Comparison of hydrogen diffusivities measured by electrochemical permeation and temperature-programmed desorption in cold-rolled pure iron

Alfredo Zafra a, Zachary Harris b, Chao Sun a, Emilio Martínez-Pañeda a,∗

a Department of Civil and Environmental Engineering, Imperial College London, London SW7 2AZ, UK
b Department of Materials Science and Engineering, University of Virginia, Charlottesville, VA 22904, USA

A R T I C L E   I N F O
Keywords:
Hydrogen
Electro-permeation
Diffusion
Thermal desorption spectroscopy
Isothermal desorption

A B S T R A C T
The diffusivity of hydrogen in cold-rolled pure iron is investigated using permeation and desorption methods. Electrochemical charging, electro-permeation and thermal desorption spectroscopy (TDS) experiments are conducted. Firstly, the relation between the charging current and the hydrogen concentration is established. Secondly, permeation experiments are conducted at 22, 40 and 67 °C to quantify the diffusivity dependence on temperature. Finally, the diffusivity is estimated by using two types of desorption experiments and Fick’s law: (i) a ‘rest time’ method, by which we measure the hydrogen content of samples held at room temperature for different times, and (ii) isothermal desorption experiments at temperatures ranging from 22 to 80 °C, fitting the resulting desorption rate versus time curves. Good agreement is obtained between the isothermal desorption and permeation approaches, with observed differences discussed and rationalized. Moreover, measured diffusivity values for cold-rolled pure iron are also found to be comparable to those reported in the literature. This work demonstrates that isothermal desorption experiments are a convenient approach to determine hydrogen diffusivity over a wide range of temperatures, as facilitated by new TDS systems with fast heating rates.

1. Introduction

Hydrogen-induced degradation is a pertinent life-limiting damage mode for many metallic structural components across the aerospace, marine, energy, transportation, and infrastructure sectors (Gangloff, 2003). Critically, the presence of hydrogen-assisted sub-critical cracking compromises structural integrity management approaches, thereby complicating life prediction and fracture control efforts (Gangloff, 2003, 2016). Such effects become increasingly important as novel approaches to increasing the viability of hydrogen energy technologies are considered (Gangloff and Somerday, 2012), which may lead to existing infrastructure being subjected to unexpected operating conditions. For example, feasibility studies have suggested that blending hydrogen into natural gas pipeline networks is one pathway by which gaseous hydrogen may be economically stored and transported (Melaina et al., 2013; Hafi et al., 2019; Ishaq and Dincer, 2020). However, recent experimental evaluations have also demonstrated that the exposure of pipeline steels to natural gas/hydrogen mixtures can result in accelerated fatigue crack growth rates (Meng et al., 2017; Shang et al., 2020), degraded fracture resistance (Nguyen et al., 2020), and reduced tensile properties (e.g., breaking stress, notch tensile strength, ductility, etc.) (Meng et al., 2017). Critically, the extent of the degradation in mechanical properties is sensitive to the hydrogen volume fraction in the natural gas/hydrogen mixture, suggesting a fundamental dependence of the degradation mechanism on the available hydrogen content (Meng et al., 2017).

Driven by this deleterious impact on performance, over a century of scientific study (Johnson, 1875) has sought to mechanistically understand the microscale processes by which hydrogen degrades the mechanical properties of structural metals. These efforts have led to the development of numerous theories (Robertson et al., 2015; Gerberich, 2012; Shishvan et al., 2020), but a growing literature database strongly suggests that hydrogen-induced degradation proceeds via the synergistic interaction of several different hydrogen-modified processes (Gangloff, 2017; Djukic et al., 2019; Robertson et al., 2015); i.e., hydrogen-induced reductions in grain boundary cohesive strength (Harris et al., 2018; Kristensen et al., 2020), hydrogen-modified plasticity behavior (Barnoush and Vehoff, 2010; Nagao et al., 2018; Wang et al., 2020),...
ized using permeation methods. However, permeation experiments can exhibit substantial scatter. For example, hydrogen diffusivities determined from permeation experiments for nominally pure Fe at ambient temperature (25 °C) can differ by multiple orders of magnitude across studies (Kumnick and Johnson, 1974). This significant variability in permeation-measured data has been attributed to a wide range of potential influences, including: testing variable sensitivities (Gonzalez, 1969; Turnbull, 1995), surface effects (Kiuchi and McLellan, 1983; Ad-dach et al., 2009), nonsteady-state conditions (Nelson and Stein, 1973), concentration-dependent diffusion (Ono and Rosales, 1968; Zafra et al., 2020), hydrogen trapping (Kumnick and Johnson, 1974; Oriani, 1970), and analysis method (Boes and Züchner, 1976; Carvalho et al., 2017).

These aforementioned challenges associated with assessing the diffusivity of hydrogen in pure Fe using permeation experiments strongly motivate exploring the use of desorption-based approaches for ‘fast’ diffusing alloys. For example, isothermal desorption experiments have been used to generate hydrogen diffusivity versus temperature relationships in stainless steels (Mine et al., 2009), Ni-based superalloys (Ai et al., 2013), Cu-Ni and Ni-Cr (Matsuo et al., 2014), a number of low-alloy steels (Yamabe et al., 2015), and precipitation-hardened steels (Yamabe et al., 2021). Critically, in order to use this isothermal method for low-alloy steels, large specimens up to 19 mm in diameter were required (Yamabe et al., 2015). Recent advances in thermal desorption equipment, including improved conduction-based heating capabilities that can induce controlled heating rates of up to 60 °C/min, vacuum systems with dedicated loading chambers for fast evacuation to reduce sample ‘rest time’, and improved resolution mass spectrometers, suggest that this desorption-based approach could be used to obtain near-ambient (< 100 °C) hydrogen diffusivity data in ‘fast’ diffusing materials, such as pure iron, without the need for large specimens. However, such an evaluation and the follow-on comparison between isothermal desorption and permeation-determined diffusivities have yet to be performed.

