

Sulfide Stress Cracking of Low Alloy Steels for Oil and Gas Production: Revisiting the Effect of Ni as an Alloying Element

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ABSTRACT

In accordance with Annex A of ANSI⁽¹⁾/NACE⁽²⁾MR0175/ISO⁽³⁾ 15156-2, low-alloy steel (LAS) components for oil and gas (O&G) are acceptable if they contain less than 1 wt.% Ni. As an alloying element in steels, nickel improves low-temperature toughness and hardenability and does not promote the formation of carbides that could retain hydrogen into the steels. In this work, a set of five steels with different nickel content was specially fabricated to study the effect of that element on the sulfide stress cracking (SSC) resistance. Quenching and tempering (Q&T) heat treatments were customized to each chemical composition to obtain a tempered martensite microstructure with a hardness level below but near the 22 HRC threshold. The effect of nickel content on the anodic and cathodic behavior of those steels was evaluated by electrochemical polarization tests in substituted NACE TM0177 A test solution, where H₂S bubbling was replaced by thiosulfate additions (i.e., Tsujikawa Method). Hydrogen permeation tests were conducted in a Devanathan-Stachurski cell, to evaluate the effect of nickel on the hydrogen diffusion. Additionally, slow strain rate tests (SSRTs) were performed at the open circuit potential (OCP) to assess the role of nickel on the SSC resistance.

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Key words: LAS, sulfide stress cracking, H₂S, hydrogen, thiosulfate, permeation, slow strain rate test

INTRODUCTION

The first reported failures of oil and gas (O&G) steel components due to sulfide stress cracking (SSC) occurred in Canada, France, and the United States in the early 1950s.¹ Since then, several combinations of chemical composition and microstructure for different grades of steels were thoroughly evaluated. Fraser, Treseder and Eldredge studied the metallurgical factors affecting SSC resistance among 104 low-alloy steels (LASs).^{2,3} In a following investigation by Treseder and Swanson, when comparing steels with the same hardness level, the SSC susceptibility increased if the nickel content was higher than 1 wt.%.⁴ Considering the metallurgical advantages of adding Ni to steels, such as the increase in hardenability and the decrease of the ductile-to-brittle transition temperature, this limit has been discussed since the late 1960s.⁵⁻⁷ Snape pointed out the possible presence of deleterious phases, i.e., retained austenite and untempered martensite, in the final microstructure of the steels studied by Treseder and Swanson.^{4,7} Nickel stabilizes the austenitic phase at lower temperatures due to its effect on the lower critical temperature (A_1). If A_1 is exceeded during tempering, untempered martensite can be present in the final microstructure, which greatly reduces SSC resistance.^{4,7} Snape proposes that steels with an adequate quenched and tempered (Q&T) microstructure can be resistant to SSC even at Ni contents beyond 1 wt.%.⁷ However, a maximum limit for nickel as an alloying element was incorporated in the requirements for SSC resistant LASs as detailed in Annex A of ANSI⁽¹⁾/NACE⁽²⁾ MR0175/ISO⁽³⁾ 15156-2 standard.⁸ The standard sets a maximum hardness level of 248 HV (22 HRC) and a nickel content below 1 wt.%, and it excludes free-machining steels and those in the cold-worked state.⁸ On the other hand, LASs that do not comply with those guidelines should be extensively qualified for SSC according to the test methods required by Annex B of ANSI/NACE MR0175/ISO 15156-2 and described in the NACE TM0177 standard.⁸ Nonetheless, many authors suggest that microstructure, rather than the content of a given alloying element, is in charge of determining SSC resistance.^{7,9,10} Another important factor to be considered is the steel cleanliness to avoid undesired effects between the alloying and residual elements.⁹

