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A MATHEMATICAL MODEL FOR THE DETERMINATION OF HYDROGEN CONCENTRATION CORRESPONDING TO CHANGES IN THE MECHANISM OF DEFORMATION

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We propose a three-dimensional mathematical model of hydrogen diffusion in a polycrystalline body taking into account the heterogeneity of diffusion parameters and the solubility of hydrogen in the grain body and on the grain boundaries. The obtained solution is verified for an iron bicrystal. It is shown that the model of grain-boundary diffusion of hydrogen enables one to determine a characteristic value of hydrogen concentration corresponding to changes in the mechanism of deformation.

Keywords: hydrogen concentration, grain-boundary hydrogen diffusion, plasticization, embrittlement.

Introduction

It is sometimes assumed (see [4, 8, 9, 17, 18]) that, in the course of fracture of iron and its alloys, hydrogen dissolved in them may either embrittle the metal at high concentrations significantly exceeding its solubility in this metal under given conditions, or promote its plasticization at very low concentrations [8], or even lead to abnormally high yielding of the metal at very high concentrations and under the conditions of cyclic oscillation of temperature within the range of polymorphic transformation of iron, high pressure of hydrogen, etc. However, the available models and hypotheses used to describe the mechanisms of influence of hydrogen on the mechanical behavior of metals (models of hydrogen pressure, its adsorptive and decohesive effects, etc. [1]) explain, as a rule, its embrittling action in the stage of fracture but neglect its influence on the deformation of metals prior to fracture.

At the same time, as early as in the 1970–80s [4, 8, 9] and, especially, in recent years [1, 5, 6, 14, 20, 21], it was established that, in the stage of deformation, which always precedes the fracture process, hydrogen promotes the initiation of dislocations, accelerates their motion, decreases the energy of stacking faults, activates transverse sliding, causes a decrease in the yield stress of the material, and promotes the relaxation of stresses. In other words, we observe manifestations of the plasticizing action of hydrogen. These assumptions form the basis of the HELP (hydrogen-enhanced localized plasticity) theory [21]. According to this theory, the macroscopic brittle fracture of a material saturated with hydrogen in a microvolume is preceded by a strongly localized plastic yield of the material (Fig. 1). This is explained by the facilitation of motion and by the appearance of dislocations on the surface as a result of the decohesion-adsorption decrease in the forces of atomic coupling in the presence of hydrogen. In this case, the enrichment of local regions of the metal with hydrogen occurs either in the diffusion way or in the dislocation way.

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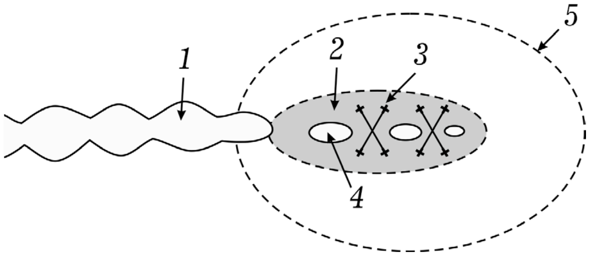
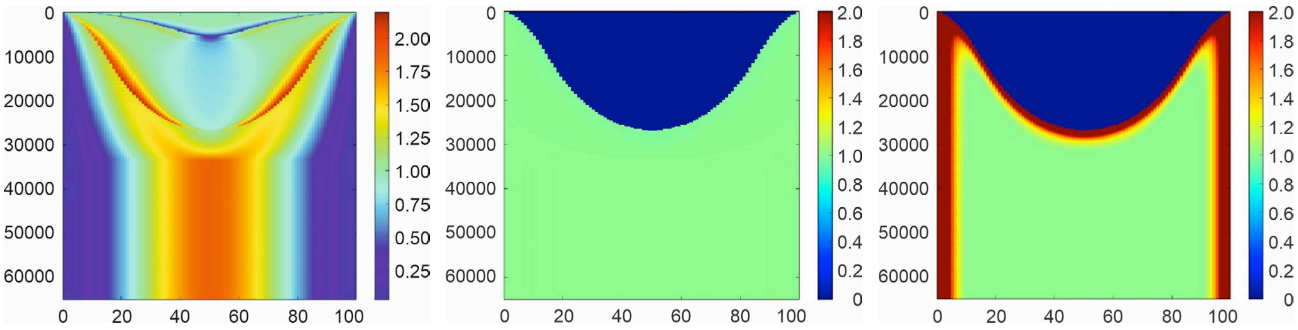


Fig. 1. Schematic diagram of the mechanism of HELP: (*1*) crack, (*2*) high hydrostatic stresses and concentration of hydrogen, (*3*) HELP, (*4*) cavities, (*5*) plastic zone without hydrogen.



