Determining the effective hydrogen diffusion coefficient in 100Cr6

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Abstract
In the present study, the diffusion constant for hydrogen in hardened 100Cr6 was measured in permeation tests. The tests were conducted on samples of different thicknesses. The diffusivity of hydrogen was also measured in pre-strained samples to study the influence of plastic strain on the diffusion rate. A finite element-based diffusion model was applied to confirm the experimental results by computing the concentrations of diffusible hydrogen and trapped hydrogen due to deformation-induced defects. The results showed that the concentration of trapped hydrogen remained very low throughout the plastic strain regime under consideration. The average effective diffusion coefficient of hydrogen in 100Cr6 at 30°C was found to be \( D_{\text{eff}} = 4.9 \times 10^{-12} \text{ m}^2/\text{s} \).

KEYWORDS
100Cr6, bearing steel, effective diffusion coefficient, hydrogen diffusion, permeation cell, trapped hydrogen

1 | INTRODUCTION

Various researchers\(^1–4\) have developed permeation cells between 1920 and 1940. Bockris and Devanathan\(^5\) analyzed the adsorption and absorption reaction of hydrogen in an aqueous solution on metal surfaces. There are two possible reactions on a surface: The adsorption of hydrogen on the surface in an anodic reaction or the recombination in a Tafel reaction.

The adsorption of hydrogen on a metal surface is a result of discharging reactions. The diffusion of hydrogen into the metal matrix could be seen as a side reaction of the overall reaction.\(^6\) Hydrogen uptake in a metal lattice is a product of a corrosion reaction or a cathodic polarization.\(^6\) McNabb and Foster\(^7\) investigated the diffusion of hydrogen in iron and steel and developed a theory to describe the influence of hydrogen traps on hydrogen diffusion in metals. The total hydrogen concentration in the material may be described as the hydrogen concentration in the lattice site and in trapping sites. Oriani\(^8\) investigated the trapping and diffusion processes of hydrogen in steel. The diffusion of hydrogen in a perfect lattice can be described with Fick’s law. In a real metal structure, dislocations, grain boundary, phase boundaries, and impurities act as hydrogen traps and significantly influence the diffusion of hydrogen. The concentration of hydrogen in the lattice can be described with the occupancy probability of the lattice site. The hydrogen concentration in traps can be described with the occupancy probability of the trapping site. According to Oriani,\(^8\) the total concentration of hydrogen in a solid body is the sum of the lattice concentration and the trap concentration.

It has been shown that the Boltzmann transport theory could be modified in a way that effects like traps, stress fields, inhomogeneous solubility, and temperature...
graduates are considered in the diffusion of hydrogen.\(^9\)–\(^11\) Hydrogen trapping is explained with irreversible trapping and reversible trapping. Irreversible traps are saturable, whereas reversible traps are nonsaturable. Permeation tests have shown\(^8\) that during the diffusion of hydrogen, the equilibrium between diffusible and reversible trapped hydrogen is formed. Reversible and irreversible trapping has a significant influence on the diffusion of hydrogen.\(^12\) The characterization of the hydrogen diffusion due to an effective diffusion constant reasonable for materials is affected by irreversible trapping of hydrogen. The hydrogen concentration in a solid body is influenced by diffusion and trapping in reversible and irreversible traps. Further permeation experiments were carried out by various researchers.\(^13\)–\(^22\)

The aim of this paper is to investigate hydrogen diffusion in hardened 100Cr6 steel plates. Permeation tests were conducted with samples of different thicknesses to measure the diffusivity of hydrogen as an independent constant. Furthermore, the diffusivity of hydrogen was investigated in pretrained samples to study the influence of higher dislocation density on its value. A finite element (FE)-based diffusion model was applied to confirm the experimental results by computing the concentration of both diffusible and trapped hydrogen due to deformation-induced defects.

