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Perspectives on hydrogen uptake, diffusion and trapping

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ABSTRACT

Contentious issues in relation to hydrogen uptake and diffusion in metals (primarily steels) are discussed in relation to recent modelling predictions and current understanding. Topics highlighted include optimising charging conditions in hydrogen permeation measurements, limits to hydrogen uptake with increase in charging current density, irreversible traps and beneficial traps, the effective diffusion coefficient, the primary source of hydrogen in relation to hydrogen assisted cracking, and outstanding challenges in modelling hydrogen diffusion.

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Introduction

Hydrogen atoms in metals can be generated from a range of sources; from dissociation of gaseous molecules of H_2 , from electrochemical processes such as general and localised corrosion, cathodic protection, galvanic coupling, electroplating, electric discharge machining, and during materials processing and welding, through dissociation of water vapour. An important distinction arises when the introduction of hydrogen is essentially a one-off process (electroplating, electric discharge machining, materials processing and welding) as in those cases the concept of beneficial traps may be of most relevance, as discussed later. The nature of the surface plays an important role in many of these examples in

determining the effective solubility of hydrogen in a metal. The presence of an oxide most commonly reduces the solubility as the hydrogen entry involves a two stage process: equilibrium between adsorbed hydrogen on the oxide surface with dissolved hydrogen atoms in the oxide, and equilibrium between dissolved hydrogen atoms in the oxide and that in the metal substrate, the latter being the primary factor reducing the solubility in the metal [1]. This is one reason why dynamic straining is often a key variable in determining hydrogen susceptibility because rupture of the oxide film enhances local hydrogen uptake. In the case of pure hydrogen gas, the oxide does not re-heal. With dynamic loading the area of oxide-free surface available for hydrogen uptake increases with exposure time.¹ In aqueous media, there is a distinction, insofar as oxide refilming will occur for corrosion resistant

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¹ This is relevant to fracture mechanics testing when fatigue precracking is undertaken in air as an air-formed oxide will be retained on the precrack walls with the area of oxide-free surface then increasing as the crack grows. However, precracking in hydrogen gas, with no oxide then present initially on the crack walls to limit hydrogen uptake, may be more practically realistic and could potentially give rise to increased crack-tip hydrogen in the earliest stage of crack growth.

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alloys and enhanced hydrogen uptake will continue to be dependent on local plastic straining.

The kinetics of generation of hydrogen will also be significantly different for gaseous and aqueous media. For hydrogen gas, crack chemistry is important but only in the restricted context of impurities in the gas stream, particularly oxygen, which competes with hydrogen for adsorption sites. This competition can result in reduced kinetics of hydrogen entry and thence crack growth, depending on the concentration of impurity and the rate of transport to the crack [2]. The latter manifests itself in a frequency dependence of fatigue crack growth rates that is impurity concentration dependent. In aqueous solutions, the kinetics of hydrogen generation will be dependent on local crack tip solution chemistry, local electrode potential, and dynamic strain rate but with the further complication that hydrogen may be generated also on the surface external to the crack (bulk charging). The distinctive nature of the factors determining the kinetics of hydrogen generation in the gaseous and aqueous media should caution against simplistic comparisons of crack growth rates and their dependence on test variables for the two environments.

In this paper the primary focus is on aqueous systems but the broader discussion on modelling hydrogen diffusion and the concept of irreversible traps and beneficial traps will be of generic relevance. The aim is not to undertake a formal review, since such a review has been published comparatively recently [3], but to present new modelling predictions, highlight contentious issues and draw attention to the potential limitations of approximate treatments of hydrogen diffusion modelling that are often overlooked.

