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On irreversible trapping of hydrogen in metals

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ABSTRACT

Calculations have been made of the discharge rate of hydrogen from a precharged steel membrane in order to clarify the definition of irreversible trapping in the context of the trap binding energy. The concept of irreversible trapping is shown to be arbitrary and the need for improved guidance in characterising such trapping is indicated.

Keywords: Hydrogen, diffusion, trapping.

CONTENTS

1.   INTRODUCTION

Hydrogen atom diffusion through a metal is governed by the rate at which the atoms hop between interstitial lattice sites[1] and the extent to which they become transiently trapped at microstructural trap sites such as dislocations, grain boundaries, vacancies and interfaces. 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 [2-7]. 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 [8]. 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). The first equation accounts for diffusion and the net rate at which hydrogen in the interstitial lattice sites is lost to trap sites and the second and third equations describe the rate of change of the trapped hydrogen concentration.

$$\frac{\partial C_L}{\partial t} = D \nabla^2 C_L - \frac{\partial C_1}{\partial t} - \frac{\partial C_2}{\partial t} \qquad (1)$$

$$\frac{\partial C_1}{\partial t} = N_1 \{ k_1 C(1 - \theta_1) - p_1 \theta_1 \} \qquad (2)$$

$$\frac{\partial C_2}{\partial t} = N_2 \{ k_2 C(1 - \theta_2) - p_2 \theta_2 \} \qquad (3)$$

Here, C_L is the concentration of hydrogen atoms in interstitial lattice sites, D is the lattice diffusion coefficient (equivalent to that for pure iron in the case of steel), C_1 and C_2 are the concentrations of hydrogen in traps of types 1 and 2, N is the density of trap sites, θ is the trap occupancy (fraction of trap sites occupied) and k and p are temperature dependent rate constants which may be expressed by:

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

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

Here, k^0 and p^0 are pre-exponential factors, ΔE is the binding energy (taken to be negative here), V_0 is the activation energy for jumping into a trap potential well (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 (height of the potential well).

In addition to the concept of deep traps, the term irreversible trap has been used with often the same meaning, the implication being that the probability of the hydrogen atom jumping out of the trap site at the temperature of interest is so low as to render the trapped hydrogen effectively immobile. Such irreversible trapping is considered for some systems to have no direct impact on cracking. In principle, the validity of this can be established by charging a test specimen (e.g. slow strain rate specimen) with hydrogen and then discharging before subsequently testing in air. Assuming that the irreversibly trapped hydrogen is retained but the readily mobile hydrogen escapes, the test will provide an assessment of the impact of the irreversibly trapped hydrogen

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[1] For iron, recent work [1] shows that quantum tunnelling of hydrogen atoms between adjacent sites is the dominant transport mechanism at ambient temperature and below.

in isolation. Using this method for a 13 Cr martensitic stainless steels (AISI 410) [9] and for some C-steels [5], no difference in cracking response was observed between results in air with and without irreversibly trapped hydrogen. Here, the charging was not so severe as to induce damage such as void development during the charging stage.

The concern is the lack of a consistent definition of what is understood by a deep, or irreversible, trap. In modelling hydrogen permeation with reversible and irreversible traps sites for near-ambient temperature conditions, the equations (2) and (3) above have been used with the rate constant p for one of the traps being set to zero (see reference [10] for example). This leads to inconsistency when modelling thermal desorption of hydrogen [11] for which finite values for p are, of necessity, used even for very deep traps. Correspondingly, there will always be leakage from the deep traps, the rate depending on temperature. Thus, the term irreversible is not fundamentally correct but has a pragmatic meaning in the context of a sufficiently long timescale for significant leakage to occur at the temperature of relevance. However, it is necessary to clarify the timescale for different binding energies.

2. MODEL CALCULATIONS

To shed some light on this topic, a theoretical analysis was undertaken in which a steel membrane was considered to be have been precharged uniformly with the hydrogen atoms in lattice and trap sites at their equilibrium concentration. The concentration of hydrogen at both surfaces was then set to zero to simulate an efficient hydrogen removal process and the leakage rate from the specimen at 22 °C was then assessed. For simplicity, only one trap was considered. The input parameters were based on experimental work conducted previously on a low alloy steel and were similar to that used for thermal desorption analysis [10]. Specifically, the initial lattice concentration was 2×10^{15} atoms cm^{-3} (typical of cathodically protected low alloy steel); the trap concentration was 2×10^{18} sites cm^{-3} and the specimen thickness was 2 mm. Values for the individual pre-exponential factors, k^0 and p^0, are not known per se but their ratio is simply the inverse of the number of lattice sites ($1/N_L$). The adopted approach is necessarily to choose values for k^0 and p^0 that are somewhat arbitrary [11] and to then assess the sensitivity to variations in the parameters. In practice, values for k^0 and p^0 of 4.4×10^{-17} s^{-1} and 2.3×10^7 mol L^{-1} s^{-1} respectively were used. Reducing the values by over two orders of magnitude, keeping the ratio constant, made a difference of only a few % to the predictions. Nevertheless, it is recognised that p^0 could be very small though non-zero. Testing is the only way to resolve this.

