Hydrogen Trapping Models in Steel

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This article describes the role of hydrogen trapping in steel. Trapping increases the solubility of hydrogen and decreases the diffusivity. Traps are characterized by their nature, *i.e.*, reversible or irreversible, saturable or unsaturable. A dislocation core is a saturable, reversible trap, while voids and crack are unsaturable, reversible traps. A trap model based on saturable, reversible traps is developed, which is slightly different from the trap model of McNabb and Foster. In equilibrium, the trap model corresponds to Oriani's trap model. Kumnick and Johnson found experimentally that the trap density increases as the plastic strain increases. Using their trap data, it is shown that equilibrium between hydrogen in lattice sites and trap sites can be assumed when strain rates are used as in standard tensile tests.

I. INTRODUCTION

IN this article, a model is derived that describes the role of trapping during hydrogen diffusion in steel. Hydrogen is not homogeneously distributed in steel, as it would be in a perfect iron crystal. Hydrogen will be found not only in the normal interstitial lattice sites but also in atomic and microstructural imperfections such as vacancies, solute atoms, dislocations, grain boundaries, boundaries of second-phase particles, and voids. The generic term for this phenomenon is trapping.[1] A general model of trapping will first be derived. It will be then demonstrated that this model can be simplified by assuming equilibrium between hydrogen in lattice sites and in trap sites. Experimental data for trap parameters are also discussed.

In voids or cracks, atomic hydrogen can recombine to form hydrogen molecules. According to Sieverts' law,[2] the hydrogen concentration in lattice sites C_L depends on the pressure p_{H_2} of the hydrogen molecules in the void:

$$C_L = k\sqrt{p_{H_2}} \qquad [1]$$

where k is the solubility of the hydrogen. Darken and Smith[3] were among the first to observe trapping of hydrogen other then void trapping. They observed that the hydrogen diffusivity increases with increasing hydrogen concentration, whereas it should be independent of the hydrogen concentration. This effect could not arise from void trapping, since, by Sieverts' law, the trapped hydrogen should be an increasing fraction of the total hydrogen concentration when the hydrogen concentration in lattice sites is increased. Consequently, the diffusivity should decrease with increasing hydrogen concentration in lattice sites, which is in contrast to what was observed.

The two prominent effects of trapping are to increase the apparent hydrogen solubility and to decrease the apparent diffusivity. When steel is equilibrated against a fixed external chemical potential of hydrogen, it will absorb hydrogen to the solubility limit of the lattice, while additional hydrogen

will occupy the traps. Equilibrium is established when the chemical potentials of the hydrogen distributions in lattice and trap sites and the external chemical potential become equal. Thus, the apparent solubility, or total hydrogen concentration, may be significantly higher than the lattice solubility. A trapped hydrogen atom must acquire an energy substantially larger than the lattice migration energy to escape the trap. Hence, the mean residence time of a diffusing hydrogen atom is considerably longer in a trap site than in a lattice site. Consequently, in the presence of trapping, the apparent diffusivity will be less than the lattice diffusivity. This behavior could be the reason why the reported diffusion constants for hydrogen in iron differ by orders of magnitude.[4]

At present, the trapping phenomena in steels are not well understood and the connection with hydrogen embrittlement is not clear. Despite this lack of understanding, it is believed that trapping plays an important role in hydrogen embrittlement. It has been difficult, however, to obtain unambiguous experimental information on the role of traps, partly because of the small hydrogen concentrations involved.[1,5]

Experimental evidence has been found only recently that hydrogen is not homogeneously distributed in steel. Gao *et al.*[6] investigated the hydrogen distribution in the vicinity of a crack tip in steel under mixed mode I/II loading using mass spectrometry, and Sun *et al.*[7] investigated the hydrogen distribution around a crack tip in an fcc single crystal. Their results show two peaks in the hydrogen distribution ahead of a notch: one peak is in the immediate vicinity of the notch, corresponding to the location of maximum equivalent strain, and another peak is located at some distance from the notch corresponding to the location of maximum hydrostatic stress. The latter effect will not be regarded here in terms of trapping, since it influences only the hydrogen diffusion through lattice sites. In Reference 8, the effect of the hydrostatic stress is considered.

II. HYDROGEN DIFFUSION WITH TRAPPING

A trap model is followed as presented by McNabb and Foster[9] and Oriani.[10] The model is based on saturable traps such as dislocation cores and grain boundaries. A saturable trap is a trap of which the physical nature is such that it can accommodate only a finite number of atoms.[11] In contrast, a nonsaturable trap can accommodate an infinite

Table I. The Number of Interstitial Sites per Atom for Bcc and Fcc Lattices

Lattice	Site	Number of Sites per Unit Cell	Number of Atoms per Unit Cell	β
Bcc	octahedral	6	2	3
Bcc	tetrahedral	12	2	6
Fcc	octahedral	4	4	1
Fcc	tetrahedral	8	4	2

number of atoms. An example of a nonsaturable trap is a void, since by Sieverts' law the amount of hydrogen in the void (pressure) increases as the hydrogen lattice concentration increases.

In the following derivations, a lattice site is denoted by the subscript L and a trap site by the subscript T. The number of lattice sites N_L per unit volume is related to the atoms constituting the host lattice:

$$N_L = \frac{N_A \beta \rho}{A_r} \qquad [2]$$

with β, the number of interstitial sites per atom (Table I); N_A, Avogadro's number, i.e., 6.022×10^{23} mol^{-1}; ρ, the density of the metal; and A_r, the atomic weight of atoms constituting the host lattice. In bcc and fcc metals, hydrogen can occupy either tetrahedral or octahedral site positions. In the case of α-iron, indirect evidence indicates tetrahedral site occupancy of hydrogen at room temperature,[12,13] in which case β is 6. The density of iron at 293 K is 7.87×10^3 kg/m^3 and its atomic weight is 55.8×10^{-3} kg/mol.[14] Hence, Eq. [2] gives $N_L = 5.1 \times 10^{29}$ m^{-3}.

