Theory for hydrogen desorption in ferritic steel

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ABSTRACT

After a concise review of the analytical models available for the interpretation of thermal desorption rates for hydrogen effusion from steel, a numerical method that incorporates the essence of local equilibrium and detrapping kinetics has been implemented to account for the real complexity of practical experiments. For example, the model permits the treatment of multiple kinds of traps, uses very few fitting parameters, and has been tested against new experimental data and to assess the influence of a variety of variables such as trap density, on the nature of the desorption process. There remain, however, significant discrepancies when attempts are made to rationalise diverse observations reported in the literature. In particular, comparisons made between the trapping of hydrogen in pure iron and interstitial-free steel indicate a much stronger binding energy for hydrogen in the former case.

1. Introduction

Hydrogen is a pernicious solute in iron in the sense that it leads to dramatic changes in the ability of the metal to absorb energy during fracture, at concentrations which are so small that it is difficult to avoid the ingress of nascent hydrogen during, for example, corrosion reactions. Studies of hydrogen embrittlement tend to be of two kinds, the first to characterise the potency of embrittlement, and the second relatively recent approach, to render it innocuous should it enter the steel [1–4].

It is established that the passage of hydrogen through a steel is hindered by lattice imperfections which tend to attract and bind it, thus rendering it immobile at temperatures where it should normally be able to diffuse readily [5]. This phenomenon, known as *trapping*, can be investigated using thermal desorption spectroscopy (TDS) which monitors the rate at which hydrogen is released from a sample during continuous heating. Strong traps release their hydrogen at higher temperatures and data such as these can be used to probe the parameters defining the interaction of hydrogen with defects. The technique is nevertheless indirect so the interpretation of the curve of desorption rate versus temperature and heating rate requires interpretation, and as will be seen later, there are difficulties with current methods. The methods and their limitations are reviewed first, and aspects of the available theory are then incorporated into a new numerical model which permits more complex problems to be resolved, for example the role of multiple trapping centres. The method is then validated using new experimental data and an assessment of published data from the literature.

2. Models

2.1. Reaction kinetics model

Kissinger proposed a generic model for differential thermal analysis covering reactions of any order $m = 1, 2, \ldots$, where m describes the relationship between the measured rate dx/dt and unreacted material $(1 - x)^m$ [6]. In this respect the model is akin to chemical reaction rate theory [7]. In its first order form, the theory has been applied to hydrogen desorption by Choo and Lee [8] in order to calculate a detrapping activation energy E_a:

$$\frac{dx}{dt} = A(1 - x) \exp\left\{\frac{-E_a}{RT}\right\} \quad \text{with} \quad x = \frac{H_0 - H_t}{H_0} \qquad (1)$$

where H_0 and H_t are the original and instantaneous hydrogen concentrations in the sample, so that x is the fraction of hydrogen released, A is a proportionality constant, R is the gas constant, T is the absolute temperature, and t the time. For a constant heating rate, ϕ, the maximum desorption rate is obtained by setting the derivative of Eq. (1) to zero, thus yielding the relationship:

$$\frac{\partial \ln\{\phi/T_p^2\}}{\partial\{1/T_p\}} = \frac{-E_a}{R} \qquad (2)$$

where T_p is the temperature corresponding to the maximum hydrogen desorption rate. It follows that the activation energy can be deduced by plotting $\ln\{\phi/T_p^2\}$ against $1/T_p$ for a variety of heating rates. Much research has been carried out using this method

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[9–12]. However, the model is based on chemical reaction kinetics and deals with homogeneous reactions, whereas the experiments involve the diffusion of hydrogen toward the sample surface. It does not contain information about the size or shape of the sample, and does not apply when the rate limiting step is diffusion rather than detrapping, as can be the case for example for hydrogen effusion from austenite.

2.2. Diffusion and trapping

A model which accounts for the capture and release of hydrogen from traps, and diffusion through the lattice, was proposed by McNabb and Foster [13]. Their analytical equations can be adapted to finite difference schemes so that the real complexity associated with experiments can be properly dealt with, for example, an arbitrary initial distribution of hydrogen [14]. If θ_t is defined as the occupancy of trap sites by hydrogen atoms,

$$\frac{d\theta_t}{dt} = kC_l(1 - \theta_t) - p\theta_t \qquad \text{where} \qquad \theta_t = \frac{C_t}{N_t} \qquad (3)$$

where N_t is the density of traps, C_l and C_t are the hydrogen concentrations in lattice and trap sites respectively, and k and p represent the rates of trapping and escaping, respectively:

$$k = k_0 \exp\left\{\frac{-Q_D}{RT}\right\} \qquad \text{and} \qquad p = p_0 \exp\left\{\frac{-(Q_D + E_b)}{RT}\right\} \qquad (4)$$

where k_0 and p_0 are constants, Q_D is the activation energy for diffusion, and E_b is the trap binding energy. The model has been used to analyse permeation test results [15], and TDS data [16–19]. Note, however, that there are a number of fitting parameters, k_0, p_0, E_b, N_t and this may be the reason why direct comparisons of calculations against experimental data have not been reported, but the model has been used to study qualitative trends [16–19].