The objective of this study is to compare permeation and thermal desorption-based assessments of hydrogen diffusivity using 1-mm thick cold-rolled pure iron to establish the efficacy of desorption-based approaches for measuring hydrogen diffusivities in a representative ‘fast’ diffusing material. The total hydrogen concentration versus applied current density relationship is first established for cold-rolled pure iron to inform the current density to be employed in subsequent experiments. Permeation measurements are performed at temperatures ranging from 22 to 67 °C and the hydrogen diffusivity is then estimated using three different approaches: breakthrough, lag time, and by fitting the permeation transient to an approximate solution of Fick’s law. These data are then compared to hydrogen diffusivity values determined from both variable rest time and isothermal (ranging from 22 to 80 °C) desorption experiments. We extensively discuss differences and similarities, as well as the implications for diffusion data extraction.

2. Experimental methods

2.1. Material

This study was conducted using cold-rolled pure iron (supplier-reported purity of >99.5 wt. %Fe) procured in the as-rolled condition from Goodfellow Ltd. as a 1-mm thick sheet. The supplier-reported average degree of cold work was 50%. All experiments were performed on thin plate specimens with nominal dimensions of 250 mm × 250 mm × 1 mm (electropermeation) and 10 mm × 10 mm × 1 mm (desorption), which were excised from the sheet using an abrasive saw. Each face of the sample was iteratively ground flat using SiC papers, finishing at 1200 grit.
2.2. Electropermeation

Electrochemical permeation experiments were performed at temperatures of 22, 40, and 67 °C using a modified Devanathan-Stachurski double-cell that was capable of being submerged in a hot bath; a schematic of this system is shown in Fig. 1. Two tests were conducted for each temperature. A masking plate was used to ensure that the specimen was inserted into the Devanathan–Stachurski double-cell and the open-circuit potential (OCP) of the sample membrane was monitored on the oxidation side of the double-cell. For the experiments conducted at 40 and 67 °C, the hot bath temperature was actively regulated by a thermostat and continuously monitored with a thermometer, which was in contact with the specimen. This setup resulted in a variation of ±1 °C in temperature over the course of a given permeation experiment. Note that the temperature of the solution at each side of the double-cell was allowed to stabilize prior to the start of each elevated temperature permeation experiment. The three-electrode hydrogen reduction cell was filled with 3 wt. % NaCl solution and contained a Pt counter electrode and a saturated calomel reference electrode. Hydrogen production was achieved by applying a current density of 5 mA/cm² to the cold-rolled Fe membrane using a Gamry 1010B potentiostat operated in galvanostatic mode. The hydrogen oxidation cell was filled with 0.1 M NaOH solution and also contained a Pt counter electrode and a saturated calomel reference electrode, with a second Gamry 1010B potentiostat operated in chronoamperometry mode to record the hydrogen permeation current density, \( J_p \), as a function of time. The hydrogen reduction and oxidation reactions taking place at the entry and exit surfaces of the specimen, respectively, are also included in Fig. 1.

Prior to conducting each permeation experiment, a thin layer of Pd (approximately 50-nm thick) was electroplated onto the specimen surface facing the oxidation side of the double-cell. Electroplating was completed by applying a current density of 1 mA/cm² to the specimen for approximately 5 min while it was immersed in a commercial solution that contained 2 g/L of Pd. The Pd layer is employed for two reasons (Manolatos et al., 1995): (1) to enhance the hydrogen oxidation reaction kinetics so as to minimize the hydrogen concentration at the sample surface in the oxidation cell, and (2) to avoid the oxidation of iron, which would obfuscate the true hydrogen permeation current. Once plated, the specimen was inserted into the Devanathan–Stachurski double-cell and the open-circuit potential (OCP) of the sample membrane was monitored on the oxidation side of the cell for 1 h. Upon completing this 1 h hold, the oxidation side of the membrane was then polarized to the final potential recorded during the OCP measurement (typically between −40 and −60 mV\(_{\text{SCCE}}\)). The permeation current density was then allowed to stabilize to a value less than 0.1 to 0.2 μA/cm² before the galvanostatic cathodic charging was started on the reduction side of the double-cell.

2.2.1. Determination of the diffusion coefficient

A representative hydrogen permeation transient versus time relationship that would be generated during an electrochemical permeation experiment is provided in Fig. 2. From these data, the hydrogen diffusivity can be calculated using three different methods (Turnbull et al., 1989): (i) the breakthrough time method, (ii) the lag time method, and (iii) by fitting the permeation transient to an approximate solution of Fick's law (Crank, 1979). The last case involves fitting the entire permeation transient, while the first two approaches use closed-form solutions to relate the time required to reach specific fractions of the steady state permeation current density, \( J_{\infty} \), to the hydrogen diffusion coefficient \( D \). In each case, it is assumed that the hydrogen subsurface concentration is a constant finite value at the entry side and zero at the exit side of the membrane.

Regarding the first method, the breakthrough time, \( t_{\text{bt}} \), is identified as the time required for \( J_p \) to reach 10% of \( J_{\infty} \) (i.e., \( J_p/J_{\infty}=0.1 \)) and is nominally considered to be the time required for the first hydrogen atoms to permeate completely through the membrane. Assuming a membrane geometry of thickness \( L \), the hydrogen diffusivity, \( D_{\text{bt}} \), can then be analytically determined for a given \( t_{\text{bt}} \) using:

\[
D_{\text{bt}} = \frac{L^2}{15.3t_{\text{bt}}}
\]

For the lag time method, the hydrogen diffusivity, \( D_{\text{lag}} \), is obtained in a similar manner as the breakthrough approach. Specifically, the lag time, \( t_{\text{lag}} \), is identified as the time required to achieve a \( J_p \) that is 63% of \( J_{\infty} \), which is then related to \( D_{\text{lag}} \) using:

\[
D_{\text{lag}} = \frac{L^2}{6t_{\text{lag}}}
\]

Lastly, the entire permeation transient as a function of time can be fit via least-squares regression to an approximate solution to Fick’s second law obtained from either a Laplace or Fourier transform (Crank, 1979), assuming 1-D diffusion. For this approach, the hydrogen diffusivity, \( D_{\text{fit}} \), is used as the sole fitting parameter to achieve the best fit between the experimental data and the approximate solution.