## 2 | MATERIALS AND EXPERIMENTS

Permeation tests were carried out to investigate the diffusion coefficient of hydrogen in 100Cr6 steel in accordance with DIN EN ISO 17081\(^23\) and ASTM G148-97.\(^24\) The permeation cell consisted of two electrochemical cells with anodic and cathodic sides separated by a thin metal sample (the test sample) that acts as a working electrode. The charging side, on which the sample acts as a cathode and hydrogen is formed by electrolysis, was filled with \(0.1 \text{ M } \text{H}_2\text{SO}_4\). A constant current density of 12 mA/cm\(^2\) was applied between the sample (cathode) and a platinum-coated titanium counter electrode (CE1) using a Keithley 6220 precision current source. The oxidation side of the permeation cell was filled with \(0.1 \text{ M } \text{NaOH}\). On this anodic side, an Ag/AgCl reference electrode (RE) containing 3 M KCl was used. Under identical current density to that applied in the charging cell, a constant voltage of +255 mV (relative to the RE) was maintained between the sample (anode) and the counter electrode (CE2) using an eDAQ ER466 potentiostat. A Luggin capillary was used to connect the sample to the RE. A schematic diagram of the permeation cell setup is shown in Figure 1.

The test samples were made of 100Cr6 steel sheet with thicknesses of 1.0- and 1.5 mm. The exposed surface area of the sample was 15 mm × 55 mm. This ensured a good thickness-to-area ratio, and thus one-dimensional diffusion.

The samples for the permeation test were hardened up to 60 HRC, which is in the range of typical hardness for bearing steel. The surface of the samples was polished and degreased with ethanol before testing. The laboratory had a controlled room temperature of 22°C. The permeation cell was heated up to 30°C by a cryostat during the permeation test. Before testing, the anodic potential was applied and the background current was measured. The permeation test was started after the background current reached a stable level lower than 0.2 µA. Each sample was tested twice with a period of 8 weeks between the first and the second tests. This holding period guarantees the release of trapped hydrogen in the sample, which may influence the results of subsequent measurements.

The permeation tests were also conducted on plastically pretrained samples. For the preparation of samples, tensile tests were conducted up to a predefined strain on 1.0-mm thick samples following DIN 50125H 20 × 80.\(^25\) The samples were made of 100Cr6 steel sheet and cut along and perpendicular to their rolling direction, after which they were hardened up to 60 HRC. During the tensile test, the deformation was measured using an extensometer with an initial gauge length of 80 mm and maximum travel of 2.5 mm.

## 3 | FE ANALYSIS

An FE simulation model of diffusion, developed in previous work\(^26\) was applied to study the difference between diffusible and trapped hydrogen due to deformation-induced defects. For this purpose, local
equilibrium was assumed between mobile and trapped hydrogen following Oriani’s theory; an equilibrium constant \( K_{eq} \) was defined by adopting the approach given by Svoboda and Fischer to set the rate of hydrogen atoms jumping from traps to lattice sites \( (\lambda) \) to the rate of hydrogen atoms jumping from lattice to trap sites \( (\kappa) \) so that

\[
K_{eq} = \frac{\kappa}{\lambda} = e^{-\frac{\Delta E_B}{RT}},
\]

where \( \Delta E_B \) is the negative trap binding energy, \( R \) is the ideal gas constant, and \( T \) is the absolute temperature in Kelvins. To model dislocation multiplication, the dislocation density was considered to be a function of plastic strain, as proposed by Hahn et al:

\[
\partial = \partial + \gamma(\partial^{pl})^\phi,
\]

where \( \partial^{pl} \) is the equivalent plastic strain \( \partial^{pl} = \int_0^t \frac{1}{3} \partial^{pl} dt \), with \( \partial^{pl} \) as the equivalent plastic strain rate, \( \partial_0 \) is the dislocation density for annealed material, set as \( \partial_0 = 10^4 \text{ mm}^{-2} \), and \( \gamma \) and \( \phi \) are material specific constants set in line with the range of values proposed by Yoshida et al. to \( 1.0 \times 10^8 \text{ mm}^{-2} \) and 1.0, respectively.

It has been shown by previous researchers (e.g., Turnbull et al. and Winzer et al.) that a single type of trap is usually sufficient to describe macroscopic hydrogen diffusion. In doing so, one is assigning an “average” binding energy to this particular trap type.

The diffusion problem is defined in terms of mass conservation of the diffusing phase as follows:

\[
\frac{\partial}{\partial t} \int_V (\bar{C}_L + \bar{C}_T) dV + \int_{\partial V} n \cdot \left( \frac{D_l V_H \bar{C}_L}{RT} \nabla \sigma_h \right) dS = 0,
\]

where \( \bar{C}_L \) is the molar hydrogen lattice concentration, \( \bar{C}_T \) is the molar hydrogen trap concentration, \( D_l \) is the lattice diffusivity, \( R \) is the universal gas constant, \( T \) is the absolute temperature in Kelvins, \( \nabla \sigma_h \) is the spatial hydrostatic stress gradient, \( V_H \) is the partial molar volume of hydrogen dissolved in the host material, \( \nabla \bar{C}_L \) is the spatial concentration gradient, \( V \) is any volume whose surface is \( S \), and \( n \) is the outward normal to \( S \).