An estimate of the trap density can be made when only dislocation cores are considered as trap sites. For example, in the case of edge dislocations with $\langle \bar{1}11 \rangle$ slip directions on {110} planes in a bcc lattice, assuming one trap per atomic plane intersected by a dislocation, the trap density N_T, i.e., the number of trap sites per unit volume, is

$$N_T = \frac{\rho_{\text{dis}}}{d_{\text{bcc}}} = \frac{\sqrt{2}}{a_{\text{bcc}}} \rho_{\text{dis}} \qquad [3]$$

where ρ_{dis} is the dislocation density and d_{bcc} is the distance between two {110} planes given by $d_{\text{bcc}} = a_{\text{bcc}}/\sqrt{2}$, where a_{bcc} is the lattice constant. The lattice constant for α-iron is 0.29 nm,[14] and the dislocation density varies from 10^{10} m^{-2} in the annealed state to 10^{16} m^{-2} in the cold-worked state. Hence, Eq. [3] gives $N_T = 5 \times 10^{19}$ to 5×10^{25} m^{-3}. A higher estimate of the trap density can be achieved by increasing the number of trap sites per intersecting plane. Experimental measurements of N_T will be discussed in Section IV. In the trap model, it is assumed that traps are isolated, i.e., that they do not form an extended network, and that transport between traps is by lattice diffusion. The hydrogen diffusion along grain boundaries and dislocations is not considered important, as these features can be considered as strong traps for hydrogen. The hydrogen transport by moving dislocations is similarly not considered important, since dislocations cannot move through grain boundaries. Hence, it is questionable whether there is a net flux of hydrogen by moving dislocations in a polycrystalline metal.[1,15] According to Oriani[10] and Johnson and Lin,[11] the time-dependent diffusion of hydrogen with trapping may be written as

$$\frac{\partial C_L}{\partial t} + \frac{\partial C_T}{\partial t} - D_L \nabla^2 C_L = 0 \qquad [4]$$

where C_L is the hydrogen concentration in lattice sites, C_T the hydrogen concentration in trap sites, D_L the diffusion coefficient, which follows an Arrhenius relation: $D_L = D_0 e^{-Q/RT}$, with D_0 the diffusion pre-exponential factor, Q the activation enthalpy, R the universal gas constant, and T the absolute temperature.[16] Equation [4] is a modification of Fick's second law: $\partial C_L/\partial t = D_L \nabla^2 C$. In situations where the hydrogen concentration in trap sites is a function only of the hydrogen concentration in lattice sites, Eq. [4] can be rewritten as

$$\frac{\partial C_L}{\partial t} - \frac{D_L}{(1 + \partial C_T/\partial C_L)} \nabla^2 C_L = 0 \qquad [5]$$

When plastic straining occurs, the concentration in lattice sites also depends on the traps created by plastic strain.[8] The exact form of $\partial C_T/\partial C_L$ will depend on the trapping mechanism. By comparison with the standard form of the diffusion equation, an effective diffusivity may be defined as

$$D_{\text{eff}} = \frac{D_L}{(1 + \partial C_T/\partial C_L)} \qquad [6]$$

In many cases, D_{eff} will be concentration dependent, and it will not usually be possible to obtain solutions of the diffusion Eq. [5] Nevertheless, some useful physical insights can be obtained from examination of Eq. [6].

A. Saturable Traps

In constructing a relation between the two hydrogen distributions, the following trapping reaction is considered:[17]

$$[H]_L \rightleftarrows [H]_T \qquad [7]$$

where $[H]_L$ is the hydrogen atom in a lattice site and $[H]_T$ is the hydrogen atom in a trap site.

The number of hydrogen atoms moving from lattice sites to trap sites is proportional to the following:

(1) the oscillation frequency ν of the hydrogen atom, which is usually taken to be equal to the Debye frequency, i.e., 10^{13} s^{-1};[18,19]
(2) the probability that an oscillation is successful, which is equal to $e^{-E_Q/RT}$,[18,19] where E_Q is an activation energy;
(3) the number of hydrogen atoms in lattice sites, i.e., the concentration; and
(4) the probability that a neighboring site is a trap site, which is equal to the number of unoccupied trap sites divided by the total number of unoccupied sites.

Hence, the derivative of the concentration of hydrogen atoms moving from lattice sites to trap sites with respect to time can be written as

$$\left. \frac{\partial C_T}{\partial t} \right|_{L \to T} = \kappa C_L \frac{N_T(1 - \theta_T)}{N_L(1 - \theta_L) + N_T(1 - \theta_T)} \qquad [8]$$

