Model of hydrogen diffusion in titanium with the formation of hydride phases

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Abstract. The problem of predicting the behavior of structural materials in hydrogen-bearing media (including extreme operating environments) cannot be solved without a thorough understanding of the mechanisms of hydrogen accumulation and transfer inside these materials. This issue is especially pressing for hydride-forming materials, such as widely used titanium alloys. Titanium and its alloys are used, in particular, in designing power and chemical reactors, for the geological disposal of highly radioactive waste. The paper presents a nonlinear mathematical model of hydrogen permeability taking into account the possible formation of hydride phases (after certain concentrations of dissolved atomic hydrogen are attained), and the iterative method for solving the corresponding boundary value problem based on implicit difference schemes.

1. Introduction

It is impossible to predict the behavior of structural materials in hydrogen-containing media without a thorough understanding of the mechanism of hydrogen uptake and transport in these materials. This problem is especially topical for hydride-forming materials, such as titanium and zirconium alloys widely used in industry. Due to mechanical strength, high corrosion, thermal and radiation resistance, titanium alloys are widely used in the military and aerospace industry, medicine, chemistry, in the nuclear industry for producing such components as steam condensers, targets for transmutation of radioactive waste, transport containers for geological disposal of highly radioactive waste.

When interacting with hydrogen, titanium is prone to hydrogen uptake accompanied by hydride formation, which leads to hydrogen embrittlement and reduced mechanical strength, and may also lead to the destruction of structural components. The mechanism of hydride embrittlement is that when the concentration of hydrogen in a solid solution reaches a certain value, the formation of a fragile hydride phase begins, which facilitates the formation and propagation of cracks under the influence of mechanical stresses. Often, this process is stimulated by thermal cycling. The mechanisms of hydrogen transport during hydride formation and other solid phase transitions are not yet fully understood.

To predict the behavior of hydride-forming alloys contacting with hydrogen-containing media, it is necessary to perform adequate computer simulations taking into account surface processes, diffusion, phase transitions, phase boundary movement, and so on. The results obtained in the
experiments on hydrogen permeation through a membrane made of titanium alloy were used to formulate and validate the model.

The mathematical research is based on the article [1]. Here, we present a nonlinear model of hydrogen permeability taking into account the possible formation of hydride phases (after certain concentrations of dissolved atomic hydrogen are attained), and the iterative method for solving the corresponding boundary value problem based on implicit difference schemes.

2. Mathematical model of hydrogen permeability of titanium

We shall briefly describe the experiment (see details in [1]). A titanium membrane is subjected to preliminary abrasive treatment in an inert medium of flowing helium and prolonged heating under vacuum conditions (for seven days at temperatures of 300 and 450°C). The sample temperature $T = 450°C$ is kept constant during the experiment. At the initial time instant, a portion of gaseous hydrogen is abruptly fed into an isolated chamber on one side of the membrane. On the outlet side, the volume is constantly pumped out by a vacuum system and hydrogen partial pressure is measured by a mass spectrometer to be then converted into the penetrating flux. During the experiment, the $H_2$ outlet pressure decreases from the initial value of 8.45 Torr to the level of 6.25 Torr. According to the phase diagram (figure 1), at the initial stage, titanium with dissolved atomic hydrogen forms an $\alpha$-phase at such temperature. Hydrogen permeability is quite slow, so one can focus on the corresponding horizontal segment of the equilibrium phase diagram at 450°C (figures 1, 2, $\gamma \equiv \delta$). The ‘path’ of the experiment is directed from left to right. The total concentration at the inlet increases monotonically and then decreases. The concentration wave passes through the membrane ‘from left to right’. The main assumption is that in such a ‘smooth’ experiment, the total concentration $c(t, x)$ of $H$ atoms uniquely determines the phase composition (figure 3). At any time instant $t$ and any point $x \in [0, \ell]$ across the thickness of the membrane, a maximum of two phases will coexist.

