Hydrogen Content and Charpy Toughness of Pipeline Steels with Different Hydrogen Charging Processes

Xin Pang and Su Xu

Abstract Hydrogen embrittlement of pipeline steels has become a major design concern for the transportation of pure hydrogen gas or hydrogen blends using pipeline, especially at high design stresses. Quantification of the effects requires measurement of hydrogen content in test samples and suitable test controls to simulate the practical service conditions. In this work, the total hydrogen content in pipeline steels pre-charged using electrolytic and gaseous methods was measured using the inert gas fusion (LECO) analysis. The analysis results showed that an average of approximately 0.2 ppm hydrogen existed in the as-received X65 steel specimens without either electrolytic or gaseous hydrogen charging. The electrolytic pre-charging in 0.1 M NaOH solution with 150 mg/L As_2O_3 was effective to introduce hydrogen into the X65 steel, and the highest total hydrogen content of 1.4 ppm was achieved at a charging current density of 2.5 mA/cm^2 and charging time of one hour. The highest total hydrogen content achieved by the gaseous charging technique in pure H_2 at 10.3 MPa pressure at room temperature for 15 days was 0.4 ppm. Pd surface coating promoted hydrogen absorption into the steel and led to almost doubled total hydrogen contents for both charging techniques. Ex-situ Charpy tests of electrolytically pre-charged X65 specimens at room temperature showed approximately maximum 20% reduction in Charpy absorbed energy (CVN) compared to uncharged specimens. The discrepancy in the pre-charging time needed to reach the saturation effect (i.e., one hour for LECO vs. five hours for Charpy) can be attributed to the different sample geometry and dimensions for the LECO and Charpy tests.

Keywords Hydrogen embrittlement · Hydrogen content · Pipeline steel · Hydrogen charging · Toughness · Charpy test

X. Pang (✉) · S. Xu
CanmetMATERIALS, Natural Resources Canada, 183 Longwood Road South, Hamilton, ON L8P 0A1, Canada
e-mail: Xin.Pang@NRCan-RNCan.gc.ca

The Minerals, Metals & Materials Society (ed.), *TMS 2024 153rd Annual Meeting & Exhibition Supplemental Proceedings*, The Minerals, Metals & Materials Series,
https://doi.org/10.1007/978-3-031-50349-8_112

Introduction

Under the Paris Agreement, many countries including Canada have committed to achieve net-zero emissions by 2050. To reach this target, hydrogen could play a valuable role as an alternative energy carrier in the decarbonisation of energy systems [1]. A widescale hydrogen economy will require a significant development of infrastructure for hydrogen storage and transport. The direct contact of gaseous hydrogen with the pipeline networks may lead to hydrogen uptake by the carbon steels, potentially triggering a variety of degradation modes that are generally referred to as hydrogen embrittlement. The deleterious effects of hydrogen on the mechanical and toughness properties of pipeline steels have become a major concern for pipeline transportation of hydrogen or hydrogen and natural gas blends, especially at high design stresses.

For a given steel tested under controlled hydrogen environment and loading conditions, the hydrogen content in the metal is a key factor determining hydrogen embrittlement effects. To quantify and compare hydrogen induced degradation in pipeline steels, accurate measurement of hydrogen content in the metal under different hydrogen charging conditions is required. It should be noted that in many previous studies the actual hydrogen content in the metal was unknown and/or the level of hydrogen uptake was assessed indirectly.

In this work, the total hydrogen content in various grades of pipeline steels precharged electrolytically or in gaseous hydrogen was measured using inert gas fusion technique, which can provide quick determination of hydrogen concentration in ppm level utilizing a commercially available and easy-to-use LECO analyzer. This can help to examine the effects of charging methods, charging conditions, and electroplated Pd surface coating on the hydrogen content of the steel specimens. Comparative ex-situ Charpy tests of hydrogen pre-charged specimens have been conducted at room temperature to investigate the hydrogen effects on the impact toughness properties of the steels. The results can help to quantify the influences of hydrogen charging process on hydrogen uptake of pipeline steels and assess their effects on the fracture toughness properties of the steels.