Fig. 1. Schematic of the electrochemical permeation testing configuration used in this work. The permeation setup is placed into a water bath to conduct high-temperature experiments.
A. Zafra et al.

The experiment and predicted \( J/J_\infty \) versus time relationship, with the predicted relationship determined from:

\[
\frac{J}{J_\infty} = \frac{2}{\pi^{1/2}} \left( D_{lp} t \right)^{1/2} \exp \left( -\frac{L^2}{4D_{lp}r} \right)
\]

The hydrogen diffusion coefficients measured with these three techniques were compared and differences discussed.

### 2.3. Hydrogen charging

Specimens were electrochemically precharged with hydrogen using a Gamry 1010B potentiostat operated in galvanostatic mode to maintain a constant cathodic current density, \( J_c \). All charging experiments were performed with the specimen fully immersed in 3 wt. % NaCl solution and referenced to a Pt electrode; a schematic of the hydrogen charging setup is shown in Fig. 3. Based on previously reported diffusivities for cold-rolled Fe (\( D \approx 8 \times 10^{-11} \text{ m}^2/\text{s}; \text{Van den Eeckhout et al., 2017} \)), all specimens were precharged for 3 h to obtain a nominally uniform hydrogen concentration across the plate thickness.

### 2.4. TDS measurements

All desorption-based experiments were completed using a dedicated thermal desorption spectroscopy (TDS) system capable of achieving heat rates as fast as 60 °C/min (3600 K/h). The system consisted of a dedicated analysis chamber, which was maintained at a vacuum pressure of 10⁻⁹ mbar using a turbomolecular pump, and a small sample loading chamber designed to minimize the time required to reach vacuum levels comparable to the analysis chamber. Hydrogen content measurements were made using a regularly calibrated Hiden Analytical RC PIC quadrupole mass spectrometer, which had a detection resolution of 4.4 \times 10⁻⁶ wppm/s. For each thermal desorption experiment, the sample was electrochemically pre-charged with hydrogen according to the process described in Section 2.3. Upon completion of the cathodic charging, the sample was rinsed with acetone and then distilled water, carefully dried with warm air, and then loaded into the transfer chamber of the TDS. The transfer system was then evacuated to approximately 10⁻⁷ mbar. After the transfer from the loading chamber was complete, the specimen was placed onto an aluminum nitride (AlN) sheet in direct contact with the controllable, 2.5 kW heating stage. Four ceramic rods were then extended to press the sample against the AlN sheet, thereby maximizing conduction as well as ensuring homogeneous heating of the entire specimen. Once the specimen had been sufficiently fixed against the AlN plate, the desorption experiment was initiated using a pre-programmed temperature versus time sequence. The typical elapsed time between the completion of cathodic charging and the beginning of the thermal desorption experiment was 30 min. A schematic illustrating this experimental setup is shown in Fig. 4.

Two types of thermal desorption experiments were performed in the current study to assess the hydrogen diffusivity of cold-rolled pure iron, as described in the following sections.

#### 2.4.1. Desorbed hydrogen tests

A series of 10 mm \( \times 10 \text{ mm} \times 1 \text{ mm} \) specimens were cathodically pre-charged in 3 wt. % NaCl solution using a current density of 5 mA/cm² during a charging time of 3 h. After charging, the samples were then allowed to rest at ambient temperature (\( \approx 22 \text{ °C} \)) in laboratory air for times (which included the TDS pump-down time) ranging from 0.5 to 48 h. Each sample was then heated from 25 to 850 °C at a rate of 30 °C/min and the total remaining hydrogen content was calculated via integration of the obtained thermal desorption spectra. The hydrogen diffusivity at ambient temperature, \( D_{des} \), can then be determined by comparing the experimental hydrogen content versus desorption time relationship to that predicted by published analytical solutions for 1-D diffusion in a plate geometry of half-thickness \( L \), such as (Crank, 1979):

\[
C - C_0 \approx \frac{C_1 - C_0}{\pi} = \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp \left( -\frac{D_{des}(2n+1)^2 \pi^2 t}{4L^2} \right) \cos \left( \frac{(2n+1)\pi x}{2L} \right)
\]

(4)
where $C$ is the hydrogen concentration at position $x$ after desorption time $t$, $C_0$ is the initial uniformly distributed hydrogen concentration at $t = 0$, and $C_1$ is the surface hydrogen concentration. A Matlab script was used to iteratively increment $C_0$ and $D_{iso}$ to obtain the optimal fit between the average concentration across the simulated specimen thickness and the measured remaining total hydrogen content for each desorption time. Note that there are several critical assumptions in this analysis. First, given that the desorbed hydrogen content contains the trapped hydrogen, which is unlikely to desorb at ambient temperature, the total hydrogen content was found to asymptotically approach a lower-bound plateau value at long desorption times. This was phenomenologically captured in this simulation by considering $C_1$ to be the trapped hydrogen concentration which, based on the desorption experiment results (see Fig. 7), was set to a constant value of 0.75 weight parts per million (wppm). Second, a constant specimen thickness of 1 mm was assumed for all simulations. Lastly, an initially uniform concentration is assumed, in accordance with the boundary conditions used for the derivation of Eq. (4) (Crank, 1979).

### 2.4.2. Isothermal TDS tests

Isothermal desorption experiments were performed at 22, 40, 60, and 80 $^\circ$C on a series of 10 mm x 10 mm x 1 mm specimens that were each cathodically pre-charged in 3 wt. % NaCl solution using a current density of 5 mA/cm$^2$ during charging time of 3 h. Duplicate experiments were also performed at 22 $^\circ$C and 80 $^\circ$C. These isothermal experiments are nominally similar to typical programmed-temperature desorption (Verbeeken, 2012), but hydrogen egress is monitored under a fixed temperature, as opposed to ramping the temperature versus time profile. For all tested temperatures greater than 22 $^\circ$C, the time required to stabilize the sample at the test temperature varied from 140 to 180 s.