![Figure 1. Phase diagram of $TiH_x$.](image)

2.1. Effective diffusion coefficient

Denote by $c(t, x)$ the total concentration of $H$ atoms; $r_{\alpha,\beta,\gamma}$ are the phase fractions:

$$r_{\alpha,\beta,\gamma} \geq 0, \quad r_{\alpha} + r_{\beta} + r_{\gamma} = 1 \Rightarrow r_{\alpha} c = c_{\alpha}, \quad r_{\beta} c = c_{\beta}, \quad r_{\gamma} c = c_{\gamma}.$$
We will focus on the notion of the effective diffusion coefficient in a two-phase medium [2]. We denote the corresponding diffusion coefficients by $D_{1,2}$ for convenience. In our case the pair of indices $(1, 2)$ can only take $(\alpha, \beta)$ or $(\beta, \gamma)$ values. In addition, for consistency (see below) we assume the following expressions for phases without impurities

$\alpha$:
$$D_{1,2} = D_{\alpha,\beta}, \quad r_1 = r_\alpha = 1, \quad r_2 = r_\beta = 0;$$

$\beta$:
$$D_{1,2} = D_{\alpha,\beta}, \quad r_1 = r_\alpha = 0, \quad r_2 = r_\beta = 1;$$

$\gamma$:
$$D_{1,2} = D_{\beta,\gamma}, \quad r_1 = r_\beta = 0, \quad r_2 = r_\gamma = 1.$$

We also note the following circumstance. The considered phases $(\alpha, \beta, \gamma)$ are mostly solutions of the diffusion-movable atomic hydrogen inside the metal (significant phase differences are determined by the lattice structure). For other materials and(or) in other conditions a qualitatively different situation is possible: a hydride with chemically bound hydrogen (formally a new material) is formed wherein ‘additional’ atomic hydrogen can dissolve and diffuse. The diffusion coefficients refer to the movable hydrogen.

**Independent fluxes model.** Parallel and sequential flux models are considered in [2] for the determination of the effective diffusion coefficient:

$$D_{\text{eff}} \equiv D_{s1} = r_1D_1 + r_2D_2, \quad \frac{1}{D_{\text{eff}}} \equiv \frac{1}{D_{s2}} = \frac{r_1}{D_1} + \frac{r_2}{D_2}.$$ 

Here, the analogy is drawn between the transfer of matter (diffusion) and of charge (electric current). The diffusion coefficient is an analogue of electrical conductivity: for parallel-connected conductors electrical conductivities are summed up, and for serially connected conductors resistances are summed up.

Due to the heterogeneity of the nucleation and phase growth processes it is possible to take the value of the convex combination $D_{s1}$ as the effective diffusion coefficient:

$$D_{\text{eff}} \equiv D_s = \xi D_{s1} + (1 - \xi)D_{s2}, \quad \xi \in [0, 1].$$ (1)

**Dependent fluxes model.** If we take the relation $J = r_1J_1 + r_2J_2$ for the total diffusion flux density, then the ‘geometric mean’ approximation $D_{s1} = D_1^{1/2}D_2^{1/2}$ is acceptable. Finally, appealing to the above analogy with electrical conductivity, we give an analogue of the Maxwell relation [2]:

$$\frac{D_{s2} - D_1}{D_{s2} + 2D_1} = \frac{r_2}{D_2} \frac{D_2 - D_1}{D_2 + 2D_1}.$$ 

Within the framework of such a model, we will accept the relation (1) for the effective diffusion coefficient with the variable weight parameter $\xi$ and the corresponding expressions for $D_{s1}$.

2.2. **Diffusion equation**

Let us accept the standard diffusion equation

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D_s(c) \frac{\partial c}{\partial x} \right), \quad D_s \equiv D_{\text{eff}}.$$
All the reasoning is set in the framework of ‘effective’ approximation. The ‘correct’ dependence of \( D_s(c) \) is determined by the theory of chemical potentials (chemical thermodynamics of heterogeneous systems). In the linear approximation, the diffusant flux density is proportional to the gradient of the chemical potential \( \mu \). If \( \mu = \mu(c; \ldots) \) (ellipsis stands for the variables that are practically independent of the spatial variable \( x \) in the context of the considered task), we obtain proportionality to the concentration gradient with a coefficient depending on \( c \). Direct use of the spatial model \( D_s(t, x) \) instead of the concentration dependence \( D_s(c(t, x)) \) can lead to a significant error, which is analyzed in detail in [3].

In the framework of an effective theory, we aim at an adequate response of \( D_s \) to the current phase composition: \( D_s = D_s(c) = D_s(r_\alpha, r_\beta, r_\gamma) \). This applies to any \( t > 0 \) and \( x \in [0, \ell] \). Even if one of the phases, for example \( \gamma \), is realized with predominantly chemical (strong) bonds, then such effective diffusion coefficient will depend both on the material and on the level of free diffusion-movable hydrogen. In this case, the total gradient \( \partial_x c \) will be numerically equal to the gradient of the diffusing component of the concentration.