The effects of Ni as an alloying element in LASs include an improvement in static and dynamic mechanical resistance, an increase in ductility and hardenability and a reduction in the ductile-to-brittle transition temperature without impacting negatively on steels' weldability.^{5,6,11,12} These attributes allow using thick-wall cross-section components with a uniform microstructure in extreme environments (e.g., high-pressure and high-temperature).¹³ Several authors have analyzed and discussed the effect of nickel in SSC resistance of low-alloy commercial and laboratory steels in H₂S-containing environments in normalized, normalized and tempered, and Q&T conditions.^{7,12,14-21} Although the selected testing method could result in discrepancies between the above mentioned authors' results, the main effect of Ni in SSC susceptibility seems to be related to the formation of trenches and their morphology. A trench is a deep pit and its presence indicates a transition between pitting and cracking.²² Other authors, consider that with a suitable microstructure containing spheroidized and fine dispersed carbides in a ferrite matrix, e.g., tempered martensite, an acceptable SSC resistance can be achieved independently of the chemical composition.^{23,24}

This work focuses on determining the effect of nickel content on some of the variables that affect SSC of quenched and tempered LASs, independently from other alloying elements.²⁵ Consequently, non-standardized tests and a simplified chemical composition were chosen for studying the effect of Ni on SSC in this work. The simplified chemical composition avoided the influence of carbide forming elements like Cr, Mo and V in the alloys used in this work. Since some authors proposed a mechanism

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for cracks initiation and propagation in H₂S-containing environments based on active path corrosion (APC) and hydrogen embrittlement (HE), electrochemical polarization tests were conducted to analyze the impact of nickel on the anodic and cathodic reaction rates.^{15,17} Gaseous hydrogen permeation tests were performed to address the role of nickel in hydrogen trapping and hydrogen diffusion. Similarly, slow strain rate tests (SSRT) were carried out to evaluate the effect of nickel on trenching and ductility loss at the open circuit potential (OCP).

EXPERIMENTAL PROCEDURE

Materials and Heat Treatment

The nickel content was varied between 0 and 5 wt.%, in a carbon steel with a base chemical composition as indicated in Table 1. Five 45 kg ingots with varying nickel content were obtained by vacuum induction melting and subsequently forged and hot-rolled to attain plates of 10 mm nominal thickness. The addition of C, Mn, and Si, as indicated in Table 1, was required to obtain a fully quenched microstructure in the 10 mm square bars, from which samples for all tests could, then, be machined.²⁶ Sulfur and phosphorus contents were limited to maximum levels of 0.0010 wt.% and 0.0006 wt.%, respectively, to avoid the presence of detrimental inclusions and embrittlement in the steels.

Specimens were normalized and Q&T to obtain a microstructure consisting of approximately 100% tempered martensite, independently of Ni content. Limits for temperatures for those heat treatments were fixed considering the effect of Ni on the lower critical temperature (A_1), which was previously evaluated with differential scanning calorimetry.²⁶ If A_1 is exceeded during tempering, austenite formation is followed by its transformation to untempered martensite in the cooling stage.⁷ Tensile tests on air, through-thickness Rockwell C hardness (HRC) measurements, and a metallographic characterization, as shown in other work, indicated that similar mechanical properties and a homogeneous Q&T martensitic microstructure were obtained after performing the heat treatments detailed in Table 1.²⁶ Additionally, HRC surface measurements were used as a rapid control of the heat treatment effectiveness for each test specimen. All the heat-treated alloys verified a hardness level below but near the 22 HRC threshold established by ANSI⁽¹⁾/NACE⁽²⁾ MR0175/ISO⁽³⁾ 15156-2 standard. Carbon steel and 0.48 wt.% Ni containing steel specimens had a hardness below 20 HRC, the lowest level measurable on this scale.

Table 1
Chemical composition and mechanical properties of the steels

N° Alloy	Chemical Composition [wt.%]					Mechanical Properties		
	C	Mn	Si	Ni	Fe	Hardness [Rockwell C]	R _{p 0.2%} [MPa, (ksi)]	Plastic Elongation (25.4 mm gauge length)
1	0.16	1.24	0.25	--	Bal.	< 20	604 (88)	0.22
3	0.17	1.22	0.25	0.48	Bal.	< 20	614 (89)	0.20
4	0.16	1.22	0.25	0.97	Bal.	21	609 (88)	0.19
7	0.16	1.32	0.22	3.06	Bal.	21	630 (91)	0.20
8	0.16	1.31	0.24	5.04	Bal.	20	608 (88)	0.26