Given the isothermal nature of these experiments, it is straightforward to determine the hydrogen diffusivity from the desorbed hydrogen content versus time profile using numerical analysis approaches (e.g., finite differences or finite element). In this work, we chose to use finite element modeling to determine the hydrogen diffusivity from the isothermal TDS tests. The magnitude of the hydrogen diffusion coefficient $D$ can be determined by fitting the experimental desorption curve with the output of a 1D finite element (FE) simulation of hydrogen transport. Specifically, diffusion is governed by Fick's second law, which in a one-dimensional form reads:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{5}$$

where $C$ is the diffusible hydrogen concentration. One must also define an initial condition ($C = C_0$ at $t = 0$) and suitable boundary conditions ($C = 0$ at $x = \pm L/2$). The simulations were then completed as follows. First, the hydrogen egress during experiments associated with the resting time required for the chamber pump-down (30 min.) and subsequent heating time to reach the targeted temperature, $T_{iso}$, was simulated by assuming the sample was held at room temperature ($T = 22 ^\circ C$) for the entire rest and heating duration. Then, upon completing this initial hold time, the temperature in the simulation was instantly increased to $T_{iso}$ and then held constant for the duration of the simulation. The diffusivity used in the initial resting step of the simulations was determined by first fitting the experimentally-measured desorbed hydrogen content versus time data obtained at 22 $^\circ$C via iteratively changing the $C_0$ and $D$ values. Once this value was known, the best $D$ at $T = 22 ^\circ C$ was then applied for the resting period for the higher temperature experiments, with $C_0$ and $D$ then adjusted to fit the observed desorption data for each respective $T_{iso}$. A sensitivity analysis revealed the existence of a unique pair of $C_0$ and $D$ values that yielded the best fit of the experimental curve for each temperature. Critically, while the simulation results were found to be nearly affected by changes in $C_0$, they were strongly sensitive to subtle changes in $D$, thereby indicating the uniqueness of the best fit $D_{iso}$ for each temperature.

### 3. Results

#### 3.1. Influence of the charging current

First, it is necessary to determine the cathodic current density, $J_c$, to be employed for subsequent hydrogen precharging and permeation experiments, as well as to establish a general relationship between applied current density and total hydrogen content for cold-rolled Fe. Towards this end, specimens were charged at seven different current densities ranging from 0.5 to 13 mA/cm$^2$. The total hydrogen content was then calculated via integration of the TDS spectra collected for each specimen over the temperature range of 25 to 850 $^\circ$C. A total of 31 specimens were evaluated: 1 specimen at 0.5 mA/cm$^2$, 1 specimen at 1 mA/cm$^2$, 1 specimen at 3 mA/cm$^2$, 22 specimens at 5 mA/cm$^2$, 1 specimen at 7 mA/cm$^2$, 3 specimens at 10 mA/cm$^2$, and 2 specimens at 13 mA/cm$^2$. The measured total hydrogen content $C$ as a function of $J_c$ is shown in Fig. 5. For the current densities where multiple experiments were performed, the average measured concentration is plotted, with the error bars representing the calculated standard deviation. These data were then fit to a power law function, yielding the following relationship: $C = 1.342 J_c^{1.102}$, as indicated by the solid line in Fig. 5. The 95% prediction bands, which represent the upper and lower bounds between which there is 95% confidence the fitted function will reside, are represented by dashed lines in Fig. 5.

Examination of Fig. 5 reveals four observations. First, the total hydrogen content exhibits an initially rapid increase with increasing $J_c$ up to 3 mA/cm$^2$, followed by a more gradual increase over the remaining range of evaluated current densities. This asymptotic-like behavior at the relatively low hydrogen contents of between 3 to 3.5 wppm is consistent with the generally low hydrogen solubility of α-iron (Choo et al., 1981). Second, regarding the solubility of hydrogen in pure Fe, the literature establishes that it is on the order of 1 wppm (Choo et al., 1981), which is lower than the values reported here. However, it should be noted that the evaluated pure Fe was cold rolled down to its final thickness of 1 mm. As such, an increase in solubility is expected due to the multiplication of defects, which will act as trap sites and increase the total hydrogen concentration (Kiuchi and McLellan, 1983; Oriani, 1970). Third, as demonstrated by both the upper and lower bounds of the prediction interval and the error bars calculated from duplicate experiments, the dataset is well described by the fitted power law equation. Lastly, the observed relative scatter of the data, especially for the 5 mA/cm$^2$ condition where 22 specimens were evaluated, is in line with expectations from other electrochemical
charging studies of hydrogen content (Ai et al., 2013; Rincon Troconis et al., 2017; Harris et al., 2021b) and suggests reasonable repeatability amongst the duplicate specimens.

3.2. Permeation tests

The permeation curves obtained for duplicate experiments on cold-rolled pure Fe at 22, 40, and 67 °C, along with their corresponding fits to Eq. (3), are shown in Fig. 6. For each experiment, the steady state permeation current density \( J_\infty \), breakthrough time \( t_b \), and lag time \( t_{lag} \) are documented in Table 1. The calculated hydrogen diffusivities using the three approaches described in Section 2.2 are also noted. First, considering the results at 22 °C, the diffusivity is found to vary between 4 and 7.4 × 10^{-11} m^2/s across the three employed methods, which is broadly consistent with reported hydrogen diffusivities for cold-rolled pure Fe (Van den Eeckhout et al., 2017). Second, both the slope of the permeation transient and the magnitude of \( J_\infty \) systematically increase with temperature, as can be seen from Table 1, across all the methodologies employed. Third, it is important to note that the assumed diffusivity employed to estimate the time required for hydrogen precharging of the desorption experiments \( D \approx 8 × 10^{-11} \) m^2/s; Van den Eeckhout et al., 2017) was a reasonable estimate. Critically, considering the calculated diffusivities for 22 °C in Table 1, it is expected that the centerline of the 1-mm thick specimens used in the current study would indeed be nominally saturated after 3 h; i.e., reached between 98.20% and 99.95% of the surface hydrogen concentration, as per Eq. (4).