Materials and Experimental Procedures

Several grades of pipe steel were tested and showed similar trends but only the results of an X65 pipe steel are presented in this paper due to the page limitation. The X65 steel pipe was from a previous R&D research project and manufactured in 2004, with a yield strength of 428 MPa, outside diameter of 914.4 mm, and wall thickness of 13.7 mm. The main chemical composition (wt%) of the steel is 0.072 C-1.4 Mn-0.19 Si-0.037 Al-0.049 Nb-0.033 Ti-0.019 Cu-0.023 Cr. The steel was machined into 5 × 5 × 10 mm specimens for hydrogen measurements using inert gas fusion (LECO) technique and standard 10 × 10 × 55 mm V-notch Charpy specimens as per ASTM E23 [2] for impact fracture toughness tests. The microstructure of the

steel was characterized using light optical microscopy and the etchant used was a Nital solution containing 4 vol.% nitric acid in ethanol. The X65 pipe steel exhibited a microstructure consistent with the modern steel processes, containing ferrite and bainite/pearlite with round-shaped inclusions.

Two types of charging methods were used to pre-charge hydrogen into the steel specimens: electrolytic and gaseous charging. For electrolytic charging, an aqueous solution containing 0.1 M NaOH and 150 mg/L As_2O_3 as hydrogen recombination poisoner was used at ambient temperature under galvanostatic conditions. During the electrolytic pre-charging, the steel specimens were subjected to a constant cathodic current in the solution for various durations up to 24 h. To prevent the potential hydrogen damage caused by a high charging current [3], current densities no more than 25 mA/cm^2 were used. During gaseous charging, the steel specimens were exposed to 99.9999% pure H_2 gas under a pressure of 10.3 MPa (1500 Psi) at room temperature for 2–10 weeks. Prior to hydrogen charging, the surface of the steel specimens was hand polished lightly using 600-grit SiC sandpaper to remove the surface oxide layer, degreased in acetone, rinsed in DI water, and blow dry using an air gun. To prevent hydrogen egress, the specimens were put in liquid nitrogen immediately after hydrogen pre-charging and then transferred to an ONH836 LECO elemental analyzer. For each charging condition, three to four repetitive specimens were examined and the average of measured hydrogen concentrations and standard deviation was reported. The effect of palladium plated surface coating on the hydrogen absorption of the steel specimens was studied. The plating was conducted using a solution bath containing 5 g/L $PdCl_2$ in 28 wt% ammonia aqueous solution [4] under a constant current density of 2.5 mA/cm^2 for 5 min.

V-notch Charpy impact test has been widely used to qualify toughness of steels and welds (e.g., [5, 6]). In this work, instrumented Charpy tests of pre-charged steel specimens were conducted at ambient temperature using a pendulum machine with a capacity of 750 J. Two to three repetitive specimens were tested for each pre-charging condition. To prevent hydrogen outgassing, the Charpy specimens were transferred and subjected to Charpy impact test within 2 min post electrolytic hydrogen pre-charging.

Results and Discussion

LECO Analysis

It is important to distinguish between diffusible and trapped hydrogen when determining hydrogen concentration using various measurement techniques. Techniques such as thermal desorption spectroscopy (TDS) can detect diffusible hydrogen [7, 8], while hydrogen extraction techniques such as LECO measure the total concentration of hydrogen and the sum of trapped and diffusible hydrogen [9, 10]. The results of LECO measurement of total hydrogen content for the X65 specimens pre-charged

electrolytically (Fig. 1) and in gaseous hydrogen (Fig. 2) under different charging conditions are listed in Table 1.

An average of around 0.2 ppm hydrogen was measured in the as-received X65 steel specimens without hydrogen pre-charging, which can be ascribed to hydrogen absorption from either the steel production and service processes (e.g., acid pickling and cathodic protection etc.) or the ambient atmosphere during storage. Previous study reported detectable hydrogen uptake in various metals including stainless steel

