

Insights Into Hydrogen Embrittlement (HE) Susceptibility of Martensitic Steels Using Finite Element Analysis (FEA) And Experiments.

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ABSTRACT

Microstructure and strength affect hydrogen embrittlement (HE) susceptibility of martensitic steels. In order to understand their respective roles, two martensitic steels with the same chemical composition, but different strength (and or hardness) levels were selected. Incremental step load (ISL) technique was used to evaluate the environmental hydrogen embrittlement susceptibilities (EHE) of the materials by in-situ charging of hydrogen at a cathodic potential of $-1.2V_{SCE}$. Microstructural characterization was performed using TEM. Stress and hydrogen concentration distributions at the time of failure were estimated from a stress coupled hydrogen diffusion finite element analysis (FEA). It was primarily observed that microstructure controlling strength has a more significant effect on HE failure, as compared to microstructure affecting hydrogen diffusion in case of EHE. This observation was further corroborated with fractographic analyses and qualitative discussion based on linear elastic fracture mechanics (LEFM).

Key words: environmental hydrogen embrittlement, finite element analysis, transmission electron microscopy, HEDE mechanism.

INTRODUCTION

Quench and tempered (Q & T) martensitic steels are widely used to manufacture fasteners. These frames, bridges and other structural components. However, premature failures of these fastener components due to hydrogen embrittlement (HE) can lead to total loss of structural integrity and catastrophic failures. For instance, the HE cracking of high strength anchor rods and structural

bolts in the San Francisco–Oakland Bay Bridge is a notable incident.¹ However, HE in martensitic steels is a complex phenomenon and has been a topic of research for decades.^{2,3} The identification of the factors responsible for HE, involves fundamental considerations implicating the entire fastener supply chain, starting from the steel mill, the fastener manufacturer, the coater, all the way to the end user. The selection of heat treatment process could be considered as a decisive factor towards the prevention of HE failure of threaded fasteners. In general, fastener specifications place broad restrictions on material selection, without any mandate on the selection of a particular grade of steel. As a result, it is necessary to develop a better understanding on the susceptibility of these materials to HE. Based on the sources of hydrogen ingress into the steel structure, there are two broad categories of HE: a) internal hydrogen embrittlement (IHE) which is a delayed failure, caused by residual hydrogen from steelmaking, surface cleaning, electroplating in particular.^{4,5} And, b) environmental hydrogen embrittlement (EHE), which occurs due to the introduction of hydrogen by sacrificial corrosion during service such as subsea applications. It is also generally accepted that strength (and or hardness) have a first-order effect on HE susceptibility in high-strength martensitic steels, with an increase in hardness and/or yield strength leading to a decrease in resistance to HE failures.⁶⁻⁸ However, the underlying mechanism(s) that make strength a significant factor in influencing HE susceptibility needs further understanding.

In this work, two Q & T steels with the same chemical composition, but heat treated to different hardness and strength levels have been selected for the current study. The susceptibility is measured by a four point bend test based on ASTM⁽¹⁾ F1624 standard test method with some modifications.^{9,10} In brief, this test involves the cathodic charging of hydrogen while performing an incremental step load (ISL) test on a notched square bar specimen. The test methodology has been designed to measure the HE cracking threshold of a material in terms of percent notch fracture strength (NFS%). An in-depth analysis reporting the validity of the test process to better understand the fundamental factors accompanied by the hydrogen distribution profile that ultimately contributes to the generation of the NFS% output value has been discussed.¹⁰

The role of microstructure in influencing material susceptibility could be also important. Therefore, an effort has also been made in this paper to separate the contributions of microstructure from strength using extensive microstructural characterization, both qualitative and quantitative. Furthermore, a stress coupled hydrogen diffusion finite element model has been developed to simulate the ISL test in order to estimate the stress and hydrogen concentration distribution in the materials at the time of failure. Finally, a qualitative description rooted in hydrogen enhanced decohesion (HEDE) mechanism and hydrogen dislocation interaction near a crack tip is presented, to provide insights into the HE failure of Q & T martensitic steels.

RESEARCH METHODOLOGY

An air-melted alloy steel grade, UNS G41350 (Cr-Mo) was selected for this study. It is a typical alloy used for manufacturing high-strength steel fasteners. The chemical composition for the alloy is given in Table 1 and the estimated carbon equivalent is 0.73. Two target hardness levels, 36.6 and 51.5 HRC, were obtained by quenching and tempering, where the 36.6 and 51.5 HRC materials will be referred to as 4135L and 4135H, respectively. The details involving the heat treatment to achieve the desired hardness levels are documented elsewhere.⁵ Following the heat treatment process, machining was performed as per ASTM⁽¹⁾ F519 type 1e specifications to obtain the specimen dimensions in the form of square single edge notched bars.¹¹ The stress concentration factor at the notch was estimated to be around 4.27 ± 0.32 , and a detailed methodology describing the machining process is also given in the reference.⁵ A stress relief heat

⁽¹⁾ American Society for Testing and Materials (ASTM), ASTM International West Conshohocken, PA, 2012.

treatment at approximately 190° C was performed for 4 hours as the last manufacturing step. Finally, the specimens were coated with light oil to prevent corrosion during transport or storage.

Table 1. Chemical composition of the AISI 4135 steel.

