



Hydrogen transport in metals: Integration of permeation, thermal desorption and degassing



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ABSTRACT

A modelling suite for hydrogen transport during electrochemical permeation, degassing and thermal desorption spectroscopy is presented. The approach is based on Fick's diffusion laws, where the initial concentration and diffusion coefficients depend on microstructure and charging conditions. The evolution equations are shown to reduce to classical models for hydrogen diffusion and thermal desorption spectroscopy. The number density of trapping sites is found to be proportional to the mean spacing of each microstructural feature, including dislocations, grain boundaries and various precipitates. The model is validated with several steel grades and polycrystalline nickel for a wide range of processing conditions and microstructures. A systematic study of the factors affecting hydrogen mobility in martensitic steels showed that dislocations control the effective diffusion coefficient of hydrogen. However, they also release hydrogen into the lattice more rapidly than other kind of traps. It is suggested that these effects contribute to the increased susceptibility to hydrogen embrittlement in martensitic and other high-strength steels. These results show that the methodology can be employed as a tool for alloy and process design, and that dislocation kinematics play a crucial role in such design.

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1. Introduction

Prescribing hydrogen transport is critical to understand hydrogen embrittlement in metals, including ingress, storage and release [1]. These mechanisms depend on the ability for hydrogen to enter and diffuse within the bulk as various lattice imperfections act as trapping sites [2]. The surface represents an initial energy well for hydrogen to ingress and initialise diffusion in the metal [3], whilst the hydrogen located in the traps must overcome a binding energy larger than that for lattice diffusion before it can be released [1]. A number of experimental methods have been employed to study hydrogen diffusion in metals with distinct microstructures. For instance, electrochemical permeation testing (EP) has been used to determine the rate of adsorption of electrolytic hydrogen and its subsequent diffusivity [4,5]. Similarly, thermal desorption spectroscopy (TDS) has been widely employed to estimate the trap binding energy by indirectly measuring the rate of hydrogen release during continuous heating [1]. Although these techniques provide good insights into hydrogen transport

for a given material, they are highly sensitive to charging/heating conditions, the geometry of the specimen and initial microstructure [6–9]. Hence, modelling methods are needed to quantitatively interpret hydrogen–microstructure interactions in complex systems, such as the case of high-strength steels.

Oriani [2] has proposed a thermodynamic model based on local equilibrium between the hydrogen situated in the lattice and in the traps. This assumption allows obtaining a direct relationship between the equilibrium hydrogen concentration in the lattice (c_L) and in the traps (c_t), as well as estimating the effective diffusion coefficient including trapping effects:

$$c_t = c_L \frac{N_t}{N_l} \exp\left(\frac{E_b}{R_{gas}T}\right)$$

$$D = \frac{D_0 \exp\left(-\frac{Q}{R_{gas}T}\right)}{1 + \frac{N_t}{N_l} \exp\left(\frac{E_b}{R_{gas}T}\right)}, \quad (1)$$

where N_l and N_t are the total lattice and trapping sites in the material, respectively, E_b is the trap binding energy with hydrogen, Q is the activation energy for hydrogen lattice diffusion, D_0 is the lat-

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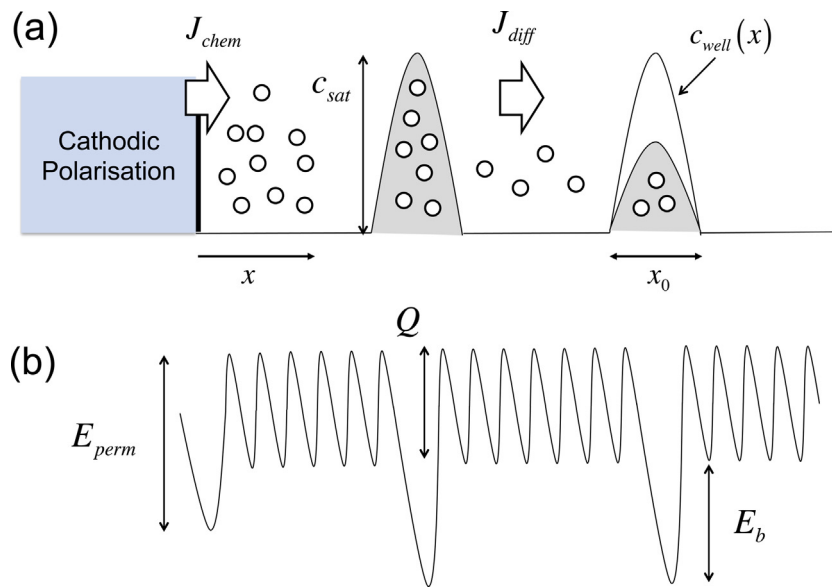