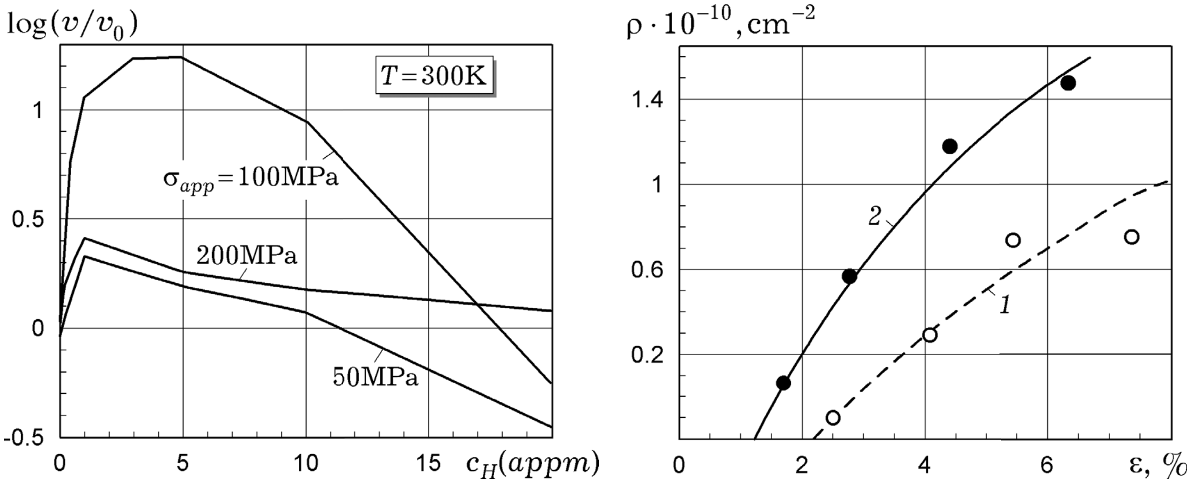
(a) **(b)** **(c)**

Fig. 2. Modeling of the redistribution of hydrogen in the lattice and its defects [11]: (a) distribution of hydrogen concentration in the metal lattice, (b) relative hydrogen concentration over the dislocation, (c) relative hydrogen concentration on the grain boundaries.

In [3], it was established that, for low-alloy pipe steels, there exists a characteristic value of hydrogen concentration in the metal $C_H = C_{H*}$ for which the mechanism of influence of hydrogen on the deformation of steel changes. Hydrogen induces the plasticization of the material for $C_H \le C_{H*}$ and its embrittlement for $C_H \ge C_{H*}$. For 20 steel, the value C_{H*} is quite low: $(1.77-2.09)\times 10^{-6}$ mole/cm^3. Hence, low hydrogen concentrations in the metal volume promote its plastic deformation. The value C_{H*} can be regarded as an important engineering parameter for the evaluation of strength and fracture of the materials and structural elements in hydrogen-containing media. Therefore, the development of a mathematical model intended for the determination of hydrogen concentration corresponding to changes in the mechanism of deformation is an important and actual problem.

1. Analysis of Investigations

It is known [1] that the diffusion of hydrogen in the metal depends not only on the type of crystal lattice of the metal but also on the degree of its perfection. Defects of the crystal lattice most significantly affect the diffusion coefficients and the solubility of hydrogen in the metal. The grain boundaries [11] form an easier path for diffusion than the grains themselves (Fig. 2). Thus, the process of transportation of atoms occurs much faster (by several orders of magnitude) than through the grains (Fig. 2c).