where θ_L is the occupancy of lattice sites: $\theta_L = C_L/N_L$; θ_T is the occupancy of trap sites: $\theta_T = C_T/N_T$; and κ is the frequency of hydrogen atoms jumping from lattice sites to trap sites: $\kappa = \nu e^{-E_{LT}/RT}$, in which E_{LT} is the activation energy for moving from a lattice site to a trap site. Referring
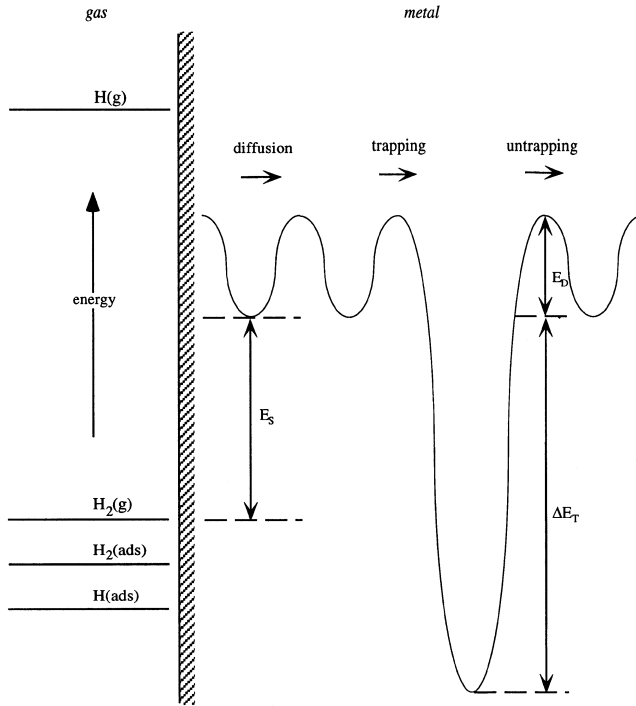
Fig. 1—Schematic view of energy relations in hydrogen-metal equilibria, including trapping.

to Figure 1, this activation energy is equal to the activation energy for moving from a lattice site to an adjacent lattice site and hence to the activation energy for normal lattice diffusion: $E_{LT} = E_{LL} = E_D$.

Similarly, the number of hydrogen atoms moving from trap sites to lattice sites is proportional to the following:

(1) the oscillation frequency ν of the hydrogen atom;
(2) the probability that an oscillation is successful;
(3) the number of hydrogen atoms in trap sites, *i.e.*, the concentration; and
(4) the probability that a neighboring site is a lattice site, which is equal to one, since it is assumed that there is no transport between trap sites.

Hence, the derivative of the concentration of hydrogen atoms moving from trap sites to lattice sites with respect to time can be written as

$$\left.\frac{\partial C_T}{\partial t}\right|_{T \to L} = -\lambda C_T \qquad [9]$$

where λ is the frequency of hydrogen atoms jumping from trap sites to lattice sites: $\lambda = \nu e^{-E_{TL}/RT}$, in which E_{TL} is the activation energy for moving from a trap site to a lattice site. Referring to Figure 1, this activation energy is the same as the activation energy for moving from a lattice site to an adjacent lattice site, E_D, minus the trap binding energy ΔE_T: $E_{TL} = E_D - \Delta E_T$. The derivative of the hydrogen concentration in trap sites with respect to time is found by adding Eq. [9] to Eq. [8]. First, the previous two equations can be simplified by taking $\theta_L \ll 1$, since the solubility of hydrogen atoms in steel is very low and $N_T \ll N_L$, as shown previously. This condition results in

$$\frac{\partial C_T}{\partial t} = \kappa \theta_L N_T (1 - \theta_T) - \lambda C_T \qquad [10]$$

When the number of trap sites is constant, using $\theta_T = C_T/N_T$, this derivative can also be written as

$$\frac{\partial C_T}{\partial t} = N_T \frac{\partial \theta_T}{\partial t} \qquad [11]$$

Equation [10] can then be rewritten as

$$\frac{\partial \theta_T}{\partial t} = \kappa \theta_L (1 - \theta_T) - \lambda \theta_T \qquad [12]$$

This relationship is the equation derived by McNabb and Foster,[9] except that θ_L is replaced by C_L. The term $1/N_L$ was "merged" in the parameter κ, as a result of which in their equation the unit of this parameter differs from that of the parameter λ. From a dimensional point of view, this arrangement is not correct.

In the case of equilibrium, the time-dependent variable is zero and Eq. [12] yields

$$\frac{\theta_T}{\theta_L(1 - \theta_T)} = \frac{\kappa}{\lambda} = e^{-\Delta E_T/RT} = K_T \qquad [13]$$

where K_T is termed as the trap equilibrium constant.

Another derivation of Eq. [13] is given by Oriani.[10] He assumed that there is local equilibrium between the hydrogen in lattice sites and the hydrogen in trap sites. This assumption means that the chemical potentials must be equal: $\mu_L = \mu_T$. The chemical potentials of the hydrogen in lattice sites and in trap sites can be expressed using a Fermi–Dirac distribution, since both types of sites can accommodate only a finite number of hydrogen atoms and it is assumed that there are no interactions between the occupied sites.[10,20] The chemical potential of the hydrogen in lattice sites is

$$\mu_L = \mu_L^0 + RT \ln \frac{\theta_L}{(1 - \theta_L)} \approx \mu_L^0 + RT \ln \theta_L \qquad [14]$$

where μ_L^0 is the chemical potential of the hydrogen in lattice sites in a reference state. Since the solubility of hydrogen atoms in steel is very low, $\theta_L \ll 1$, which justifies the simplification in Eq. [14]. The chemical potential of hydrogen in trap sites is given by

$$\mu_T = \mu_T^0 + RT \ln \frac{\theta_T}{(1 - \theta_T)} \qquad [15]$$

where μ_T^0 is the chemical potential of hydrogen in trap sites in a reference state. Equalizing Eqs. [14] and [15] results in Eq. [13], where $\Delta E_T = \mu_T^0 - \mu_L^0$.

