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Review of Hydrogen Diffusion Models for the Analysis of Hydrogen Embrittlement of Materials

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Abstract Hydrogen-assisted fracture (HAF) of metals is the problem of major concern in structural integrity. HAF is rate limited by hydrogen accumulation in fracture sites in metals. Diffusion is a relevant stage of transport that supplies hydrogen to fracture process zones. Addressing the purposes of HAF analysis, modelling of hydrogen diffusion with account for physical-mechanical fields and factors of material microstructure (hydrogen trapping) is revisited. Generalised system of equations of trapping-affected hydrogen diffusion is derived from the kinetics principles. For circumstances, which are relevant to plenty of engineering HAF cases, specialised models of "microstructure informed" stress-strain-assisted hydrogen diffusion in metals are retrieved and collated under the prism of their suitability for HAF analyses.

Keywords Hydrogen assisted fracture, Hydrogen diffusion, Modelling

1. Introduction

Hydrogen is often the key factor in environmentally assisted fracture of metals, as far as it may be present *per se* in the environment or discharge in cracks due to favourable local electrochemistry [1]. Harmful effects of hydrogen on metals ("hydrogen embrittlement") form the long-standing problem of the mechanics of materials. Hydrogen transport to damage sites is ubiquitous component of every hydrogen assisted fracture (HAF) process, which is rate-limited by hydrogen delivery to meet requirements of operating fracture mechanism. A series of kinetic processes involved in HAF have been identified, among which hydrogen diffusion has been substantiated as the governing mode of hydrogen supply to fracture nuclei [1-3]. Continuum modelling of hydrogen diffusion has been focused as the key issue of HAF studies and their engineering applications [1,3-6].

Concerning hydrogen behaviour in metals, important disconformities [2,7,8] were witnessed between experience and the Fick's diffusion laws. Various issues have been pointed out as potential causes of these inconsistencies, and several analyses have been performed culminating in continuum equations of diffusion built up from microscopic or phenomenological considerations [1,4-11]. However, comprehensive accounting for a variety of potentially influencing factors is complicated undertaking, and numerous specialised diffusion models, which attended to different microstrictural features, have been raised [8]. An outlook of hydrogen diffusion modelling for the purposes of HAF analysis is here presented.

2. Background Theory of HAF [1,5]

HAF is considered a result of synergic action of stress, strain and hydrogen amount in material. Fracture event takes place in a locus identified by position vector **x,** when hydrogen concentration C accumulated there over time t reaches the critical level C_{cr} dependent on stress-strain state:

$$C(\mathbf{x},t) = C_{cr}\big(\boldsymbol{\sigma}(\mathbf{x},t), \boldsymbol{\varepsilon}_p(\mathbf{x},t)\big), \tag{1}$$

where $\boldsymbol{\sigma}$ y $\boldsymbol{\varepsilon}_p$ are, respectively, the tensors of stress and plastic strain. Condition of contact between the concentration and the criterial surfaces, $C(\mathbf{x},t)$ and $C_{cr}(\mathbf{x},t)$, respectively, which reads

$$\partial C(\mathbf{x},t)/\partial \mathbf{x} = C_{cr}\left(\boldsymbol{\sigma}(\mathbf{x},t), \boldsymbol{\varepsilon}_p(\mathbf{x},t)\right)/\partial \mathbf{x}, \tag{2}$$

accompanies the fracture criterion (1) to form the system of equations to define the location $\mathbf{x}_{cr}$ and time t_{cr} of HAF event [12]. Hydrogen transport towards fracture sites is dominated by diffusion, which defines the left-hand parts of Eqs. (1) and (2).

It is known that material damage is associated with crystal imperfections, and that they act as hydrogen traps (T-sites) for H atoms where their free energies G_T are less than that for ordinary lattice (L-)sites G_L (Fig. 1a). The ratio at.H/at.Me can there substantially exceed that in L-sites [2,3,4,6], as follows from the equilibrium partition of hydrogen between T- and L-sites [2,4,6,13]

$$\frac{\theta_T}{1-\theta_T} = \frac{\theta_L}{1-\theta_L} K \quad \left(K = e^{\beta E_b}\right), \tag{3}$$

