



Article Effect of Cold Deformation on the Hydrogen Permeation Behavior of X65 Pipeline Steel

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Abstract: In this study, an electrochemical hydrogen permeation experiment was used to determine the diffusion parameters, and a hydrogen microprint test was used to visualize the distribution of hydrogen in X65 pipeline steel with different levels of cold deformation. The hydrogen permeation curves show that both hydrogen permeation current density and effective hydrogen diffusion coefficient decrease with increasing cold deformation. The density of reversible and irreversible hydrogen traps is calculated from the permeation parameters, and it is found that the amount of both traps increases with increasing deformation, especially a significant increase in reversible hydrogen traps, which is in agreement with the results measured by thermal desorption spectroscopy. Hydrogen microprint test results indicate that the degree of hydrogen aggregation on the specimen surface increases with increasing cold deformation, especially at phase and grain boundaries. In addition, the dislocation configuration after cold deformation was further investigated by transmission electron microscopy.

Keywords: pipeline steel; hydrogen permeation; hydrogen microprint test



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1. Introduction

With the rapid development of the global population, economy, and industry, human demand for energy is rising. Transporting crude oil and natural gas at higher working pressure to increase the capacity is now an important requirement [1,2]. Due to the advantages of low investment cost, large scale, high transport efficiency, safety, and reliability, pipeline transportation has become the main way for oil and gas transportation [3–6].

However, during the service of pipeline steel, hydrogen atoms can enter into the material due to not only the cathodic protection but also the influence of the transport medium and other issues. In general, the entrance of hydrogen into the metals is a prerequisite for hydrogen-related failure. There are usually three sources of hydrogen entering the interior of metals [7]. One is the hydrogen atoms introduced directly into the steel in certain amounts during the production process, e.g., during smelting, pickling, electroplating, etc. This hydrogen existing internally before the usage of a material is called internal hydrogen. The second one is the hydrogen absorbed directly from the gases containing H atoms in the service environment, e.g., the H in the lattice by collision, adsorption, dissociation, and the reaction of gases such as H₂ on the material surface during the service of pipeline steel. The third one is the absorption of hydrogen atoms from the liquid phase in the service environment of the steel. When the corrosion potential in the service environment is below the hydrogen evolution line, hydrogen atoms will be generated and adsorbed on the surface of the steel and then enter into the steel.

In addition, the large plastic strain may present during the production, construction, and usage of pipeline steels, and it will have a significant effect on hydrogen permeation behaviors [8]. Previous studies have found that the effect of plastic strain on hydrogen permeation is mainly due to the alteration of dislocations [9,10]. Dislocations are generally

considered to be important reversible hydrogen traps in materials [11,12]. Therefore, dislocation proliferation caused by plastic deformation is expected to affect hydrogen permeation. For cold-rolled iron and ferritic steels, the effect of dislocations on the hydrogen diffusion behaviors was often investigated by electrochemical permeation tests [13–17]. In these tests, the number of hydrogen atoms diffused from the charging side of a Devanathan-Stachurski cell through a metal specimen would be measured by the oxidation current density on the detection side. Kim and Lee investigated the relationship between plastic deformation and hydrogen transport behavior of quenched and partitioned (Q&P) steels by electrochemical hydrogen permeation tests and thermal desorption spectroscopy (TDS). They concluded that the trapped hydrogen content increased with increasing deformation level [10]. The increase in hydrogen traps in Q&P steels could be attributed to the increase in dislocation density in the ferrite and martensite from the substable austenite phase transformation. Cabrini et al. studied the hydrogen transport behavior of low alloy steels under cyclic loading conditions by electrochemical permeation techniques [18]. The results showed that the decrease in the apparent diffusion coefficient was also related to the increase in dislocation density with increasing deformation or the change in trap binding energy. Wang and Hui et al. studied the hydrogen permeation process in low alloy steels after pre-deformation and obtained the same results, where plastic pre-deformation promoted the absorption and permeation of hydrogen in the material, leading to an increase in hydrogen content [19]. In conclusion, it is found that hydrogen permeation behavior is sensitive to the dislocation density caused by plastic deformation [20]. In addition, the hydrogen diffusion kinetic parameters obtained by hydrogen permeation tests are crucial.

