Modelling of zirconium alloy hydrogenation

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Abstract. Zirconium alloys are the construction materials for critical elements in active zones of nuclear power reactors. During the operation of reactors such materials are subject to hydrogenation. Hydrogenation results in a decrease of alloy plasticity and cracking resistance. The formation of brittle hydrides at crack tips can result in severe embrittlement. One of the most important requirements for the reactor’s active zone materials is low hydrogen absorptivity. The mathematical model of hydride layer formation and growth is developed. The problem is to determine the dynamics of the free boundary of phase interface and the distributions of hydrogen concentration in hydride and in solution. Iterative computational algorithm for solving the nonlinear boundary-value problem with the Stefan condition based on implicit difference schemes is developed.

1. Introduction
The interest in the interaction of hydrogen and its isotopes with metals, alloys and intermetallic compounds is multifarious [1–8]. It is sufficient to mention problems in power production, protection of metals from hydrogen corrosion, chemical reactor design, rocket production. Enthusiasts have been speaking about hydrogen economy along with hydrogen energy [4]. Some mathematical models of dehydrogenation and hydrogen permeability connected with this article are presented in [9–11]. One of the most important requirements for the reactor’s active zone materials (made of zirconium alloys) is low hydrogen absorptivity since hydrogen embrittlement may cause zirconium cladding damage. Depending on the hydrogen content and operation temperature, hydrogen may be present in zirconium alloys as a solid solution or as hydrides. Hydrides have the greatest embrittlement effect on alloys as they can form and enlarge cracks.

We briefly describe the experiment (see details in [12]). A plate is placed into a chamber. The plate is polished on one side. The other side is nearly impermeable to hydrogen due to the presence of impurities, oxides and such. We disregard butt ends. The temperature of the sample and input pressure $p \approx 2$ atm. are constant during the experiment (sample cooling is carried out).

The alloy absorbs hydrogen quite well. A thin volume layer at which the hydrogen distribution can be considered uniform at a relatively high input pressure $p = \text{const} (\approx 2 \text{ atm.})$ is selected. Diffusion resistance starts to set only at a certain initial depth $\ell_0$. When the concentration of dissolved hydrogen reaches a certain value, this layer forms the initial hydride crust. Further transport of hydrogen proceeds through the growing hydride layer. The problem is to model the dynamics of the moving boundary of phase transition and to estimate the concentration distribution in hydride and in solution.
2. Mathematical model

The notations are the following. \( L \) is the plate thickness; \( \ell_0 \) is the thickness of the layer that absorbs hydrogen relatively easily and there is no diffusion resistance inside this layer yet (future initial hydride crust); \( u(t) \) is the concentration of atomic hydrogen \((H)\) in \( \ell_0 \)-layer \((1H/cm^3)\); \( Q \) is the concentration \((1H/cm^3)\), when \( u(t) \) becomes equal to \( Q \) the lattice is rearranged and the solution is converted to hydride; \( c(t, x) \) is \( H \) concentration in \((L - \ell_0)\)-layer; \( \mu \) is the kinetic constant. During the experiment the temperature and input pressure are constant \((T = \text{const}, p = \text{const})\). The notations are schematically represented in Fig. 1. The \( \alpha \)-phase is the \( H \) solution in Zr–1Nb alloy and \( \delta \)-phase is the hydride wherein atomic \( H \) is also dissolved and diffuses.

According to the gas kinetic theory the particle flux density \( J_p \) incoming to the surface (in this case the flux of \( H_2 \) molecules) is connected with the pressure \( p \) by the Hertz–Knudsen formula: \( J_p = p/\sqrt{2\pi mkT} \) \((k \text{ is the Boltzmann constant, } m \text{ is the mass of } H_2 \text{ molecule})\). In the context of the experiment it is convenient to select the following units \([x, t, L] = \text{cm}, [p] = \text{Torr}\). Then we numerically obtain the dependence \( J_p = \mu p, \mu(T) \approx 2.474 \cdot 10^{22}/\sqrt{T} \) \((\mu = 1 H_2/(\text{Torr cm}^2 s), [T] = \text{K})\). Since the atomic hydrogen diffuses, for consistency we will calculate the flux in \( H \) atoms: \( J_p = 2\mu p \). Only a small part of \( H \) will however be absorbed into the alloy: \( J_{\text{abs}} = 2\mu sp \) \((s \ll 1)\). Multiplier \( s \) is the fraction of incoming \( H \) that gets to the near-to-surface volume. We combine the elementary stages of physisorption, chemosorption, dissociation and dissolution itself into one stage: \( s \) is the effective coefficient of absorption.

