

The Susceptibility of Nanostructured Steel to Sulfide Stress Corrosion Cracking as a function of H₂S concentration, pH and Heat Treatment

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ABSTRACT

The present work evaluates the sulfide corrosion cracking susceptibility of nanostructured bainitic steel with a dual-phase structure of bainite and retained austenite. Notch Tensile Slow Strain Rate Testing (NTSSRT) method was employed to assess the threshold stress intensity values (K_{ISSCC}). Microscopic morphology and analysis of fracture surface were carried out by scanning electronic microscope (SEM). Hydrogen sulfide (H₂S) concentration with the range from 0.02 mole% to 35 mole% and pH value of 3.5 and 5.5 were controlled in 1% sodium chloride (NaCl) solution using sodium acetate/acetic acid buffer solution.

The results show that K_{ISSCC} values are much lower in a more acidic environment. Heat treatment makes nanostructured steel more susceptible to SSC. Many secondary cracks were observed on the fracture surface, which may initiate from quasi cleavage caused by hydrogen in brittle fracture region. Inclusions can accelerate the crack propagation and failure process. Microscopic observation shows cracks can initiate from or arrested in austenite. Further relation between crack propagation and microstructure can be explored by employing Electron Backscatter Diffraction (EBSD) technique.

Key words: Nanostructured steel, sulfide stress corrosion cracking, pH, hydrogen sulfide concentration

INTRODUCTION

Nanostructured bainitic steel, a new class of ultrahigh-strength steel, has high potential applications in the oil and gas industry. Its superior mechanical properties come from fine bainitic ferrite and retained austenite structure.¹⁻³ Hydrogen embrittlement is a potential problem in the oil and gas industry, characterized by a reduced mechanical properties.^{4,5} Hydrogen sulfide (H₂S) sour environment leads to issues of sulfide corrosion cracking (SSC).^{6,7} The formation of iron sulfide on the metal surface leads to localized corrosion and initiation of cracks. Hydrogen embrittlement follows the pitting related active path corrosion, causing fast failure of steels.⁸

The main factors that are responsible for SSC include the external environment, internal stress, and metallurgy.⁹ Environmental factors are H₂S concentration, pH, temperature, chloride content and so on. Increasing H₂S concentration increases hydrogen absorption and diffusion into metal.¹⁰ Low pH H₂S environment promotes the destructive effect of H⁺ on iron sulfide film.¹¹

Internal stress of materials can be produced in the manufacturing process. Microstructural features such as phase, grain size, grain boundary characteristics, inclusions, and precipitations play a vital role in SSC susceptibility. Specifically, microvoids, grain boundary, and dislocation act as reversible traps, and inclusions, carbides, and oxides are irreversible trap sites due to different trap binding energy.¹²⁻¹³ Hydrogen can be captured by inclusions and precipitates and transported by dislocation to potential crack sites.¹⁴⁻¹⁵ The diffusivity of hydrogen in the iron body-centered cubic (BCC) structure is higher than that in the face-centered cubic (FCC) structure, but solubility in BCC is much lower. Trapping more hydrogen can make materials more susceptible to SSC.¹⁶⁻¹⁷ Flexible heat treatment helps to manufacture nanostructured steel in large dimensions, but makes coarser microstructure and non-uniform dislocation density.¹⁸ Nanostructured bainitic steel with an ultra-high strength has a high content of retained austenite and high dislocation density. The corresponding SSC susceptibility needs further investigation.

In this work, the SSC susceptibility of an ultra-high strength nanostructured bainitic steel was evaluated as a function of H₂S concentration, acidity of solutions and heat treatment via notch tensile slow strain rate testing method. Microstructural analysis was performed to illustrate the fracture mechanism and effects of microstructure on sulfide corrosion cracking.

EXPERIMENTAL PROCEDURE

Experimental Design

The International Organization for Standardization (ISO)⁽¹⁾ 15156 standard defines a series of possible sour environments depending on brine pH and H₂S content in associated gas.¹⁹ Based on the definitions of the sour environments an experimental design test matrix for the evaluation of the SSC susceptibility can be proposed as shown in Table 1.

Table 1
Experimental matrix to study the K_{ISSC} of nanostructured steel

pH	Test condition	H ₂ S concentration (mole %)
3.5	Brine solution	0.7, 3.5, 5.75, 35
5.5	Brine solution	0.02, 0.35, 3.5, 30

The experimental design shown in Table 1, considers the H₂S content and the solution pH as independent variables. Additionally, the test matrix is also applied nanostructured steel after tempering to evaluate the possible effect of the carbide formation on SSC

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behavior. The dependent variables in the present study will be the evaluation of the susceptibility to SSC, by means of the evaluation of the K_{ISSC} parameter.