The hydrogen concentration in trap sites as a function of the hydrogen concentration in lattice sites is obtained by substitution of $\theta_L = C_L/N_L$ and $\theta_T = C_T/N_T$ in Eq. [13]:

$$C_T = \frac{N_T}{\left(1 + \dfrac{N_L}{K_T C_L}\right)} \qquad [16]$$

If the trap density and temperature remain constant, the partial derivative of the hydrogen concentration in trap sites with respect to the hydrogen concentration in lattice sites, using Eq. [16], is

$$\frac{\partial C_T}{\partial C_L} = \frac{C_T(1 - \theta_T)}{C_L} \qquad [17]$$

Substituting in Eq. [6], the following relation is obtained for the effective diffusivity:

$$D_{\text{eff}} = D_L \frac{C_L}{C_L + C_T(1 - \theta_T)} \qquad [18]$$

When the occupancy of trap sites by hydrogen is also low ($\theta_T \ll 1$), Eq. [13] reduces to

$$C_T = K_T \frac{N_T}{N_L} C_L \qquad [19]$$

Hence, in the regime of low trap occupancy, saturable traps are equivalent to linear, nonsaturable traps. Using Eq. [18], the effective diffusivity now becomes

$$D_{\text{eff}} = D_L \frac{1}{1 + K_T N_T/N_L} \qquad [20]$$

Since Eq. [20] is independent of the hydrogen concentration, Oriani[10] used it to determine trap parameters in the regime of low trap occupancy. The validity of Eq. [20] was acknowledged by Monte Carlo simulations of Kircheim.[21]

B. *Void Traps*

The surface of a void can trap atomic hydrogen, but the void itself can trap molecular hydrogen. At the surface of the void, the following absorption reaction (inverse trapping reaction) takes place:

$$\frac{1}{2} H_2 \rightleftarrows [H]_L \qquad [21]$$
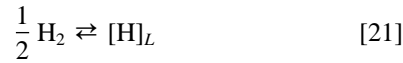
where the brackets mean that the hydrogen is absorbed in lattice sites. If we assume equilibrium between the hydrogen gas in the void and the hydrogen in lattice sites, the chemical potential of the hydrogen molecules in the void must be equal to the chemical potential of hydrogen in lattice sites: $\mu_L - 1/2\, \mu_{H_2} = 0$. The chemical potential of the hydrogen gas is

$$\mu_{H_2} = \mu_{H_2}^0 + RT \ln \frac{f_{H_2}}{p_{H_2}^0} \qquad [22]$$

where $\theta_{H_2}^0$ is the chemical potential in a reference state, f_{H_2} the fugacity of the hydrogen gas, and $p_{H_2}^0$ a reference pressure. Equalizing Eqs. [14] and Eq. [22],

$$\frac{C_L}{N_L \sqrt{f_{H_2}}} = \frac{e^{-\left(\mu_L^0 - \frac{1}{2}\mu_{H_2}^0\right)/RT}}{\sqrt{p_{H_2}^0}} \qquad [23]$$

Equation [23] rearranges to

$$C_L = k\sqrt{f_{H_2}} \qquad [24]$$

where k contains all constants of Eq. [23]. Experimental data show that k follows an Arrhenius relation, $k = k_0 e^{-\Delta H_s/RT}$, with k_0 the solution pre-exponential factor and ΔH_s the enthalpy of solution, for iron 5×10^{23} m^{-3}Pa$^{-1/2}$ and 28.6 kJ/mol, respectively.[22] At low hydrogen pressures, the hydrogen gas can be regarded as an ideal gas and the fugacity may be replaced by the pressure p, which leads to Eq. [1]. Otherwise, the fugacity has to be related to the pressure.[23] For molecular trapping in voids, Chew[24] derives for the effective diffusivity

$$D_{\text{eff}} = \frac{D_L}{\left(1 + \frac{2V_f}{kRT}\sqrt{p_{H_2}}\right)} \qquad [25]$$

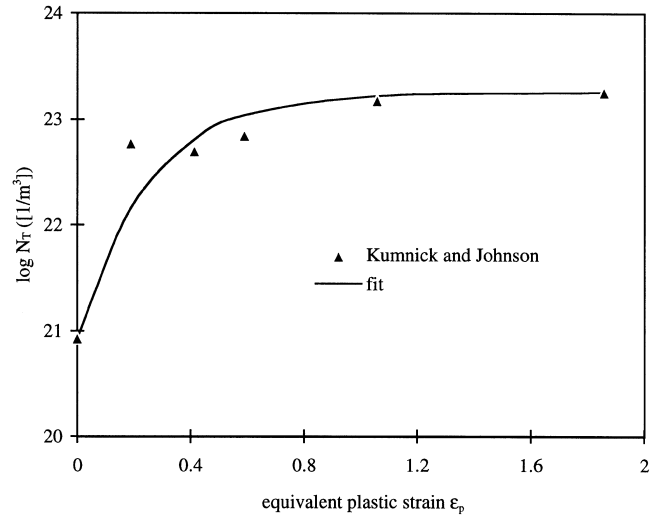Fig. 2—The number of trap sites in α-iron as a function of equivalent plastic strain along with the fit $\log N_T = 23.3 - 2.33e^{-4.0\varepsilon_p}$.

where V_f is the void volume fraction. Chew[24] extended this relation for high hydrogen pressures in the voids. Johnson and Lin[11] derive a similar relation for molecar trapping. Johnson[5] analyzed diffusion data for hydrogen in this relation. However, the nature of the experiments was such that trends with lattice concentration or temperature could not be examined.

