

Permeation Testing under Tensile Loading Combined with FEM Modelling for the Study of Hydrogen Embrittlement of Tempered Martensitic Steels

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ABSTRACT

The present work explores permeation testing of specimens which are simultaneously loaded in tension to investigate hydrogen-assisted cracking. In this experimental technique, the global hydrogen flux and the mechanical loading are continuously monitored during a tensile test of specimens with U- and V-notches at various cathodic polarization current densities. These experimental conditions allow assessment of the susceptibility of steels under various intensities of hydrogen flux and concentration in several mechanical states. Diffusible hydrogen led to quasi-cleavage fracture at the hydrogen entry surfaces for all the tested conditions. The results of the permeation test (under tensile loading) are incorporated into finite element modeling (FEM) for the evaluation of local conditions for the development of quasi-cleavage fracture, as well as the sensitivity of these threshold conditions (stress, plastic strain, hydrogen flux and concentration) to the intensity of the applied cathodic polarization.

Key words: hydrogen-assisted cracking, martensitic steel, quasi-cleavage, hydrogen flux

INTRODUCTION

The present work addressed the challenge of developing higher-strength low-alloy martensitic steels for sour service which are resistant to hydrogen-assisted cracking by evaluating a test method in which a permeation test is performed on a specimen which is simultaneously subjected to an applied tensile load. The design of this experimental technique consists of an electrochemical permeation Devanathan-Stachurski cell built on a 100 kN tensile machine, which allows continuous monitoring of the global hydrogen flux and mechanical loading during the tensile test of prismatic notched and unnotched specimens until fracture.

Hydrogen changes considerably the fracture mechanisms of martensitic steels. Intergranular and quasi-cleavage hydrogen-induced fracture surfaces are often observed in the presence of hydrogen instead of ductile morphology of air-tested specimens.¹⁻³ Despite the numerous studies on hydrogen embrittlement of martensitic steels,¹⁻⁸ it is still not clear how hydrogen promotes quasi-cleavage fracture and the role of plasticity in this process. Recent studies have shown that the damage is a result of a combined effect of local hydrogen concentration, hydrogen flux, hydrostatic stress and plastic strain.^{7,8} This paper continues these investigations and increases comprehension of the local threshold conditions (hydrogen flux and concentration, mechanical state), which are necessary for the appearance and development of hydrogen-assisted quasi-cleavage fracture in martensitic steels.

EXPERIMENTAL PROCEDURE

The present work studied a 0.3C-0.4Mn-1.0Cr-0.8Mo wt.% steel with small amounts (< 0.04%) of Nb, Ni, Cu, Al and Ti. Samples were submitted to water quenching followed by tempering at 670°C for 30 minutes providing a fully tempered lath martensitic structure.

Structural characterization was conducted using differential scanning calorimetry, X-ray diffraction, optical microscopy, scanning electron microscopy with electron back-scattered diffraction (SEM-EBSD) and transmission electron microscopy (TEM). Hydrogen distribution quantification was completed using permeation tests and thermal desorption spectroscopy (TDS) measurements. Activation energies and number densities of interstitial and trapping sites were obtained using the data of permeation tests performed at four different temperatures and TDS conducted at seven distinct heating rates. A detailed description of these experimental techniques as well as the diffusion and trapping models has already been published in previous works.⁹⁻¹¹

Under hydrogen flux, tensile testing was performed in a permeation cell assembled directly on an INSTRON[†] 100 kN machine with notched prismatic specimens (see Appendix A) using a strain rate of 10^{-5} s^{-1} until fracture. The cell has two compartments with saturated sulfate reference electrodes (SSE, $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$) and platinum counter electrodes. Solutions of 1 mol/L H_2SO_4 and 0.1 mol/L NaOH were respectively used in the charging and detection compartments. Constant cathodic charging current densities from 5 to 100 mA/cm² were applied. The temperature was fixed to 20°C and the cell was kept under argon flux. The tensile tests were started after the permeation reached the steady state (constant hydrogen flux to assess the impact of diffusible hydrogen). After the tensile tests, a hydrogen analyzer Jobin Yvon Horiba EMGA-621W[†] was used to perform TDS measurements of the hydrogen concentration and the fracture surfaces were observed using the scanning electron microscope Philips FEI: Quanta 200FEG/ESEM[†]. Figure 1 summarizes the experimental methodology including 1) stable passive layer formation, 2) hydrogen cathodic charging, 3) tensile testing, 4) hydrogen measurement and fracture surfaces imaging and 5) finite element method (FEM) calculations. The last step is performed using the elasto-plastic and hydrogen diffusion models explained hereafter.