![Figure 1. Stage I.](image1)

![Figure 2. Stage II.](image2)

**Stage I: preliminary stage — \( H \) dissolution in Zr–1Nb**

For the diffusion \((L - \ell_0)\)-layer we formulate the standard boundary-value problem:

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}, \quad x \in (\ell_0, L), \quad t > 0; \quad c(0, x) = 0, \quad x \in [\ell_0, L]; \quad c(t, \ell_0) = u(t), \quad \frac{\partial c}{\partial x} \bigg|_{L} = 0. \tag{1}
\]

The boundary condition \( c(t, \ell_0) = u(t) \) indicates that the \( H \) distribution with respect to sample thickness is continuous, while \( \partial_x c \big|_L = 0 \) indicates that the plate side \( x = L \) is impermeable. Hereinafter, we assume that coefficients depend on the temperature in an Arrhenius way: \( D = D_0 \exp\{-E_D/[RT]\} \), \( s = s_0 \exp\{-E_s/[RT]\} \), ... The temperature \( T = \text{const} \) is maintained throughout one experiment.

From the fluxes balance we derive the ordinary differential equation (ODE) for the concentration \( u(t) \):

\[
\dot{u}(t)\ell_0 = 2\mu sp - bu^2 + D \frac{\partial c}{\partial x} \bigg|_{\ell_0}, \quad u(0) = 0. \tag{2}
\]
The meaning of this equation is the following. The amount of $H$ atoms that has been absorbed through $cm^2$ during $1s$ due to the hydrogen pressure is $2μsp$, but there are the opposing desorption flux $bu^2$ ($b$ is the effective coefficient of recombination) and the diffusion outflow. The imbalance of these flux densities determines the accumulation of hydrogen atoms within the $\ell_0$-layer ($u\ell_0$). This equation should be considered together with (1) since $u(t)$ determines the boundary concentration in (1). When $p$ is not too large (without hydride formation), in the equilibrium situation (when all derivatives are zero) we have

$$2μsp - bu^2 = 0 \Rightarrow \bar{u} = Γ√p, \quad Γ \equiv 2μs/b.$$  

Therefore, under static conditions the dynamics of (2) is consistent with the Sieverts law $\bar{u} \propto √p$, where $Γ$ is the solubility coefficient. Let us emphasize that we speak about the dissolved diffusion-movable atomic hydrogen. In the “saturation–degassing” experiment the total absorption of hydrogen is taken into account, including reversible capture, hydride phases ... — the coefficient $Γ$ may have another meaning and numerical value. Technically it is easy to add the reversible capture of $H$ atoms in the $(L - \ell_0)$-layer by different types of “traps” (defects of the material), but in this problem we consider the reversible capture to be a minor factor.

**Stage II: hydride formation and phase boundary movement**

At some time instant the concentration $u(t)$ becomes equal to the threshold concentration $Q = Q(T)$, at which the lattice is rearranged and hydride is formed ($δ$-phase). We consider that this transition process is relatively fast. Thus, $u(t) = Q \Rightarrow \ell_0$-crust turns into a hydride. We set a new time zero ($t = 0$) and model the growth of the hydride phase. By this time we have $c(0, x) = \varphi(x), \varphi(\ell_0) = Q$ (the distribution of dissolved hydrogen is taken from the previous stage). Now the hydrogen begins to diffuse through the hydride $\ell_0$-layer. Denote by $v(t, x)$ the $H$ concentration in the $δ$-layer. We emphasize that $v(t, x)$ is the concentration of diffusing hydrogen, the total concentration is equal to $Q + v(t, x)$. Notations are schematically represented in Fig. 2. We put down the diffusion equations:

$$\frac{∂v}{∂t} = D_∗ \frac{∂^2v}{∂x^2}, \quad x \in (0, \ell(t)), \quad v(0, x) = 0, \quad x \in [0, \ell_0],$$  