(a) **(b)**

Fig. 3. (a) Influence of hydrogen on the mobility of dislocations (logarithm of the velocity of dislocation with hydrogen normalized to the velocity without hydrogen) [15]; (b) variation of the density of dislocations as a function of the tensile deformation of specimens made of ARMCO-iron in air (curve 1) and after hydrogenation (curve 2) [9].

The process of accumulation of hydrogen on grain boundaries up to a certain critical level and the formation of hydrogen clusters decrease the energy of interaction of atoms in the metal, stack faults, and distortions of the lattice [12, 15, 16, 19, 22], which facilitates the motion of dislocations in various sliding systems (Fig. 3a). In particular, this activates transverse sliding, causes an increase in the number of dislocations (Fig. 3b) and fragments of shear, bending-torsion, and rotation, and decreases the local yield stresses in the material.

As a result of saturation of the grain boundaries with hydrogen, we observe its redistribution into the volume of grains and blocking of the motion of dislocations, which leads to hydrogen embrittlement.

2. Classical Model of Grain-Boundary Diffusion of Hydrogen. Fisher Model

In view of high importance of the process of diffusion on the grain boundaries, we consider it in more detail. For the classical analysis of the diffusion process on grain boundaries, it is necessary to develop a model of the boundary and make assumptions concerning the relationship between the diffusive flows on the boundary and in the volume of the grain. In other words, the chosen model must include, in a certain way, the process of "suction" of atoms from the boundary into the grain. The analysis of the diffusion exchange between the boundary and the volume of the grain is indeed necessary because the fraction of boundaries in the volume of the crystal is small. Indeed, for the mean grain size $a = 100$ μm, the fraction of grain boundaries $f_{gb} = \delta / a$ does not exceed 10^{-5}.

The diffusion transport from the boundary into the bulk of the grain is independent of the phenomenological model of diffusion [13] and is realized in three stages in the course of time. In the first stage, corresponding to the condition

$$\ell = \sqrt{D_g t} \le 0.1\delta ,$$

we observe no exchange by atoms between the boundary and the volume of grains. Here, ℓ is the diffusion length, δ is the width of grain boundary, D_g is the diffusion coefficient of hydrogen in the volume of grains, and t is the time variable. In the second stage, under the condition

$$10^2 < \ell \le (0.2\text{–}0.4)a,$$

we observe the intense transportation of atoms between the boundary and the volume of grains. The third stage is realized under the condition

$$\ell > (0.8\text{–}1.0)a,$$

when the flow of atoms from the zone of grain boundaries is balanced by the flow from the undistorted lattice.

The simplest description of the grain-boundary diffusion was proposed by Fisher in [10]. Later, the Fisher model was modified by other researchers but its essence remained invariable. The Fisher model is based on the following assumptions:

1) the grain boundary is a thin layer of the material with high diffusion coefficient located between two semiinfinite grains characterized by lower diffusion coefficients;

2) the process of transport into the volume is directed only perpendicular to the boundary;

3) the diffusion coefficients on the grain boundary and in its volume are independent of the concentration of diffusing atoms.

The diffusing material in the form of a thin layer is placed on the specimen surface in the plane $x = 0$ (Fig. 4). The concentration of the material in the layer is supposed to be constant and equal to C_0. The problem is reduced to the determination of the concentration $C(x,y,t)$ from the system of equations

$$\frac{\partial c}{\partial t} = D_g \Delta c, \qquad |y| \ge \frac{\delta}{2},$$

$$\frac{\partial c_{gb}}{\partial t} = D_{gb} \frac{\partial^2 c_{gb}}{\partial^2 x} + \frac{2}{\delta} D_g \left.\frac{\partial c}{\partial y}\right|_{|y|=\delta/2}, \qquad |y| < \frac{\delta}{2},$$

$$c\left(x, \pm\frac{\delta}{2}, t\right) = c_{gb}(x,t)$$

with the following boundary conditions:

$$c(0,y,t) = C_0 H(t), \qquad c(\infty,y,t) = 0, \qquad c(x,y,0) = 0, \qquad x > 0,$$