X65 is one of the most important kinds of pipeline steels used for natural gas transportation domestically, and it is now considered to be one of the potential materials for the transport of natural gas doped with hydrogen. Large residual strain may exceed 20%, usually present adjacent to the welds. Hence, the purpose of this study is to clarify the effect of strain level on the hydrogen permeation behavior of X65 pipeline steel, and the mechanism of hydrogen permeation is explored. This study used double hydrogen permeation tests to determine the hydrogen permeation parameters with different cold deformation levels. The parameters include the hydrogen diffusion flux (N_{∞}), effective hydrogen diffusion coefficient (D_{eff}), apparent solubility (c_0), and hydrogen trap density (N_T). A hydrogen microprint test (HMT) was used to characterize the hydrogen distribution on the surface of the material after cold deformation. The mechanism of the effect of cold deformation on hydrogen permeation was also investigated by TDS and transmission electron microscopy (TEM).

2. Materials and Methods

2.1. Materials

X65 pipeline steel was used in this study and its chemical compositions are listed in Table 1. The content of all main elements of X65 pipeline steel meets the requirements of API 5L. The optical microstructure of X65 pipeline steel was observed with an optical microscope (OM, Axio Observer Z1, Zeiss, Oberkochen, Germany), as shown in Figure 1. It can be found that the material is composed of polygonal ferrite (PF) and a small amount of pearlite (P).

Table 1. Chemical compositions of API X65 steel (wt.%).

Steel	С	Si	Р	S	Cr	Mn	Ni	Cu	Мо	Fe
X65	0.081	0.190	0.014	< 0.001	0.050	1.320	< 0.030	< 0.030	< 0.030	Bal.

Plate tensile specimens were taken from the direction perpendicular to the diameter of the pipe, with the dimensions of 150 mm \times 25 mm \times 2 mm, as shown in Figure 2a. Tensile tests were carried out by using a universal testing machine (Zwick Z150, Zwick, North Rhine-Westphalia, Germany) at room temperature with a stretching rate of 0.75 mm/min to simulate different cold deformations. A certain deformation was applied to the specimens and the actual deformation after unloading was measured to obtain the real cold deformation level. Three kinds of specimens were prepared, 0.00% for undeformed specimens, 4.25% and 7.25% for deformed ones, respectively, as shown in Figure 2b. Hydrogen permeation specimens were cut from the parallel sections of the tensile specimens, as shown in Figure 2a.



Figure 1. Optical microstructure of X65 pipeline steel.



Figure 2. (a) Hydrogen permeation specimen sampling diagram, (b) engineering strain curves in the cold deformation loaded–unloaded condition.

The dislocation configuration after cold deformation was further investigated using TEM (TEM, JEM-2100F, JEOL, Tokyo Metropolis, Japan) with an accelerating voltage of 200 kV. The specimens used for TEM observation were first mechanically ground to a thickness of 60 μ m and then were electrolytically double sprayed with a 10% perchloric acid ethanol solution at a voltage of 30 V below -20 °C.

2.2. Hydrogen Permeation Experiment

A modified Devanthan–Stachurski dual cell (Figure 3) was used for electrochemical hydrogen permeation tests in this study. The apparatus consists of two electrolytic cells that are not in contact with each other. The two cells are separated by a specimen. The cathode cell is on one side of the specimen. A constant cathodic current is applied to the specimen and hence the hydrogen ions in solution will be transformed into hydrogen atoms by gaining electrons on the surface of the specimen. Some of the hydrogen molecules and then escape to the atmosphere, while others will diffuse to the other side of the specimen driven by the hydrogen concentration gradient. On the other side of the specimen is the anode cell, where an electrochemical workstation applies a constant anodic potential to the specimen, and then the hydrogen atoms penetrating from the cathode chamber will be oxidized into hydrogen ions again.