III. DETERMINATION OF TRAP PARAMETERS

Kumnick and Johnson[26] used the following equation to measure the trap density and binding energy in very pure iron.

$$\frac{t_T}{t_L} = 1 + \frac{3N_T}{k\sqrt{p_{H_2}}} \qquad [26]$$

where t_T and t_L are the lag times with and without trapping, respectively. This equation is based on the work of Caskey and Pillinger.[25] They measured the lag time at various hydrogen pressures and at various deformation levels. The experimental data were analyzed for trap densities and binding energies through plots of ($t_T/t_L - 1$) versus $1/\sqrt{p_{H_2}}$. The slope at high pressures was determined through which the trap density is known. Using this trap density, a fit was made through all data points by changing the trap binding energy. This procedure was done for several deformation levels. It was found that the trap density increases sharply with plastic strain at low plastic strain levels and then increases more gradually with further straining (Figure 2). A fit close to their observations (Figure 2 also) is

$$\log N_T = 23.3 - 2.33e^{-4.0\varepsilon_p} \qquad [27]$$

Kumnick and Johnson estimated a trap binding energy of -60 ± 5 kJ/mol, independent of temperature within the range of 288 to 343 K and independent of plastic deformations within the range of 0 to 80 pct. The physical picture that may be inferred from these observations is one of deep and isolated traps with a single binding energy and a concentration that is dependent on deformation level. The variation

in the trap density with deformations is similar to the variation in quantities such as yield strength, hardness, and dislocation density with deformation level. This correlation implies that the traps are associated with the imperfection structure, probably dislocations, and perhaps point defects, developed during plastic deformation.[26] Other trap sites may be newly created microvoid surfaces. In the annealed state, the measured trap density, N_T, which is approximately 10^{21} m^{-3}, can be identified with the dislocation density, since according to Eq. [3], the trap density varies between 5×10^{19} and 5×10^{21} m^{-3}. On the other hand, in the heavily deformed state, the measured trap density is approximately 10^{23} m^{-3}, while according to Eq. [3], the trap density is 5×10^{25} m^{-3}. This result can be explained by the fact that not all dislocations are edge dislocations, as assumed in Eq. [3]. The trap binding energy seems very high, but Hirth[12] argued that this is easily possible, as there are even stronger traps, for example, grain boundaries and the Fe$_3$C interface. Weak traps are voids and the stress field of dislocations. Riecke and Bohnenkamp[27] carried out the same analysis as Kumnick and Johnson. They found for iron a trap binding energy of -56 kJ/mol and a trap density of 1.9×10^{23} m^{-3} at 60 pct deformation, approximately the same values as found by Kumnick and Johnson.

Perng and Altstetter[28] investigated trapping in austenitic stainless steel by measuring the hydrogen flux, from which the diffusivity and the permeation were deduced. The gas permeation experiments were performed in the temperature range 100 to 350 °C and in the hydrogen pressure range of 0.1 to 30 kPa. They observed that the amount of trapped hydrogen increases rapidly at first and then less rapidly with increasing deformation. However, the estimated increase in the trap density, from 5×10^{26} to 5×10^{27} m^{-3}, was not large compared with Kumnick and Johnson. This result was probably because the number of traps such as carbide interfaces was already large, so that the increase due to plasticity could not be detected. In ferritic stainless steel, Perng *et al.*[29] did not observe a significant increase in the effective hydrogen diffusivity due to the increase in hydrogen pressure, probably because the hydrogen pressure range was not large enough to detect any trapping.[29] Kumnick and Johnson varied the hydrogen pressure between 1 and 100 kPa. As in the austenitic stainless steel, the number of traps such as carbide interfaces could already be large, so that the increase in trap sites could not be detected.

Xie and Hirth[30] examined hydrogen trapping in spheroidized carbon steel by cathodic charging permeation tests. They found that trapping increases with increasing deformation. Since the specimens were charged cathodically, an analysis such as that carried out by Kumnick and Johnson could not be performed.

Oriani[10] used Eq. [20] to analyze the existing experimental data and observed the following trend: the trap density increases with increasing deformations, carbon content, and the strength level of the steel. He found a surprisingly uniform trap binding energy of -27 kJ/mol and a trap density of the order of 10^{25} m^{-3} for undeformed steel. Considering Eq. [3], with a dislocation density of l0^{12} m^{-2}, gives a trap density of 5×10^{21} m^{-3}. Oriani's trap density is therefore too large to be due to dislocations alone. For undeformed steel, a dislocation density of the order of 10^{15} lines/m^2 would be needed to justify this. Oriani concluded that interfaces and
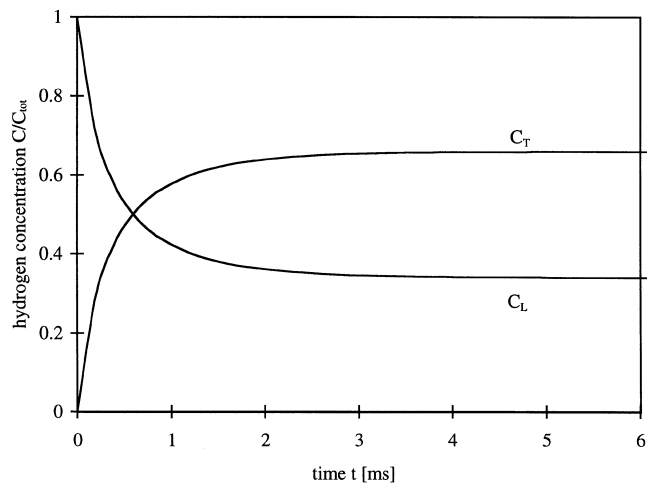

Fig. 3—Plot of Eq. [29] using $N_T = 2 \times 10^{21}$ m^{-3}, $\Delta E_T = -60$ kJ/mol, $C_{tot} = 3 \times 10^{21}$ m^{-3}, $N_L = 5.1 \times 10^{29}$ m^{-3}, $T = 293$ K, $E_D = 6.9$ kJ/mol, $v = 1 \times 10^{13}$ s^{-1}, and $C_{T_0} = 0$.

microcracks are involved in trapping. It is, however, doubtful whether Oriani determined dislocations as trap sites, since the measured trap binding energy is approximately the same as the heat of solution but of opposite sign. In addition, Eq. [20], used by Oriani, is similar to Eq. [25], which can be used for void trapping. Furthermore, the hydrogen concentrations were also orders of magnitude higher than the hydrogen concentrations used by Kumnick and Johnson,[26] diminishing the effect of dislocation trapping and increasing the chance of hydrogen damage (voids). Hence, it is very reasonable to assume that Oriani investigated void traps.

