



Modelling the influence of trapping on hydrogen permeation in metals

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ABSTRACT

Hydrogen permeation (diffusion) is strongly influenced by the local hydrogen concentration and by the density and depth of traps. Consequently hydrogen diffusion cannot be described by a constant effective diffusivity as suggested in standards and several papers.

A modelling study for diffusion of hydrogen in metals with traps is presented. Simulations are performed for a charging and discharging process, showing a remarkable asymmetry. The actual chemical diffusivity ranges over several orders of magnitude depending on the hydrogen concentration as well as the density and depth of traps. Consequently, the concept of effective diffusivity outlined in standards and many publications fails.

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1. Introduction

1.1. Technical relevance of hydrogen diffusion in corrosion science

Currently large efforts are undertaken by steel industry to fulfill needs of the markets for higher strength steels. In oil and gas production new deep reservoirs with high pressure and high temperature (HPHT) are explored having a need for such steels. Many new wells in addition contain increasing amounts of H₂S. Just recently the new high strength sour gas steel grade C110 has been introduced to NACE TM0177. Similar developments happen in automotive industry. Due to lightweight design there are big efforts to apply high strength steels in the car body. Just recently several German premium producers use windscreen pillars and other parts made of high strength steels. A third example for the increasing application of high strength steels is the development of fine-grained steel for structural use, e.g. in cranes. This trend to use higher strength steels is driven by lightweight construction demands to save energy and resources yielding more sustainable technologies. The major drawback of such steels is that an increase of strength corresponds with an increasing susceptibility to hydrogen induced damaged especially to stress corrosion cracking. In consequence when hydrogen can enter a material by corrosive or other processes it is of large interest to understand its diffusion and trapping behaviour.

1.2. State of scientific and technical research

Hydrogen embrittlement and hydrogen assisted cracking of metals are also topics of scientific and technical research, see the overviews published in the last three decades, e.g. by Oriani [1] in 1993 or by Somerday et al. [2] in 2009. Most of the reports deal with Fe-based alloys as steels. Since the permeation of hydrogen is performed by a diffusion process combined with retaining hydrogen in traps, a proper description of this process by standard diffusion equations with constant diffusion coefficient is not correct. Such a description is, however, followed in many practical applications, e.g. the ASTM standard G148-97 (2003) [3], or EN ISO 17081 [4], or only as a representative example for the large amount of papers [5], providing an extremely simple relation for determination and use of an “effective” hydrogen diffusivity D_{eff} . The reader can also find several references concerning experimental investigations of hydrogen diffusion in Section 3.1 of this paper.

A central aspect of the sound treatment of the hydrogen permeation process is the proper handling of trapping. First steps to imply the role of traps into the diffusion equations were taken by McNabb and Foster [6] in 1963, assuming a kinetic equation for capture in and release from traps. With respect to handling of the role of traps in the diffusion equations we refer to the overview by Turnbull [7]. For steels we specifically refer to a detailed investigation by Krom and Bakker [8] for trapping models. Most recently a French group [9] published a categorization of the traps with respect to the trapping energy ΔE_k , expressed in kJ/mol, of a specific sort k of traps.

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1.3. Research goals of the paper

The first goal of this paper is to introduce a diffusion equation for hydrogen, which incorporates the role of traps in the system by a concentration-dependent chemical diffusion coefficient.

The second goal of this paper is then to apply the derived diffusion equation to the simulation of hydrogen permeation through a ferritic steel plate, which may be coated by a Pd layer.

Modelling studies demonstrate in detail how to handle the current model for this practical application. The study allows also analyzing the, sometimes very pronounced, asymmetry between a charging and discharging process.

2. Theory

This section introduces shortly the derivation of the leading diffusion equation to calculate the evolution of the hydrogen concentration profile in the system with traps; for details see [10].

2.1. Problem definition and theoretical basis

2.1.1. Molar concentrations and site fractions

Hydrogen acts as an interstitial component in a crystal. Its amount in the solid can be described by its molar concentration c in mol/m³, being the sum of the molar concentration of freely diffusing hydrogen in the (defect-free) lattice denoted as c_L and the molar concentration c_T of the hydrogen situated in the immobile and localized traps

$$c = c_L + c_T. \quad (1)$$

From now on subscript “L” refers to a lattice-relevant quantity and “T” to a trap-relevant quantity; for sake of simplicity we work with only one sort of traps with the same trapping energy ΔE .

We introduce the molar volume V_L in m³/mol of one mole of interstitial positions in the lattice, and analogously the molar volume V_T in m³/mol of one mole of possible trap positions. Obviously the higher the value of V_T the lower is the amount of traps in a specimen.