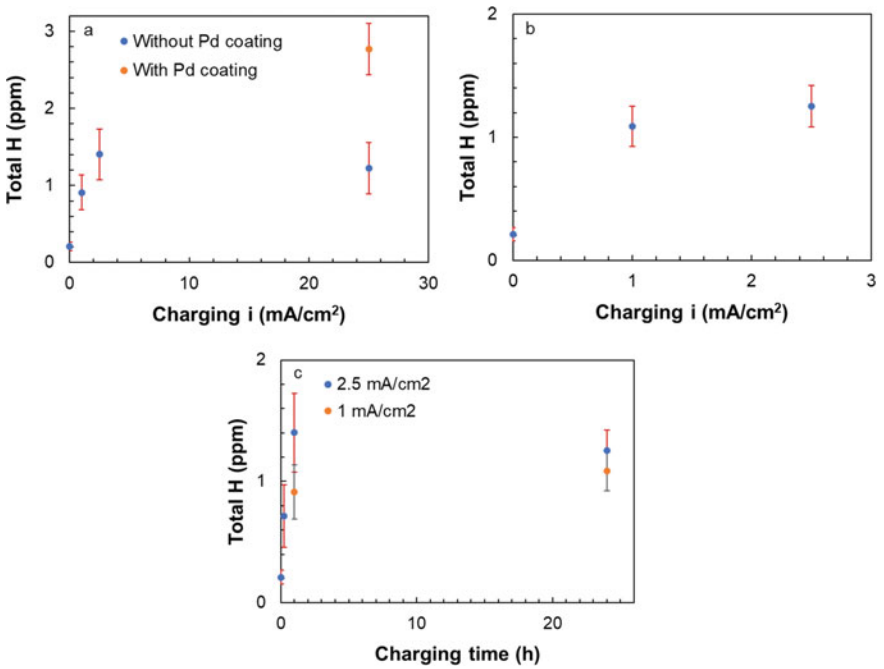

Fig. 1 Total hydrogen content for X65 specimens electrolytically pre-charged at various current densities for **a** 1 h and **b** 24 h, and at **c** 2.5 mA/cm^2 for different time durations

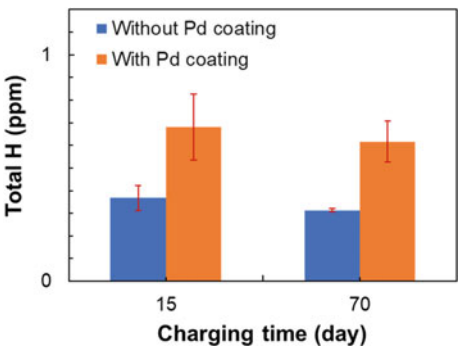

Fig. 2 Total hydrogen content for X65 specimens pre-charged in gaseous hydrogen at 10.3 MPa (1500 Psi) for different time durations

Table 1 Total H content measured by LECO for X65 specimens pre-charged under various conditions

Charging method	Pre-charging conditions		Pd coating	Average (individual) hydrogen content (ppm)
	Current density (mA/cm^2)	Time (h)		
Electrolytic	0	0	No	0.2 (0.3, 0.2, 0.3, 0.1)
	1	1	No	0.9 (0.6, 0.9, 1.0, 1.2)
	2.5	1	No	1.4 (1.6, 1.8, 1.2, 1.1)
	25	1	No	1.2 (1.4, 0.7, 1.4, 1.3)
	25	1	Yes	2.8 (2.6, 3.2, 2.8, 2.4)
	1	24	No	1.1 (1.1, 1.2, 1.3, 0.9)
	2.5	24	No	1.3 (1.1, 1.4, 1.1, 1.4)
	2.5	0.25	No	0.7 (1.0, 0.8, 0.4)
	Pressure (MPa)	Time (day)		
Gaseous	10.3	15	No	0.4 (0.4, 0.3, 0.4, 0.4)
	10.3	15	Yes	0.7 (0.8, 0.7, 0.5)
	10.3	70	No	0.3 (0.3, 0.3, 0.3)
	10.3	70	Yes	0.6 (0.5, 0.7, 0.7)

after a long-term exposure to ambient humid air at room temperature [11]. To confirm this, the as-received X65 steel specimens were baked at 200 °C in flowing N_2 environment for 3 h and then stored in a sealed vial filled with N_2 gas. The measured hydrogen content of the baked specimens was less than 0.1 ppm or undetectable (i.e., showing negative H-concentration in LECO analysis).