Examination of the Laplace Fick's law fit for each experiment in Fig. 6 demonstrates that steady state conditions were attained in each experiment, as shown by the good agreement between the experimental and fitted curves. The exception is the 22 °C (1) case, where stabilization of the permeation curve was not observed. Speculatively, the difficulty in reaching steady state for this experiment may be due either to surface effects taking place in the cathodic or anodic sides of the specimen (Kiuchi and McLellan, 1983; Addach et al., 2009) or to incomplete filling of the hydrogen traps (Kumnick and Johnson, 1974; Oriani, 1970). As such, it is likely that the reported diffusivities determined for this test are biased to slightly higher values. This situation exemplifies a primary limitation of electropermeation tests when assessing hydrogen diffusivity in metals as numerous variables can hinder the attainment of steady state, thereby obfuscating subsequent analysis efforts.

Comparing the calculated diffusivities for each method in Table 1, it is interesting to note that the lag time and the Laplace methods resulted in similar hydrogen diffusivities across all tested specimens, with the largest differences being less than 12%. Conversely, the diffusivities determined with the breakthrough method at 22 °C were noticeably higher than those obtained with the lag time and Laplace methods, but then found to be lower in the case of the tests performed at higher temperatures. Speculatively, this behavior could be explained in terms of the progressive loss of importance of trapping phenomena over lattice diffusion as the temperature is increased (Oriani, 1970). It is worth noting that the differences in diffusivity between the breakthrough and the lag time/Laplace methods increased to nearly 40% in some cases, which is greater than the scatter reported between duplicate experiments.

3.3. Desorption curve

The results of the ‘rest time’-based approach to measuring hydrogen diffusivity via desorption methods is shown in Fig. 7. As expected, the total hydrogen concentration within the specimen exhibits an initially strong reduction with increasing rest time at ambient temperature, eventually leveling out at a nominal concentration of 0.75 wppm after approximately 10–15 h. This initial steep reduction is consistent with the egress of the diffusible hydrogen concentration, while the observed plateau is indicative of the trapped hydrogen content. These data were then iteratively fit to Eq. (4), with \( C_0 \) and \( D_{des} \) used as fitting parameters. The results of the best obtained fit are indicated by the red line in Fig. 7, which corresponded to \( C_0 = 3.0 \) wppm and \( D_{des} = 1 × 10^{-11} \) m^2/s. Comparing this value to those obtained from the various permeation methods at 22 °C (Table 1), it is clear that the ‘rest time’ desorption approach yields a tangibly lower diffusivity. Possible reasons for this decreased diffusivity will be enumerated in the Discussion section.

![Fig. 6. Permeation transients obtained in pure Fe at different temperatures, including a fit using Fick’s law.](image_url)

![Fig. 7. Desorption curve. Hydrogen concentration as a function of elapsed time in air at room temperature. The datapoint and error bars at 0.5 h represent the average and standard deviation of the total content measured from 22 experiments.](image_url)

| Test | \( J_\infty \) (μA/cm²) | \( t_b \) (s) | \( D_{obs} \) (m²/s) | \( t_{lag} \) (s) | \( D_{lag} \) (m²/s) | \( D_{lap} \) (m²/s) |
|------|---------------------|---------|------------------|---------|------------------|------------------|
| 22 °C (1) | 4.85 | 870 | 7.36 × 10^{-11} | 4110 | 3.97 × 10^{-11} | 4.53 × 10^{-11} |
| 22 °C (2) | 3.24 | 834 | 6.78 × 10^{-11} | 2596 | 5.55 × 10^{-11} | 5.89 × 10^{-11} |
| 40 °C (1) | 6.52 | 245 | 2.21 × 10^{-10} | 377 | 3.66 × 10^{-10} | 3.31 × 10^{-10} |
| 40 °C (2) | 7.73 | 315 | 1.83 × 10^{-10} | 570 | 2.57 × 10^{-10} | 2.41 × 10^{-10} |
| 67 °C (1) | 13.60 | 87 | 6.22 × 10^{-10} | 145 | 9.52 × 10^{-10} | 8.52 × 10^{-10} |
| 67 °C (2) | 13.56 | 80 | 7.19 × 10^{-10} | 151 | 9.71 × 10^{-10} | 9.24 × 10^{-10} |
3.4. Isothermal TDS tests

The measured desorption rate versus time profiles during isothermal desorption experiments at temperatures of 22, 40, 60 and 80 °C are shown in Fig. 8. The initial slope of the desorption rate versus time relationship is noted to increase with increasing temperature, consistent with expectations for an increasing hydrogen diffusivity and with the behavior observed during the permeation experiments (Fig. 6). The best fit to Fick’s second law, determined from finite element (FE) simulations, is indicated by the corresponding dashed lines for each respective condition. For all cases, the FE calculations closely capture the experimentally observed initial slope, which is a strong function of the hydrogen diffusivity. The initial diffusible hydrogen concentration \( C_0 \) and diffusion coefficient \( D_{iso} \) that yielded the best fit of the experimental curve with Fick’s second law (FE model) are shown in Table 2. As expected, and in line with the permeation results, the calculated diffusivity exhibits a systematic increase with increasing temperature.

Finally, it is worth noting that very similar diffusion coefficients were obtained for the replicate tests performed at 22 °C and 80 °C, respectively. This is observed even though noticeable differences are seen in the fitted \( C_0 \) values, though these variations in \( C_0 \) lie within the scattering reported in Fig. 5. This excellent repeatability suggests this method – isothermal TDS tests combined with numerical fitting – is a robust approach for the determination of hydrogen diffusivities.