where $\theta_X = C_X/N_X$ is hydrogen saturation of X-type sites (X = L or T) defined by volume concentrations of these sites in metal, N_X, and of hydrogen allocated to them, C_X, so that the total concentration $C = \Sigma C_X$, $E_b = G_L - G_T$ is the binding energy of hydrogen to trap, and $\beta = (RT)^{-1}$ is the Boltzmann's factor in terms of the gas constant R and temperature T. Then, e.g., for steels at usual HAF occurrence conditions $T \approx 300$ K and $\theta_L \sim 10^{-6}$ at utmost [3,6], reported values of E_b, being approximately in the range from 0.25 to 1.5 eV [2,14,15] yield $K \geq \sim 10^4$ and $\theta_T/\theta_L \geq \sim 10^4$.

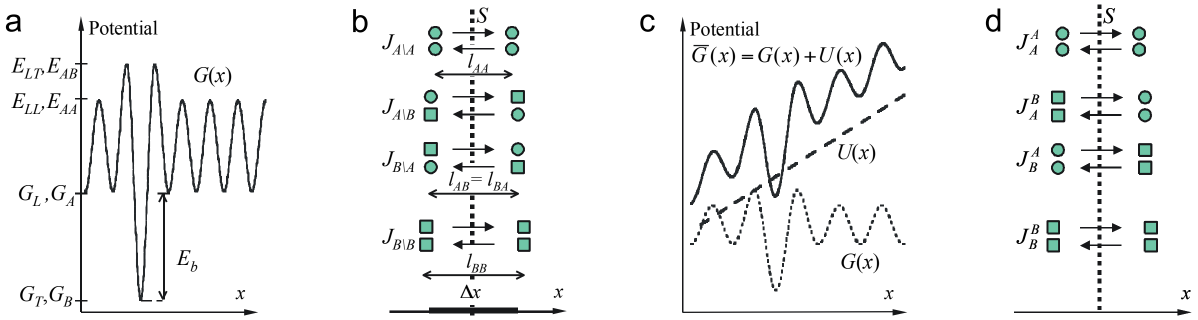

Figure 1. Schematics of (a) potential-position trace $G(x)$ for H in a lattice with different type sites L and T (or A and B); (b) combination of diffusion jumps between sites of different kinds (A – circles, B – quads) to evaluate partial fluxes; (c) distortion of lattice potential $G(x)$ by superposed field U; (d) combination of hops to establish partial balances.

To this end, whenever L/T-partition of hydrogen in volume element $d^3\mathbf{x}$ around a point $\mathbf{x}$ is in equilibrium, all partial concentrations $C_i(\mathbf{x},t)$ ($i = 1,2,\ldots$) are related one to another via Eq. (3), so that all them, including the one corresponding to crystal imperfections responsible for HAF micro-mechanism, are biunivocally related to the total one $C(\mathbf{x},t)$. In this case, continuum description of local HAF event by Eqs. (1)-(2) holds, as well as it may be rewritten explicitly in terms of the responsible partial concentration C_X merely by changing there the variable according to Eq. (3). Otherwise, HAF should be described taking in Eqs. (1)-(2) responsible concentration C_X instead of C, and accounting for L/T-exchange kinetics in analysis of hydrogen transportation.

At any rate, hydrogen delivery to fracture sites proceeds by thermally activated hopping of H atoms between available sites in metal, i.e., by diffusion that turns out to be affected by trapping [2,4,6,7,10,13]. In this context, diffusion modelling is crucial for HAF analysis, prediction and control, as far as, combining with HAF experiments able to reveal fracture initiation time t_{cr} and location $\mathbf{x}_{cr}$, this allows to specify the critical concentration $C_{cr}(\boldsymbol{\sigma},\boldsymbol{\varepsilon}_p)$, i.e., the fracture criterion (1), and to employ this criterion for assessment of fracture time of structures [12,16].

3. Modelling of Hydrogen Diffusion with Trapping: Backgrounds Revisited

Both atomistic and thermodynamic arguments have been used to derive diffusion equations [1,4-11,13,15]. These approaches are not contradictory, but complementary [11] and capable to converge into the same field equations with certain insights about specific factors. Concerning traps, they were incorporated into resulting field equations in some cases via plausible postulating [4,6,7,17], but not from background principles (excepting few attempts with limited offspring [10,18,19] for HAF). In this section, diffusion equations grounding upon diffuser jumps probabilities is revisited.