Slow Strain Rate Test Coupling with H₂S

The fracture mechanics approach is used to evaluate the SSC susceptibility of high-strength low-alloy steels by using threshold stress intensity parameter, K_{ISSC} .²⁰ Notch Tensile Slow Strain Rate Testing (NTSSRT) method was employed to evaluate K_{ISSC} value with a strain rate of 10^{-6} s^{-1} which is highly recommended and widely used. Contest Load Frame Test System* was used to carry out NTSSRT experiments with a load capacity of 10000 lbf (4450 N), equipped with a digital stepper motor to ensure a steady extension rate. The diagram of the notched sample is displayed in Figure 1. The notch is 30% of gage diameter 0.25 inch (6.35mm) with 60° and notch tip radius of 0.5 mils (0.012 mm). Smooth samples were also tested in an inert environment with a diameter of 0.125 inch (3.175mm).

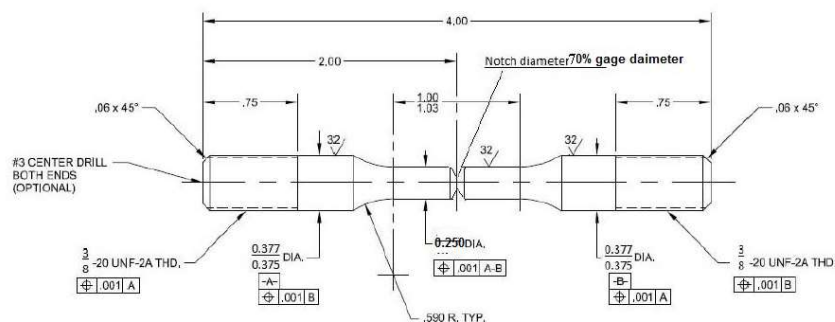


Figure 1: Diagram of the notched tensile sample used for SSRT experiment

Different levels of H₂S concentrations and pH values were considered in this study to evaluate the susceptibility to SSC as shown in the test matrix in Table 2.

The control of H₂S concentration in aqueous condition was realized by introducing sulfide species (sodium sulfide in this work) at a sour aqueous environment, following the recipe in Table 2. The H₂S in gas phase ranges from 0.02 mol% to 35 mol% was transformed into H₂S activity in liquid state by OLI system based on thermodynamics.

Before applying a load, the tensile sample was immersed in 250 mL brine solution (containing sodium chloride, sodium acetate, and sodium sulfide) and purged with nitrogen gas for 1 hour. The oxygen contamination can enhance corrosion rate, affect the nature of corrosion products and lower the hydrogen uptake due to the formation of H₂S-O₂ reaction products.²¹⁻²² The dissolved oxygen content decreases to lower than 35 (parts per billion) ppb after N₂ purge, which meets the requirement of NACE TM0177 standard.²³ Continuous oxygen contamination at low concentration is always possible during the standardized experiments.²⁴ In this work, the oxygen was controlled in low concentration at the same level to reduce the effects of oxygen. The acid part of the

* Trade name.

solution recipe was injected into the solution after completion of the nitrogen purging step, after which the loading process was started.

Table 2
Composition of brines used for producing different concentrations of H₂S

pH	Chemicals	0.7 mole%	3.5 mole%	5.75 mole%	35 mole%
3.5	Sodium Chloride(g/L)	10	10	10	10
	Sodium Acetate(g/L)	4	4	4	4
	Sodium Sulfide (g/L)	0.2	1	1.67	11
	Acetic acid (mL/L)	30	30	30	30
	Hydrochloride acid (mL/L)	0.2	1	1.3	8.4
	Chemicals	0.02 mole%	0.35 mole%	3.5 mole%	30 mole%
5.5	Sodium Chloride (g/L)	10	10	10	10
	Sodium Acetate (g/L)	4	4	4	4
	Sodium Sulfide (g/L)	0.005	0.1	1	9
	Acetic acid (mL/L)	0.6	0.3	0.3	0.3
	Hydrochloride acid (mL/L)	/	0.1	0.8	7