In the analysis the flux variation with time is calculated. This is readily converted to a total amount of hydrogen discharged at a specific time (C_{disch}). The ratio of this to the initial concentration (C_{init}) in the steel (trapped plus interstitial) is then determined as a function of time and gives a simple measure of the leakage rate.

A plot of this ratio versus time for different values of the binding energy is shown in Figure 1 for very long times and in more detail at shorter times in Figure 2. For the binding energy of 70 kJ/mole an extended run to 313 days was carried out. At this time the ratio was 0.41.
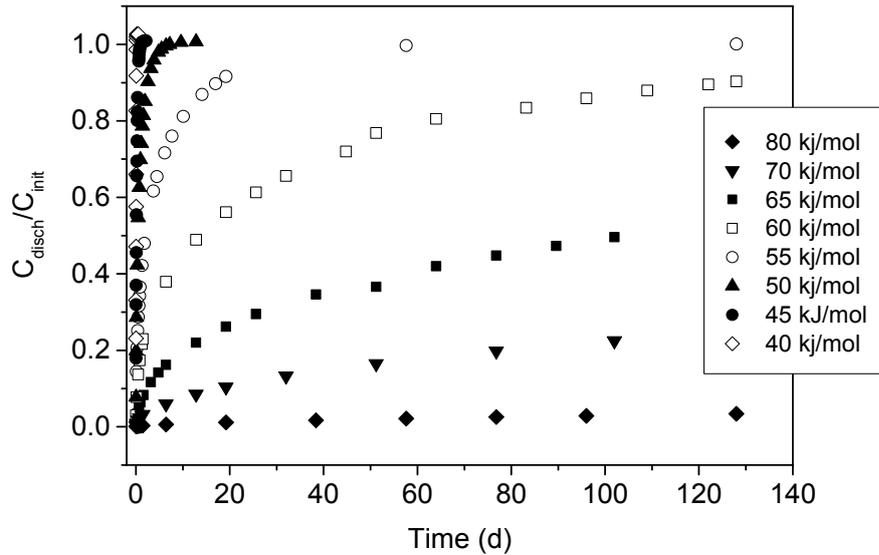
Figure 1: Leakage rate of hydrogen from uniformly precharged steel as a function of binding energy.

The leakage rate decreases with time but of course is finite in all cases. The hydrogen is mobile but the rate of jumping over the potential energy barrier is of course so very low at the highest binding energy that the flux is very small. In the latter context, one might argue that the amount of hydrogen available to affect cracking is always going to be low compared with that associated with lower binding energy trap sites and the hydrogen can be treated as effectively immobile.
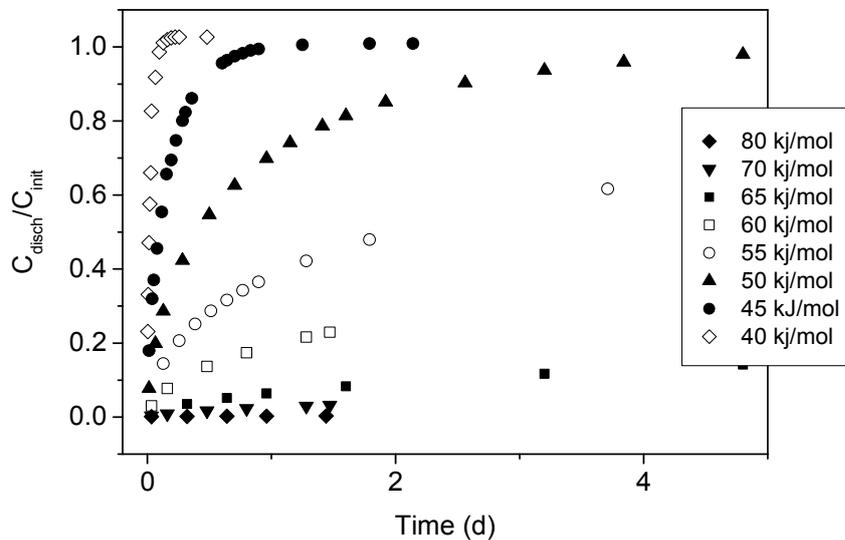

Figure 2: Leakage rate of hydrogen from uniformly precharged steel as a function of binding energy.