Let us complete a dependency table 1 for \( r_\alpha, r_\beta, r_\gamma(c) \).

Table 1. Dependency table for \( r_\alpha, r_\beta, r_\gamma(c) \).

| \( \alpha \) | \( \alpha + \beta \) | \( \beta \) | \( \beta + \gamma \) | \( \gamma \) |
|---|---|---|---|---|
| \( r_\alpha \) | 1 | \( \frac{c_\alpha - c}{c_\beta - c_\alpha} \) | 0 | 0 | 0 |
| \( r_\beta \) | 0 | \( \frac{c - c_\beta}{c_\beta - c_\alpha} \) | 1 | \( \frac{c - c_\gamma}{c_\gamma - c_\beta} \) | 0 |
| \( r_\gamma \) | 0 | 0 | 0 | \( \frac{c - c_\alpha}{c_\gamma - c_\beta} \) | 1 |

2.3. Boundary conditions

The surface will not explicitly stand out in the model. When describing desorption from the outlet side into the vacuumized volume, we operate with the effective recombination coefficient directly related to the near-surface bulk concentration \( c(t, \ell) \).

The boundary condition at \( x = \ell \) is

\[
-D_s \frac{\partial c}{\partial x} \bigg|_{x=\ell} = J_{\text{des}} = r_1 b_1 \left[ \frac{c_1}{r_1 c} \right]^2 + r_2 b_2 \left[ \frac{c_2}{r_2 c} \right]^2 = \left[ \frac{r_3 b_\alpha + r_3 b_\beta + r_3 b_\gamma}{b_{\text{eff}} = b_\ast(r_\alpha, r_\beta, r_\gamma)} \right] c^2(t, \ell). \tag{2}
\]

The notation for the bulk desorption coefficients is similar to that for the diffusion coefficients above: \( b_{1,2} = b_{r_\alpha, r_\beta} \) or \( b_{1,2} = b_{r_\beta, r_\gamma} \) depending on the concentration \( c(t, \ell) \). We note that the effective desorption coefficient \( b_{\text{eff}} = b_\ast(r_\alpha, r_\beta, r_\gamma) \) was found to depend on the concentration \( c = c(t, \ell) \). Thus, in the general case, desorption is not quadratic in the classical sense.

We now look at the boundary conditions at the inlet side. We use the ideal gas equation in the inlet volume (in the SI system):

\[
p(t)V = N(t)kT \Rightarrow \dot{N} = \frac{\dot{p}V}{kT} \Rightarrow D_s \frac{\partial c}{\partial x} \bigg|_{x=0} = f(t) = 2 \frac{\dot{N}}{S}. \tag{3}
\]
Here, $S$ is the area of the membrane side (converted back to cm, $[S] = \text{cm}^2$), and factor 2 means that the hydrogen fluxes are calculated in $H$ atoms for consistency. The permeability is quite slow, so the problem of differentiating the measured pressure $p(t)$ is effectively solved using the numerical differentiation formulas. The authors used a procedure for smoothing the observations on a seven-point pattern using a cubic polynomial [4].

Alternative variant: we assume that the pressure $p(t)$ in the inlet volume is large enough to meet the condition of quasi-equilibrium solubility $c(t, 0) = \Gamma \sqrt{p(t)}$, where $\Gamma$ is the Sieverts’ constant. To reconcile this condition with zero initial data

$$S\in(2) \text{ for } c,$$

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3. Computational algorithm

We fix the time step $\Delta t$ and choose uniform grids for spatial variables. The initial distribution $c(0, x)$ is zero. The diffusion and desorption coefficients are given implicitly and calculated algorithmically (using calculated total concentration $c(t, x)$). Therefore, the computational algorithm will be based on the implicit conservative scheme of second–order accuracy in space and first–order accuracy in time, and will have an iterative character. Iterations are meant to more precisely define $c(t, x)$ at each time layer. We use a standard four-point pattern to approximate the diffusion equation and then solve the resultant linear equation system applying the Thomas algorithm. We now describe the way to more precisely define the values of $c(t, x)$ at each time layer.