Figure 3. Schematic diagram of the electrochemical hydrogen permeation cell.

The specimen dimensions were 20 mm \times 20 mm \times 1 mm, with a diameter of 16 mm exposed to the solution. The specimens were first polished and then nickel-plated on one side. The nickel-plating solution was 300 g/L NiSO₄·6H₂O, 30 g/L NiCl₂·6H₂O, 40 g/L H_3BO_3 , and 0.1 g/L $C_{12}H_{25}$ -OSO₃Na; the plating was performed at a current density of 5 mA/cm² and with a duration of 5 min. After the specimen was connected to the wire and tested for conductivity, it was mounted in the middle of the electrolytic cells, with the nickelplated side facing the anode cell and the other side facing the cathode cell. After adding 0.2 mol/L NaOH solution into the anode cell, a constant potential of 0.3 V (vs. Hg/HgO) would be applied to the specimen via a Gamry 600 electrochemical workstation. Until the background current was less than $0.1 \,\mu\text{A/cm}^2$, $0.5 \,\text{mol/L}$ H₂SO₄ + 2 g/L CH₄N₂S solution would be added to the cathode cell and a constant cathodic current of 5 mA/cm^2 then be applied to the specimen via a constant current source. The change in current of the anode cell should be detected during the whole test until the current reached a steady state. In this study, the same specimen was subjected to a double hydrogen permeation test to investigate the effect of reversible and irreversible hydrogen traps on the changes in the hydrogen permeation behavior of pipeline steel.

2.3. Hydrogen Microprint Test

The specimen with dimensions of 20 mm \times 20 mm \times 1 mm was polished and then hydrogen was charged on one side with a current density of 5 mA/cm² for 5 h. After that, a microstamping solution (5 g AgBr + 10 mL 1.4 mol/L NaNO₂) was applied to the uncharged side and held for 30 min. Then immediately, the specimen was placed in a fixing solution (0.6 mol/L Na₂S₂O₃ + 1.4 mol/L NaNO₂) and soaked for 30 min. The specimen was then carefully cleaned with ethanol and dried in air. Afterward, the coated side was slightly etched with a 4% nitric acid ethanol solution to present the microstructure of the material. The whole process should be carried out in a light-proof environment. In the end, scanning electron microscope (SEM, XL30-FEG, FEI, Hillsboro, OR, USA) was used to observe the distribution of the silver particles. Silvery particles represent the distribution of hydrogen atoms.

2.4. Hydrogen Desorption Spectroscopy

The specimen with a diameter of 20 mm and a thickness of 1 mm was polished to 2000# to remove the surface oxide layer on both sides, followed by rinsing it with distilled water and ethanol before hydrogen charging. The specimen was charged within a 0.5 mol/L $H_2SO_4 + 2 g/L CH_4N_2S$ solution for 12 h at a current density of 5 mA/cm². After that, the specimen was immediately placed in liquid nitrogen and quickly transferred to the quartz tube of the thermal desorber. The rate of hydrogen desorption from the steel was

measured by a quadrupole mass spectrometer and set at a ramp-up rate of 300 $^{\circ}$ C/h from room temperature to 800 $^{\circ}$ C.

3. Results and Discussion

3.1. Hydrogen Permeation

The hydrogen permeation curves for X65 pipeline steel with different cold deformation levels after a double test are shown in Figure 4. The trends of the hydrogen permeation curves are consistent and can be roughly divided into three stages, which are the permeation current incubation stage, the permeation current rise stage, and the permeation current stabilization stage. However, it is obvious that the cold deformation not only slightly delays the current incubation time but also affects the steady current density (J_{∞}). The J_{∞} slightly decreases with increasing the cold deformation levels for both the first and second hydrogen permeation tests, especially for the second test, and this is consistent with the findings in Refs. [21,22]. The J_{∞} responds to the magnitude of hydrogen diffusion flux (N_{∞}) and is also related to D_{eff} and c_0 . D_{eff} is the quantity of hydrogen that diffuses through a unit cross-sectional area of the specimen in unit time due to the different H concentration between two surfaces, and c_0 corresponds to the hydrogen concentration in the lattice, reversible and irreversible traps [23]. Researchers commonly use the time lag method to calculate the hydrogen permeation parameters by using the following equations [24–26]:

$$N_{\infty} = \frac{J_{\infty}}{F} \tag{1}$$

$$D_{eff=}\frac{d^2}{6t_L} \tag{2}$$

$$c_0 = \frac{N_\infty \times d}{D_{eff}} \tag{3}$$

where N_{∞} is the hydrogen diffusion flux (mol/(cm²·s)), J_{∞} is the steady-state current density (A/cm²), *F* is Faraday's constant(96,500 Coulombs/mol) [27], D_{eff} is the effective hydrogen diffusion coefficient (cm²/s), *d* is the specimen thickness (0.8 mm in this study), t_L is the lag time, i.e., the time corresponding to $J/J_{\infty} = 0.63$, and c_0 is the apparent solubility (mol/cm³). See Appendix A Table A1 for parameters and the corresponding abbreviations.



Figure 4. Hydrogen permeation curves of X65 steel with different cold deformation levels: (**a**) the first hydrogen permeation curves, (**b**) the second hydrogen permeation curves.

The electrochemical hydrogen permeation parameters are derived from the measured hydrogen permeation curves and the results are listed in Tables 2 and 3, respectively. In order to visually compare the effect of cold deformation on the N_{∞} , D_{eff} , and c_0 for the first and second hydrogen permeation, the calculated parameters are plotted against the cold deformation levels in Figure 5. It can be found that N_{∞} fluctuates within a very small range and remains almost constant. When comparing the results, it can be seen that the D_{eff} of the second hydrogen permeation test is greater than that of the first test. The analysis concluded that X65 pipeline steel contains both reversible and irreversible hydrogen traps. During the first hydrogen permeation test, the hydrogen entering the specimen is trapped by both the reversible and irreversible hydrogen traps during diffusion, while during the second test, the irreversible hydrogen traps have been already filled. Hence, the second hydrogen permeation curve only reflects the capture of hydrogen in the reversible traps [28]. Therefore, the D_{eff} for the second test is higher. Moreover, the D_{eff} decreases from 3.553×10^{-6} to 1.775×10^{-6} cm²/s for the first hydrogen permeation test and from 4.265×10^{-6} to 1.903×10^{-6} cm²/s for the second one as the cold deformation level increases from 0.00% to 7.25%, while the c_0 shows an opposite trend. From the above results, it is found that cold deformation inhibits the hydrogen permeation behavior for X65 pipeline steel, and this should be related to the microstructure changes caused by cold deformation.

Table 2. Parameters from the first hydrogen permeation curves of X65 pipeline steel with different cold deformation levels.

Cold Deformation (%)	$N_{\infty} imes$ 10 ⁻⁹ (mol/(cm ² ·s))	$D_{e\!f\!f} imes 10^{-6}\ ({ m cm}^2/{ m s})$	$c_0 imes 10^{-5}$ (mol/cm ³)
0.00	2.451 ± 0.052	3.553 ± 0.311	5.551 ± 0.368
4.25	2.473 ± 0.026	2.717 ± 0.090	7.288 ± 0.163
7.25	2.342 ± 0.022	1.775 ± 0.006	10.557 ± 0.133

Table 3. Parameters from the second hydrogen permeation curves of X65 pipeline steel with different cold deformation levels.

Cold Deformation (%)	$N_{\infty} imes 10^{-9}$ (mol/(cm $^2\cdot$ s))	$D_{eff} imes 10^{-6}$ (cm ² /s)	$c_0 imes 10^{-5}$ (mol/cm ³)
0.00	2.331 ± 0.022	4.265 ± 0.455	4.418 ± 0.431
4.25	2.137 ± 0.013	2.947 ± 0.024	5.801 ± 0.013
7.25	2.122 ± 0.062	1.903 ± 0.058	8.922 ± 0.010



Figure 5. Effect of cold deformation on hydrogen permeation behavior: (**a**) hydrogen permeation parameters from the first permeation curves, (**b**) hydrogen permeation parameters from the second permeation curves.