where

$$H(t) = \begin{cases} 1, & t \ge 0, \\ 0, & t < 0. \end{cases}$$

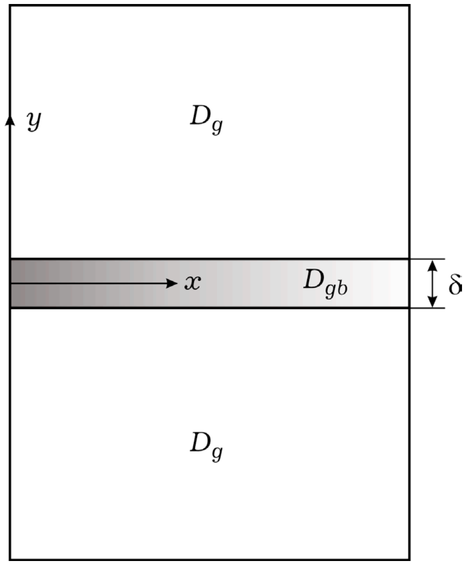


Fig. 4. Schematic diagram of grain-boundary diffusion in the Fisher model [10].

In the two-dimensional case, the solution takes the following form [10]:

$$c(\xi,\eta,\beta) = c_1(\eta) + c_2(\xi,\eta,\beta), \qquad c_1(\eta) = C_0 \operatorname{erfc}\left(\frac{\eta}{2}\right),$$

$$c_2(\xi,\eta,\beta) = \frac{C_0\eta}{4\sqrt{\pi}} \int_1^{\theta} \frac{\exp(-\eta^2/4\sigma)}{\sqrt{\sigma^3}} \left(\frac{\sigma-1}{\beta} + \xi\right) \frac{\theta-1}{\theta-\sigma}\, d\sigma.$$

Here, $\xi = (|y| - \delta/2)\ell^{-1}$, $|y| \ge \delta/2$, $\eta = x/\ell$, $\beta = (\theta-1)\delta/(2\ell)$, and $\theta = D_{gb}/D_g$.

3. Mathematical Modeling of the Diffusion of Hydrogen in a Polycrystalline Body with Regard for the Inhomogeneity of the Parameters of Diffusion and Solubility of Hydrogen Inside the Body and on the Grain Boundaries

In what follows, we propose a mathematical model of the diffusion of hydrogen in a polycrystalline body taking into account the inhomogeneous behavior of the parameters of diffusion and solubility of hydrogen both inside the body and on the grain boundaries. In the case of piecewise inhomogeneous bodies, the hydrogen solubility function has a jump on the boundary between the domains of homogeneity. Hence, the function of hydrogen concentration also has a jump, as follows from the condition of continuity of the chemical potential of hydrogen over the entire region [1].

Instead of the hydrogen concentration, we introduce a hydrogen potential function Π continuous in the entire region and proposed in [1]:

$$\Pi_i(x,y,z,t) = \frac{C_i(x,y,z,t)}{K_i(x,y,z,t)}. \tag{1}$$

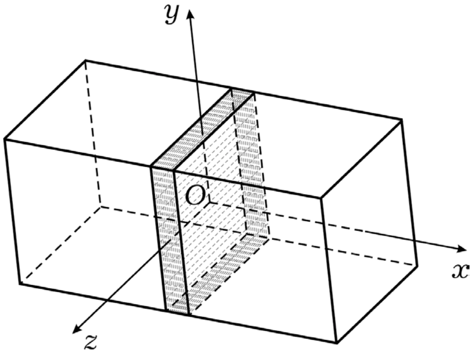


Fig. 5. Schematic diagram of a bicrystal.

We seek the distribution of the field of hydrogen concentration according to the generalized Fick law, which takes the following form (in terms of the function Π):

$$\frac{\partial \Pi_i}{\partial t} = D_i \Delta \Pi_i . \tag{2}$$

In the parallelepiped $-\ell_1 < x < \ell_1$, $-\ell_2 < y < \ell_2$, $-\ell_3 < z < \ell_3$, for the following initial and boundary conditions:

$$\begin{gathered} \Pi_i(x,y,z,0) = \Pi_0 , \\ \Pi_i(\pm\ell_1,y,z,t) = \Pi_i(x,\pm\ell_2,z,t) = \Pi_i(x,y,\pm\ell_3,t) = \Pi_1 , \end{gathered} \tag{3}$$