Moving on to the $(n + 1)$-time layer, we use explicit schemes for the diffusion equation to calculate the initial approximation for the first two grid nodes with respect to the spatial variable $x = x_{1,2}$. Using second–order accuracy approximation for $\partial_x c|_{x=0}$, we solve the linear equation (3) for $c(t_n+1, 0)$ and find the first sweep coefficients. Using these coefficients we calculate the remaining sweep coefficients. We use the boundary condition (2) at $x = \ell$ in order to find $c(t_n+1, \ell)$ using second–order accuracy approximation for $\partial_x c|_{x=\ell}$. We have a quadratic equation in (2) for $c(t_n+1, \ell)$ and choose the positive root. Find the distribution (approximation) $c(t_{n+1}, x)$, $x \in [0, \ell]$ using the Thomas algorithm for solving the system of algebraic equations with a tridiagonal matrix. Continue improving $c(t_{n+1}, 0)$ in virtue of (3) (the values of $c$ at $x = x_{1,2}$ used to calculate $\partial_x c|_{x=0}$ have already changed). The iterations proceed until the distribution $c(t_{n+1}, x)$, $x \in [0, \ell]$ becomes stable. The time step is small enough, so a few iterations will suffice.

Now we describe how the coefficients $D_x$ and $b_\alpha$ are computed, knowing the current concentration $c(t, x)$. For every $x = x_k \in [0, \ell]$ we determine which column of table 1 the value $c(t_{n+1}, x_k)$ belongs to, then compute the fractions $r_\alpha, \beta, \gamma$, the diffusion coefficient according to the formula (1) (in the framework of the models with dependent or independent fluxes), and the desorption coefficient according to the notations in (2). Then, we move on to the next time layer.

4. Numerical modelling of hydrogen permeability

The proposed model is adapted to the experimental conditions and the data range for titanium alloys. We fix $\ell = 0.01 \text{ cm}$, $S = 0.8 \text{ cm}^2$, $T = 350^\circ \text{C}$, $V_{in} = 7 \times 10^{-3} \text{m}^3$, $D_o = 3.18 \times 10^{-7} \text{cm}^2 \text{s}^{-1}$, $D_\beta = 2.5 \times 10^{-5} \text{cm}^2 \text{s}^{-1}$, $D_\gamma = 2 \times 10^{-6} \text{cm}^2 \text{s}^{-1}$, $b_\alpha = 4.2 \times 10^{-29} \text{cm}^4 \text{s}^{-1}$, $b_\beta = 1.4 \times 10^{-30} \text{cm}^4 \text{s}^{-1}$, $b_\gamma = 1 \times 10^{-30} \text{cm}^4 \text{s}^{-1}$, $c_{\alpha}^* = 0$, $c_{\alpha}^+ = 4.9 \times 10^{21} \text{cm}^{-3}$, $c_{\beta}^* = 2.4 \times 10^{22} \text{cm}^{-3}$, $c_{\beta}^+ = 5 \times 10^{22} \text{cm}^{-3}$, $c_{\gamma}^* = 7.8 \times 10^{22} \text{cm}^{-3}$, $c_{\gamma}^+ = 1.3 \times 10^{23} \text{cm}^{-3}$.

Figures 4, 5 show the qualitative coincidence of the desorption flux curves.
Let us sum up the results of the presented work. The problem of modeling hydrogen permeability was as follows. A monotonous penetrating flux is usually observed under the stated experimental conditions. In this case however, a characteristic deflection of the experimental curve was registered at the output. What causes it? The physical interpretation is that as the concentration of dissolved atomic hydrogen increases, a phase transition occurs at some point. A hydride is formed, some of the hydrogen atoms chemically bind to the metal atoms and the amount of free diffusing hydrogen decreases for some time. But the hydride is permeable to dissolved (now in the new material) atomic hydrogen. A sufficiently high pressure on the input side initiates the subsequent growth of the penetrating flux through the ‘hydride-metal’ layered (multilayer) material with a phase transition moving boundary. The presented model confirms at a qualitative level the described scenario and gives quantitative indications of parameter values. To improve the modeling accuracy the model needs to be developed in the following direction. Desorption is taken into account in the form of bulk desorption ($b$ is the effective coefficient of the recombination of atoms into hydrogen molecules). More detailed modeling of surface processes (similar to [5,6]) will complicate the model but its approximation capabilities will be augmented.

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