(3)

$$\frac{∂c}{∂t} = D \frac{∂^2c}{∂x^2}, \quad x \in (\ell(t), L), \quad c(0, x) = \varphi(x), \quad x \in [\ell_0, L].$$  

(4)

Here, $D_*$ is the $H$ diffusion coefficient in the new material (in the hydride, in $δ$-phase). We write the “input-output” boundary conditions similarly to stage I:

$$2μs_∗p - b_*v^2(t, 0) = -D_∗ \frac{∂v}{∂x} \bigg|_{x=0}, \quad \frac{∂c}{∂x} \bigg|_{L} = 0.$$  

(5)

In the hydride, the concentration gradient appears almost immediately since it is much harder to diffuse through the $δ$-phase. There is no “cumulative” layer (the analogue of the $\ell_0$-layer in stage I). The free phase boundary $x = \ell(t)$ is now movable and two conditions at the interface $x = \ell(t)$ are needed to “sew together” the diffusion equations.

We begin with the Stefan type condition describing the dynamics of the phase boundary:

$$\left[ v(t, \ell(t)) + Q - c(t, \ell(t)) \right] \dot{\ell}(t) = -D_∗ \frac{∂v}{∂x} \bigg|_{\ell(t)} + D \frac{∂c}{∂x} \bigg|_{\ell(t)}.$$  

A jump of concentrations occurs: $v(t, \ell) + Q > Q > c(t, \ell), \ell = \ell(t), t > 0$. Still, the concentration $v(t, \ell)$ is negligible (the alloy “does not resist” the penetration of hydrogen). We assume that
v(t, ℓ(t)) = 0. The incoming flux from the δ-phase almost completely goes to hydride formation (movement of the boundary x = ℓ(t)) and to the solution (α-phase).

Thus, we accept the following conditions on the moving free boundary:

\[ v(t, ℓ(t)) = 0, \quad [Q - c(t, ℓ(t))]\dot{ℓ}(t) = -D_v \frac{∂v}{∂x} \big|_t + D_c \frac{∂c}{∂x} \big|_t. \]  

(6)

At the beginning \([…] = 0\) \((c(0, ℓ_0) = ϕ(ℓ_0) = Q)\), and then \((t > 0)\) a jump of concentrations occurs \([(…)] > 0\) and \(\dot{ℓ}(t) > 0\). The front moves with the concentration \(Q\) (total) towards \(x = L\). Passing to the limit \((t \to +\infty)\) we have \(ℓ(t) \to L\), but phase boundary movement slows down appreciably. The concentration distribution \(c(t, x)\) tends to uniformity and slowly increases up to the limit value \(Q\), when one can practically neglect the Zr–1Nb layer.

3. Computational algorithm

Stage I. The main computational challenges are to solve the nonlinear boundary-value problem with moving phase boundary (Stage II). Therefore, we only briefly describe here the general scheme for Stage I. The authors approximate the diffusion equation (1) (using four-point pattern) and ODE (2) by implicit difference schemes of second–order accuracy. The algorithm is of iterative nature due to the model nonlinearity. Moving on to the next time layer, we use explicit schemes for the diffusion equation to calculate the initial approximation for the first three grid nodes with respect to the spatial variable. Knowing the current approximations of the concentration in the boundary nodes \((x = ℓ_0, L)\), we used the Thomas algorithm for solving the system of algebraic equations with tridiagonal matrix. After correcting the concentration values in internal nodes, the concentration in the boundary node \(x = ℓ_0\) is recalculated as a positive root of quadratic equation (from the difference approximation of the boundary condition (2)). The iterations proceed until the distribution \(c(t, x), x \in [ℓ_0, L]\) becomes stable. Then we move on to the next time layer.

Stage II. Transformation of the boundary-value problem

The authors chose the following variant: the moving segments \([0, ℓ(t)]\) and \([ℓ(t), L]\) are transformed into \([0,1]\). Then uniform grids are chosen. We introduce a change of variables with a new time zero \((t_0 = 0): (t, x) \leftrightarrow (t, y), x = ℓ(t)y, \hat{v}(t, y) = v(x, t(y)); (t, x) \leftrightarrow (t, z), x = ℓ(t) + z[1 - ℓ(t)], \hat{c}(t, z) = c(x, t(z))\).