IV. THE EQUILIBRIUM BETWEEN HYDROGEN IN LATTICE SITES AND IN TRAP SITES

In this section, it is investigated whether equilibrium can be assumed between the hydrogen in lattice sites and in trap sites by using the experimental data of the previous section. Equation [10] can be solved analytically when the total hydrogen concentration, $C_{tot} = C_L + C_T$, and the trap density are held constant during time. Equation [10] then becomes

$$\frac{\partial C_T}{\partial t} = \frac{1}{N_L} [\kappa C_T^2 - \{\kappa C_{tot} + \kappa N_T + \lambda N_L\} C_T + \kappa C_{tot} N_T] \quad [28]$$

which has the following solution:

$$C_T = \frac{r_1 - r_2}{2r_3} + \frac{e^{r_1 t}}{\dfrac{2r_3}{2r_3 C_{T_0} + r_2 - r_1} + \dfrac{r_3}{r_1} - \dfrac{r_3}{r_1} e^{r_1 t}} \quad [29]$$

where C_{T_0} is the hydrogen concentration in trap sites at $t = 0$ and

$$r_1 = -\frac{1}{N_L} \sqrt{\{\kappa C_{tot} + \kappa N_T + \lambda N_L\}^2 - 4\kappa^2 C_{tot} N_T}$$

$$r_2 = \frac{-1}{N_L} \{\kappa C_{tot} + \kappa N_T + \lambda N_L\}$$

$$r_3 = \frac{\kappa}{N_L}$$

Equation [29] with $C_{T_0} = 0$ is plotted in Figure 3 using the

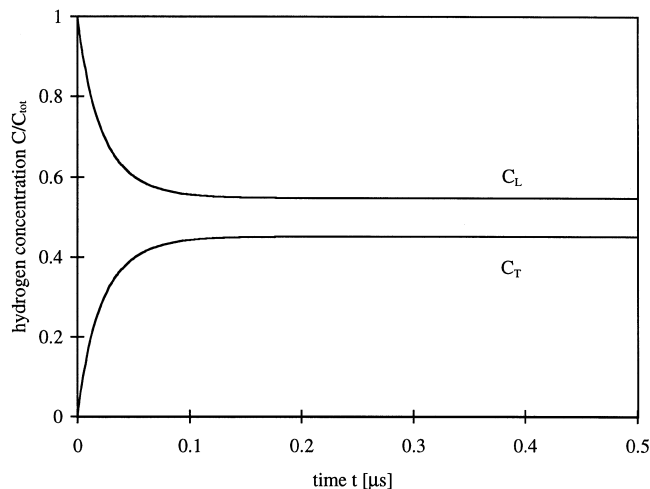Fig. 4—Plot of Eq. [29] using $N_T = 2 \times 10^{25}$ m^{-3}, $\Delta E_T = -27$ kJ/mol, $C_{tot} = 3 \times 10^{25}$ m^{-3}, $N_L = 5.1 \times 10^{29}$ m^{-3}, $T = 293$ K, $E_D = 6.9$ kJ/mol, $\nu = 1 \times 10^{13}$ s^{-1}, and $C_{T_0} = 0$.

Fig. 5—Plot of Eq. [29] with N_T depending on the strain, using $\Delta E_T = -60$ kJ/mol, $C_{tot} = 3 \times 10^{21}$ m^{-3}, $N_L = 5.1 \times 10^{29}$ m^{-3}, $T = 293$ K, $E_D = 6.9$ kJ/mol, and $\nu = 1 \times 10^{13}$ s^{-1}.

data of Kumnick and Johnson, *i.e.*, a low trap density and a high trap binding energy, and in Figure 4 using Oriani's data, *i.e.*, a high trap density and a low trap binding energy. Oriani's data are used for comparison purposes, despite the fact that these data are believed to reflect void traps. The vibration frequency is as usual taken equal to the Debye frequency, *i.e.*, $\approx 10^{13}$ s^{-1}. In the first case, equilibrium is found within 4 ms, and in the second case, it is found within 0.2 μs. It is found that by increasing the trap density, the temperature, or the total hydrogen concentration, the time to reach equilibrium decreases, while changing the trap binding energy has a small influence on the time to reach equilibrium. The trap binding energy influences the ratio of the hydrogen concentrations in the equilibrium situation.

The preceding analytical solution of Eq. [28] corresponds to the situation in which at $t = 0$ a number of trap sites are suddenly present. It is more appropriate to follow the hydrogen distribution in time starting from an equilibrium situation and then changing the trap density. The equilibrium hydrogen concentration in trap sites, $C_{T,eq}$, can be calculated using Eq. [16] with $C_L = C_{tot} - C_T$. This condition results in

$$C_{T,eq}^2 - \left(\frac{N_L}{K_T} + C_{tot} + N_T\right)C_{T,eq} + N_T C_{tot} = 0 \quad [30]$$

This quadratic equation of the hydrogen concentration in trap sites has one correct solution, given by

$$C_{T,eq} = \frac{1}{2}\left(\frac{N_L}{K_T} + C_{tot} + N_T\right.$$
$$\left. - \sqrt{\left(\frac{N_L}{K_T} + C_{tot} + N_T\right)^2 - 4N_T C_{tot}}\right) \quad [31]$$