3.1. Flux Equations

Isothermal diffusion by particles hopping among sites of kinds A and B is considered adopting the techniques used elsewhere [11,13,15,18-20]. Concerning the flux of the species through unit surface S normal to x-axis and situated there at position x, eight possible elementary steps can be grouped in pairs as shown in Fig. 1b, where l_{IJ} (I,J = A or B) are jump distances between specified sites, so that each couple renders the net flux $J_{A\backslash B}$ by forth and back hops between transboundary A and B sites, which are here diffuser releasers and receptors, respectively. The transition frequency Γ_{AB} from A-sites located at x' to B-ones at x'' per unit time depends on attempt frequency Ω_{AB} controlled by particle vibration frequency at given site ω_{0A} and by potential barrier $\Delta E_{AB} = E_{AB} - G_A$, where E_{AB} is the free energy at saddle point of lattice potential $G(x)$ between A and B (Fig. 1a). The frequency of successful hops depends on combined probability Y_B, which merges the probabilities γ_B that encountered receptor sites are the B-type ones and Θ_B that they are empty, that is

$$\Gamma_{AB} = \left[\Omega_{AB}\right]_{x'}\left[Y_B\right]_{x''} \text{ at } \Omega_{AB} = \omega_{0A}^{x}\exp\left(-\beta\Delta E_{AB}\right),\ Y_B = \gamma_B\Theta_B,\ \gamma_B = N_B/N,\ \Theta_B = 1-\theta_B, \qquad (4)$$

where $\omega_{0A}^{x} = \omega_{0A} f_A^{x}$ to reckon up the fraction f_A^{x} of hops that contribute to the flux through S having directions towards it, and $N = \Sigma N_i$ is the volume concentration of all available sites. (Note, that process parameters f_A, l_{AB} and ΔE_{AB}, according to the crystal symmetry, can depend on the x-axis orientation with respect to the lattice, causing this way diffusion anisotropy. They are isotropic, e.g., for interstitial sites in cubic lattice, and can be for “spherical” point-wise defects there, yielding $f_A = f = 1/6$ irrespectively of orientation.) Jump probability to any site is assumed to be not conditioned by that to another.

When some imposed potential field $U(x)$ distorts the lattice relief $G(x)$, Fig. 1c, ΔE_{AB} depends on jump sense, which biases the hopping probabilities. This implies modification of hopping frequency (4) with the factor $\exp(\pm\frac{1}{2}\beta\Delta x\nabla_x U)$, where the lower/upper sign corresponds to jumps pro-/counter-wise the x-direction, $\Delta x = x' - x''$, and ∇_x is the x-component of a gradient.

Reckoning up the hops of particles from A to B sites through control surface S at position x, using Taylor series expansions of involved variables about x with respect to $\varDelta x$ and truncating them at the second term, the net partial transfer by forth and back A→B jumps can be obtained

$$\mathbf{J}_{A\backslash B} = -d_{AB}\left\{Y_B \nabla C_A - C_A\left(\nabla Y_B - \beta Y_B \nabla U\right)\right\}, \tag{5}$$

where the diffusivity $d_{AB} = \varOmega_{AB} l_{AB}^2$ when $\varDelta x = l_{AB}$ is taken. The total diffuser flux vector $\mathbf{J}$ is the sum of the net partial ones $\mathbf{J}_{A\backslash B}$ over all pairs of site kinds A and B, which reads:

$$\mathbf{J} = \sum_{A,B} \mathbf{J}_{A\backslash B} = -\sum_{A,B} d_{AB} Y_B C_A \nabla \ln\left(e^{\beta U} C_A / Y_B\right). \tag{6}$$

This holds for arbitrary number m of site types, e.g., the L-sites and $(m - 1)$ kinds of traps T$_i$ (i=1,…,$m - 1$). Presented flux equations advance those derived elsewhere [18] in that arbitrary occupation degrees θ_i ($i = 1,\ldots,m$) towards saturation are here admitted for all kinds of sites, and that alteration of lattice potential relief by some superposed field $U(x)$ is taken into account.

