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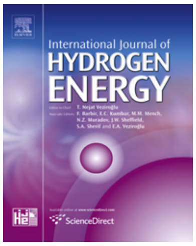

Computational analysis of geometrical factors affecting experimental data extracted from hydrogen permeation tests: II – Consequences of trapping and an oxide layer

E. Legrand [a], J. Bouhattate [a,*], X. Feaugas [a], H. Garmestani [b]

[a] Laboratoire d'Etudes des Matériaux en Milieux Agressifs, LEMMA, Bat. Marie Curie, Av. Michel Crépeau, 17042 La Rochelle, France
[b] Laboratory of Micromechanics of Material, LMM, Georgia Institute of Technology, Materials Science and Engineering, 771 Ferst Drive, N.W., Atlanta, GA 30332-0245, USA

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ABSTRACT

Although electrochemical permeation tests are used to determine the diffusion coefficients of hydrogen through metals, these measures are affected by various phenomena such as trapping or surface states. In this work, we analyzed the combined effects on diffusion of hydrogen trapping and the presence of an oxide layer at the exit side of the material. We numerically simulated the diffusion of hydrogen through a 1 mm thick martensitic steel membrane, using Finite Elements Method. Trapping densities are taken between 10^{-4} and 100 mol/m^3, for an oxide layer 5 nm thick. We studied oxide layers with hydrogen diffusion coefficients between 10^{-21} and 10^{-10} m^2/s. It appears that the diffusion is withheld by trapping and the oxide layer. However both parameters exhibit opposite effects on hydrogen subsurface concentrations; analytical equations have been proposed to correct the experimental results obtained by electrochemical permeation tests, using the material properties. It appears that the ratios between the membrane and the oxide diffusion coefficients and thicknesses guide the influence of trapping and the oxide layer.

1. Introduction

The resistance to environmental degradation, especially hydrogen embrittlement (HE) is one of the major concerns for the durability of materials and structures in severe loading conditions. These damages are caused by a hydrogen surface adsorption followed by absorption and diffusion/trapping phenomena. Consequently, the quantification of hydrogen concentrations in the material and the assessment of trap sites interactions with hydrogen atoms are necessary to understand failure mechanisms. According to exhaustive statistical analysis of a large data set, the values of hydrogen solubility and diffusivity in metals and alloys exhibit some time incoherence [1]. To gather reliable information on hydrogen diffusion, two main types of experimental techniques are generally used in metals and alloys: the electrochemical permeation technique (EP) and the thermal desorption spectroscopy (TDS). In spite of both techniques contributing in a complementary way to understand hydrogen interactions with a metallurgical state [2,3], there is few information on the errors caused by the presence of traps, the surface layer, electrochemical adsorption steps, etc., which may induce uncertainty in hydrogen ingress measurements. Recently, to reach a better understanding and a correction of experimental measures

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* Corresponding author.
E-mail address: jamaa.bouhattate@univ-lr.fr (J. Bouhattate).

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Nomenclature

J	Hydrogen flux, mol m^{-2} s^{-1}
J_{max}	Steady-state hydrogen flux, mol m^{-2} s^{-1}
$J^{\sim}{}_{max}$	Calculated steady-state hydrogen flux, mol m^{-2} s^{-1}
t_B	Breakthrough-time, s
e_m	Membrane thickness, m
e_{ox}	Oxide thickness, m
D_L	Lattice hydrogen diffusion coefficient, m^2/s
D_{ox}	Oxide hydrogen diffusion coefficient, m^2/s
D_{eff}	Effective hydrogen diffusion coefficient, m^2/s
$D^{\sim}{}_{eff}$	Calculated effective hydrogen diffusion coefficient, m^2/s
C_0	Initial hydrogen concentration, mol/m^3
C_{0eff}	Effective hydrogen concentration, mol/m^3
$C^{\sim}{}_{0eff}$	Calculated hydrogen concentration, mol/m^3
C_s	Exit side hydrogen concentration, mol/m^3
C_L	Lattice hydrogen concentration, mol/m^3
C_T	Trapped hydrogen concentration, mol/m^3
$<C_L>$	Average lattice hydrogen concentration, mol/m^3
$<C_T>$	Average trapped hydrogen concentration, mol/m^3
$<C>$	Average total hydrogen concentration ($<C> = <C_T> + <C_L>$), mol/m^3
N_L	Lattice hydrogen concentration, mol/m^3
N_T	Trap sites density, mol/m^3
ΔE_T	Trap binding energy, eV
K_T	Trap equilibrium constant
T	Temperature, K
μ	Trapping effect parameter
η	Trapping effect parameter affected by C_0
β	Oxide effect parameter