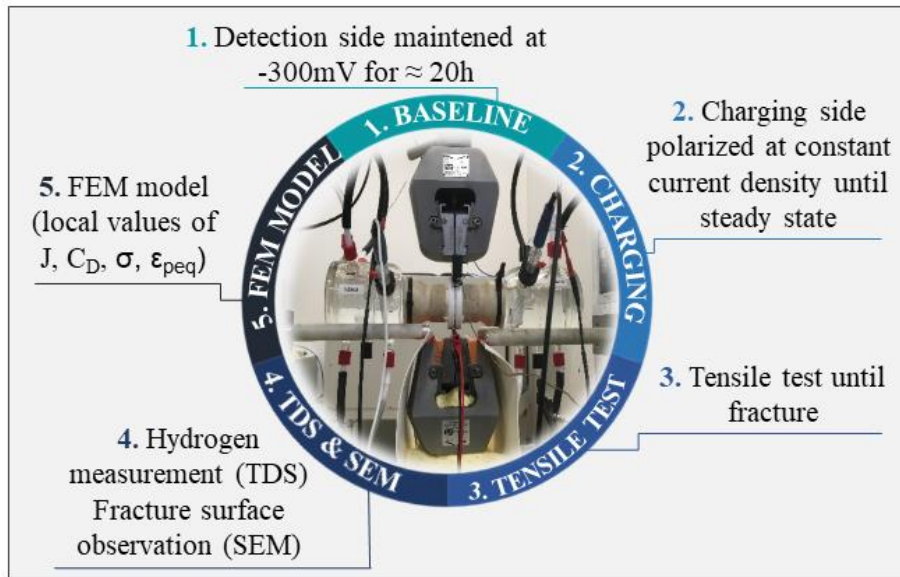


Figure 1: Illustration of the experimental approach of tensile testing under hydrogen flux with a photo of the setup of the permeation cell built on the tensile machine.

Elastoplastic Model

Based on the classical local approach of fracture,¹²⁻¹⁴ a finite element calculation was performed for each specimen design to provide the mechanical parameters' distributions within the bulk of the specimen during loading to fracture. Mesh was reorganized to take into account the displacement. An elastoplastic law was identified from the plastic behavior of the alloy before necking, in the framework of the classical elastoplastic theory based on thermodynamics of irreversible processes with internal variables.¹⁵ The validity of such finite element modeling calculations was checked by comparing the calculated variations of true stress as well as the average longitudinal true strain with the experimental data.

The model uses a function $f(\bar{\sigma})$ as a plasticity yield criterion where $f(\bar{\sigma}) = 0$ is a state at the border of the yield surface. Equation 1 shows how this function is calculated based on the von Mises equivalent stress (σ_{eqVM}), the yield strength (σ_{YS}) and three hardening terms: R_0 , X_1 and X_2 (R_0 is isotropic, whereas X_1 and X_2 are kinematic components). In the definition of σ_{eqVM} , $\bar{S}$ is the deviatoric stress tensor.

$$f(\bar{\sigma}) = \sigma_{eqVM} - [\sigma_{YS} + R_0 + X_1 + X_2] \quad \text{where} \quad \sigma_{eqVM} = \sqrt{\frac{3}{2}(\bar{S}) : (\bar{S})} \quad (1)$$

It is explained below how the stress and strain were obtained by the model for the elastic and plastic regimes.

