

Modeling of the processes of hydrogen absorption and hydrogen cracking of steels

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Abstract

Quantitative physical-mechanical models of hydrogen action on metal at different mechanisms of its storing were suggested. The first mechanism is related to atomic hydrogen diffusion and storing at the interface of two metals accompanied by cracklike defect formation and growth. The crack grows under the action of hydrogen pressure on its surfaces and the crack speed is dependent on the stress intensity factor. The hydrogen pressure and stress intensity factor are self-consistently determined on the basis of solving diffusion and elasticity problems accounting for the crack growth.

The second mechanism models the storing of hydrogen in bulk on dislocation defects of the metal crystalline lattice which represent energetic traps. The hydrogen storing process is accompanied by volume deformation of metal and generation of inner stresses. A kinetic model of inner stresses variation at hydrogen storing versus the concentration of coupled hydrogen in the crystalline lattice is suggested in the paper.

1. Introduction

Problems of hydrogen action on mechanical behavior of steels are very actual (see, e.g. [1-5]). The process of hydrogen atoms diffusion in metal is the limiting one for nucleation and growth of cracks and crack-like defects [1-7]. Hydrogen accumulation leads to the increasing of hydrogen pressure in micropores and microcracks and other hydrogen sinks. The hydrogen pressure serves as a cause of defect growth and metal embrittlement. The process of hydrogen embrittlement because of the “pressure mechanism” was modeled, in particular in [2, 8-15].

The growth of a single hydrogen crack was modeled in [10, 11] while formation of ordered systems of hydrogen cracks (structures of fracture) in dependence on inner hydrogen pressure and stress field caused by external mechanical loading was modeled in [12-15].

In the given paper two problems were considered.

In the first problem the process of atomic hydrogen diffusion into a crack at the interface between the cladding layer and base metal is modeled with the emphasis

to the nonsteady (transient) regimes. This problem is related to evaluation of the cladding layer longevity in the reaction vessels for oil refining.

In the second problem the process of atomic hydrogen diffusion and its accumulation in metal (steel) leading to metal embrittlement was modeled. This problem is related to the behavior of apparatus and technological pipeline operating in conditions of hydrogen absorption. The known NACE hydrogen absorption criterion implies measuring the hydrogen outflow at the outer surface. The model suggested in the given paper enables to evaluate the amount of coupled hydrogen in metal on the basis of the data of these measurements. Then the embrittlement degree and the residual lifetime of the component can be evaluated. The last two questions require a special analysis which is not performed here.

2. Modeling of the processes of hydrogen accumulation at the interface of two metals

The 2D problem on atomic hydrogen diffusion into the crack of length $L = 2\ell$ at the depth H on the interface of the elastic layer of thickness H and rigid halfspace is considered. It is assumed that hydrogen diffusion through the interface outside of the crack is blocked. Hydrogen pressure inside the crack will be determined by the model of an ideal gas

$$P = C_* kT \quad (1)$$

where P is the hydrogen pressure, C_* is the hydrogen concentration inside the crack, T is temperature of metal and gas, k is the Boltzmann constant.

Denote by $V(t) = d\ell/dt$ the velocity of the crack. Assume that the equation which determines the interrelation of the crack velocity and the stress intensity factor K_I has the following form

$$V(t) = V_0 (K_I/K_C)^\alpha, K_I \leq K_C ; \quad V(t) = V_0, K_I \geq K_C \quad (2)$$

where K_C is the critical stress intensity factor, V_0 and α are constants.

Hence, to describe the interface crack growth one needs to solve the self-consistent problem on atomic hydrogen diffusion in the metal and crack and problem on deformation of the material containing the crack. The concentration of atomic hydrogen inside the crack is determined by its diffusion from the outer material surface into the crack. The diffusion equations in 2D case have the following form in the Cartesian coordinate system x_1x_2 (axis x_2 is directed into the bulk of material from the outer surface)

$$\frac{\partial C}{\partial t} = -\frac{\partial q_i}{\partial x_i}; \quad q_t = -D \frac{\partial C}{\partial x_i} \quad (3)$$

where C is the atomic hydrogen concentration in metal, D is the diffusion coefficient, q_i are the hydrogen flux components ($i = 1,2$). The boundary conditions at the outer surface and at the interface can be written as follows

$$\begin{aligned} C(x_1, H, t) &= C_0, & |x_1| \leq \infty, x_2 &= 0 \\ C(x_1, H, t) &= C_{**}(t), & |x_1| \leq \ell, x_2 &= H \\ q_2(x_1, H, t) &= 0, & |x_1| \geq 1, x_2 &= H \end{aligned} \quad (4)$$

where C_0 is the gas concentration at the outer surface C_{**} is the atomic hydrogen concentration at the microcrack surface. Hydrogen concentration inside the crack is self-consistently determined by the following nonlinear equation

$$\int_{-\ell}^{\ell} \frac{\partial}{\partial x_2} q_2(x_1, H, t) dx_1 = L(t) \frac{\partial C}{\partial t} \quad (5)$$