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Testing Environment

All the tests were conducted in a deaerated NACE TM0177 A base solution (5 wt.% NaCl and 0.5 wt.% glacial acetic acid) at a pH between 2.7 – 2.8, at room temperature and 1 atm pressure.²⁷ In all cases, the H₂S bubbling was substituted by adding sodium thiosulfate (Na₂S₂O₃) to simulate an H₂S-containing environment. This alternative was proposed by Tsujikawa et al. for SSC testing of LASs and corrosion resistant alloys.²⁸ In comparison with conventional gaseous H₂S evaluations, laboratory tests with thiosulfate are simpler because sodium thiosulfate is an innocuous salt. According to Tsujikawa, in acid environments and at the corrosion potentials of LASs, thiosulfate reduces to H₂S, generating this gas locally at the surface of the metal.²⁸ The optimum concentration of thiosulfate as a substitute of H₂S in NACE TM0177 A base solution is 10⁻³ M.^{28–31} At a higher concentration the corrosion rate increases, promoting the formation of thicker corrosion product films on the steels' surface which inhibits the amount of absorbed hydrogen.^{29–31} Kappes et al. determined that at a concentration of 10⁻³ M S₂O₃²⁻ in the TM0177 A base solution, the effective H₂S concentration in the vicinity of a carbon steel electrode's surface, is equivalent to that obtained in the same base solution saturated with a partial pressure of 0.56 kPa H₂S in nitrogen.³⁰ Additionally, Tsujikawa reported that the ductility loss in a SSRT due to SSC in a 10⁻³ M S₂O₃²⁻ substituted TM0177 A base solution was similar to that obtained in simulated ocean water saturated with 0.1 MPa H₂S.²⁸

Unless stated otherwise, all the tests reported in this work were conducted in a 10⁻³ M S₂O₃²⁻ substituted TM0177 A base solution, which was prepared by adding 5 ml of a fresh 0.2 M Na₂S₂O₃ solution per liter of TM0177 A base solution. Special considerations were taken to avoid potential contamination of the electrolyte with oxygen. Firstly, the solution and the testing cell were deaerated with N₂ bubbling before thiosulfate was added to the solution. After adding thiosulfate to the deaerated solution, it was transferred to the cell, where the steel electrode was placed, and the corresponding test was started. Additionally, in tests that required electrochemical polarization, the counter electrode (CE) was placed in a bridge tube that allowed ionic conduction through a frit-glass but avoided the contamination of the test solution with products of the reactions occurring at the surface of the CE.

Electrochemical Tests

Anodic and cathodic potentiodynamic polarization curves in a deaerated 10⁻³ M S₂O₃²⁻ substituted TM0177 A base solution were obtained to determine the effect of nickel in the electrochemical behavior of each steel composition. The OCP was measured for 24 h before polarizing the electrode. A scan rate of 0.167 mV/s was used. For each experimental condition, all the tests were conducted in duplicate.

Specimens were cut from the plates and ground with SiC emery paper up to 600 grit. The specimens were coated with epoxy resin, leaving an area of 1.5 cm² of the plane containing the rolling and transverse directions of the plate exposed to the solution. A five-port glass cell with N₂ deaeration capabilities was used. The steel specimen was immersed in the solution once it was deaerated. The potential was measured *versus* a KCl saturated calomel reference electrode (SCE) and a graphite bar served as a counter electrode. For safety reasons, the gas exiting the cell was passed through a trap containing 0.1 M NaOH to neutralize and capture the H₂S formed during the thiosulfate reduction.