RESULTS AND DISCUSSION

Materials Investigated

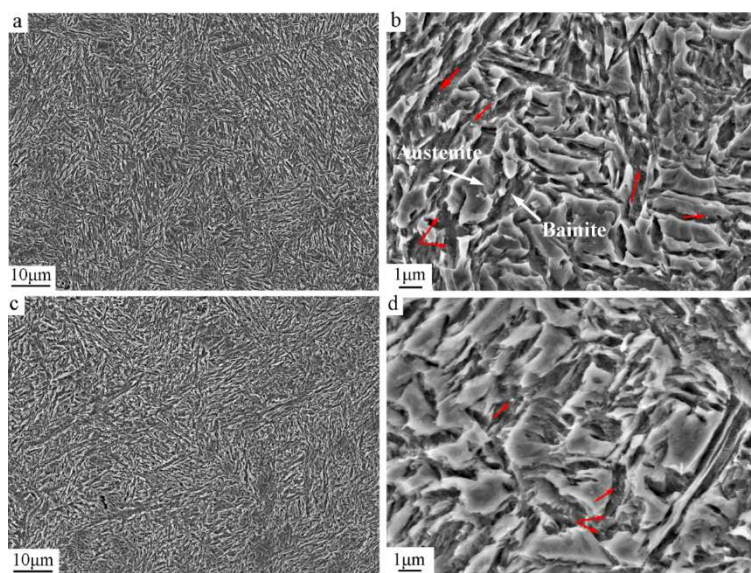


Figure 2: Microstructure of (a-b) nanostructured steel, and (c-d) heat treated specimens

The microstructure of nanostructured steel before and after heat treatment was characterized by scanning electronic microscope (JCM-7000 NeoScope Benchtop SEM [†]) and is shown in Figure 2. Fine acicular matrix of bainite was surrounded by thin film retained austenite. Nano-scaled precipitates were found to be randomly distributed in the bainitic matrix (labelled by red arrows). Unmelted particles in the size range of 3-10 μm were observed with a composition of (Nb, V, Mn, Al) carbide as determined by Energy-Dispersive X-Ray Spectroscopy (EDS) analysis. Austenite phase becomes larger and the bainite/austenite interface becomes coarser after heat treatment (Figure 2 [b] and Figure 2 [d]). Meanwhile, the austenite fraction increases a little as indicated by 62.72% and 71.63% of regular and heat-treated specimens, respectively.

Results of SSRT Test

Stress-strain curves in the air

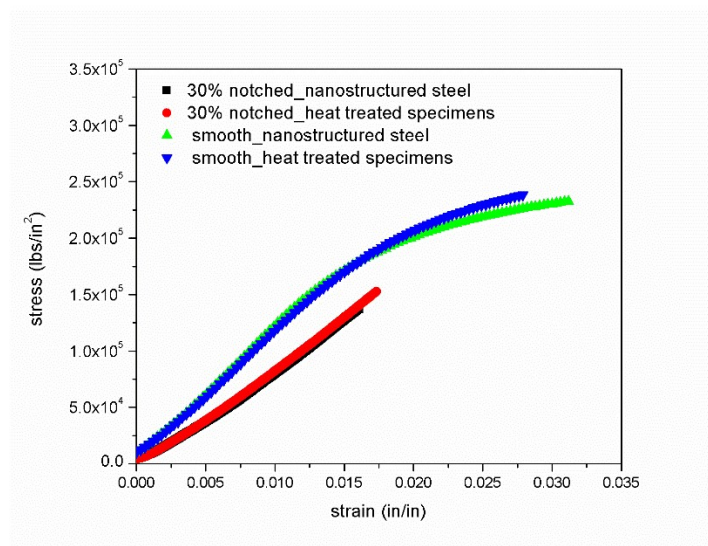


Figure 3: Stress-strain curves of nanostructured steel and heat-treated specimens under tensile test in air

Mechanical parameters of nanostructured steels were obtained by tensile tests in air. From stress-strain curves in Figure 3, both nanostructured steel (smooth nanostructured steel) and heat treated specimens (smooth heat treated specimens) have close yield stress of 200 ksi (1379 MPa) and ultimate tensile stress of 240 ksi (1654 MPa), respectively. The heat-treated specimen is more brittle due to lower fracture strain. Notch hardening effect can be observed for notched specimens as evidenced by almost doubled ultimate stress and halved fracture strain. Linear fitting was carried out to obtain Young's modulus with a value of 1.216×10^7 psi (84 GPa) and 1.157×10^7 psi (80 GPa), corresponding to regular and heat-treated nanostructured steels, respectively. For the 30% notched nanostructured steel and heat treated specimens, only elastic deformation was observed with the 30% notched heat treated specimens have a little bit higher ultimate stress and strain.

[†] Trade name.