One can determine the hydrogen pressure inside the crack according to Eq. (1) if the diffusion problem (Eqs (3), (4)) was solved and the hydrogen concentration inside the crack was determined too.

Hence, the system of equations and boundary conditions, Eqs (1)-(5) allows to calculate the hydrogen pressure inside the crack as a function of its length and time. The given coupled system of equations of fracture mechanics and diffusion was solved numerically accounting for variations of geometry of diffusion and deformation regions. The numerical method suggested in [16, 17] for solving the diffusion equation in 1D-regions with the moving boundaries was used. Time dependences of the gas concentration and crack length during the diffusion process are given in Fig. 1 for the following parameters of the problem; $\alpha = 2$, $C_{**} = 0$. The dependences show that the crack speed is low at the initial stage of hydrogen accumulation inside the defect. The crack length increases two times during 50% of the whole time of the crack growth, while the rate of hydrogen accumulation is the highest during the same period. The residual 50% of the crack growth time are characterized by essential reduction of the hydrogen accumulation rate and three times increasing the crack length.

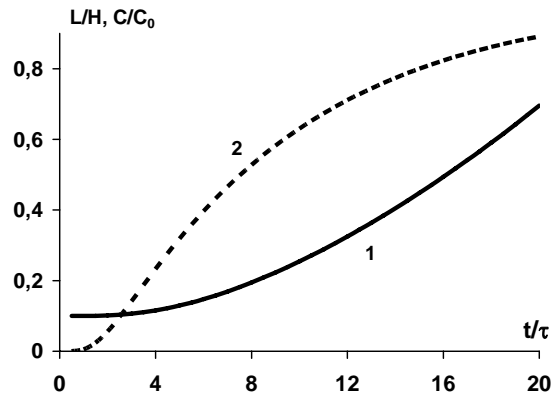


Fig. 1. The time dependences of the crack length (curve 1) and gas concentration (curve 2) ($\tau = H^2/D$ is the characteristic time)

3. Modeling of the processes of steel hydrogen absorption and embrittlement. An analysis of the processes of steel embrittlement

Hydrogen-metal interaction consists of several stages: adsorption, dissolving diffusion, bulk-surface transition, desorption. Solubility is the most important characteristic which adjusts hydrogen accumulation in metal and its embrittlement.

The dependence of hydrogen solubility in metal on the temperature and pressure can be described by the following formula [1]

$$S = K_0 \exp(-\Delta H / 2RT) \cdot \sqrt{P_{H_2}} \quad (6)$$

where S is the hydrogen solubility; T is temperature, K ; ΔH is dissolving heat; R is the universal gas constant, P_{H_2} is the partial hydrogen pressure in the gas at the outer metal surface. The values of the constant K_0 and ΔH are given in [1] for some stainless steels. The embrittlement process is determined by the hydrogen concentration in the traps. In particular, dislocations belong to the essential traps for the deformed material. The dislocations as the hydrogen traps in alloy X-750 were considered in [18, 19]. The traps density per unit of volume was evaluated by the following formula within the assumption that each dislocation can serve as a trap per one atom in an atomic plane

$$N_T = \sqrt{2} \cdot \rho / a \quad (7)$$

where ρ is the dislocation density, a is the lattice parameter. This assumption was confirmed by the experimental study described in [20]. In this paper it was obtained the better fitting to experimental data in case when the trap radius was equal to 1-2 lattice parameter values. Eq. (7) can be used for evaluation of the

traps density if the dislocation density is known in dependence of the plastic deformation level [19]. A model for computing hydrogen diffusion and accumulation in traps accounting for the stress-deformation state of the material is presented in the next section.