3.2. Hydrogen Microprinting

The purpose of using the HMT is to understand more clearly the effect of cold deformation on the hydrogen permeation behavior, as it can visually indicate the distribution of hydrogen atoms. In this study, the hydrogen atoms diffuse from one side of the specimen to the other side and are oxidized by the Ag⁺, allowing us to observe the distribution of hydrogen by Ag particles. The hydrogen content is higher in areas with a higher density of Ag particles. HMT was performed on specimens with 0.00% and 7.25% deformation (Figure 6). Figure 6a,c shows the low magnification images of the silver particle distribution on the surface of the specimens with 0.00% and 7.25% cold deformation, respectively. It can be clearly seen that the silver particles are relatively uniformly distributed on the surface of the specimens, with a greater enrichment on the surface with higher cold deformation levels. The explanation for this is that the N_{∞} remains almost constant after cold deformation, while the D_{eff} decreases. The reason for the decrease in the permeability coefficient is the increase in hydrogen traps, which will be clearly explained in the next section. The increase in trapped hydrogen leads to an increase in the enrichment of the silver particles. Figure 6b,d shows higher magnification images of Figure 6a,c, respectively, the silver particles are more likely to be distributed at the grain boundaries and phase boundaries than in other regions. Grain boundaries and phase boundaries act as hydrogen trapping points and have a higher capacity for hydrogen enrichment than interstitial positions [29,30].



Figure 6. SEM images of X65 steel with different cold deformation levels after hydrogen microprinting: **(a,b)** without cold deformation (0.00%), **(c,d)** with 7.25% cold deformation.

3.3. Effect of Cold Deformation on Hydrogen Permeation

Exploring the potential mechanisms and the underlying causes of the hydrogen permeation behavior of X65 pipeline steel requires an in-depth understanding of the interactions between hydrogen and microstructural features. In a previous study [31], hydrogen diffusivity in various sheets of steel exhibited unique behavior, mainly due to the presence of various hydrogen traps. Hydrogen atoms in steel not only occupy interstitial sites but also can be captured by defects, such as vacancies, dislocations, grain boundaries, voids, interstitial atoms, second phases, and nonmetallic inclusions, etc. These defects are usually referred to as hydrogen traps. According to the binding energy of hydrogen with traps, traps can be divided into reversible and irreversible ones. Reversible traps are low energy traps that will not permanently trap hydrogen, such as dislocations, small angle grain boundaries, voids, etc. Irreversible traps are high-binding energy traps at ambient temperatures, which include nonmetallic inclusion, second phases, interstitial atoms, vacancies, etc. [32,33].

The D_{eff} for two hydrogen permeations decreases with increasing cold deformation because of the increasing N_T . Some researchers have suggested that the N_T in the material can be calculated from the following equation [34]:

$$N_T = \frac{c_0}{3} \left(\frac{D_L}{D_{eff}} - 1 \right) \tag{4}$$

where the value of the lattice diffusion coefficient in trap-free bcc iron is supposed as $D_L = 1.28 \times 10^{-4} \text{ cm}^2/\text{s}$. The results of the second hydrogen permeation test reflect the reversible hydrogen trap density (N_{RT}). The N_T of the first hydrogen permeation test