The other solution is not valid, as it results in a negative hydrogen concentration in lattice sites. Since the trap density N_T is time dependent, Eq. [28] can only be solved numerically. For $N_T = N_T(\varepsilon_p) = N_T(\dot{\varepsilon}_p t)$, Eq. [27] is used. In Figure 5, the hydrogen concentration in trap sites as a function of time is shown for various plastic strain rates in the case of strong trapping. The time axis is normalized by the strain rate and the concentration axis by the equilibrium hydrogen
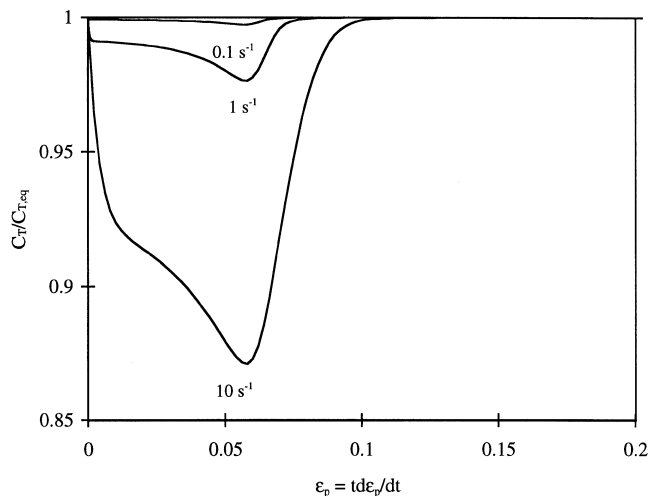
concentration in trap sites. The analysis is started in an equilibrium situation. As trap sites are created, hydrogen will move from lattice sites to trap sites in order to reach equilibrium. When the strain rate is less than 0.1 s^{-1} the filling of trap sites may follow the creation of trap sites. With increasing strain rate, the hydrogen concentration deviates from the equilibrium concentration, as less time becomes available for filling the newly created traps. However, this deviation has a maximum of 0.13 for a strain rate of 10 s^{-1}. At a certain time, the trap creation rate decreases down to zero and the hydrogen concentration in trap sites becomes equal to the equilibrium hydrogen concentration in trap sites. For weak trapping, $\Delta E_T = -27$ kJ/mol, there is no effect of the plastic strain rate for strain rates lower than 10 s^{-1}. In tensile tests, the average strain rate is around 0.1 to 1 s^{-1}. The strain rate in tensile tests conducted in a hydrogen environment is even lower. Thus, local equilibrium can be assumed between the hydrogen concentration in lattice sites and trap sites as long as the strain rate is less than 1 s^{-1}. In the preceding solutions the total hydrogen concentration was constant. When the total hydrogen concentration may increase, as is the case when the hydrogen concentration is prescribed on the boundaries, the time to reach equilibrium will be shorter, since more hydrogen is available.

Now that it has been demonstrated that equilibrium can be assumed, the effect of trapping on the effective diffusion constant will be considered. In Figure 6, the effective diffusion constant is shown according to Eq. [18] using a high binding energy. As the hydrogen concentration in lattice sites increases, the effective diffusion constant also increases from zero up to the lattice diffusion constant. This behavior was observed by Darken and Smith.[3] Thus, the effect of trapping becomes less significant as the hydrogen concentration in lattice sites increases. Ultimately, there will be no effect at all, since all trap sites are filled. When the trap density is increased, the effective diffusion constant becomes the lattice diffusion constant at higher hydrogen concentrations in lattice sites. The same trends can be seen when the trap binding energy is low (Figure 7). However, the effective diffusion constant will now not become zero as is the case
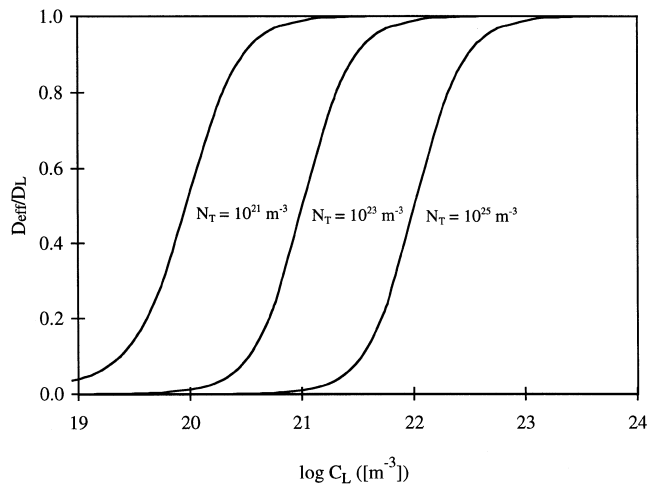
Fig. 6—Ratio D_{eff}/D_L in the case of strong trapping as a function of the hydrogen concentration in lattice sites for various trap densities: $T = 293$ K and $\Delta E_T = -60$ kJ/mol.
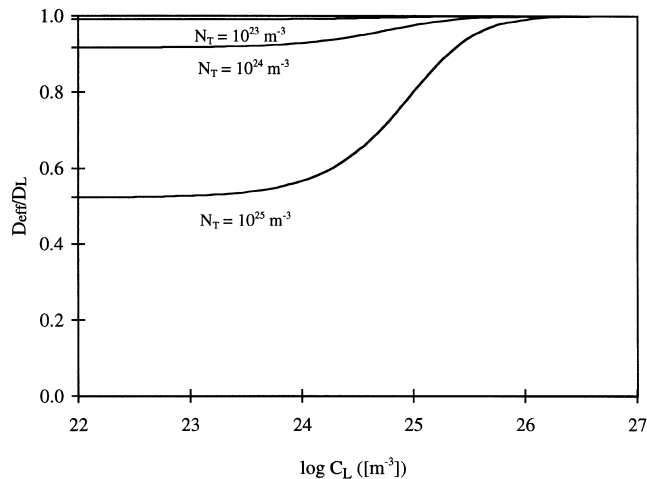

Fig. 7—Ratio D_{eff}/D_L in the case of weak trapping as a function of the hydrogen concentration in lattice sites for various trap densities: $T = 293$ K and $\Delta E_T = -27$ kJ/mol.