4. Modeling of the processes of hydrogen diffusion and accumulation in metal

Let us formulate a model and the basic equation which describe the processes of hydrogen diffusion and accumulation in the traps in metal. According to papers [20, 21] assume that hydrogen can be located in an internode or trap. These both distributions are equilibrium which is determined by the relation [22, 23]

$$\frac{\theta_T}{\theta_T - 1} = \frac{\theta_L}{\theta_L - 1} \cdot K, \quad K = \exp(W_B / RT) \quad (8)$$

where θ_L is the portion of places in the internode and θ_T is the portion of places in the trap which can be occupied by hydrogen atoms; K is constant of equilibrium; W_B is the hydrogen bonding energy in the trap. The hydrogen concentration in the unit of metal volume in the traps, C_T , is determined by the following expression

$$C_T = \theta_T \cdot \alpha \cdot N_T \quad (9)$$

where α is the amount of places in the trap; N_T is the traps density in metal (the amount of traps in the unit volume) which is the function of the plastic deformation value, $N_T = N_T(\varepsilon_p)$. The hydrogen concentration in the internodes, C_L , is determined by the following expression

$$C_L = \theta_L \cdot \beta \cdot N_L \quad (10)$$

where β is the amount of places in the internode; N_L is the amount of atoms in the unit of volume of crystalline lattice. If the amount of places in the traps in the unit of volume αN_T is small as compared to the amount of internode places, βN_L , then one can write in this case (11)

$$N_L = N_A / V_M \quad (11)$$

where $N_A = 6,0221 \cdot 10^{23}$ atoms/mole is the Avogadro number; V_M is the molar volume of crystalline lattice (measured in the units of volume per mole). Using Eqs (8)-(11) we obtained the expression for the hydrogen concentration in traps

$$C_T = \frac{C_L \cdot K}{N_L \cdot \beta + C_L (K - 1)} \cdot \alpha N_T \quad (12)$$

The hydrogen concentration C in metal is determined by the sum of hydrogen concentration in internodes and traps $C=C_L+C_T$. The concentration of the diffusing hydrogen C_L in arbitrary point of metal (x_1, x_2, x_3) is determined by the following diffusion equation

$$\frac{\partial C_L}{\partial t} + \nabla_i q_i = F_H(x_1, x_2, x_3, t), \quad (13)$$

where $\nabla_i q_i \equiv \nabla_1 q_1 + \nabla_2 q_2 + \nabla_3 q_3$ (here and later on summation with respect to the repeating indexes is implied), $C_L(x_1, x_2, x_3, t)$ is the concentration of diffusing hydrogen, $\nabla_i = \partial/\partial x_i$; q_i is the i -component of the diffusion flux, $F_H(x_1, x_2, x_3, t)$ is the sink function describing the hydrogen absorption by the traps. Generally the sink function depends on the hydrogen concentrations in internodes and traps as well as on the characteristic time of hydrogen transition from the internode space into the trap. Following the model suggested in (23) we assume that the transition time is essentially smaller than the characteristic diffusion time. In this case $F_H(x_1, x_2, x_3, t) = -\partial C_T/\partial t$ and by incorporating Eq. (12) we obtain

$$F_H(x_1, x_2, x_3, t) = -\frac{\partial}{\partial t} \left(\frac{C_L \cdot K}{N_L \cdot \beta + C_L (K-1)} \cdot \alpha N_T \right)$$

The flux, $q_i(x_1, x_2, x_3, t)$, equals in the case of the combined action of the concentration gradient and mechanical stresses

$$q_i = D \left(-\nabla_i C_L + \frac{C_L \Delta v}{kT} \frac{\partial \sigma}{\partial x_i} \right) \quad (14)$$

where D is the coefficient of hydrogen diffusion in metal, $\sigma(x_1, x_2, x_3, t) = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$ is the spherical part of the stress tensor σ_{ij} ; Δv is the elastic volume deformation caused by the volume extension at intruding the hydrogen atom in the internode space.

The boundary and initial conditions have the following form

$$\begin{aligned} C(x_1, x_2, x_3, 0) &= C_0(x_1, x_2, x_3, 0) & (15) \\ C(x_1, x_2, x_3, t) &= S(x_1, x_2, x_3, t), \quad (x_1, x_2, x_3) \in \Gamma_i \\ C(x_1, x_2, x_3, t) &= 0, \quad (x_1, x_2, x_3) \in \Gamma_e \end{aligned}$$

where S is the hydrogen solubility at the inner surface Γ_i determined by Eq. (6); C_0 is the initial hydrogen concentration in metal Γ_e ; hydrogen is absent at the outer surface. The hydrogen distribution in the internodes and traps in the initial moment of time at the inner surface is determined by incorporating Eq. (12). Hence, the system of equations and the given initial and boundary conditions, Eqs (12)-(15), determines the process of hydrogen absorption in metal. The given

system of equations can be solved for the given field of mechanical stresses. This generally implies solving the problem on diffusion and deformation in the self-consistent statement accounting for the equations of elastoplastic deformation of metal, since the hydrogen absorption process is accompanied by an additional metal deformation caused by the hydrogen absorption process.