Elastic Regime

When $f(\bar{\sigma}) < 0$, the stress state ($\bar{\sigma}$) is inside the yield surface, meaning it is elastic. In this case, the stress state can be calculated by applying Hooke's law, written in the Equation 2, where C is the fourth order stiffness tensor that describes the isotropic elasticity.

$$\bar{\sigma} = C : \bar{\epsilon}_e \quad (2)$$

The strain tensor is obtained as a function of the deformation gradient ($\bar{F}e$) and the second-order identity ($\bar{I}$) tensors according to Equation 3.

$$\bar{\varepsilon} = \frac{1}{2}(\overline{Fe^T Fe} - \bar{I}) \quad (3)$$

Plastic Regime

When the condition $f(\bar{\sigma}) = 0$ is reached, the stress state ($\bar{\sigma}$) lies on the yield surface and the material starts to be plastically deformed. During further plastic deformation, the stress always remains at the yield surface satisfying $f(\bar{\sigma}) = 0$. Therefore, the von Mises equivalent stress (σ_{eqVM}) can be obtained by using Equation 1, once the yield strength and the hardening terms are known.

Equation 4 describes the hardening parameters (R_0 , X_1 and X_2) as a function of the empirical constants (S_i and Z_i) and the equivalent plastic strain (ε_{peq}), defined, as usual, in terms of the strain tensor ($\bar{\varepsilon}_p$).

$$R_0 \text{ or } X_1 \text{ or } X_2 = \frac{S_0 \text{ or } S_1 \text{ or } S_2}{Z_0 \text{ or } Z_1 \text{ or } Z_2} [1 - \exp(-(Z_0 \text{ or } Z_1 \text{ or } Z_2)\varepsilon_{peq})] \quad (4)$$

$$\text{where } \varepsilon_{peq} = \sqrt{2/3 (\bar{\varepsilon}_p) : (\bar{\varepsilon}_p)}$$

Lastly, the plastic strain is calculated using Equation 5 where λ is a plastic multiplier.¹⁵

$$\bar{\varepsilon}_p = \lambda \frac{\partial f(\bar{\sigma})}{\partial \bar{\sigma}} \quad (5)$$

By using this model, the elastoplastic behavior is defined in terms of nine variables: Poisson's ratio (considered equal to 0.3 for the material evaluated), Young's modulus ($E = 200 \pm 10$ GPa), yield strength (YS or σ_{YS}), and six empirical hardening constants (S_0 , S_1 , S_2 , Z_0 , Z_1 and Z_2) obtained by trial and error, i.e. through successive calculations until obtaining satisfactory fitting of the experimental tensile curves and reductions of section.

Model of Hydrogen Diffusion and Trapping Coupled with Hydrostatic Stress

The model considers Equations 6 to 8 from the theory of diffusion and trapping.¹⁶⁻¹⁸ In these equations, D_L is the interstitial diffusion coefficient, N_L and N_T are the number density of lattice and trapping sites, and ΔE_T is the binding energy of trap sites (see Table 1). Additionally, k_B is the Boltzmann constant, V_H is the partial molar volume of hydrogen (considered 2×10^{-6} m³/mol)¹⁹ and T is temperature (in this case room temperature, 298K). The model presents only two hydrogen states, trapped (C_T) and diffusible (C_D). It does not distinguish the interstitial hydrogen (C_L) from the reversible trapped hydrogen (C_{Tr}). For Equations 7 and 8, it is considered $C_L = 0.05C_D$, based on the electrochemical permeation observations that C_L corresponds to less than 5% of the sub-surface concentration (C_0). This consideration provides apparent diffusion coefficient (D_{app}) values similar to those observed experimentally (around 7×10^{-11} m²/s), validating the simulation of hydrogen diffusion.

$$\frac{\partial C_D}{\partial t} - D_{app} \left[\Delta C_D - \nabla \left(\frac{V_H}{RT} C_D \nabla \sigma_m \right) \right] = 0 \quad (6)$$

$$D_{app} = \frac{D_L}{1 + \frac{\partial C_T}{\partial C_L}} \quad (7)$$