minus the N_T of the second test should then be the irreversible hydrogen trap density (N_{IRT}) [34]. The calculated results are shown in Figure 7a, and it can be found that both N_{RT} and N_{IRT} increase with increasing cold deformation, especially the N_{RT} . The N_{RT} increases significantly from 1.93×10^{20} to 1.19×10^{21} cm⁻³, an increase of approximately six times. A comparison of D_{eff} and c_0 reveals that N_T is positively proportional to c_0 and inversely proportional to D_{eff} . This is consistent with the results from previous studies [34]. The researchers found that reduced permeability and diffusivity, as well as increased solubility, led to more hydrogen being trapped in the steel. This also explains the greater abundance and density of silver particles with increasing cold deformation in 3.2. Figure 7b demonstrates the effect of cold deformation on the TDS results of X65, showing a similar trend as in Figure 7a. The TDS curves show two types of desorption peaks, peak 1 and peak 2, for both the specimen without deformation and the specimen with 7.25% deformation. Peak 1 is the low-temperature peak where hydrogen is desorbed from the reversible hydrogen traps while peak 2 is the high-temperature peak where hydrogen is desorbed from the irreversible hydrogen traps. Peak 1 appears at around 130 °C and peak 2 at around 400 °C when without deformation. However, when deformation reaches 7.25%, peak 1 shifts to around 165 $^{\circ}$ C and peak 2 to 600 $^{\circ}$ C. It can be found that after deformation, both the two peaks shift to potions with higher temperatures. In addition, the intensity of both peaks increases after deformation. It is generally believed that peak 1 corresponds to reversible hydrogen traps (mainly dislocations) and the increase in the intensity of peak 1 indicates an increase in dislocation density [9,35]. TEM micrographs of specimens with cold deformation of 4.25% and 7.25% are shown in Figure 7c, d. From Figure 7c, it is found that after 4.25% cold deformation, clearly visible dislocation lines are found in the material, with slight dislocation entanglement in the middle of the dislocation. For 7.25% cold deformation material (Figure 7d), a significant increase in dislocation density is observed, accompanied by dislocation build-up and entanglement. The increase in dislocation density confirms that the density of reversible hydrogen traps increases with increasing cold deformation, and this is the main reason for the different hydrogen permeation behavior after cold deformation.



Figure 7. (**a**) Hydrogen trap density diagram for X65 pipeline steel from the electrochemical hydrogen permeation test, (**b**) TDS curves for X65 pipeline steel with different cold deformation levels, (**c**) TEM micrographs of X65 steel with 4.25% cold deformation, (**d**) TEM micrographs of X65 steel with 7.25% cold deformation.

4. Conclusions

The effect of cold deformation on the hydrogen permeation behavior of X65 pipeline steel is investigated in combination with electrochemical hydrogen permeation tests, TDS, TEM, and HMT, and the following conclusions can be drawn:

- (1) The D_{eff} decreases with increasing cold deformation (from 0.00% to 7.25%), from 3.553×10^{-6} to 1.775×10^{-6} cm²/s for the first penetration test and from 4.265×10^{-6} to 1.903×10^{-6} cm²/s for the second one, while c_0 increases with increasing cold deformation. The increase in cold deformation level inhibits hydrogen permeation.
- (2) In the HMT tests, the enrichment of silver particles on the surface increases with the cold deformation level and particles are more likely to be enriched at the grain boundaries and phase boundaries.
- (3) Both N_T and N_{RT} increase with increasing cold deformation which is proved by hydrogen penetration tests as well as by TDS. The dislocation density increases significantly after cold deformation and is accompanied by dislocation entanglement.

The current method for studying hydrogen permeation behavior is still the traditional electrochemical hydrogen permeation test. However, with a large number of applications of hydrogen-doped natural gas pipelines and pure hydrogen pipelines, studying the hydrogen permeation behavior in gaseous hydrogen environments will be more valuable for engineering. We will modify the cathode cell of the Devanthan–Stachurski dual cell so that the cathode cell can hold high pressure gaseous hydrogen. This will enable hydrogen permeation study in high-pressure hydrogen environments and compare the effect of liquid and gas phase hydrogen charging on the hydrogen permeation behavior.

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Appendix A

Table A1. Parameters and the corresponding abbreviations in this study.

Parameters	Abbreviations
Hydrogen diffusion flux	N_{∞}
Steady current density	J_{∞}
Effective hydrogen diffusion coefficient	D_{eff}
Apparent solubility	c_0
Specimen thickness	d
Lag time	t_L
Faraday constant	F
Trap free bcc iron	D_L
Hydrogen trap density	N_T
Reversible hydrogen trap density	N_{RT}
Irreversible hydrogen trap density	N_{IRT}

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