Fig. 8—Ratio D_{eff}/D_L in the case of strong trapping ($\Delta E_T = -60$ kJ/mol) as a function of the temperature for various trap densities. The hydrogen concentration in lattice sites is in equilibrium at 0.1 MPa: $C_L = k_0 e^{-\Delta H_S/RT}\sqrt{p}$ with $k_0 = 4.9 \times 10^{23}$ m^{-3}Pa$^{-1/2}$ and $\Delta H_S = 28.6$ kJ/mol.[22]

Fig. 9—Ratio D_{eff}/D_L in the case of weak trapping ($\Delta E_T = -27$ kJ/mol) as a function of the temperature for various trap densities. The hydrogen concentration in lattice sites is in equilibrium at 0.1 MPa: $C_L = k_0 e^{-\Delta H_S/RT}\sqrt{p}$ with $k_0 = 4.9 \times 10^{23}$ m^{-3} Pa$^{-1/2}$ and $\Delta H_S = 28.6$ kJ/mol.[22]

with a high trap binding energy. Moreover, the effective diffusion constant becomes the lattice diffusion constant at higher hydrogen concentrations. Note that in Figure 7 the hydrogen concentrations in lattice sites are so high that the equilibrium pressure will result in the formation of voids in steel. The effect of temperature for various trap densities is shown in Figures 8 and 9 according to Eq. [18] in the temperature range where the trap parameters are valid (Section III). The hydrogen concentration in lattice sites is in equilibrium at a constant hydrogen pressure of 0.1 MPa. By increasing the temperature, the solubility of hydrogen increases, since hydrogen dissolves endothermally. Consequently, the hydrogen concentration in lattice sites increases as the temperature increases. Moreover, the equilibrium situation, Eq. [16], shifts to the hydrogen in lattice sites as the temperature increases, since this reaction is exothermal. Nevertheless, the effect of temperature on the effective diffusion constant is small when trap sites have a high trap binding energy (Figure 8). For weak trapping, the effect of the temperature is much greater (Figure 9).
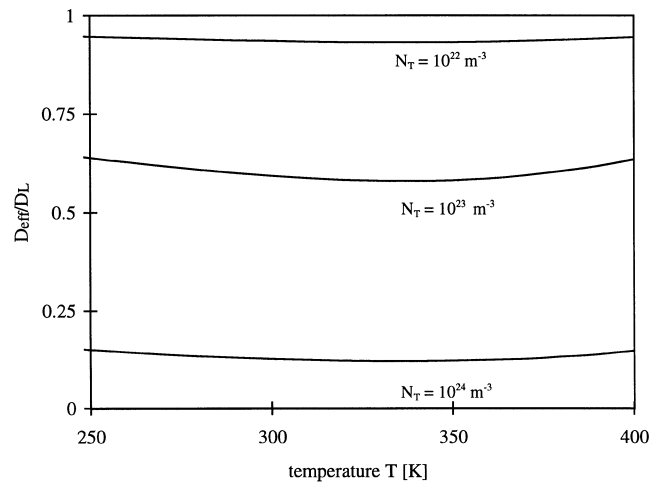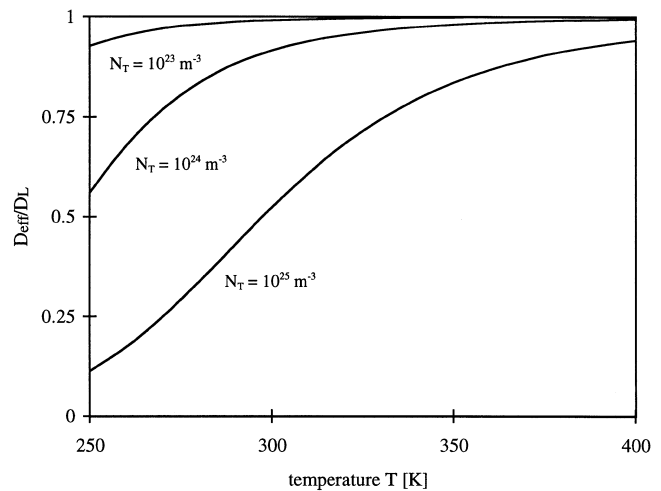
V. CONCLUSIONS

In steel, various traps exist for hydrogen atoms. Trapping enhances the solubility of hydrogen but decreases the diffusivity. Traps are, for example, dislocations and voids. To investigate the effect of traps on the hydrogen distribution in steel, a model for trapping was derived, which resembles the McNabb and Foster model.[9] Assuming equilibrium between the hydrogen in lattice sites and in trap sites, Oriani's trap model[10] is obtained.

Experimental data show an increasing trap density as the amount of plastic deformation increases. These traps can be identified as dislocations and other imperfections created by plastic deformations. Experimentally, it is difficult to determine the number of traps as a function of plastic strain. Only the experimental data of Kumnick and Johnson[26] obtained from pure iron can be used to obtain a relation for the number of traps as a function of equivalent plastic strain.

Modeling of traps in iron and steel can be done on the

basis of local equilibrium between hydrogen in lattice sites and hydrogen in trap sites as long as strain rates are less than $\approx 1 \text{ s}^{-1}$. This situation has the advantage that the rate of the hydrogen concentration in trap sites can be expressed as a function of the hydrogen concentration in lattice sites. The effect of traps on the diffusion depends strongly on the trap binding energy and the trap density with respect to hydrogen concentration in lattice sites.

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