Very large binding energies of order of 80 kJ/mol do not provide challenges in assessment; the problem is for values in the range 50-60 kJ/mol. Here, the concept of immobile hydrogen is more arbitrary as, quite clearly, there is a significant loss of hydrogen in a modest timescale. The data indicate that significant leakage may occur at trap sites with a binding energy of 55 kJ/mol, typical of the value assigned by Grabke and Riecke [6] to deep, immobile, traps. In their study, they conducted stepwise permeation measurements such that the first charging step

fills the deep traps primarily and the second step, using more severe charging conditions, fills the shallower traps.

The occupancy of trap sites is readily calculated using

$$\theta = \frac{C_L/N_L \exp[-\Delta E/RT)}{1+C_L/N_L \exp[-\Delta E/RT)} \ .$$

Values for different binding energies are summarised in Table 1.

Table 1. Occupancy of trap sites as a function of binding energy assuming a low uniform lattice concentration of 2×10^{15} atoms cm^{-3} (4.2×10^{-4} ppm by mass)

Binding Energy / kJ/mole	Trap occupancy
40	0.045
45	0.26
50	0.73
55	0.95
60	0.99
65	1.00
70	1.00
75	1.00
80	1.00

Assuming a lattice concentration of 2×10^{15} atoms cm^{-3} and a binding energy of 55 kJ/mole, the trap occupancy is about 95% (Table 1) so there is no doubt that this represents a deep trap and would be mostly filled during the first permeation stage. In the context of the testing of Grabke and Riecke, the traps would be nearly filled during the first permeation so their analysis is not affected. However, Figure 1 shows that it is clearly imprecise to suggest that the trapped hydrogen is immobile; given time, if the charging were ceased the hydrogen would discharge.

In the model calculations, it is assumed also that hydrogen is removed efficiently from the exit surface. Following metal processing, oxide scales can present barriers to hydrogen atom discharge but it is necessary to distinguish between trapping and its effects on mobility of hydrogen in the metal from effects imposed by oxide transport constraints.

3.   DISCUSSION

Recognising the arbitrariness of the concept of irreversible trapping, it is important to assess the implications for testing. In separating out reversible and irreversible traps during permeation studies, it is advocated that repeated permeation tests are carried out [12]. After the first transient, the hydrogen is usually allowed to discharge from the steel, the assumption being that remaining hydrogen is irreversibly trapped. That procedure now needs better definition, as the extent to which the deep traps have emptied requires resolution. If electrochemical discharge is carried out, the oxidation current gives an indication of the extent to which hydrogen is still leaking from the specimen and by implication from the trap sites.   When the oxidation current falls to the background level, it is usually assumed that the reversible traps have emptied and that the remaining hydrogen is irreversibly held in very deep traps. In view of the calculations above, it is feasible that a rather slow leakage is proceeding and that the occupancy of deep traps has diminished somewhat. In the short timescale of the repeated permeation experiments this leakage may not be significant. As an alternative to electrochemical discharge, the

specimen may be removed and left to discharge in an oven at an elevated temperature (e.g. 100 °C). However, this still remains a somewhat arbitrary procedure as the time allowed for detrapping is often unspecified. It is essentially the same problem encountered with the tests near ambient temperature.

It is apparent that in modelling of hydrogen permeation and fitting to experimental data, the treatment of deep traps should allow for the rate of hydrogen egress from the deep traps rather than making *a priori* assumptions that it is negligible. Further experimental measurement is required to clarify the concept of irreversible trapping. The term is recognisably arbitrary but perhaps now needs definition in terms of a rate of loss of hydrogen below some specified value (e.g. <0.1% per day). Repeated permeation measurements for varying discharge periods and discharge temperatures would provide insight and allow a consistent definition.

4.   CONCLUSIONS

Deep traps may be considered as those traps for which the trap occupancy approaches unity. However, this does not necessarily imply that these traps are irreversible at ambient temperature.

There will always be some leakage of hydrogen from traps at ambient temperature, even very deep ones, and the concept of irreversibility of hydrogen trapping is not fundamental but based loosely on experimental observation and approximate models. As such, more thought needs to be given to exploration of the effect of discharge time on retained hydrogen at the appropriate test temperature and a pragmatic definition of "irreversibility" that is based on the rate of release of hydrogen compared to experimental test times. Arguably, the term may be considered an artificial construct and should be dropped altogether.

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