Description of diffusion in terms of specified partial fluxes can be supplemented with mass-balance relation being now the usual continuity equation:

$$\frac{C(\mathbf{x},t)}{\partial t} = -\nabla \cdot \mathbf{J}\left(= \nabla \cdot \sum_{A,B} d_{AB} Y_B \left[\nabla C_A - C_A \nabla \ln\left(e^{-\beta U} Y_B\right)\right]\right). \tag{7}$$

3.2. Mass Balance

In contrast to the one-level system (single kind of sites), Eq. (7) does not accomplish description of diffusion in terms of concentrations C_i ($i = 1,\ldots,m$) for the m-level case ($m > 1$) where a system of m balance equations must be built up. This requires to combine the same diffusion steps as shown in Fig. 2d to gather all forth and back jumps across S that fill/vacate the sites of the sort A in a region $\varDelta x$ around a point x by surmounting saddle points at $x \pm \varDelta x/2$. Desired equations are derived here following the random walk theory and its continuum implementation [19,20].

Considering two-level system and addressing the net species supply into A-sites in a domain $\varDelta x \ni x$ by overcoming saddle point at $x - \varDelta x/2$ from all outer A- and B-sites, involved diffusion steps include the net income flux $J_{A\backslash A}$, and the resulting B⇆A-exchange flux, which is as follows:

$$J_A^B = \left\{e^{-\frac{1}{2}\beta \varDelta x \nabla_x U}\left[C_B l_{AB} \varOmega_{BA}\right]_{x-\varDelta x}\left[Y_A\right]_x - e^{\frac{1}{2}\beta \varDelta x \nabla_x U}\left[C_A l_{AB} \varOmega_{AB}\right]_x \left[Y_B\right]_{x-\varDelta x}\right\}. \tag{8}$$

The net exit from A-sites in a domain $\varDelta x$ towards all sites beyond $x + \varDelta x/2$ is defined similarly. Then, balancing transitions at both extremes of $\varDelta x$, using power series expansions and disregarding higher order terms with $\varDelta x$, mass balance for the species dwelling in A-sites can be derived. However, calculations in general terms are overly long and tedious, so that now we content ourselves with particular case when the sites characteristics are isotropic and uniform, i.e., jump frequencies $\varOmega_{\ldots}$ and lengths $l_{\ldots}$ are constant, for which the following is deduced:

$$\frac{\partial C_A}{\partial t} = d_{AA}\nabla\cdot\left[Y_A C_A \nabla \ln\left(e^{\beta U} C_A / Y_A\right)\right] + d_{BA} Y_A \nabla\cdot\left[C_B \nabla \ln\left(e^{\beta U} C_B\right)\right] - d_{AB} C_A\left(\nabla^2 Y_B - \beta \nabla Y_B \cdot \nabla U\right) + \\ + \left[k_{BA} C_B\left(N_A - C_A\right) - k_{AB} C_A\left(N_B - C_B\right)\right], \tag{9}$$

where $k_{AB} = f^{-1}\Omega_{AB} / N = d_{AB} /(fNl_{AB}^2)$. Similarly, balance for a diffuser dwelling in B-sites can be derived rendering the result that differs from Eq. (9) by permutation of the site labels A and B. This description is extensible for arbitrary number *m* of site types by taking in the right-hand part of Eq. (9) the sum over all site kinds from a set {B;B≠A}. The last term in brackets in Eq. (9) represents transitions between the nearest neighbour sites of different types in a volume $d^3\mathbf{x}$ around a point **x**.

This way, the system of nonlinear differential equations (9) is derived for partial concentrations C_i ($i=A,B,\ldots$ or $1,\ldots,m$). Balance in terms of total concentration $C = \Sigma C_i$ can be obtained summing up the equations of the system (9) over site kinds totality {A}. After all, the result coincides with Eq. (7). One may notice here the similarity with equations built up by Leblond-Dubois [10] following distinct approach based on construction of Boltzmann type transport equations. Present derivation advances the previous one [19] with respect to the sites saturability, their concentrations non-uniformity, and the contribution of a field *U*.

