such as Cr, Mo or Cu are studied to reach better material properties. But the relationship between chemical composition and failure mechanism at low pH is still unclear due to the complexity of sour environment.

In this context, this study focused on laboratory stainless steel heats containing different controlled amounts of Ni and Mo. Not only simple electrochemical tests in sour medium have shown better behavior of alloys with high content of Mo, but electrochemical impedance spectroscopy and proof rings tests also confirmed these corrosion resistance improvements. Slow strain rate traction measurements have been performed in sour medium to estimate hydrogen sulfide effects on mechanical properties. To highlight hydrogen embrittlement effect on our structure, hydrogen permeation analysis is used to estimate diffusion coefficient. Besides the amount of hydrogen in samples after stress corrosion tests have been also determined with hydrogen analyzer based on thermal conductivity measurements.

Keywords: Martensitic Stainless Steels, Sulfide Stress Cracking, Electrochemical Impedance Spectroscopy, Slow Strain Rate Traction, Hydrogen Permeation
Introduction

Martensitic stainless steels are commonly used in oil and gas industry. They present good mechanical and corrosion resistance properties with lower production costs compared to duplex stainless steels [1]. Moreover they can be used in severe conditions without using inhibitors or coatings thanks to a low carbon content. Martensitic stainless steel EN 1.4418 presents passive behavior for sour media at pH superior than 4 [2]. But at lower pH, corrosion products are formed and failures occurred. In most cases, the failure is associated to hydrogen embrittlement induced by hydrogen sulfide (H$_2$S). But the corrosion mechanism in this medium is not completely clear.

Many studies deal with hydrogen sulfide corrosion resistance at different partial pressure of hydrogen sulfide, pH and temperature [3]–[5]. But it seems difficult to dissociate experimental parameters effects. Several authors explain the cracking by hydrogen embrittlement induced by hydrogen sulfide [6]–[8]. Hydrogen sulfide would react with metal surface to produce sulfides. These sulfides would encourage hydrogen absorption and consequently a locally decrease in mechanical properties [7], [9].

The aim of this study is to highlight molybdenum effect on corrosion resistance in sour media. Different laboratory heats containing controlled amount of molybdenum have been characterized in terms of electrochemical behavior, stress corrosion resistance and electrochemical impedance.

Materials and methods

Materials

Microstructure and electrochemical properties were investigated on three laboratory heats. Chemical compositions of the different tested laboratory heats are detailed in Table 1. Each heat was carefully quenched at 1100°C and aged around 600°C. The aging temperature was chosen so that each heat has comparable microstructure in terms of retained austenite content.

<table>
<thead>
<tr>
<th>Heats</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4418</td>
<td>15</td>
<td>5.0</td>
<td>0.8</td>
</tr>
<tr>
<td>Steel A</td>
<td>15</td>
<td>5.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Steel B</td>
<td>15</td>
<td>5.0</td>
<td>2.25</td>
</tr>
</tbody>
</table>

Stress corrosion cracking

To evaluate the resistance of the different samples to stress corrosion cracking, measurements were conducted using applied load with proof rings, following the NACE standard TM0177-05 method A. The solution contained 50 g/L NaCl, 25 g/L acetic acid, 4.1 g/L sodium acetate, with 10% of H$_2$S in CO$_2$ and the pH was adjusted with NaOH droplets if necessary. First, the
solution was deoxygenated with \( \text{N}_2 \) at least for one hour and gas bubbling was maintained during the whole test duration. This electrolyte corresponds to NACE B medium.

The applied stress was at 90% of yield strength. Measurements were conducted in triplicate for each test condition to ensure reproducibility.

Slow strain rate traction (SSRT) tests had been performed on all laboratory heats with specimens of gauge length 25 x 5 mm. Specimens were polished up to 1200, then washed and rinsed. The nominal strain rate was \( 10^{-6} \text{ s}^{-1} \). Two samples of each composition were tested in air as reference. Measurements in corrosive environments were performed in NACE B at pH=3.5 and 23 °C. Open-circuit voltage (OCV) was measured with a classical three electrodes cell, with platinum as counter electrode and saturated calomel electrode as reference.

Electrochemical measurements

Samples were polished until 1200 SiC, then, the surface was washed in a solution of ethanol and acetone (50/50) in an ultrasonic bath for a few minutes. After that, samples were rinsed with distilled water and dried with compressed air. Finally, they stayed 24 hours in air before running the experiments in order to have a good reproducibility of the passive film.

The measurement system was a standard three electrodes cell, consisting of the investigated sample (exposed surface of 0.785 cm²) as the working electrode, a platinum disc as counter electrode and a saturated calomel electrode as the reference electrode. The electrolyte was NACE B.