Steel Grade	C	Mn	Ni	Cr	Mo	Si	S	P	Cu	Al	V
UNS G41350	0.35	0.90	0.04	0.95	0.16	0.25	0.015	0.01	0.06	0.001	0.02

The ISL tests can be conducted based on a self-programmed loading protocol, such as 2%–2 h (10% increment in load in first one hour followed by another 10% in the next two hours and 2% increments in load with two hours of holding time in the following hours) to determine the susceptible condition.¹⁰ The environmental tests were carried out at room temperature by in-situ charging of hydrogen using 3.5 wt.% NaCl electrolyte under potentiostatic control by imposing a cathodic potential of -1.2V_{SCE}. A fast fracture test methodology at a continuous loading rate of 445 N/min (100 lbs/min) was used to determine the baseline load measurements. The percent notch fracture strength (NFS%), which is the measure of the degree of material susceptibility to HE could be determined using Eq. (1):

$$\text{Percent notch fracture strength (NFS\%)} = \frac{\text{Fracture Load in } H_2 \text{ environment}}{\text{Fast Fracture Load}} \times 100 \quad (1)$$

At least three tests were performed to obtain an average percent NFS (NFS%). At the end of each ISL test, the fracture surfaces were preserved for fractographic analysis. A detailed methodology to obtain an NFS% value is already reported elsewhere.¹⁰

The microstructural characterization using transmission electron microscope (TEM), along with the sample preparation technique has been documented elsewhere.¹² The fracture surfaces obtained at the end of the ISL tests were studied using a Field Emission Gun- Scanning Electron Microscope (FEG-SEM) to perform fracture surface mapping.

The hydrogen transport kinetics inside a material is controlled by both concentration and stress gradient factors. At a constant temperature, the hydrogen diffusion for an arbitrary domain of volume Ω bounded by a surface $\partial\Omega$ can be studied by using Eq. (2):

$$\frac{\partial C_L}{\partial t} - \nabla \cdot (D_L \nabla C_L) + \nabla \cdot \left(\frac{D_L C_L V_H}{RT} \nabla \sigma_h \right) = 0 \quad (2)$$

where D_L is the lattice diffusion constant, C_L is the lattice H concentration per unit volume, σ_h is the hydrostatic stress (i.e. $\sigma_h = \frac{1}{3} \sum_{n=1}^3 \sigma_{nn}$, σ_{nn} = normal stress components) and V_H is the partial molar volume of hydrogen, R and T are the gas constant (8.314 Jmol⁻¹K⁻¹) and temperature respectively.¹³ A weak formulation of the stress coupled hydrogen diffusion problem along-with the complete formulation of the coupled transport-mechanical scheme has been documented in a preceding study.¹⁴ A 2D plane strain condition with an isotropic strain hardening process where the elastic-plastic behavior based on J2 plasticity has been considered to carry out the simulations.¹⁵ Thus, the principle of virtual work can provide the weak formulation accounting the elastoplastic deformation of the material.¹⁵ Since, no significant influence of hydrogen on the constitutive behavior of Q & T steels have been observed, the effect of hydrogen on the macroscopic stress-strain relation of the materials has been neglected in this study.^{16,17}

A load controlled boundary condition was used to simulate the elastoplastic deformation during the ISL test. A constant hydrogen concentration of C_0 (=0.204 mol/m³) was assumed along the

surface of the sample for each simulation. The estimation of C_0 was done based on the Henrian behavior of hydrogen dissolved in steels given by Eq. (3) as:

$$C_0 = K_S \sqrt{f^0} \quad (3)$$

where K_S is the solubility constant with an approximate value of $3.8 \times 10^{-3} \text{ mol m}^{-3} \text{ atm}^{-1/2}$ in case of pure Fe.^{14,18} Equation (3) is the modified expression of Sievert's law for electrolytic charging where the hydrogen activity is expressed in terms of fugacity, f^0 , instead of pressure. An equilibrium relation between hydrogen fugacity and cathodic electrochemical charging overpotential is given as:

$$f^0 = 560 \exp\left(-\frac{\beta F}{14.35RT}\right) \quad (4)$$

where F is the Faraday constant. A discussion on the assumptions in the development and application of the above relations is reported elsewhere.¹⁴ The implementation of the FEA model in the commercial program ABAQUS[†] has been carried out following the analogy between heat transfer and mass diffusion, as reported in the papers.^{19,20} Finally, the stress coupled diffusion equation (Eq. (2)) was implemented with the help of a user subroutine, UMATHT[†]. A mesh study was performed to obtain the optimum number of elements. The geometry was then meshed with a total number of 8986 nodes and 8707 elements, with 100 elements being distributed at the notch tip. The plane strain quadrilateral elements (CPE4) and the quadrilateral heat transfer elements (DC2D4) available in the FEA software were used for stress and diffusion analyses respectively. All the important materials parameters are listed in Table 2. A more detailed description of the implementation process will be reported in a successive paper.

Table 2. Material parameters

Parameters	Symbols	4135L	4135H
Elastic modulus (GPa)	E	211	211
Poisson ratio	ν	0.3	0.3
Density (kgm^{-3})	ρ	7850	7850
Yield strength (MPa)	σ_0	1080	1500
Lattice H diffusivity (m^2s^{-1})	D_L	1.5E-08	1.5E-08
Partial molar volume of hydrogen ($\text{m}^3\text{mol}^{-1}$)	V_H	2 E-06	2E-06
Temperature (K)	T	293	

The 2D diffusion FEA model was first utilized to calculate the time at which the sample geometry reaches equilibrium with the surface concentration, C_0 . Figure 1 shows the hydrogen concentration distribution along the notch length for time intervals starting from 1 s to 1 hour, and it can be noted that approximately 45 mins is required to reach equilibrium. Hence, in the present study 1 hour of holding time with a maximum time step of 100s was allotted for the stress-coupled hydrogen diffusion simulations instead of 2 hours of holding time (as was used in the experiments) to minimize computational time and cost.

RESULTS AND DISCUSSION

The NFS_% values as a measure of HE susceptibility were first calculated using Eq. (1) from the average fast fracture load values and the average failure load values in presence of hydrogen; all the values are reported in Table 3. It can be observed that the difference in NFS_% between 4135L

[†] Trade name.