Modelling hydrogen uptake and diffusion

Hydrogen atom diffusion through a metal is governed by the rate at which the atoms hop or quantum tunnel between interstitial lattice sites [4] and the extent to which they become transiently trapped at microstructural trap sites such as dislocations, grain boundaries, vacancies and interfaces [5]. The impact of trapping will depend on the density and distribution of trap sites and the depth of the associated potential well. Traps are often classified as shallow or deep according to the magnitude of their binding energies but with varied views as to what constitutes a shallow trap and a deep trap in relation to specific microstructural features [6–10]. In practice, there can be a spectrum of trap sites in a metal each of which will have a characteristic binding energy, as illustrated by thermal desorption spectroscopy [11]. Often one or two traps will tend to dominate at a particular temperature.

Transport by diffusion with two types of trap site is described by equations (1)–(3), which are adapted from the early work of McNabb and Foster [12] and Leblond and Dubois [13,14]. The first equation accounts for diffusion driven by the concentration gradient of hydrogen atoms, migration due to a lowering of the chemical potential induced by hydrostatic stress, and the net rate at which hydrogen in the interstitial lattice sites is captured by trap sites of Types 1 and 2. The second and third equations describe the rate of change of the trapped hydrogen concentration.

$$\frac{\partial C_L}{\partial t} = \omega D_L \nabla^2 C_L + \nabla \left(-\frac{\omega D_L C_L}{RT} \cdot V_H \nabla \sigma_H \right) - \frac{\partial C_1}{\partial t} - \frac{\partial C_2}{\partial t} \quad (1)$$

$$\frac{\partial C_1}{\partial t} = N_1 [k_1 C_L (1 - \theta_1) - p_1 \theta_1] \quad (2)$$

$$\frac{\partial C_2}{\partial t} = N_2 [k_2 C_L (1 - \theta_2) - p_2 \theta_2] \quad (3)$$

C_L is the concentration of hydrogen atoms in interstitial lattice sites, C_1 and C_2 are the concentration of hydrogen atoms in traps of Types 1 and 2 respectively, ω is the tortuosity factor (important in two-phase system where diffusivity in the embedded phase is relatively very low and hydrogen atoms preferentially diffuse around that phase), V_H is the partial molar volume of the hydrogen atom, σ_H is the hydrostatic stress, R is the gas constant, T is the temperature, θ is the trap occupancy, and k and p are rate constants given by

$$k = k^0 \exp[-(V_0)/RT] \quad (4)$$

and

$$p = p^0 \exp[-(V_0 - \Delta E)/RT] \quad (5)$$

ΔE is the binding energy (sign is negative), V_0 is the activation energy for a hydrogen atom jumping from an interstitial site into a trap site (often assumed to be the same as that for lattice diffusion) and $(V_0 - \Delta E)$ is the activation energy barrier for jumping out of the trap site (height of the potential well). The pre-exponential factor k^0 will have dimensions of $\text{cm}^{-3} \text{s}^{-1}$ per site while p^0 will have dimensions of s^{-1} and is sometimes referred to as the frequency factor. Gradients in temperature and material properties can be present in some engineering applications and the basic equations should be adapted to include those features as appropriate.

The physical nature of the reactions at the metal-solution interface in aqueous solution is illustrated schematically in Fig. 1.

The predominant cathodic reduction reactions involve reduction of both protons and water with the relative magnitude dependent on the local pH in the solution at the metal-solution interface. The evolution of hydrogen also comprises two processes, chemical recombination (Tafel reaction) of adsorbed hydrogen atoms and electrochemical

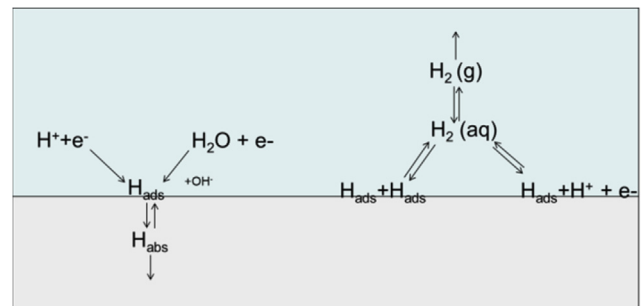


Fig. 1 – Schematic illustration of reaction processes at charging surface.

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