It can be seen that even one hour of electrolytic charging was effective to introduce hydrogen into the 5 × 5 × 10 mm specimens of X65 steel. The variation of total hydrogen content with the charging current density for X65 specimens pre-charged for 1 h is given in Fig. 1a. The total hydrogen content increased with the increasing current density and saturated (1.4 ppm) at 2.5 mA/cm^2. A much higher charging current density of 25 mA/cm^2 for 1 h did not lead to any further increase in the total hydrogen content and no test with longer charging time was conducted at this current density. The gradual increase in the hydrogen content with the increase of charging current density up to 2.5 mA/cm^2 was also observed for specimens charged for 24 h (Fig. 1b). An extension of charging time from 1 to 24 h did not bring significant increase in the hydrogen content in the steel under both 1 and 2.5 mA/cm^2 charging current densities (Fig. 1c). When exposed to the same electrolytic charging process (at 25 mA/cm^2 for 1 h), the Pd plated X65 specimens showed an average total hydrogen content of 2.8 ppm, while the bare X65 specimens had 1.2 ppm hydrogen on average (Fig. 1a). Similar effect of Pd coating on the hydrogen uptake of the steel was also seen in the gaseous hydrogen charged conditions (Fig. 2).

It is worth noting that merely 15 min of electrolytic charging at 2.5 mA/cm^2 was able to introduce 0.7 ppm hydrogen into the steel (Fig. 1c), manifesting the

effectiveness of the electrolytic charging method. In contrast, only 0.4 ppm hydrogen was introduced into the X65 steel after 15 days of gaseous charging in 10.3 MPa of high purity hydrogen at room temperature (Fig. 2). In a recent work [12], the diffusible hydrogen was found to be about 0.1 ppm in an X65 pipe steel after gaseous hydrogen charging at a pressure of 25 MPa for 25 h at room temperature. It might be estimated that the trapped hydrogen in the current pipe steel after gaseous charging would be 0.2–0.3 ppm assuming that the same level of diffusible hydrogen was achieved as in [12]. The effect of Pd coating on hydrogen content was also evident in gaseous charging. Further extension of the charging time to 70 days in the gaseous environment did not result in a higher hydrogen content. The effectiveness of the electrolytic charging was also demonstrated in the studies conducted by Atrens and Liu et al. [13, 14] on determination of the hydrogen activity (or pressure) during gaseous hydrogen charging that is equivalent to the hydrogen activity during the electrolytic charging. It was reported that under the most severe charging condition in 0.1 M NaOH solution, the calculated hydrogen fugacity at an overpotential of 0.9 V was 658.6 MPa (6500 atm) [14].

Pd has a strong affinity to hydrogen and promotes hydrogen molecular dissociation on its surface as well as atom diffusion into the bulk [15, 16]. In this work, the application of electroplated Pd surface coating resulted in a considerable increase in the total hydrogen content measured for the steel specimens. With the electroplated Pd coating, the total hydrogen content in the steel specimens almost doubled compared to the uncoated specimens for both charging time durations. However, it must be pointed out that it is unknown whether the hydrogen is uniformly distributed in the Pd coated steel or more hydrogen gathers in the Pd surface layer than in the steel. Further investigation is needed to ascertain the hydrogen distribution in the Pd coated steel. Currently work is also underway to further analyze the diffusible and total hydrogen contents in pipeline steels using thermal desorption spectroscopy (hot extraction technique).

Charpy Test

The results of the Charpy impact tests at ambient temperature for electrolytically pre-charged X65 specimens are summarized in Table 2. The average Charpy absorbed energy (CVN) values for the pipeline steel specimens under different pre-charging conditions are plotted in Fig. 3, where the error bars show the CVN variation range of the repetitive specimens. It can be seen from Fig. 3 that the hydrogen pre-charged into the X65 steel led to obviously reduced Charpy toughness of the steel. The effect aggravated with an increase in charging current density (Fig. 3a) and charging time (Fig. 3b), and saturated at around 2.5 mA/cm^2 of charging current density and 5 h of charging time. It should be noted that the results of LECO measurements showed that the total hydrogen content in the steel also increased with the charging current density (Fig. 1a, b) and charging time (Fig. 1c), but reached saturation at 2.5 mA/cm^2 and 1 h. The hydrogen resulted in approximately maximum 20% decrease in

CNV for the steel. Further increase of charging time to 24 h and charging current density to 20 mA/cm^2 did not result in any further degradation of Charpy toughness for X65 steel. These trends agreed well with the results of the LECO analysis of the electrolytically pre-charged X65 specimens. The discrepancy in the pre-charging time needed to reach the saturation (i.e., 1 h for LECO vs. 5 h for Charpy) can be attributed to the different sample geometry and dimensions for the LECO and Charpy tests.