The boundary-value problem (3)–(6) for zirconium alloy hydrogenation after the change of variables is

\[ \frac{∂\hat{v}}{∂t} = \frac{D_v}{ℓ^2(t)} \cdot \frac{∂^2\hat{v}}{∂y^2} + \frac{\dot{ℓ}(t)y}{ℓ(t)} \cdot \frac{∂\hat{v}}{∂y}, \quad y \in (0, 1), \quad \hat{v}(0, y) = 0, \quad y \in [0, 1], \]  

(7)

\[ \dot{v}(t, 1) = 0, \quad 2μs_k - b_k\hat{v}^2(0, 0) = -\frac{D_v}{ℓ(t)} \cdot \frac{∂\hat{v}}{∂y} \big|_{y=0}; \]  

(8)

\[ \frac{∂\hat{c}}{∂t} = \frac{D}{[L - ℓ(t)]^2} \cdot \frac{∂^2\hat{c}}{∂z^2} + \frac{\dot{ℓ}(t)(1 - z)}{L - ℓ(t)} \cdot \frac{∂\hat{c}}{∂z}, \quad \hat{c}(0, z) = ψ(z), \quad \frac{∂\hat{c}}{∂z} \big|_{z=1} = 0; \]  

(9)

\[ [Q - \hat{c}(t, 0)]\dot{ℓ}(t) = -\frac{D_v}{ℓ(t)} \cdot \frac{∂\hat{v}}{∂y} \big|_{y=1} + \frac{D}{L - ℓ(t)} \cdot \frac{∂\hat{c}}{∂z} \big|_{z=0}. \]  

(10)

The initial distribution \(ψ(z)\) is taken from the previous stage. Formally, one can forget about the physical meaning of \(ℓ(t)\) as the phase bound and consider it as a functional parameter. Model coefficients in the boundary-value problem are nonlinear functionals with respect to solutions \(\hat{v}, \hat{c}\). Indeed, if we consider the functions \(\hat{v}(t, y), \hat{c}(t, z)\) as formally known we get
a nonlinear functional differential equation for \( \ell(t) \): 
\[
\ell(t) = G(t, \ell(t)) \quad \text{from the Stefan condition (10).}
\]
All model coefficients are unambiguously determined using the solution \( \ell(t) \). Therefore, the computational algorithm will be based on the implicit scheme and will have an iterative character. Iterations will be related to more precise definition of \( \ell(t) \) at every time layer. We use a standard four-point pattern to approximate the diffusion equations (7), (9) and then solve the resultant linear equation systems applying the Thomas algorithm. We now describe how to “sew together” the diffusion equations using the Stefan condition (10). We have to restrict ourselves to the case of the initial stage only (\( \ell(0) = \ldots \)), we proceed similarly on the next time layers) to avoid cumbersome technical manipulations.

We first assume that \( \ell_0 = \ell(0) = 0 \) (later on we use the value from the previous layer). The parameter \( \ell_0 \) is subject to iterative improvement, the value of \( \ell_0 \) is known.

We fix the time step \( \Delta t \) and suppose that \( \ell = 0, \ell = \ell_0 \) in the boundary-value problem (7)–(8). At the initial stage we assume \( \hat{v} = 0 \) at \( y = y_{1.2} \) in the standard three-point pattern. We have a quadratic equation in (8) for \( \hat{v}(t_1, 0) \) and choose the positive root. Find the distribution (approximation) \( \hat{v}(t_1, y), y \in [0, 1] \) using the Thomas algorithm. Go back to the improvement of \( \hat{v}(t_1, 0) \) in virtue of (8) (the values of \( \hat{v} \) at \( y = y_{1.2} \) used to calculate \( \partial_y \hat{v} |_{y=0} \) have already changed). Proceed with this process until the distribution \( v(t_1, y) \) becomes stable. The time step is small enough, so a few iterations will suffice.

