



Determination of trapping parameters and the chemical diffusion coefficient from hydrogen permeation experiments



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ABSTRACT

An improved diffusion theory accounting for trapping effects is applied to evaluation of hydrogen permeation experiments performed for pure iron and pearlitic and martensitic steels. The trapping parameters as molar volume and depth of traps are determined by fitting experiments by simulations based on the theory. The concentration-dependent chemical diffusion coefficient of hydrogen is extracted indicating that the trapping effect on diffusion in pure iron and pearlitic steel is negligible. However, it is significant for martensitic steel, for which the chemical diffusion coefficient cannot be considered as concentration-independent as it is established in current standards.

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1. Introduction

It is a first matter of fact that hydrogen permeation (diffusion) in metals, e.g. Fe-based alloys, is strongly influenced by the activity of traps, described by their densities and depths. Traps can be, e.g. substitutional solute atoms, dislocation cores, grain boundaries and interfaces of incoherent particles, listed in the sense of increasing trap depth, which is expressed in terms of the trapping energy ΔE_k with the label “ k ” denoting the sort of trap. The reader is referred with respect to data for ΔE_k to the instructive paper (specifically for martensitic steels) by Thomas et al. [1], the recent papers by Frappart et al., e.g. [2], the data reported by Verbeken [3] and to Mine and Horita [4]. The trap density is characterized by the volume V_{Tk} of a sort k of trap corresponding to one mole of possible trap positions.

A second matter of fact is that permeation experiments, as they have been performed since several decades (according references and related discussions can be found at the end of Section 2), can deliver measured hydrogen fluxes on the output (out-flux) side of a test specimen in the form of a plate, but cannot provide a direct information on the traps and their activity in the material. Since in technical applications the chemical, electrical and mechanical environment conditions as well as materials can differ significantly, the treatment of the role of traps must be performed

with high caution, and a utilization of data as an effective diffusion coefficient D_{eff} stemming from a standard evaluation of permeation tests (ASTM, EN ISO, for details see later) may be misleading.

A third matter of fact is that the actual flux of hydrogen \mathbf{j} is proportional to the negative gradient of the hydrogen concentration c via a chemical diffusion coefficient \tilde{D} , which depends strongly on the concentration c , the trap parameters as V_{Tk} and ΔE_k (the subscript $k = 1$ for only one sort of trap is skipped from now on) and the temperature T , for details see [5–7]. The ratio of \tilde{D}/D_{Fe} , with D_{Fe} being the diffusion coefficient of hydrogen in a trap-free iron lattice, can vary over several orders of magnitude. This fact is illustrated by the well established collection of diffusion coefficients in the Fe–H system, see e.g. Landolt–Börnstein, [8], Section 9 there, and Fig. 11 of [5]. An explanation of the obviously enormous scatter of diffusion coefficients is given by Svoboda and Fischer, [5], Section 5 there, clearly addressing the role of traps to this scatter. A consequence of this fact is that any procedure used to measure D_{eff} , which is based on the assumption of a constant diffusion coefficient, does not reflect the real situation. One must keep in mind that an analytical framework to solve the diffusion equation, e.g. for the calculation of effective diffusion coefficient D_{eff} , enforces a diffusion coefficient constant in space and time. It should also be mentioned that some groups denote the chemical diffusion coefficient as effective diffusion coefficient, see e.g. Novak et al. [9].

One major goal of new steel concepts is to increase strength. Therefore importance of future research in the field of hydrogen and its effect in steels will further increase. In recent few years

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many works and efforts have been made in corrosion research to bring more understanding about hydrogen in steels. Nanninga et al. [10] have investigated the effect of microstructure, composition and hardness on hydrogen embrittlement of carbon steel, concluding that hardness is more important than microstructure or chemical composition. In many applications H_2S will play an important role due to sour wells in oil and gas production. Zhou et al. [11] showed recently that the iron sulfide layer at high partial pressures of H_2S changes charging conditions completely resulting first in an increasing of permeation current followed by a decrease when the layer is building up more dense. Xue and Cheng [12] evaluated the trap density of their X80 pipeline steel by means of permeation experiments. Sojka et al. [13] and Perez Escobar et al. [14] investigated new high strength multiphase steels and their behavior during hydrogen uptake.

Many papers [15–18] deal with the effect of traps on hydrogen embrittlement of steels. Qi et al. [15] made a distinction between hydrogen dissolved in the lattice and hydrogen being trapped. Jebaraj et al. [16] investigated the effect of dislocations and precipitates in Inconel 718 on hydrogen diffusion coefficient. Lamoutsi et al. [17] showed different modes of trapping in differently heat treated conditions for Aluminium alloy 2024 and under strain. Wang et al. [18] found out that the threshold stress intensity factor for hydrogen embrittlement of a high strength steel increases, when the diffusion coefficient determined by permeation increases as well. In contradiction they found no clear dependency of crack growth rate as function of hydrogen diffusion coefficient.

The goals of this paper are now

1. to present recent results of permeation experiments,
2. to present their interpretation by conventional evaluation concepts according to standards [19,20],
3. to present their interpretation by an evaluation concept following the chemical diffusion coefficient \tilde{D} , taking into account the role of one sort of trap,
4. to extract from experiments the data for the trap density V_T and trap depth ΔE for different steel grades,
5. to show comparisons between experiments and their simulations using the concentration independent effective diffusion coefficient D_{eff} and the concentration-dependent chemical diffusion coefficient \tilde{D} .