An elastic–plastic material model with kinematic strain hardening was adopted for steel; its parameters were obtained by conducting tensile tests (see Section 4). An elastic modulus of \( E = 200.2 \text{ GPa} \) and a Poisson’s ratio of \( \nu = 0.3 \) defined the elastic response of the material. To account for plasticity, the initial yield strength was set to \( \sigma_0 = 1.195.1 \text{ MPa} \); linear kinematic strain hardening was modeled by defining a constant hardening modulus of \( H = 185.5 \text{ GPa} \) throughout the plastic strain regime under consideration. The gage section of the tensile sample was modeled as a sheet with dimensions of \( 80 \text{ mm} \times 20 \text{ mm} \times 1 \text{ mm} \). The tensile stress of \( \text{Ca 1,640 MPa} \) was applied and released to deform the sample to a permanent equivalent plastic strain of \( \partial^{pl} = 2.4 \times 10^{-3} \). Subsequently, hydrogen diffusion was modeled through a middle section of the sample with dimensions \( 55 \text{ mm} \times 15 \text{ mm} \times 1 \text{ mm} \), as given in Figure 2.

Due to the uncertainty regarding hydrogen influx, hypothetical boundary conditions were applied. An initial hydrogen concentration of \( 1.0 \text{ ppm} (1.41 \times 10^{-10} \text{ mol/mm}^3) \) was assumed throughout the sample. Diffusion was triggered by maintaining a constant hydrogen concentration of \( 1.41 \times 10^{-9} \text{ mol/mm}^3 \) at the charging side of the sample, whereas the concentration at the oxidation side was maintained at \( 1.41 \times 10^{-10} \text{ mol/mm}^3 \). This enabled studying the concentration distribution of both diffusible and trapped hydrogen under the effect of plastic strain. The hydrogen diffusion was computed for a period of \( 3,600 \text{ s} \). To discretize the geometry, 20-node second-order reduced integration hexahedral elements with displacement and temperature degrees of freedom (C3D20RT) were used. The diffusion parameters used to run the simulation are listed in Table 1.

| Property       | Value           | Reference(s) |
|----------------|-----------------|--------------|
| \( D_l \) (mm\(^2\)/s) | \( 1.1 \times 10^{-3} \) | [32]         |
| \( \partial_0 \) (mm\(^{-2}\)) | \( 1.0 \times 10^4 \) | [29]         |
| \( \gamma \) (mm\(^2\)/s) | \( 1.0 \times 10^8 \) | [33]         |
| \( \phi \) (-) | 1.0             |              |
| \( R \) (J/mol·K) | 8.314           |              |
| \( V_H \) (mm\(^3\)/mol) | \( 2.3 \times 10^3 \) | [34]         |
| \( T \) (K)     | 298.15          |              |
Figure 3 shows the stress–strain diagram for hardened 100Cr6 plates in tension. The tests were conducted along the rolling direction (Figure 3a) and perpendicular to the rolling direction (Figure 3b). The mean values of the measured material data are listed in Tables 2 and 3. The dashed lines in Figure 3a,b and represent the plastic strain at which pretrained samples were tested in the permeation cell.

Figure 4a shows the normalized permeation curves for a permeation test with a 1.0 and 1.5‐mm thick sample. Figure 4b shows the normalized permeation curves for a permeation test with a 1.0‐mm thick pretrained sample. The samples were manufactured along and perpendicular to the rolling direction of the sheet and strained in tension to plastic strains of 1.0 × 10⁻³ and 2.4 × 10⁻³, respectively. The measured curves in Figure 4 are compared with the analytical solution to Fick’s second law (assuming constant D_eff).

Figure 4 shows the measured diffusion constants for different thicknesses, rolling directions, pretrained, and unstrained samples. The diffusion constant was measured as independent from these variations. The averaged diffusion constant for hydrogen in hardened 100Cr6 is D_eff = [4.9 ± 1.24] × 10⁻¹² m²/s.