Move on to the boundary-value problem (9) returning to the previous time layer \( t = 0 \). The missing boundary condition is determined from the Stefan equation (10): 
\[
\ell_0 = 0, \hat{v} = 0 \quad \Rightarrow \partial_x \hat{c}|_{z=0} = 0.
\]
We proceed with the iterative calculations until the distribution \( \hat{c}(t_1, z) \) becomes stable. Note that the input concentration will then go down \( \hat{c}(t_1, 0) < Q \).

As a result of these calculations we get \([\ldots] > 0 \) and a positive right-hand side into the Stefan equation (10). We find a new approximation of \( \ell_0 > 0 \) and return to the beginning of the described subalgorithm. After some iterations we obtain a steady-state value of \( \ell_0 \) and determine \( \ell_1 = \ell_0 + \ell_0 \Delta t \). We go on to the layer \( t_1 = \Delta t \) and begin with the following equality \( \ell_1 = \ell_0 \).

Next, we specify the value of \( \ell_1 \) and the corresponding distributions \( \hat{v}(t_2, y), \hat{c}(t_2, z) \) according to the scheme drafted above.

**Numerical algorithm testing.** The iterative algorithm is developed on the basis of implicit difference schemes and the Thomas algorithm. Computational experiments confirming the algorithm efficiency have been conducted. The input data, for example, are \( L = 6 \cdot 10^{-2} \) cm, \( \ell_0 = 1.3 \cdot 10^{-3} \) cm, \( p = 1520 \) Torr, \( T = 593 \) K, \( Q = 6.4 \cdot 10^{20} \) cm\(^{-3}\), \( D_0 = 2.2 \cdot 10^{-3} \) cm\(^2\) s\(^{-1}\), \( E_D = 35 \cdot 10^3 \) J mol\(^{-1}\), \( D_0 = 1.5 \cdot 10^{-3} \) cm\(^2\) s\(^{-1}\), \( E_{D*} = 59 \cdot 10^3 \) J mol\(^{-1}\), \( b = 5 \cdot 10^{-23} \) cm\(^3\) s\(^{-1}\), \( \beta = 3 \cdot 10^{-24} \) cm\(^4\) s\(^{-1}\), \( s = 7 \cdot 10^{-6} \), \( s_a = 6 \cdot 10^{-7} \).

The possibility to analyze the distribution dynamics of dissolved hydrogen concentrations across the hydride and the alloy layers is shown in Fig. 3.

**Conclusions**

Zirconium alloys are the construction materials for critical elements in active zones of nuclear power reactors. During the operation of reactors such materials are subject to hydrogenation. Hydrogenation results in a decrease of alloy plasticity and cracking resistance. The formation of brittle hydrides at crack tips can result in severe embrittlement. One of the most important requirements for the reactor’s active zone materials is low hydrogen absorptivity.

Since dissolved atomic hydrogen represents an extremely mobile interstitial phase, it is practically impossible in experimental studies to determine time-dependent hydrogen distribution in the material (even within the experiment time scale) based on the available external measurements.

The article presents a model taking into account nonlinear dynamics of adsorption-desorption processes and the movement of free phase boundary (hydride–metal). In the asymptotic (under chemical equilibrium conditions) the model corresponds to the experimental Sieverts law of
solubility. The algorithm that allows to numerically model the dynamics of phase boundary and distribution of dissolved hydrogen concentrations across the hydride and the alloy layers is briefly presented. Particularly important is the model-based forecast on the time horizon much exceeding experimental capabilities.

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References
[1] Alefeld G and Völk J (Eds) 1978 Hydrogen in Metals (Berlin; New York: Springer) vol I Basic Properties p 427, vol II Application-oriented Properties p 387
[2] Pisarev A A, Tsvetkov I V, Marenkov E D and Yarko S S 2008 Hydrogen Permeability through Metals (Moscow: MEFPI) p 144
[3] Varin R A, Czuiko T and Wronska Z S 2009 Nanomaterials for solid state hydrogen storage (Springer) p 338
[4] Ball M and Wietschel M (Eds) 2009 The hydrogen economy (Cambridge University Press) p 646
[5] Hirscher M (Ed) 2010 Handbook of Hydrogen Storage (Wiley–VCH) p 353
[6] Evard E A, Gabis I E and Yartys V A 2010 Kinetics of hydrogen evolution from MgH2: experimental studies, mechanism and modelling Int. J. