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Correlation of Hydrogen Diffusion and Trapping Behaviour with Hydrogen Embrittlement Resistance in Line Pipe Steels

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ABSTRACT

In this study the hydrogen diffusion and trapping characteristics of four API line pipe grade steels were investigated during electrochemical charging. In addition, the slow strain rate (SSRT) method was used to determine the steels resistance to hydrogen embrittlement in terms of ductility ratio and time to failure. Permeation tests were used to characterise the hydrogen diffusivity and apparent solubility, whilst complimentary thermal desorption tests were used to assess the hydrogen solubility and to characterise the nature of the trapped hydrogen. From the results obtained, it was shown that irreversibly trapped hydrogen was present in all steels in the absence of hydrogen charging (as-received state). Furthermore, hydrogen introduced during electrochemical charging was reversible in nature for all steels. Comparison of hydrogen embrittlement resistance with the determined diffusion and trapping characteristics revealed improved performance for steels with lower diffusivity and higher hydrogen solubility. The trend with diffusivity was explained in terms of a critical hydrogen concentration for failure, which was shown to be higher in steels with lower diffusivity. This critical concentration was reached much later in the steels with lower diffusivities, thus giving improved ductility ratios and longer failure times in the SSRT tests.

Key words: Hydrogen embrittlement, hydrogen diffusion, line pipe, permeation, thermal desorption, hydrogen trapping, slow strain rate tests

INTRODUCTION

In line pipe steels exposed to sour service conditions and under stress, hydrogen atoms may be generated on the exposed pipe surface. Over time, this hydrogen can diffuse into the metal bulk, leading to reduced ductility and increased susceptibility to cracking. This is known as hydrogen embrittlement.¹ Apart from sour service, hydrogen embrittlement in linepipe may also arise from the use of cathodic protection systems.² Considering the above processes, the bulk diffusion of hydrogen in the steel is expected to influence a pipelines resistance to embrittlement. Furthermore, hydrogen diffusion is strongly influenced by the microstructure i.e. trapping. Generally, hydrogen may be bound strongly to some trap sites e.g. fine incoherent precipitates, and dislocation cores, which are then known as irreversible traps.^{3,4} On the other hand hydrogen may also interact more weakly with other microstructural features (reversible traps), e.g. dislocation strain fields and semi-coherent precipitates.³ In terms of hydrogen embrittlement resistance, characterisation of the hydrogen diffusion coefficient, as well as the concentration of trapped hydrogen and its nature, i.e. reversibly or irreversibly trapped, may help to rationalise different line pipe steels performance.

In the present study, four API grade line pipe steels have been characterised in terms of hydrogen diffusion and trapping characteristics. The diffusivity and apparent hydrogen solubility have been assessed by the permeation method, whilst hydrogen solubility and nature (in terms of reversible and irreversibly trapped), was investigated using thermal desorption. Finally, the results obtained have been compared with hydrogen embrittlement resistance (ductility ratios and time to failure), as evaluated with slow strain rate tests on the linepipe steels.

MATERIALS AND EXPERIMENTAL PROCEDURES

Materials

The line pipe steels for study consisted of 4 different seamless pipe body materials, produced by quenching and tempering. Table 1 shows the general pipe properties.

Table 1
General properties for investigated seamless pipe materials

Pipe name	Wall thickness (mm) and outer diameter (mm)	CE _{Pcm}	P	S
X65-25mm	25 - 273	0.17	<0.015	<0.001
X65-30mm	30 - 219	0.19	<0.015	<0.001
X65-46mm	46 - 273	0.20	<0.015	<0.001
X70-15mm	15 - 251	0.18	<0.015	<0.001

As can be seen, three X65 grade pipes and one X70 grade has been chosen for study. These materials were selected varying chemistry (carbon equivalent CE_{Pcm}), microstructure, and residual hydrogen content, as part of a wider study on hydrogen embrittlement resistance of line pipe steels. Finally, it should be pointed out that these steels were produced with calcium treatment for inclusion shape control.

Table 2 shows the mechanical properties of the pipe materials.

Table 2
Mechanical properties for investigated seamless pipe materials

Pipe	Yield strength at 0.5% strain (MPa)	Ultimate tensile strength (MPa)	Yield to tensile strength ratio
X65-25mm	499	586	0.85
X65-30mm	519	593	0.88
X65-46mm	510	601	0.85
X70-15mm	570	643	0.89

As expected, the X65 materials all have very similar strength levels (499 – 519 MPa yield strength), whilst the X70 grade has a slightly higher strength.

Experimental procedure for permeation tests

Hydrogen permeation tests were performed at ambient temperature following the procedures given in ASTM G148.⁵ For all pipes, disc specimens with 2 mm thickness (selected to ensure volume controlled diffusion) were machined close to the inner surface of each pipe. One side of each specimen (the oxidation side in permeation tests) was then mechanically polished to a 600 grit finish, degreased, then palladium coated. This layer makes sure that all hydrogen produced will be oxidised and measured.⁶ The other side of each specimen (charging side in permeation tests) was left in the as machined condition and degreased. Figure 1 shows the experimental setup used for the permeation tests.