The results are generally in agreement with the effect of hydrogen on tensile curve, i.e., hydrogen has little effect on strengths before necking [17]. However, as impact loading decreases the effect of hydrogen embrittlement, slow-rate in-situ tests would be more suitable than ex-situ tests at impact rates for quantifying the hydrogen effect on toughness of pipeline steels, because under normal operational conditions pipelines are exposed to pressure loading similar to the in-situ slow-rate loading. The development of three-point bend testing facility and procedures with in-situ electrolytic hydrogen charging capacity is currently underway at the authors laboratory.

Table 2 Charpy impact test data for X65 steel specimens pre-charged under difference conditions

Steel grade	Pre-charging current density (mA/cm^2)	Pre-charging time (h)	Average (individual) Charpy absorbed energy CVN (J)
X65	0	0	234 (233, 237, 233)
	1.0	24	201 (205, 196)
	2.5	24	188 (194, 182)
	20.0	24	192 (188, 195)
	2.5	1	207 (215, 199)
	2.5	5	192 (192, 191)

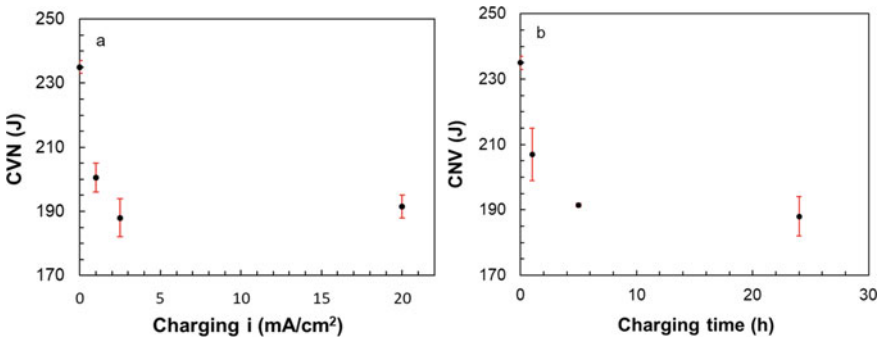

Fig. 3 Charpy absorption energy for X65 steel specimens **a** pre-charged for 24 h as a function of pre-charging current density and **b** pre-charged at 2.5 mA/cm^2 as a function of pre-charging time

Conclusions

The effects of charging methods, charging conditions, and electroplated Pd surface coating on the hydrogen content of the specimens were studied. Ex-situ Charpy tests have been conducted at room temperature to investigate the hydrogen effects on the impact fracture toughness properties of the steels. Following conclusions can be drawn:

1. The inert gas fusion (LECO) analysis showed that an average of approximately 0.2 ppm hydrogen existed in the as-received X65 steel specimens without hydrogen pre-charging, which can be ascribed to hydrogen absorption from either the steel production or service processes.
2. Electrolytic pre-charging in 0.1 M NaOH with 150 mg/L As_2O_3 at 2.5 mA/cm^2 was effective for introducing hydrogen into X65 pipeline steel. Results of LECO analysis showed that an average of 1.4 ppm total hydrogen in X65 was seen for specimens pre-charged at 2.5 mA/cm^2 for 1 h. Further increase of charging current density and time did not result in noticeable increase in the hydrogen content. The electrolytic charging method was a more aggressive charging condition than the gaseous charging technique.
3. Pd electroplated surface coating promoted hydrogen absorption into the steel and led to doubled total hydrogen content under both electrolytic and gaseous hydrogen charging conditions. However, further investigation is needed to ascertain the hydrogen distribution in the Pd coated steel.
4. Ex-situ Charpy tests of electrolytically pre-charged X65 specimens at room temperature showed approximately maximum 20% reduction in CVN compared to uncharged specimens. The results could be correlated with the hydrogen content after pre-charging. The discrepancy in the pre-charging time needed to reach the saturation effect (i.e., 1 h for LECO vs. 5 h for Charpy) can be attributed to the different sample geometry and dimensions for the LECO and Charpy tests.

Acknowledgements Financial support from the Hydrogen Codes and Standards R&D program, Office of Energy Research and Development (OERD), and Natural Resource of Canada (NRCan) is gratefully acknowledged. The authors would like to express their appreciation to David Saleh, Jie Liang, Magdalene Matchim, Chao Shi, and Renata Zavadil of CanmetMATERIALS, NRCan for their technical assistance.

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