3.3. Equilibrium

The chemical potential μ_A of hydrogen residing in metal in sites of whichever type A is [13,15]

$$\mu_A(\theta_A) = \overline{G}_A + RT \ln\left(\theta_A/(1-\theta_A)\right), \tag{10}$$

where $\overline{G}_A$ is the free energy at the site with account for imposed potential *U*, $\overline{G}_A = G_A + U$ (Fig, 1c). At equilibrium, μ_A must be the same throughout a solid and in equilibrium with the input fugacity of hydrogen imposed by an environment, e.g., H_2 gas at pressure *p* that has chemical potential of hydrogen μ_p = const. Then, for all sites at equilibrium $\mu_A = \mu_p$, which yields

$$\left[\frac{\theta_A}{1-\theta_A}\right]_{eq} = e^{\beta\left(\mu_p - \overline{G}_A\right)} = e^{\beta\left[\mu_p - (G_A + U)\right]} \text{ or } \left[\frac{C_A}{\left(N_A - C_A\right)S_A}\right]_{eq} = \frac{1}{NS_A}\left[\frac{C_A}{Y_A}\right]_{eq} = e^{\beta\mu_p}, \tag{11}$$

where $S_A = \exp\left(-\beta\overline{G}_A\right)$ is the solubility factor. From the kinetics point of view, the numbers of forward and backward jumps between the nearest neighbour sites of distinct types in equilibrium are equal to each other in a volume $d^3\mathbf{x}$ around a point **x**. This is expressed by detailed balance relation [20] being nothing else than equilibrium partition Eq. (3), which gets now more forms:

$$C_A \Omega_{AB} Y_B = C_B \Omega_{BA} Y_A \text{ or } C_A d_{AB} Y_B = C_B d_{BA} Y_A \text{ or } \theta_B\left(1-\theta_A\right) = \theta_A\left(1-\theta_B\right)\exp\left[\beta\left(G_A - G_B\right)\right]. \tag{12}$$

One can verify that fluxes $J_{I\backslash I}$ (I = A,B,…) are nil at equilibrium by virtue of Eq. (11), and that the sum $J_{A\backslash B} + J_{B\backslash A}$, A ≠ B, does the same with the aid of detailed balance (12). So, the total flux (6) is nil at equilibrium. As well, Eq. (9) at equilibrium yields $\partial C_A/\partial t = 0$ for all A-s by virtue of Eqs. (11) and (12), being the last term in brackets in Eq. (9) a paraphrase of the detailed balance (12).

4. Special Field Equations and Retrieval of the Known Models

4.1. One-level System

In the case of diffusion over identical sites, say L-sites, Eqs. (5), (6), and (9) in the absence of any potential field $U(\mathbf{x})$ render Fick's laws for isothermal diffusion with lattice diffusivity $D_L = d_{LL} = \Omega_{LL} l_{LL}^2$ [11,13,15]. As well, they lead to the equations of uphill diffusion under imposed potential U, e.g., due to lattice dilatation under hydrostatic stress σ, when $U = - V_H \beta \sigma$, V_H is the partial molar volume of H in metal, as they are known both for dilute solutions at $\theta << 1$ [1,2,11,21] (hereafter the site type labelling is skipped wherever convenient) and for arbitrary degree of saturation $\theta = C/N$ [22]. For the latter more general case, corresponding reduction of Eq. (5) reads:

$$\mathbf{J} = -D_L \left[\nabla C + \beta C (1 - \theta) \nabla U \right]. \tag{13}$$

The balance equation is established then by common continuity relation, cf. Eq. (7).

4.2. Multi-level System, Implicit Description of Trapping: The Variable Solubility Model

Since the origin of potential $U(\mathbf{x})$ was not relevant in derivations, it can incorporate the intrinsic own lattice potential relief with variable depths of wells at interstitial sites, which yields variable solubility $S(\mathbf{x})$ according to the well bottom $\overline{G}(\mathbf{x})$at location $\mathbf{x}$. This can be complemented with variable saddle point energy $E(\mathbf{x})$. Then, skipping site labels that become irrelevant, both Eqs. (5) and (6) can be rewritten in terms of the non-uniform both solubility and diffusivity as follows:

$$\mathbf{J} = -D(1 - \theta) C \nabla \ln \left(\frac{C}{(1 - \theta) S} \right) = -D (1 - \theta)^2 S \nabla \left(\frac{C}{(1 - \theta) S} \right), \tag{14}$$

where (cf. expressions (4), (5) and (11))

$$D(\mathbf{x}) = \omega_0(\mathbf{x}) \exp\left[-\beta \left(E(\mathbf{x}) - \overline{G}(\mathbf{x}) \right) \right] l^2 \quad \text{and} \quad S(\mathbf{x}) = \exp\left(-\beta \overline{G}(\mathbf{x}) \right). \tag{15}$$

With these flux equations, the mass balance is established by usual continuity relation, cf. Eq. (7).