associated with the permeation technique, we started investigations on the effects of hydrogen trapping and surface layer on the diffusion through a metallic membrane by simulating the system with a FEM model. The first part of these investigations has been focused on the scale transition between diffusion and trapping phenomenon at microscopic scale and the average data extracted at macroscopic scale [4]. This approach, conducted without any surface layer or surface limited kinetics shows that no scale effect occurs and that the effective subsurface concentration, currently evaluated by Fick's laws, sometimes does not correspond directly to the hydrogen concentration in the membrane (non-proportional relationship). Now, the second step of our analysis (the aim of the present paper) is focused on the consequences of a layer on the exit side of a membrane on the permeation data extracted from EP experiments.

In accordance with an extensive data set extracted from that kind of experimental tests [5–8], the hydrogen transport inside a metallic membrane is affected by its thickness. EP experiments provide the steady-state flux, J_{max} and the time t_B (breakthrough-time) required for the first hydrogen atoms to cross through the membrane. The effective values of, respectively, the diffusion coefficient and the subsurface concentration are generally evaluated using the classical resolution of the Fick's equations with:

$$D_{eff} = \frac{e^2}{M \times t_B} \tag{1}$$

and

$$J_{max} = \left[C_0 D_{eff}\right] \frac{1}{e} \tag{2}$$

To suppress all effects of surface kinetics on the entry side, thicknesses over 1 mm are required. Even though Eqs. (1) and (2) are verified with these thicknesses, an oxide layer on the exit side decreases D_{eff} and C_{0eff}. This does not occur with quasi "neutral surfaces" such as palladium coatings [7,9–11]. We can analyze the literature data on the membrane thickness, by separating the cases of palladium-coated and oxidized membranes. α-iron was chosen as reference material, because of its small density of strong hydrogen traps. On the opposite, martensitic steels possess numerous interfaces and precipitates that can trap hydrogen. In case of Pd-coated membranes, the steady state flux J_{max} is inversely proportional to the membrane thickness, in agreement with Fick's laws solution at a steady-state (Eq. (1)). For α-iron, the hydrogen concentration C_{0eff} can be calculated knowing D_{eff}. Even though D_{eff} fluctuates with the thickness [10,11], Eq. (2) is confirmed by experimental results. Still, an oxide layer considerably alters these results [5,6,12]. Thus, getting correct hydrogen concentrations $C_{0eff} \approx C_0$ requires several analyses of diffusion coefficients D_{eff}. The sole data on the effects of the membrane thickness for martensitic steels are given with an oxidized exit side [7]. High trapping means an increase in C_{0eff}. Moreover, the oxide has almost no effect when the hydrogen diffusion coefficient is similar to that in the membrane. Thus, the effects of an oxide layer cannot be considered without taking into account the trapping process.

This work bestows a numerical analysis by finite element method of the diffusion of hydrogen by simulating EP tests. We studied the effects of trapping alone in our previous work [4]. In order to increase our knowledge of the effects of an oxide layer on diffusion, we now study the effects of trapping combined with an oxide layer. This should enable us to correct the errors committed on the data extracted from EP tests. Literature data on oxide layers are first recalled, and the numerical model is described. Results and discussions are then detailed.

2. Oxide and protective layer

The diffusion model used in this work [13–15] has already been described in our previous paper [4]. We propose to take into account the oxide layer in order to get a better understanding of its effects on the diffusion of hydrogen. We consider that the oxide layer is homogeneous with a constant thickness and a low hydrogen diffusion coefficient. Moreover, no hydrogen is trapped inside the oxide layer.

The oxide layer is usually about 3–5 nm-thick in steels [16]. Its hydrogen diffusion coefficient is included between 10^{14} m^2/s (wustite) [16] and 10^{-21} m^2/s (hematite) [17].