5. Numerical modeling of the hydrogen absorption processes

The calculations were performed for the following values of the parameters: $T = 300\text{K}$; the coefficient of atomic hydrogen diffusion $D = 1.27 \cdot 10^{-8} \text{ m}^2/\text{s}$ [25]; the bonding energy of hydrogen in trap $W_B = 60 \text{ kJ/mole}$ [21]; the molar volume $\Omega = 7.116 \cdot 10^{-6} \text{ m}^3/\text{mole}$; $N_L = 8.46 \cdot 10^{28} \text{ atom/m}^3$; coefficients $\alpha = 1$, $\beta = 1$ [26]. According to the analysis of data given [1] we used the value of solubility $S_0 = 5.0 \cdot 10^{21} \text{ atom/m}^3$ at $T = 300\text{K}$ and $P = 0.1 \text{ MPa}$. This value of S_0 is close to the data used in [24] in calculations ($S_0 = 2.084 \cdot 10^{21} \text{ atom/m}^3$). Solubility increasing with pressure increasing is determined by Eq. (6): $S = S_0 \cdot P^{1/2}$. The traps density, N_T , in dependence on the plastic deformation value was evaluated on the basis of the results given in [21].

Model numerical calculations of hydrogen absorption were performed for a thin-walled steel pipe of radius R and wall thickness b , $b \ll R$, being under the action of the inner pressure P . The circumferential stresses in the pipe wall were determined by the formulae: $\sigma = PR/b$.

Further, deformations are equal to $\varepsilon = \varepsilon_e + \varepsilon_p$, $\varepsilon_e = \sigma/E$, $\varepsilon_p = 0$ at $\sigma \leq \sigma_Y$ and,

$$\varepsilon_p = \varepsilon_{\text{res}} \frac{\sigma - \sigma_Y}{\sigma_B - \sigma_Y} \text{ at } \sigma_Y < \sigma \leq \sigma_B$$

where $E = 200\text{GPa}$, $\sigma_Y = 250 \text{ MPa}$ for steels of austenite class and $\sigma_Y = 270 \div 300 \text{ MPa}$ for low-alloy steels of chrome-molybdenum and chrome-molybdenum-vanadium class at the temperature range $20 \div 100^\circ\text{C}$; σ_B is the ultimate strength which varies in the range $500 \div 550 \text{ MPa}$ and $450 \div 500 \text{ MPa}$ for the same steels at the temperature $20 \div 100^\circ\text{C}$, respectively; ε_{res} is the residual deformation at fracture which is about $35 \div 40\%$.

The circumferential stresses are equal $\sim 1 \text{ MPa}$ for the pipe of radius $R = 50 \text{ mm}$ and wall thickness $b = 3 \text{ mm}$ at the pressure $P = 0.1 \text{ MPa}$. This value of stresses is essentially less as compared to the yield stress. Hence, in this case within the framework of the given model hydrogen absorption in the pipe wall is only determined by the initial traps distribution. However, some zones of stress concentration are present in real components (e.g., zones of welds, pipe connections, etc.). The computing model of hydrogen absorption both at the absence of plastic deformations and accounting for their influence on the hydrogen absorption process is given later on. In the first case the amount of traps

related to the dislocations is determined by the initial properties of the material while in the second case the amount of traps increases with the increasing of plastic deformations. The problem on calculation of the space-time distribution of the hydrogen concentration in the pipe wall was solved numerically by the method of finite differences on the basis of the algorithm suggested in [17] for modeling of similar process of metal deformation at the vacancies diffusion. The following dimensionless variables were introduced

$$\xi = \frac{x}{b}, \quad \eta = \frac{D \cdot t}{b^2}, \quad S_L = \frac{C_L}{S},$$

The calculated variations of the diffusing hydrogen concentration and concentration of hydrogen in traps through the wall thickness are given in Figs 2, 3 in case of absence of plastic deformations and in Figs 4, 5 for the case when $\varepsilon_p = 0.5$.