This mode to describe diffusion, named [10] the non-uniform solubility model, deals with a system where neither interstitial positions nor saddle points are all identical, and so, it treats in effect a multilevel system. Though, specific sites are here indiscernible within each elementary volume $d^3\mathbf{x}$ around a point $\mathbf{x}$, where the values $\overline{G}(\mathbf{x})$ and $E(\mathbf{x})$ can be interpreted as effective averages over different sites with account for their amounts in regions, which are small in macroscopic sense, but large enough in microscopic one. Such averaging counts implicitly on equilibrium partition of a diffuser between sites of different kinds in $d^3\mathbf{x}$ disregarding traps filling/emptying kinetics.

Anyhow, excepting the term $(1 - \theta)$ that accounts for sites saturability, these equations render fairly the same as established for dilute solutions ($\theta << 1$) elsewhere booth within the frameworks of microscopic kinetics [10] and macroscopic thermodynamics [1,5,9]. To this end, built up upon phenomenological account of measurable variables, but not relying on specification of atomic mechanisms, the latter approach extends the suitability of hydrogen diffusion description by means of Eq. (14) over much wider range of circumstances, such as non-uniformity of alloy composition, transient external fields (e.g., mechanical stresses), simultaneous (e.g., strain induced) phase transformations, cold working, non-isothermal diffusion (Soret effect), etc. [1,5,9,11]. Till now, these factors could not be incorporated satisfactorily in diffusion models via kinetics considerations. From another side, diffusion modelling accounting for the kinetics of H transitions between different microstructural entities ("sites") is not feasible on the way of thermodynamics.

4.3. Multi-level System, Explicit Description of Trapping

When conditions of system equilibrium are not fulfilled, it evolves to equilibrium. Various transitions can be discerned there. One of them is rather long-distance transfer that drives to global equilibrium via fluxes represented by respective equations of the previous section. Besides, localised processes of H exchange between the nearest sites of different kinds are there involved, too, which tend to local equilibrium expressed by the detailed balance (12). Corresponding process rates, which may depend on both intrinsic (e.g., vibration frequency and jump length) and extrinsic (such as diffusion distance) factors, may be so distinct, that in the time scale of interest (e.g., for membrane permeation or for hydrogen delivery to fracture locations) some processes may have attained equilibrium while others have not yet.

4.3.1. Diffusion under Traps-Lattice Equilibrium

One possibility of the mentioned partial equilibrium is when detailed balance is quickly reached and maintained during diffusion, e.g., when relatively long diffusion distances x_{cr} with corresponding times $t \sim x_{cr}^2/(4D)$ [23] are of interest. Suggested by Oriani [17] to be kept during diffusion, the hypothesis of local equilibrium assumes that detailed balance (12) holds for all nearest neighbour A and B sites, so that partial balance (9) in the case of multiple B-sites yields the following:

$$\frac{\partial C_A}{\partial t} = d_{AA}\nabla\cdot\left[Y_A C_A \nabla \ln\left(\left(e^{\beta U} C_A / Y_A\right)\right)\right] + \sum_B d_{AB} \frac{C_A}{C_B} \nabla\cdot\left[Y_B C_B \nabla \ln\left(\left(e^{\beta U} C_B / Y_B\right)\right)\right]. \tag{16}$$

The global balance (7) for two-level system (for multi-level one the sum is to be taken over all site types) under local equilibrium is reduced to the next:

$$\frac{\partial C}{\partial t} \equiv \frac{\partial\left(C_A + C_B\right)}{\partial t} = \nabla\cdot\left[\left(d_{AA} Y_A C_A + 2 d_{AB} Y_B C_A + d_{BB} Y_B C_B\right)\nabla \ln\left(\frac{C_A}{S_A Y_A}\right)\right]. \tag{17}$$

Accompanying Eq. (17) with the detailed balance (12), which may be solved with respect to C_B,

$$C_B = \frac{N_B C_A K / N_A}{1 + C_A (K-1)/N_A} \quad \left(K = e^{\beta E_b},\ E_b = G_A - G_B\right), \tag{18}$$

the system of partial-differential equations of diffusion with trapping converts into the system of one partial-differential and a series of algebraic equations (17) and (18) with respect to partial concentrations C_I (I = A,B,…). This system transforms into the sole differential equation (17) with respect to C_A by substitution there C_B according to Eq. (18).