2. Theoretical concept for diffusion

2.1. Derivation of the chemical diffusion coefficient \tilde{D}

The theoretical concept is outlined in detail in [5–7]. Therefore, we repeat only some definitions necessary for the interpretation of the results.

We assume only one sort of traps and, thus, the subscript k can be omitted. Then one can denote by c , $[c] = \text{mol m}^{-3}$, the total molar concentration of hydrogen, by c_L the molar concentration of freely diffusing hydrogen as interstitial component in a defect (trap)-free lattice, and by c_T the molar concentration of hydrogen situated in the (immobile) traps. The concentrations are additive as

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

We introduce the volume V_L , $[V_L] = \text{m}^3 \text{mol}^{-1}$, corresponding to one mole of interstitial positions in the lattice (lattice positions, where hydrogen can freely diffuse), and as already explained the volume V_T , $[V_T] = \text{m}^3 \text{mol}^{-1}$, corresponding to one mole of possible trap positions (where hydrogen gets immobile). Obviously the higher the value of V_T the lower is the density of traps in a specimen. Since the unit volume of material (in our case 1 m^3) contains $1/V_L$ moles of interstitial lattice positions and $1/V_T$ moles of possible trap

positions, the volume $V = 1/(1/V_L + 1/V_T)$ contains one mole of possible hydrogen positions.

Some comments concerning the relation between c_L and c_T may be useful. Obviously the first attempt to describe the trapping process goes back to McNabb and Foster [21] in 1963, who postulated a kinetic equation for c_T . This concept was used also for the interpretation of experimental results, e.g. in [22] and recently [23]. Koiwa [24] presented in 1974 a concept based on stochastic processes (trapping process, escape process). Already some years earlier Oriani offered a relation between c_T and c_L based on local thermodynamic equilibrium between the hydrogen atoms in the traps and the interstitial lattice positions. This relation was discussed by Kim et al. [25] in 1981 and derived within the classical thermodynamic framework by Svoboda and Fischer for several sorts of trap, see [5,6]. It can be shown that Koiwa's proposal [24] can be considered as a special solution of the equilibrium concept for dilute traps. Finally, the concept offered by Oriani and generalized by Svoboda and Fischer has proven to be successful in several experimental and numerical studies. Based on this local equilibrium concept we repeat from [5,6]

$$c_T/c = \frac{V_L c_L}{V_T c} \cdot \frac{1}{K + V_L c_L (1 - K)}. \quad (2)$$

Note that $c_L = c - c_T$; the quantity K is the so-called equilibrium constant $K = \exp(-\Delta E/R_g T)$, R_g is the gas constant, T the temperature. For $c \rightarrow 0$ the ratio c_T/c approaches $V_L/(V_L + V_T K)$; for $c \rightarrow 1/V$ the value $c_T/c = V_L/(V_L + V_T)$ is obtained. Since K depends in a nonlinear way on the temperature T , the temperature dependence of the process occurs in a nonlinear way. Furthermore, one can recognize from Eq. (1) that the pairs (c_T, c) , (c_L, c) , (c_T, c_L) are linked together in a nonlinear way. After some algebra one finds the following relation between c_L and c as

$$c_L = \frac{cV_L(1-K) - (V_T K + V_L)}{2(1-K)V_L} + \frac{\left\{ [cV_L V_T (1-K) - (V_T K + V_L)]^2 + 4cV_L V_T^2 (1-K)K \right\}^{1/2}}{2V_T(1-K)V_L}. \quad (3)$$

The diffusion equations, expressed in the molar concentration c , are derived in [5], Section 4 there, and read as

$$\mathbf{j} = -\tilde{D} \text{grad}(c), \quad \frac{dc}{dt} = -\text{div}(\mathbf{j}). \quad (4)$$

The operators “grad” and “div” are the gradient and divergence operator, resp., in the actual configuration. The diffusive flux \mathbf{j} , $[\mathbf{j}] = \text{mol m}^{-2} \text{s}^{-1}$, is related to the gradient of c via the chemical diffusion coefficient \tilde{D} , which follows as

$$\tilde{D} = \frac{D}{2} \left(1 + \frac{cV_L(1-K) - V_L/V_T + K}{\sqrt{(cV_L(1-K) - K - V_L/V_T)^2 + 4cV_L K(1-K)}} \right), \quad (5)$$

where D is the tracer diffusion coefficient of hydrogen in the trap-free lattice.

One can easily see that \tilde{D} is a function of the concentration c and of the parameters V_L , V_T and K , which depends on the temperature.

For $c \rightarrow 0$ the ratio \tilde{D}/D approaches the value $(V_T/V_L)K$, for $c \rightarrow 1/V$ the value 1. Of course, for no traps, i.e. $V_T \rightarrow \infty$, Eq. (5) yields $\tilde{D} = D$.

Finally, it should be mentioned that first formulations of \tilde{D} as functions of c_L and c_T go back to Koiwa [24] in 1974 and Johnson et al. in 1979 [26]. Further according references can be found in [5].

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