4. Discussion

We proceed to compare and analyze the results obtained by the various permeation and desorption methods. The estimated diffusivities are shown versus the inverse of temperature in Fig. 9, using a log-linear plot. Here, the solid lines represent a fit of each respective dataset to the following Arrhenius expression:

\[
D = D_0 \exp \left(- \frac{E_a}{RT} \right)
\]

where \( D_0 \) is the pre-exponential factor, \( E_a \) the activation energy for hydrogen diffusion, and \( R \) is the gas constant. The independent term of the linear regression is equal to \( \log(D_0) \) and \( E_a \) is obtained by multiplying the slope by \( R \). The fitted values of \( D_0 \) and \( E_a \) are shown in Table 3.

Four observations can be made from these data. First, the desorption-based ‘rest time’ method yielded a significantly lower hydrogen diffusivity at 22 °C (nearly five-fold) as compared to the other four approaches. Given that this approach is based on fitting the measured remaining hydrogen content as a function of outgassing time, it is speculated that variations in absorbed hydrogen concentration are likely responsible for the low observed diffusivity. As demonstrated by the error bars shown in Fig. 7 for the 22 duplicate measurements performed at 0.5 h, test-to-test scatter in initially absorbed hydrogen content is non-negligible, which would introduce increased variability into this method relative to other approaches. Second, the isothermal desorption method yielded generally similar diffusivity values for a given temperature relative to the three permeation based approaches. Such agreement between the diffusivity values measured through both methods was not expected, as considerable differences between absorption-based and desorption-based measurements of diffusivity have been previously reported for elevated temperature (> 400 °C)-based evolution experiments in pure iron (Carmichael et al., 1960). Third, examination of the spread in diffusivities at ambient temperature indicates a maximum of two-fold difference across the four best methods (permeation and isothermal desorption), which represents excellent agreement relative to the reported spread in ambient temperature diffusivity for pure Fe in the literature (Ono and Rosales, 1968; Kumnick and Johnson, 1974;
Kiuchi and McLellan, 1983). Lastly, examination of the calculated $E_a$ for the four approaches that were conducted at multiple temperatures demonstrates that the isothermal desorption-based $E_a$ sits in the middle of the three permeation-based approaches. Speculatively, it is likely that the agreement between these different methods would only increase if the isothermal desorption results were compared against the second permeation transient, which represents a scenario where the deep hydrogen traps are already filled.

As expected, the diffusion coefficients determined from the current experiments shown in Table 3 are significantly different from those measured in the literature for well-annealed pure Fe. For example, a thorough analysis of the existing diffusivity literature in well-annealed iron was performed by Kiuchi and McLellan, who suggested that hydrogen diffusion is best described by $D_0 = 7.23 \times 10^{-8}$ m²/s and an activation energy $E_a = 5.69$ kJ/mol up to a temperature of 80 °C (Kiuchi and McLellan, 1983). Considering the activation energy parameter, it is expected that the significantly increased dislocation density induced during the cold-rolling process will result in the widespread distribution of modestly strong hydrogen trap sites, thereby increasing the macroscale barrier for hydrogen diffusion (Oriani, 1970). For example, Choo and Lee (1983) observed a progressive increase in both $D_0$ and $E_a$ with the degree of cold rolling for pure iron. As such, the measured diffusivity is no longer controlled simply by lattice diffusion, but rather becomes dependent on the trapping behavior, resulting in diffusion being best described by an effective diffusivity (Oriani, 1970).

Given this expected departure from the behavior of annealed pure Fe, the current study’s results should be compared to the diffusivity versus temperature data reported from studies on cold-rolled Fe. This comparison is shown in Fig. 10 for six relevant studies (Addach et al., 2005; Choo and Lee, 1983; Drexler et al., 2020; Siegl et al., 2019; Van den Eeckhout et al., 2017; Li et al., 2014). The degree of cold rolling involved in each study has been included next to the corresponding data point in Fig. 10. As was discussed previously based on analyses conducted in the literature (Kiuchi and McLellan, 1983), literature data exhibits substantial scatter in measured diffusivity at ambient temperature (300 K). Fig. 10 demonstrates that this large variability persists in cold-worked iron, as iron with similar degrees of cold work (~50%) exhibits one order of magnitude differences in measured diffusivity. However, it is notable that the current results fall approximately in the middle of the observed scatter, suggesting general agreement with these prior data. Less literature data on cold-rolled iron is available at elevated temperatures, but the trend of the current results residing in the nominal middle of the scatter band appears to generally hold as the temperature is increased.

Collectively, these comparisons with prior literature data and the reasonable agreement with the three different permeation-based approaches (Fig. 9 and Table 3) strongly support the viability of the employed isothermal desorption approach for assessing hydrogen diffusivity in cold-rolled Fe and other ‘fast’ diffusion alloy systems. Moreover, the efficacy of this method was demonstrated using a relatively thin material form (1-mm thick sheet), indicating that the approach does not become dependent on the trapping behavior, resulting in diffusion being best described by an effective diffusivity (Oriani, 1970).

5. Conclusions

The hydrogen diffusivity for cold-rolled pure Fe was measured using both electrochemical permeation and thermal desorption-based techniques, offering an opportunity to compare these approaches. Based on these experiments, the following conclusions were made:

- Analysis of permeation data using the breakthrough time method, the lag time method, and a Laplace solution to the entire permeation transient yielded nominally similar hydrogen diffusivities across methodologies for each temperature (22 °C, 40 °C and 67 °C). The hydrogen diffusivity values obtained at 22 °C were found to be generally consistent with those reported in the literature for cold-rolled pure Fe.
- Comparison of two desorption-based approaches to calculating the hydrogen diffusion resulted in significantly different values, with differences between isothermal desorption and the rest time method being of almost an order of magnitude. This difference is speculatively attributed to the strong sensitivity of the rest time method to lag time and Laplace permeation approaches. However, a collective analysis suggests that isothermal desorption is generally consistent with the permeation results.
- Hydrogen diffusivity values reported in the literature as a function of temperature for cold-rolled Fe are in excellent agreement with those determined in the current study using permeation and isothermal desorption.
- The results of this study demonstrate the efficacy of the isothermal desorption technique for evaluating hydrogen diffusivity in thin-section specimens of ‘fast’ diffusing materials. Additional studies are needed to evaluate the experimental scatter of this approach relative to that observed for permeation-based experiments, but initial results suggest that isothermal desorption exhibits reduced levels of scatter.