From the FE simulation, the normalized hydrogen lattice concentration (C_l/C_s) and total concentration (C/C_s) to the surface concentration (C_s = 1.41 × 10⁻⁹ mol/mm³) are plotted against the distance along with the thickness of the sample for different simulation times in Figure 5a. Figure 5b shows the normalized hydrogen concentration at traps (C_T/C_s) plotted against the distance along with the thickness of the sample for different simulation times; it reached saturation along with the sample thickness after approximately 300 s.

The simulation results indicate a very little influence of trapped hydrogen on the total hydrogen concentration.

## DISCUSSION

In the present study, the effective diffusion coefficient for hydrogen in hardened 100Cr6 at 30°C was measured in a permeation test. The diffusivity of hydrogen in hardened 100Cr6 was measured using samples of different thicknesses. The analysis showed the measured diffusion constant to be independent of the sample thickness. The measured diffusion constant for 100Cr6 was found to be 4.9 × 10⁻¹² m²/s. A value of 7.54 × 10⁻⁹ m²/s was reported for body-centered cubic annealed iron by Kiuchi and

### TABLE 2 Material data measured in the tensile tests

| Material parameters | Along rolling direction | 90° to rolling direction |
|---------------------|-------------------------|--------------------------|
| Tensile strength (MPa) | 1,982.2                 | 2,090.2                  |
| Elastic modulus (GPa)  | 200.2                   | 200.5                    |
| Strain to rupture     | 1.2 × 10⁻²              | 1.3 × 10⁻²               |
| Thickness (mm)        | 1.0                     | 1.0                      |

### TABLE 3 Measured diffusion constants for hydrogen in pretrained and unstrained samples

| Thickness (mm) | Permanent strain (−) | D_eff (x 10⁻¹² m²/s) Initial test | D_eff (x 10⁻¹² m²/s) Repeat test |
|----------------|----------------------|-----------------------------------|---------------------------------|
| 1.0            | –                    | 4.57                              | 3.24                            |
| 1.5            | –                    | 5.86                              | 3.85                            |
| 1.0 (0°)*      | 1.0 × 10⁻³           | 6.25                              | –                               |
| 1.0 (90°)**    | 2.4 × 10⁻³           | 5.92                              | –                               |

*Load along rolling direction.
**Load perpendicular to rolling direction.
The disparity in the value is mainly due to the different crystal structure, microstructure, chemical composition, and defect density (e.g., dislocation density) between hardened 100Cr6 and annealed iron. Moreover, the solubility of hydrogen in iron is reduced by alloying elements such as chromium, molybdenum, tungsten, and nickel. In iron, the hydrogen is trapped on grain boundaries and dislocations that are influenced by these alloying materials. The trapped hydrogen is detracted from the lattice diffusion. The solubility of hydrogen is increased by trapping and the diffusivity is decreased. The results indicated almost no change in diffusivity with plastic strains up to $2.4 \times 10^{-3}$; the numerical simulations (compare Figure 5a,b) confirmed that the concentration of trapped hydrogen in dislocations comprises only a small and negligible fraction of the total hydrogen concentration. This may be attributed to the insignificant increase in dislocation density due to the brittle nature of martensitic steel, which does not allow the accumulation of considerable plastic strains. The simulations showed a very slight increase in the normalized trapped hydrogen concentration up to 300 s, after which the value reaches saturation (Figure 5b). The measured plastic strain at rupture was below $3.0 \times 10^{-3}$ in all tested samples, which, according to Equation (2), results in a dislocation density of $3.1 \times 10^6$ mm$^{-2}$. Here, it should be noted that the applicability of this argument is restricted by the dependence of trap density on the dislocation density, which is a function of plastic strain. Nonetheless, and although plastic strains had a minor effect on the diffusion behavior in this particular case, the alteration of internal stresses as a result of plastic deformation, that is, residual stresses in the material, may have a more significant effect on the diffusion and accumulation of hydrogen (cf. Khader et al. [26]).

### 6 | CONCLUSION

The diffusion constant for hydrogen in hardened 100Cr6 steel was measured in permeation tests. The measured effective diffusion coefficient was found to be independent of the sample thickness and plastic strain. The averaged diffusion coefficient of hydrogen in 100Cr6 at 30°C was found to be $D_{eff} = 4.9 \times 10^{-12}$ m$^2$/s.

An FE analysis of the diffusion process indicated a negligible effect of dislocation multiplication on the
concentration of trapped hydrogen. This was attributed to the brittle nature of 100Cr6 and its limited accumulation of plastic strain.

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