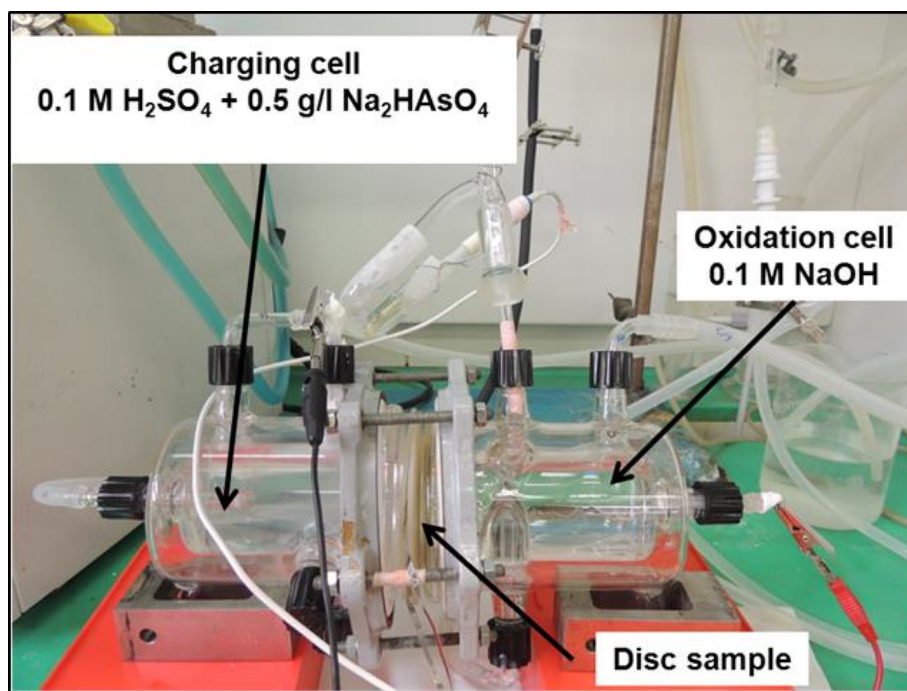


Figure 1: Permeation experimental setup.

For each test, the prepared steel disc was placed between the two cells. Both cells were constantly deaerated during the test (N_2). A constant current density of 2 mA/cm^2 was applied to the charging cell which resulted in generation of hydrogen atoms at the charging side of the steel disc. The presence of sodium arsenate inhibited the formation of hydrogen gas (H_2), thus improving the efficiency of hydrogen

charging into the steel. The atomic hydrogen diffused through the disc and was oxidised at the exit face, by application of an applied potential (+0.3V versus SCE). The oxidation current density was then measured. After subtraction of the background the permeation current density as a function of charging time could be obtained from each test. The data was then analysed to determine the effective bulk diffusion coefficient of hydrogen in each steel (D_{eff}), and the apparent hydrogen solubility (C_{app}). The diffusion coefficient was obtained by fitting equation (1) to the rising permeation transient for each steel.⁷

$$\frac{i(t)}{i_{ss}} = \frac{2L}{\sqrt{\pi D_{eff} t}} \sum_{n=0}^{\infty} \exp\left(-\frac{(2n+1)^2 L^2}{4 D_{eff} t}\right) \quad (1)$$

Where i is the permeation current density at time t , i_{ss} is the steady state current density and L is the sample thickness. C_{app} (in ppm by weight) was then obtained via equation (2).^{3,5,7}

$$C_{app} = \left[\frac{i_{ss} L}{F D_{eff}} \right] \left[\frac{M_H \times 10^6}{\rho} \right] \times 0.5 \quad (2)$$

Where F is Faradays constant, M_H is the molar mass of hydrogen and ρ is the density of the steel.

Experimental procedure for thermal desorption analysis

For thermal desorption tests small rectangular specimens were machined from each pipe, close to the inner surface. After degreasing samples were subjected to electrochemical hydrogen charging at ambient temperature, with the same test solution and current density as was used for permeation tests. In addition, the test solution was constantly deaerated with N_2 during charging. After the charging period specimens were removed, washed in distilled water and cleaned with acetone. Next the samples were transferred to the hydrogen analyser. The whole process between the end of electrochemical charging and measurement was no-more than 5 minutes. The hydrogen content was measured by melt-extraction. The technique involves melting of the sample in a graphite crucible, allowing all of the trapped hydrogen to escape. The hydrogen is converted to water, which is then analysed by an infra-red detector. The content of hydrogen in the steel sample is then obtained in ppm by weight. With this method the uncertainty in hydrogen content measurement is ± 0.5 ppm.

For each steel, 3 types of test were made in order to determine the diffusible and irreversible hydrogen contents:

- Hydrogen content measurement on uncharged specimens to determine the residual level (C_{RES}).
- Hydrogen content measurement on specimens charged for a time sufficient to saturate each sample ($t_{sat} = 24$ hours). In this way the total hydrogen content for each steel could be obtained (C_{TOT}).
- Specimens first charged for $t = t_{sat} = 24$ hours. Hydrogen content measured after delay time ($t_{out} = 24$ hours) in air sufficient for hydrogen level to fall to a constant level (C_{MIN}).

Experimental procedure for slow strain rate tests

Slow strain rate tests (SSRT) were performed for each steel following the procedures in NACE TM0198.⁸ Cylindrical test specimens with a diameter of 3.81 mm and gauge length of 25.4 mm, were