![Fig. 10. Measured and reported values of the diffusion coefficient of hydrogen in cold-rolled iron as a function of temperature. The degree of cold rolling is indicated; the data from the present work corresponds to a supplier-reported average degree of cold work of 50%.

Collectively, these comparisons with prior literature data and the reasonable agreement with the three different permeation-based approaches (Fig. 9 and Table 3) strongly support the viability of the employed isothermal desorption approach for assessing hydrogen diffusivity in cold-rolled Fe and other ‘fast’ diffusion alloy systems. Moreover, the efficacy of this method was demonstrated using a relatively thin material form (1-mm thick sheet), indicating that the approach does not become dependent on the trapping behavior, resulting in diffusion being best described by an effective diffusivity (Oriani, 1970).

5. Conclusions

The hydrogen diffusivity for cold-rolled pure Fe was measured using both electrochemical permeation and thermal desorption-based techniques, offering an opportunity to compare these approaches. Based on these experiments, the following conclusions were made:

- Analysis of permeation data using the breakthrough time method, the lag time method, and a Laplace solution to the entire permeation transient yielded nominally similar hydrogen diffusivities across methodologies for each temperature (22 °C, 40 °C and 67 °C). The hydrogen diffusivity values obtained at 22 °C were found to be generally consistent with those reported in the literature for cold-rolled pure Fe.
- Comparison of two desorption-based approaches to calculating the hydrogen diffusion resulted in significantly different values, with differences between isothermal desorption and the rest time method being of almost an order of magnitude. This difference is speculatively attributed to the strong sensitivity of the rest time method to lag time and Laplace permeation approaches. However, a collective analysis suggests that isothermal desorption is generally consistent with the permeation results.
- Hydrogen diffusivity values reported in the literature as a function of temperature for cold-rolled Fe are in excellent agreement with those determined in the current study using permeation and isothermal desorption.
- The results of this study demonstrate the efficacy of the isothermal desorption technique for evaluating hydrogen diffusivity in thin-section specimens of ‘fast’ diffusing materials. Additional studies are needed to evaluate the experimental scatter of this approach relative to that observed for permeation-based experiments, but initial results suggest that isothermal desorption exhibits reduced levels of scatter.
Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Emilio Martínez-Pañeda acknowledges discussions with A. Díaz (University of Burgos). The authors acknowledge financial support from the EPSRC, UK (grants EP/V04902X/1 and EP/V009680/1).

References

Addach, H., Berquot, P., Rezrazi, M., Takadoum, J., 2009. Study of the electrochemical permeation of hydrogen in iron. Corros. Sci. 51 (2), 263–267.
Addach, H., Berquot, P., Rezrazi, M., Vergy, M., 2005. Hydrogen permeation in iron at different temperatures. Mater. Lett. 59 (11), 1347–1351.
Ai, J.H., Ha, H.M., Gangloff, R.P., Scully, J.R., 2013. Hydrogen diffusion and trapping in a precipitation-hardened nickel-copper-aluminum alloy Monel K-500 (UNS N05500). Acta Mater. 61 (9), 3186–3199.
Akhurst, R.N., Baker, T.J., 1981. The threshold stress intensity for hydrogen-induced crack growth. Metall. Trans. A 12 (6), 1059–1070.
Barnoush, A., Vehoff, H., 2010. Recent developments in the study of hydrogen embrittlement: Hydrogen effect on dislocation nucleation. Acta Metall. 58 (16), 5274–5283.
Barrer, R.M., 1940. Stationary and non-stationary states of flow of hydrogen in palladium and iron. Trans. Faraday Soc. 36, 1235–1248.
Bhadeshia, H.K.D.H., 2016. Prevention of hydrogen embrittlement in steels. ISIJ Int. 56 (1), 24–36.
Boes, N., Züchner, H., 1976. Electrochemical methods for studying diffusion, permeation and solubility of hydrogen in metals. J. Less-Common Metals 49 (C), 223–240.
Carmichael, D., Hornaday, J., Morris, A., Parlee, N., 1960. The absorption and effusion of hydrogen in alpha iron. Trans. Metall. Soc. AIME 218, 826–832.
Carvalho, J.P., Vilar, E.O., Araújo, B.A., 2017. A critical review and experimental analysis of the equation recommended by ASTM G148-97 and ISO 17081: 2004 for the calculation of the hydrogen diffusivity in metals and alloys. Int. J. Hydrogen Energy 42 (1), 681–688.
Choi, J.Y., 1970. Diffusion of hydrogen in iron. Metall. Trans. 1 (4), 911–919.
Choo, W.Y., Lee, J.Y., 1983. Thermal analysis of trapped hydrogen in pure iron. Metall. Trans. A 13, 423–427.
Choo, W.Y., Lee, J.Y., 1983. Effect of cold working on the hydrogen trapping phenomena in pure iron. Metall. Trans. A 14 (7), 1299–1305.
Choo, W.Y., Lee, J.Y., Cho, C.G., Hwang, S.H., 1981. Hydrogen solubility in pure iron and effects of alloying elements on the solubility in the temperature range 20 to 500 °C. J. Mater. Sci. 16 (5), 1285–1292.
Crane, J., 1979. The Mathematics of Diffusion. Oxford University Press, Oxford, viii, 414 p.
DeLucia, J., Berman, D., 1981. An electrochemical technique to measure diffusible hydrogen in metals (barnacle electrode). In: Mansfeld, F., Bertocci, U. (Eds.), Electrochemical Corrosion Testing. ASTM STP 727. American Society for Testing and Materials, pp. 256–273.
Depoer, T., Verbeken, K., 2021. Hydrogen diffusion in metals: a topic requiring specific attention from the experimentalist. In: Van der Voorede, M. (Ed.), Hydrogen Storage for Sustainability, vol. II. Walter de Gruyter GmbH, Berlin, pp. 247–280.
Diaz, A., Cuesta, I.L., Martinez-Pañeda, E., Alegre, J.M., 2020a. Analysis of hydrogen permeation tests considering two different modelling approaches for grain boundary trapping in iron. Int. J. Fract. 223, 17–35.
Diaz, A., Cuesta, I.L., Martinez-Pañeda, E., Alegre, J.M., 2020b. Influence of charging conditions on simulated temperature-programmed desorption for hydrogen in metals. Int. J. Hydrogen Energy 45, 23704–23720.
Diaz, A., Zafra, A., Martinez-Pañeda, E., Alegre, J.M., Beltrane, J., Cuesta, I.L., 2020c. Simulation of hydrogen permeation through pure iron for trapping and surface phenomena characterisation. Theor. Appl. Fract. Mech. 110, 102818.
Martínez-Pañeda, E., Niordson, C.F., Gangloff, R.P., 2016. Strain gradient plasticity-based modeling of hydrogen environment assisted cracking. Acta Mater. 117, 321–332.