One can now define as a dimension-free quantity the site fraction y_L of freely diffusing hydrogen in the lattice as

$$y_L = c_L V_L, \quad (2)$$

and the site fraction y_T , of immobilized trapped hydrogen as

$$y_T = c_T V_T. \quad (3)$$

Since the unit volume of matter (in our case 1 m³) contains $1/V_L$ moles of interstitial positions and $1/V_T$ moles of possible trap positions, the volume $V = 1/(1/V_L + 1/V_T)$ corresponds to one mole of possible hydrogen positions. Therefore, a mean site fraction y of hydrogen in the system can be related to the molar concentration c , using Eqs. (1)–(3) and V , as

$$y = cV = \frac{V_L}{V_L + V_T} y_T + \frac{V_T}{V_L + V_T} y_L. \quad (4)$$

This relation leads with $y_T = 1$ and $y_L = 1$ trivially to $y = 1$. One should keep in mind that V_T may evolve with time, e.g. according with ongoing plastification. Mostly $V_T \gg V_L$, so V obtains practically the value of V_L . Since V can be considered to be constant, then consequently V_L can also be assumed to be constant.

2.1.2. Trapping

Trapping takes place only, if it leads to the reduction of the total energy of the system. Figuratively written, several hydrogen atoms fall in the traps and are captured there. If one mole of trapped hydrogen lowers the total energy of the system by ΔE , then one

can show [10], Section 3.2, that due to local thermodynamic equilibrium the ratio between y_T and y_L follows as

$$\frac{y_T}{y_L} = \frac{1}{K_T + y_L(1 - K_T)}, \quad (5.1)$$

$$K_T = \exp\left(-\frac{\Delta E}{R_g T}\right). \quad (5.2)$$

R_g is the gas constant being 8.314 J/(mol K), T is the temperature in K. The quantity K_T , $0 \leq K_T \leq 1$, is denoted as equilibrium constant and may obtain for steel at room temperature a value of 10^{-8} , see the discussion in Section 3.2. Eq. (5.1) is known in the open literature as “Oriani equation”, although Oriani has originally published in [1] a different formulation tacitly assuming $V_L \ll V_T$, $K_T \ll 1$, $y_L \ll K_T$ (in the notation of our paper). One can immediately see from Eq. (5.2) for $\Delta E = 0$, $K_T = 1$ that the site fraction y_T is identical to that of the freely diffusing hydrogen, y_L , or in other words, the traps provide “no advantage” to the hydrogen atoms staying in them. For $\Delta E = \infty$, $K_T = 0$, the site fraction y_T becomes 1, or in other words, all traps are fully occupied provided that a sufficient amount of hydrogen exists in the system.

The minimization of the total Gibbs energy of the system yields the following chemical potentials μ_L , μ_T , expressed in kJ/mol, as

$$\mu_L = \mu_0 + R_g T \ln \frac{y_L}{1 - y_L}, \quad (6.1)$$

$$\mu_T = \mu_0 + R_g T \ln \frac{y_T}{1 - y_T} - \Delta E. \quad (6.2)$$

The quantity μ_0 includes the contribution to the chemical potential independent of y_L and y_T and is usually denoted as μ_L^0 , which may vary significantly for different metals, e.g. μ_L^0 for Fe is appr. by 33 kJ/mol higher (i.e. $14R_g T$ at 300 K) than μ_L^0 for Pd. If a hydrostatic stress state σ_H exists, then $\mu_0 = \mu_L^0 - \sigma_H \Omega_H$ with Ω_H being the partial molar volume of hydrogen (i.e. 2×10^{-6} m³/mol), so a hydrostatic pressure of 1 GPa in the metal increases μ_0 by an amount of 2 kJ/mol.

2.1.3. Diffusion equations

The mass balance and Fick’s first law, expressed in the molar concentration c , see e.g. [10], Section 4 read as

$$\frac{dc}{dt} = -\text{div}(j), \quad (7.1)$$

$$j = -\tilde{D} \text{grad}(c). \quad (7.2)$$

Combining of the equations for the mass balance, Eq. (7.1), and the diffusive flux, Eq. (7.2), yields

$$\frac{dc}{dt} = \text{div}(\tilde{D} \text{grad} c). \quad (7.3)$$

According boundary and initial conditions are discussed in Section 3.2 of this paper.

The diffusive flux j , expressed in mol/(m² s), is related to the gradient of the molar concentration c via the chemical diffusion coefficient \tilde{D} , see [10], which follows as

$$\tilde{D} = \frac{D}{2} \left(1 + \frac{cV_L(1 - K_T) - V_L/V_T + K_T}{\sqrt{(cV_L(1 - K_T) - K_T - V_L/V_T)^2 + 4cV_L K_T(1 - K_T)}} \right). \quad (8)$$

D is the tracer diffusion coefficient of hydrogen in the trap-free lattice. Note that \tilde{D}/D depends on

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