Hence, the numerical modeling of the hydrogen absorption process in the pipe wall was performed. It was shown that the amount of trapped hydrogen increases with increasing the value of plastic deformation. The time of transition to the stationary hydrogen distribution equals $0.5 \div 0.7$ of the characteristic diffusion time, b^2/D (slightly more long with increasing the traps amount).

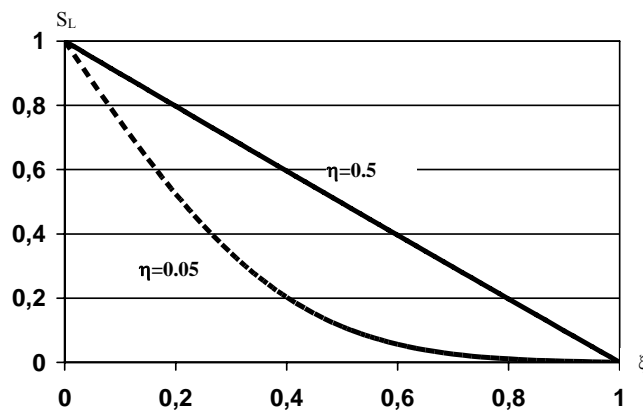


Fig. 2. Hydrogen concentration variation in the internode through the wall thickness, $\varepsilon_p=0$

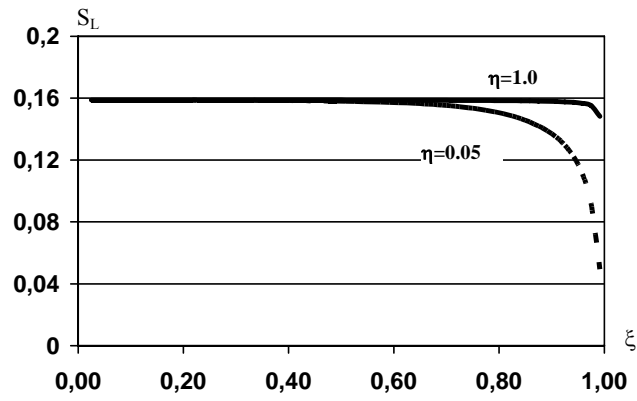


Fig.3. Hydrogen concentration variation in the traps through the wall thickness, $\epsilon_p=0$

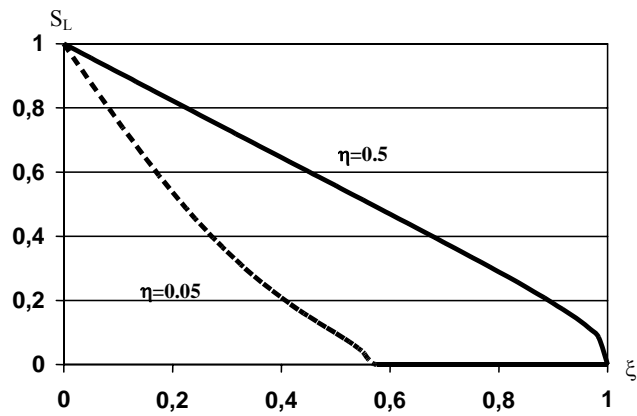


Fig. 4. Hydrogen concentration variation in the internode through the wall thickness, $\epsilon_p=0.5$

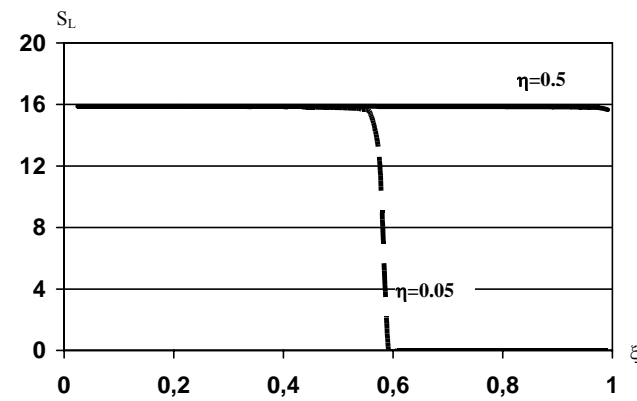


Fig. 5. Hydrogen concentration variation in the traps through the wall thickness, $\epsilon_p=0.5$

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