It can be verified that, labelling A ≡ L to be lattice sites and B ≡ T traps, at $\theta_L << 1$ and $\gamma_T << \gamma_L \approx 1$, and so, $Y_T << 1$, which are usually met in HAF of engineering alloys [6], and $d_{BX}/d_{AX} \sim \exp(-\beta E_b) <$ $\sim 10^{-4}$ at $E_b > 0.2$ eV [2,14,15] for X = L or T, Eqs. (17)-(18) convert into the equation of trap-assisted diffusion [4] as implementation of Oriani's [17] equilibrium hypothesis:

$$\left(1+\frac{\partial C_T}{\partial C_L}\right)\frac{\partial C_L}{\partial t}=\nabla\cdot\left[D_L\left(\nabla C_L-C_L\nabla\ln S_L\right)\right] \text{ at } C_T=C_L K N_T/\left(N_L+KC_L\right). \tag{19}$$

4.3.2. Diffusion with Account for Lattice/Trap Exchange Kinetics

The system of equations (9), which describes hydrogen diffusion affected by traps in rather general terms, is tough to solve. Taking advantage of circumstances usually met in HAF, it can be reduced to more suitable forms. Namely, $\theta_L << 1$, $\gamma_T << \gamma_L \approx 1$, and thus $Y_T << Y_L \approx 1$, as well as $d_{TX}/d_{LX} << 1$ (X = T and L) usually hold in HAF, but the matter of local L/T-equilibrium is not ensured *a priori*. Then, taken for granted that T→T jumps are fairly improbable, the total flux **J**, Eq. (6), and the partial balance for C_T, Eq. (9), can be assessed as follows:

$$\mathbf{J}=\mathbf{J}_{L\backslash L}\left\{1+\frac{d_{TT}}{d_{LL}}\left[Y_T O\left(\frac{|\nabla C_T|}{|\nabla C_L|}\right)+O\left(\frac{C_T}{C_L}\right)\right]+\frac{d_{LT}}{d_{LL}}\left[Y_T O(1)+o(C_L)\right]+\frac{d_{TL}}{d_{LL}}O\left(\frac{|\nabla C_T|}{|\nabla C_L|}\right)\right\}, \tag{20}$$

$$\frac{\partial C_T}{\partial t}=\frac{d_{LT}}{d_{LL}}Y_T\nabla\cdot\mathbf{J}_{L\backslash L}+\frac{1}{fl^2}\left(d_{LT}Y_T C_L-d_{TL}C_T\right). \tag{21}$$

Accordingly, if neither ratios of partial concentrations C_T to C_L and their gradients nor the divergence of lattice-hopping flux $\mathbf{J}_{L\backslash L}$ are too large to forbid the disregard of terms with $d_{TX}/d_{LX} << 1$ and $Y_T << 1$ in Eqs. (20) and (21), then Eqs. (17)-(18) convert into the system of partial- and ordinary-differential equations postulated by McNabb-Foster [7], which is now extended for variable solubility S_L:

$$\frac{\partial}{\partial t}\left(C_L+C_T\right)=\nabla\cdot\left[D_L\left(\nabla C_L-C_L\nabla\ln S_L\right)\right];\ \frac{dC_T}{dt}=\left(k_{LT}/N\right)\left(N_T-C_T\right)C_L-k_{TL}C_T. \tag{22}$$

Obviously, these specialised equations of trap-affected diffusion are additively extensible for the case of multiple trap kinds T_i (i = 1,…) as the antecedent general Eqs. (7) and (9) do.

The system of equations (22) with respect to a number of concentrations C_i (i = 1,…,m) may complicate numerical simulations of diffusion making corresponding discrete approximations of the boundary-value problems oversized. However, the second of Eqs. (22) has the closed-form solution

$$C_T=\exp\left(-\int_0^t P_T(\zeta)d\zeta\right)\left[\int_0^t\left(\exp\left(\int_0^\xi P_T(\zeta)d\zeta\right)Q(\xi)\right)d\xi+C_T^0\right], \tag{23}$$

where $P_T(t) = k_{TL} + k_{LT}C_L(t)/N$, $Q(t) = k_{LT}N_TC_L(t)/N$, and $C_T^0 = C_T\big|_{t=0}$ is the initial condition. Substitution of the expression (23) into the first of Eqs. (22) reduces the problem to the sole integro-differential-equation with respect to C_L. Its computational implementation, e.g., via available finite element routines [4-6], requires modification only of calculation of concentration capacity matrices.