the solution of problem (1)–(3) was obtained [2, 7] in the form

$$\begin{aligned} \frac{\Pi_i(x,y,z,t)-\Pi_1}{\Pi_0-\Pi_1} &= 8 \sum_{i,j,k=1}^{\infty} \frac{(-1)^{i+j+k+1}}{\beta_i \beta_j \beta_k} \cos\frac{\beta_i x}{\ell_1} \cos\frac{\beta_j y}{\ell_2} \cos\frac{\beta_k z}{\ell_3} \\ &\times \exp\left(-\left(\beta_i^2 K_1^2 + \beta_j^2 K_2^2 + \beta_k^2 K_3^2\right) \left(\frac{1}{\ell_1^2} + \frac{1}{\ell_2^2} + \frac{1}{\ell_3^2} \right) D_i t \right), \end{aligned} \tag{4}$$

where

$$\beta_\alpha = \frac{2\alpha - 1}{2}\pi , \quad \alpha = \{i,j,k\} , \quad K_i = \frac{1}{\ell_i \sqrt{\ell_1^{-2} + \ell_2^{-2} + \ell_3^{-2}}} .$$

Thus, according to (1), the concentration of hydrogen can be found from the relations:

$$\begin{gathered} C_{g_i}(x,y,z,t) = K_{g_i}(x,y,z,t)\Pi_{g_i}(x,y,z,t) , \\ C_{gb_i}(x,y,z,t) = K_{gb_i}(x,y,z,t)\Pi_{gb_i}(x,y,z,t) . \end{gathered} \tag{5}$$

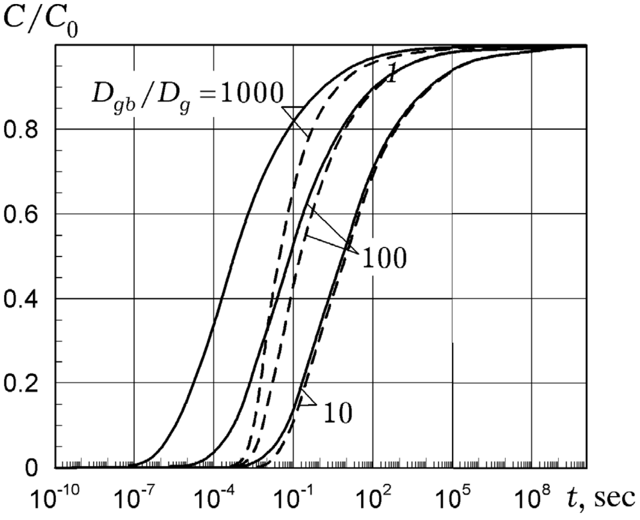


Fig. 6. Time dependences of the grain-boundary (solid lines) and volume (dashed lines) concentrations of hydrogen in the bicrystal.

4. Approbation of the Model

We checked the obtained solution for a bicrystal of iron (Fig. 5), the initial concentration equal to zero, a constant external concentration C_0, $D_g = 2.27 \cdot 10^{-13}\ \mathrm{m}^2/\mathrm{sec}$, and a saturation time of 1000 nsec.

In Fig. 6, we present the time dependences of the concentration of hydrogen on the grain boundary (solid lines) and in the volume of the grain (dashed curves) for different ratios θ. We observe a delay of the volume flow of hydrogen by a certain time. This shows that hydrogen first diffuses on the grain boundaries and the diffusion of hydrogen through the grains originates only after their saturation. It is worth noting that, as the ratio θ decreases from 1000 to 100 and 10 (Fig. 6), the difference between the concentration profiles also decreases.

5. Determination of the Characteristic Value of C_{H*} Corresponding to Changes in the Mechanism of the Influence of Hydrogen on the Deformation of Steel

We computed the redistribution of hydrogen for 20 steel. The results of investigations for this type of steel were presented in [3]. The specimens hydrogenated to a given value of concentration C_H [mole/cm^3] were subjected to uniaxial tension up to fracture. In the process of deformation of specimens in the automated mode, we recorded the dependences of the applied load on the elongation of the specimens with the help of a personal computer. The dependence of the concentration of hydrogen C_H on the duration of hydrogenation τ was accepted in the form

$$C_H = A\tau^m, \tag{6}$$

where A and m are constants of the analyzed "material–medium" system. For the "20 steel–NS4 solution" system, we take $A = 0.28 \cdot 10^{-6}$, and $m = 0.65$.