Additionally, OCP evolution was measured during 72 h in a deaerated 10⁻³ M S₂O₃²⁻ substituted TM0177 A base solution to allow the formation of a sulfide film on the exposed area of the specimen. The nature of the films formed in 3 and 5 wt.% Ni LASs was analyzed by grazing incidence X-ray diffraction at an angle of 1° and a 0.02° step using a multipurpose diffractometer with Cu radiation. Subsequently, the sulfide film was removed from each specimen by a 30 s immersion in an inhibited HCl solution, containing 20 g of antimony trioxide and 50 g of stannous chloride per liter of concentrated HCl solution (36.5%).³² Scanning electron microscopy (SEM) was used to analyze the morphology of the metallic surface after the sulfide film removal. Blank tests (i.e., specimens polished to 600 grit and subsequently immersed for 30 s in the inhibited HCl solution) were also observed under SEM to avoid spurious interpretations from the specimens' exposed metallic surface analysis.

Hydrogen Permeation Tests

The effect of Ni on hydrogen transport was studied using hydrogen permeation tests conducted in a Devanathan-Stachurski cell.³³ Gaseous H₂ (purity higher than 99.999%) circulated in the charging cell at atmospheric pressure. On the detection side, the surface of the steel specimen was polarized at 200 mV above the hydrogen reversible potential for each test temperature, in a deaerated 0.1 M NaOH solution (pH ~ 13).

The steel membrane had a thickness of 1.5 mm and its surface was ground with SiC emery paper up to 600 grit. Both sides of the membranes were electropolished in a solution of 10% HClO₄ and 90% ethylene glycol monobutyl ether to remove the plastic deformation imparted during grinding operations. Finally, a thin palladium coating was electrodeposited on both sides of the sample following the procedure proposed by Bruzzoni.³⁴ After Pd electrodeposition, the specimens were heat-treated in air at 120°C for 16 hs to remove hydrogen absorbed in the steel during the previous processes.

Gaseous hydrogen charging transients' curves were obtained at 30°C, 50°C, and 70°C. The temperature was controlled by immersing both charging and detection cells in a thermostatic silicone oil bath, thus minimizing temperature fluctuations that strongly affect the hydrogen diffusion process and hence the measurements of the hydrogen oxidation current on the detection cell.³⁵ Tests were conducted in duplicate. Hydrogen charging was initiated by circulating H₂ in the charging side of the cell once a stable background density current around 0.001 µA/cm² was attained. On the other hand, air was circulated to obtain the decaying transients. Using the same specimen and maintaining the same overpotential on the detection side, the test temperature was modified and typically, after a 12 h temperature stabilization period with air circulating on the charging side, a low and stable background current density was attained on the detection side before each H buildup transient.

In this work, an effective diffusion coefficient (D_{eff}) was calculated from each transient with the time-lag method as recommended in previous works.³⁶ This method considers the time elapsed to achieve a H flux equivalent to 63% of the corresponding H permeation flux at steady state, τ_{lag} .³⁷ For a membrane of thickness L , the effective diffusion coefficient is calculated as in Equation 1³⁷:

$$D_{\text{eff}} = L^2 / 6\tau_{\text{lag}} \quad (1)$$

Slow Strain Rate Tests

Slow strain rate tests were conducted to evaluate SSC susceptibility at OCP as a function of nickel content. Considering the exposed steel area and the expected duration of the SSRT, a 3.5 l poly (methyl methacrylate) cell was specially constructed. The large capacity of the cell ensured a solution volume to exposed steel area ratio of 0.54 l/cm² that prevented consumption of thiosulfate during the test.³⁰ The cell had five ports for the working electrode, counter electrode (in case electrochemical polarization was required), reference electrode, and N₂ inlet/outlet. The N₂ outlet was connected to a caustic trap to neutralize produced H₂S.

Cylindrical specimens with threaded ends were machined from the plates with the axis parallel to the rolling direction. The bars were heat-treated to produce a Q&T microstructure with mechanical properties as detailed in Table 1. The gauge diameter and length were 3.81 mm and 25.4 mm, respectively, and machining was conducted following the recommendations in NACE TM0198.³⁸ The gauge section was longitudinally polished with SiC emery paper up to 4000 grit to obtain an average roughness below 0.25 µm as required in the standard.³⁸ Specimens were threaded in pull rods and an epoxy coating was applied to the shoulders of the specimens and the pull rods, leaving only the gauge length uncoated, thus avoiding undesired galvanic effects and corrosion reactions on the pull rods.