The open-circuit potential was measured for four hours. Then, the sample was polarized from -20 mV vs. open-circuit voltage (OCV) to the potential for which a current of 5 mA/cm² was reached. The scan rate was 1.67mV/s. For electrochemical impedance spectroscopy (EIS), measurements were performed at open-circuit voltage from 50 mHz to 20 kHz. The amplitude signal was 20 mV.

Results and discussion

Polarization curves of all heats recorded in NACE B solution at pH=3.5 are presented in Figure 1. First, 1.4418 and steel A appear active in this medium whereas steel B is passive. Corrosion current for 1.4418 is around 100 \( \mu \text{A/cm}^2 \) and for steel A around 40 \( \mu \text{A/cm}^2 \). These currents are too high to consider both heats as passive. Moreover, after polarizations measurements, black corrosion products are visible on sample surfaces. For steel B, corrosion current is around 0.2 \( \mu \text{A/cm}^2 \), which corresponds to a passivation current for a passive steel. So increase of molybdenum content as in steel B decrease corrosion current and improve passivity. Moreover, corrosion potential increases with molybdenum content, confirming that corrosion resistance is improved.
In order to compare corrosion resistance performance of all heats, different parameters (Traction limit resistance, area reduction and total elongation) are compared. To normalized values, the value obtained in corrosive medium is divided by the value obtained in the air. The calculated percentage corresponds to remaining properties in the corrosive medium. For all parameters, molybdenum content increases this ratio (Figure 2). In corrosive medium, the loss of necking is between 66 and 80%, probably due to hydrogen embrittlement. But the traction limit resistance does not seem to decrease sharply with corrosion and for all heats yield strength is not affected by corrosion. This suggests that corrosion process does not seem to affect the elastic part of traction curve but modifies the ductility, particularly near traction limit resistance, where retained austenite transformation into martensite can occur.

After SSRT tests, only specimens from steel B remain with corrosion products-free surface, but failure surface was not completely ductile. Intergranular facies is observed in edge, characteristic of hydrogen absorption. So passivity would not prevent hydrogen absorption, but could reduce it.
During stress corrosion measurements, potential evolution is always divided in three steps for all heats. At the beginning of the test, the potential is around $-0.2 \text{ V}_{\text{SCE}}$. Then potential falls down to $-0.5 \text{ V}_{\text{SCE}}$ and stays around $-0.5 \text{ V}_{\text{SCE}}$. Finally, the potential drops to $-0.6\text{V}_{\text{SCE}}$ few hours before the failure. Typical curve shape is represented on Figure 3. Electrochemical impedance spectroscopy has been performed on all heats to characterize corrosion process during SCC tests. Impedance diagram was recorded at the beginning and at the end of the potential plateau around $-0.5\text{V}_{\text{SCE}}$ (Figure 3) for each heat. Impedance diagrams are presented on Figure 4. At the beginning of the plateau, steel B presents a higher polarization resistance than the two other. Then, at the end of the plateau, few hours before failure, 1.4418 and steel A present a very low impedance with a diffusion contribution at low frequencies. Indeed, diagram presents an angle of 45° for low frequencies, which is characteristic for diffusion process. For steel B, the polarization resistance is much higher, but the diffusion contribution is also visible. This means that for the three grades hydrogen absorption should be considered, but the process seems to be slowed down by increasing molybdenum content.

For all heats, diffusion contribution has been identified even if the grade is passive as steel B. This diffusion contribution could be associated to hydrogen diffusion in the matrix leading to hydrogen embrittlement [10], [11]. So molybdenum content increase would not prevent from hydrogen embrittlement but would slow down its effects.
Figure 3: Typical shape of open-circuit evolution during a stress corrosion test in NACE B solution at pH=3.5

Figure 4: Impedance spectra of 1.4418 (−), steel A (−), steel B (−) in NACE B solution (pH=3.5) under 90% of yield strength at begin (●) and end (▲) of the potential plateau around −0.5V\text{SCE}

**Conclusions**

Molybdenum has a positive effect on stress corrosion resistance. At pH=3.5 in NACE B solution, corrosion current decreases for high content of molybdenum and corrosion potential
increases with it. On SSRT tests, loss of mechanical properties is reduced by increasing molybdenum content. But, in all cases, necking is strongly reduced, which is characteristic for a brittle fracture. Hydrogen embrittlement could be responsible for this loss and electrochemical impedance spectroscopy showed that diffusion process was present for all heats. Moreover, polarization resistance decreases with time for all heats indicating decrease of corrosion resistance.

References