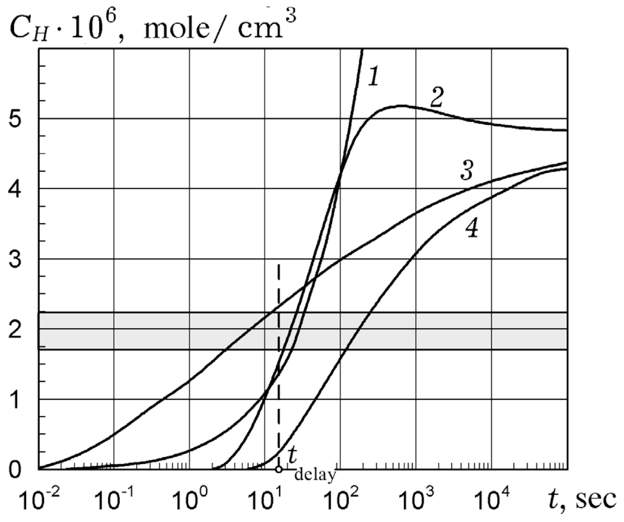


Fig. 7. Time dependences of the total (curves *1* and *2*), grain-boundary (curve *3*), and volume (curve *4*) concentrations of hydrogen.

Table 1. True values of the Cross-Sectional Area, Yield Limit σ_y, Ultimate Strength σ_u, and Fracture Stress σ_f for Specimens of 20 Steel in Different Stages of Deformation for Different Volume Concentrations of Hydrogen C_H [3]

C_H [mole/cm^3]	S_{σ_y}	S_{σ_u}	S_{σ_f}	σ_y	σ_u	σ_f
	mm^2			MPa		
0	19.60	16.48	7.67	271	590	932
$0.57 \cdot 10^{-6}$	19.44	16.10	7.34	261	585	939
$1.77 \cdot 10^{-6}$	19.63	16.07	7.11	230	589	960
$2.09 \cdot 10^{-6}$	19.54	16.20	7.04	294	581	969
$2.93 \cdot 10^{-6}$	19.63	16.43	7.33	307	575	919
$5.40 \cdot 10^{-6}$	19.58	16.65	7.28	291	570	937

By using the “applied load–elongation of the specimen” curves, the “stress σ – strain ε” dependences were constructed in [3] for various values of the volume concentration of hydrogen C_H in the metal. It is worth noting that the evaluation of stresses σ was based on taking into account the true values of the cross-sectional area of the deformed specimen. For this reason, the true values of the yield limit σ_y, ultimate strength σ_u, and fracture stress σ_f were computed for steel for various values of C_H (Table 1). The accumulated results make it possible to state that, for low-alloy pipe steels, there exists a characteristic value of the concentration of hydrogen $C_H = C_{H*}$ in the metal corresponding to changes in the mechanism of influence of hydrogen on the deformation and fracture processes.

In Fig. 7, we display the time dependences of the concentration of hydrogen computed by using relations (4)–(6): curves *1* and *2* correspond to the total concentration of hydrogen; here, curve *1* is obtained by using the empirical relation (6), whereas *2* is obtained by using relation (4). Moreover, curve *3* corresponds to the diffusion of hydrogen on the grain boundary and curve *4* describes the diffusion flow in the volume of the grain originating with a certain delay. The concentration in curve *3* corresponding to the time of delay of the volume flow is just the required characteristic value of the concentration of hydrogen in the metal corresponding to changes in the mechanism of the influence of hydrogen on the deformation of steel.

CONCLUSIONS

We propose a mathematical model of the diffusion of hydrogen in polycrystalline bodies with regard for the inhomogeneity of the parameters of diffusion and the solubility of hydrogen inside the body and on the grain boundaries in the three-dimensional statement. The solution is verified for a bicrystal of iron.

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