Fig. 1. Schematic representation of the (a) energy and (b) concentration landscape for hydrogen transport in the traps.

tice diffusion coefficient prefactor, R_{gas} is the gas constant and T is the absolute temperature. These equations do not account for kinetic effects and hydrogen interactions with the traps. Similarly, Fischer et al. [10] have also used the local equilibrium assumption to describe interstitial diffusion in metals with multiple trapping species.

A number of models for mass transport and desorption have been proposed to understand hydrogen diffusion under the presence of single or multiple trap species [3,11–16]. For instance, Choo and Young Lee [1] applied the Kissinger equation [11] to describe the rate of hydrogen release during thermal desorption spectroscopy; although this relationship has been widely applied to estimate E_b via identifying the peak temperature T_c (maximum desorption rate) [17–19], it has been shown that the sample dimensions and density of traps affect T_c [9,16]. Another important approach for hydrogen transport was introduced by McNabb and Foster [12]. They proposed two coupled diffusion equations for lattice (c_L) and trapped (c_t) hydrogen, where the rates of capture and escape depend on E_b . This model has been applied to study permeation and desorption tests [20,21], however it requires a number of parameters to be identified.

Due to the need to incorporate various fitting parameters, these models fall short in identifying optimal microstructures for hydrogen resistance, especially when various metallic systems are considered. Another implication of these limitations is the scatter in trapping parameter values reported by different authors [22–24]. This issue is critical in materials susceptible to hydrogen embrittlement due to the presence of multiple trap species altering the overall mobility of hydrogen. Moreover, it has been observed experimentally that the apparent diffusivity during electrochemical permeation not only depends on the microstructure but also on the charging conditions [8,22]. This shows that, in spite of the previous results, there is no unified description for hydrogen transport able to describe hydrogen permeation, desorption and release, including the relevant processing parameters, sample geometries and microstructural features. The wide application of Oriani's equations to estimate hydrogen diffusivity in various materials suggests that, to some extent, local-equilibrium may hold for the time and length scales of EP and TDS, and for low H content. This also implies that Fickian diffusion models could be sufficient to describe hydrogen diffusion.

The objective of this work is to introduce a unified description for hydrogen transport combining electrochemical permeation, thermal desorption and degassing. This is to define a methodology for process design and to identify optimal microstructures reducing hydrogen diffusivity. The formulation is based on postulating Fickian diffusion equations including the relevant microstructural features, testing conditions and (three-dimensional) geometries affecting the overall diffusion behaviour. An expression for the apparent diffusion coefficient during permeation D_{perm} including the effects of charging conditions and microstructural features is obtained. Additionally, using the local equilibrium assumption to compute the diffusion coefficient, it is possible to estimate the egress of hydrogen when various microstructural features act as trapping sites. This allows to consolidate the descriptions of diffusion during ingress, storage and release adopting the same set of parameters for various alloy grades and similar microstructures. This is demonstrated by applying the models to several steel grades, including ferritic, martensitic, bainitic, pearlitic and austenitic, as well as in polycrystalline nickel. A parametric analysis on hydrogen transport in martensitic steels, a system with multiple kinds of traps, is performed to understand the role of different microstructural features in trapping events.

2. Modelling transport kinetics during electrochemical charging

Electrochemical charging allows to measure the hydrogen permeation rate and the apparent diffusion within a metal. There are two regimes during permeation [4,25,26]: (I) a transient region induced by electrochemical reactions at the sample's surface; and (II) a steady state, where the variation in the concentration and current density is constant. Additionally, electrochemical charging is widely employed for thermal desorption spectroscopy studies to increase the hydrogen content in the material to understand trapping behaviour. Hence, it is also important to study hydrogen ingress not only to understand diffusion but also to provide the initial spatial concentration distribution of hydrogen for TDS.

The H permeation rate depends on several factors including oxide layer formation, cathodic current density, sample dimensions and internal microstructure [4,5,26,27]. Permeation can be described by standard diffusion equations if it is assumed that

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