Matsu, T., Yamabe, J., Furukawa, H., Seki, K., Shimizu, K., Watanabe, S., Matsouka, S., 2014. Development of new strain gage for high-pressure hydrogen gas use. Exp. Mech. 54 (3), 431–442.

Melaina, M., Antonia, O., Penev, M., 2013. NREL/TP-5600-51995: Blending hydrogen into natural gas pipelines networks: a review of key issues. National Renewable Energy Laboratory, Golden, CO, pp. 1–30.

Meng, B., Gu, C., Zhang, L., Zhou, C., Li, X., Zhao, Y., Zheng, J., Chen, X., Han, Y., 2017. Hydrogen effects on X80 pipeline steel in high-pressure natural gas/hydrogen mixtures. Int. J. Hydrogen Energy 42 (11), 7404–7412.

Mine, Y., Narazaki, C., Murakami, K., Matsuoka, S., Murakami, Y., 2009. Hydrogen transport in solution-treated and pre-strained austenitic stainless steels and its role in hydrogen-enhanced fatigue crack growth. Int. J. Hydrogen Energy 34 (2), 1097–1107.

Nagao, A., Dadfarnia, M., Somerday, B.P., Sofronis, P., Ritchie, R.O., 2018. Hydrogen-enhanced-plasticity mediated decohesion for hydrogen-induced intergranular and “quasi-cleavage” fracture of lath martensitic steels. J. Mech. Phys. Solids 112, 403–430.

Nagumo, M., Takai, K., 2019. The predominant role of strain-induced vacancies in hydrogen embrittlement of steels: Overview. Acta Mater. 165, 722–733.

Nelson, H., Stein, J., 1973. NASA TN D-7265: Gas-phase Hydrogen Permeation Through Alpha Iron, 4130 Steel, and 304 Stainless Steel from Less than 100° C to near 600° C. Technical Report, Ames Research Center, Moffat Field, CA, pp. 1–18.

Nguyen, T.T., Park, J.S., Kim, W.S., Nahm, S.H., Beak, U.B., 2020. Environment hydrogen-enhanced-plasticity mediated decohesion for hydrogen-induced intergranular and “quasi-cleavage” fracture of lath martensitic steels. J. Mech. Phys. Solids 112, 403–430.

Shang, J., Chen, W., Zheng, J., Hua, Z., Zhang, L., Zhou, C., Gu, C., 2020. Enhanced hydrogen embrittlement of low-carbon steel to natural gas/hydrogen mixtures. Scr. Mater. 189, 67–71.

Siegl, W., Ecker, W., Klammer, J., Kloesch, G., Mori, G., Drexler, A., Winter, G., Schniederitsch, H., 2019. Hydrogen trapping in heat treated and deformed armco iron. NACE - International Corrosion Conference Series 2019-March.

Stross, T., Tompkins, F.C., 1956. The diffusion coefficient of hydrogen in iron. Proc. Chem. Soc. London 1, 230–234.

Subramanyan, P., 1981. Electrochemical aspects of hydrogen in metals. In: Bockris, J., Conway, B., Yeager, E., White, R. (Eds.), Comprehensive Treatise on Electrochemistry. Plenum Press, New York, pp. 411–462.

Turnbull, A., 1995. Factors affecting the reliability of hydrogen permeation measurement. Mater. Sci. Forum 192-194 (pt 1), 63–78.

Van den Eeckhout, E., Laureys, A., Verbeken, K., 2017. Hydrogen permeation through deformed and heat-treated Armco pure iron. Mater. Sci. Technol. 33 (13), 1515–1523.

Verbeken, K., 2012. Analysing hydrogen in metals: bulk thermal desorption spectroscopy (TDS) methods. In: Gangloff, R.P., Somerday, B.P. (Eds.), Gaseous Hydrogen Embrittlement of Materials in Energy Technologies, vol. II. Woodhead Publishing, pp. 27–55.

Wang, S., Martin, M.L., Sofronis, P., Ohnuki, S., Hashimoto, N., Robertson, I.M., 2014. Hydrogen-induced intergranular failure of iron. Acta Mater. 69, 275–282.

Yamabe, J., Awane, T., Matsouka, S., 2015. Investigation of hydrogen transport behavior of various low-alloy steels with high-pressure hydrogen gas. Int. J. Hydrogen Energy 40 (34), 11075–11086.

Yamabe, J., Sezgin, J.-G., Wada, K., 2021. Interpretation of complex, tensile-fracture phenomena in precipitation-hardened, martensitic stainless steels, 17-4PH, in presence of hydrogen. Mater. Sci. Eng. A 823, 141717.