5. Summation: Suitability of Models for HAF Analysis

The system of equations of diffusion with trapping, which is derived here from kinetics principles, provides generalisation of pertinent previously suggested models, as well as it retrieves special ones typically either raised on the thermodynamics bases or postulated partially from microscopic arguments. This way, simpler equations of specialised models gain clarification of involved approximations and, respectively, of the requisites of their applicability. This allows reasoned pondering of their advantages and limitations to select optimal models for HAF-case analyses.

Demonstrated relation of general kinetics-based equations of trapping-affected diffusion with thermodynamics-grounded variable-solubility model visualises the incorporation of traps in this latter. However, its solid thermodynamics foundation makes it capable of accounting of wider variety of factors that influence hydrogen diffusion in metals, but are not amenable to incorporation in kinetics analysis. These are phase transformations under loading (e.g., $\gamma \rightarrow \alpha$ transition in steels), variable alloy composition, thermodiffusion, and all microstructural features, such as inclusions, grain boundaries or dislocations, which, strictly speaking, can hardly be treated as point-wise lattice irregularities that the majority of kinetics-based models deal with. With variable solubility model, numerous factors of H behaviour in metals can be incorporated in HAF analyses and simulations through macro-level determined, i.e., apparent or measurable, diffusivities and solubilities dependent on microstructure, cold working, etc. It is the advantage of this model in addition to its linearity, which substantially streamlines computations. However, the prominent deficiency of this model is inability to describe dissymmetry between hydrogenation and dehydrogenation kinetics. Meanwhile, the significance of this fault for HAF analysis seems to be case-dependent, e.g., it may be irrelevant whenever only monotonic hydrogenation occurs, but can be substantial under load or hydrogenation cycling. As well, this model discounts the lattice/trap exchange kinetics, which may be desired in particular HAF analyses. The importance of these deficiencies is also case-dependent, as far as HAF involves definite diffusion distances towards fracture sites x_{cr}, and corresponding diffusion times $t_{dif} \sim x_{cr}^2/(4D)$, which may be short or long compared with the characteristic time of approaching trap-lattice equilibrium $t_{T\text{-}L}^{-1} \sim k_{TL} + k_{LT}C_L/N$ according to the solution (23). E.g., the role of trap-filling kinetics may be noticeable for hydrogen assisted crack growth in high-strength or brittle materials, where sub-micrometer diffusion distances of the order of crack-tip opening displacement are involved [1,5], and it can be irrelevant otherwise.

Concerning diffusion models that account for trapping explicitly, they lack of the majority of attractions of the preceding one, as far as they cannot account for a series of cited diffusion-influencing factors. In return, they describe hydrogenation-degassing dissymmetry and a series of other trap-related abnormalities of diffusion. However, this improvement raises computational expenses of managing non-linear partial-differential or integro-differential equations. These models count on micro-level determined mobility, binding and kinetics rates characteristics, which complicates their implementation in engineering. Regarding suitability for HAF description of explicit models of trapping-affected diffusion with or without lattice-trap equilibrium, this is basically the matter of transportation distances and corresponding times relevant to HAF process, so that whenever they are short, account for lattice-trap exchange kinetics may be advisable. However, one ought to be aware that large concentration gradients that can be met, e.g., in the proximity of hydrogen entry surface at short diffusion times can invalidate the requisites of smallness of the ratios of partial concentrations and their gradients, which justify the reduction of general system of diffusion equations (9) to the special case (22) of McNabb-Foster.

At any rate, recognising that trap populations may be affected by plastic deformation ε_p, $N_T = N_T(\varepsilon_p)$, and that the most relevant field for HAF is the stress field, $U \propto \sigma$, all considered equations describe the process of stress-strain assisted diffusion [1,4-6,16]. This way, present study gives an outlook of "microstructure informed" models of stress-strain affected hydrogen diffusion able to account for various physical variables relevant to HAF.

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