2.3. Local equilibrium

Oriani's model assumes that local equilibrium exists between the concentrations of hydrogen in the lattice and at traps, both for a static and dynamic population of hydrogen (i.e., during diffusion) and assuming no interactions between the occupied sites, [20]:

$$\frac{\theta_t(1 - \theta_l)}{\theta_l(1 - \theta_t)} = \exp\left\{\frac{E_b}{RT}\right\}. \qquad (5)$$

If both $\theta_t \ll 1$ and $\theta_l \ll 1$ then this equation simplifies to

$$C_t \approx \frac{N_t}{N_l} C_l \exp\left\{\frac{E_b}{RT}\right\}. \qquad (6)$$

Since $N_t \ll N_l$, the cross-section available for diffusion is not significantly diminished by traps so the diffusion flux can be written in terms of just the lattice sites as

$$J = -D_l \frac{dC_l}{dz} \qquad (7)$$

where D_l is the diffusivity of hydrogen in the undisturbed lattice. However, hydrogen at traps also contributes to the concentration gradient so an apparent diffusivity D_a can be defined such that

$$J = -D_a \frac{d(C_l + C_t)}{dz} \qquad (8)$$

On comparing the diffusion coefficients in Eqs. (7) and (8), and substituting the relationship between C_l and C_t from Eq. (6), it can be shown [20] that

$$D_a = D_l \frac{dC_l}{d(C_l + C_t)} = D_l \frac{C_l}{C_l + C_t(1 - \theta_t)} \approx \frac{D_l}{1 + \frac{N_t}{N_l} \exp\left\{\frac{E_b}{RT}\right\}} \qquad (9)$$

with the approximation justified as long as $\theta_t \ll 1$. Note that the $(1 - \theta_t)$ term arises because there is no gradient in the concentration of traps if all traps are occupied.

Oriani's model has been applied extensively to extract the apparent diffusivity, trap density and binding energy from permeation experiments [15,21–24, for example]. It is, however, limited by the apparent diffusivity approach to dealing with the characteristics of just one kind of trap. The simplifying assumption $\theta_t \ll 1$ used to derive Eq. (9) is unlikely to be justified when dealing with TDS data on samples which are charged with significant concentrations of hydrogen. This is illustrated in Fig. 1 for a variety of binding energies; naturally, the approximation is particularly weak for high binding energies or large hydrogen concentrations. This might explain the poor agreement between experiment and theory reported by Yamaguchi and Nagumo when they applied the apparent diffusivity into a diffusion model to explain TDS results [25]; a further difficulty is that the apparent diffusivity, designed for isothermal conditions is applied to experiments involving continuous heating.

3. Numerical analysis of hydrogen desorption

To cope with the limitations of the methods described above, a numerical finite difference method was programmed as described in Fig. 2. It is important to emphasise that the method permits multiple binding sites, here implemented for two trap sites with different binding energies. It is assumed that there is no interaction between the trapped and free hydrogen and that one-dimensional diffusion occurs through the lattice in a direction normal to the plane of a steel sheet. Hydrogen is first introduced into the sample and distributed between the trap sites and lattice sites either assuming local equilibrium or via a "kinetic model" based on the McNabb and Foster scheme. The lattice hydrogen is then allowed to diffuse out to the free surface using a finite difference method (FDM). This process is repeated until the sample reaches the target temperature.

Using symmetry it is only necessary to model half of the specimen, which for 1 mm length was divided into 50 elements after demonstrating that further subdivision did not make a significant difference to the calculated outcomes. In the case of austenite where diffusion is much slower, the number of elements per mm was increased to 800.

Hydrogen is first introduced into the sample assuming a constant surface concentration of 0.03 ppm, consistent with the extrapolated phase boundary of the Fe_α-H phase diagram [26]. The time interval was chosen to be less than $\frac{1}{3}(\Delta z)^2 D^{-1}$, where Δz is the dimension of the FDM element. The hydrogen that enters
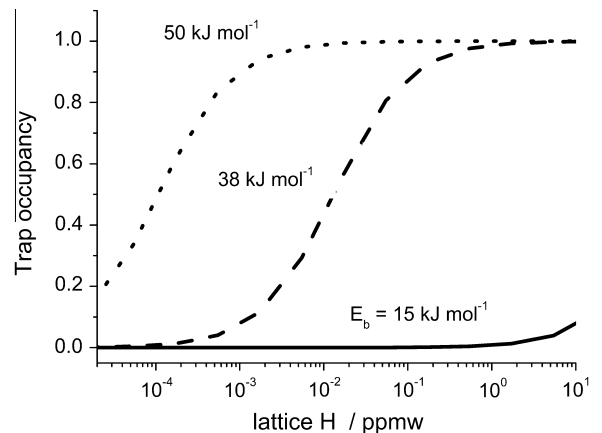

Fig. 1. Trap occupancy as a function of hydrogen content at 300 K.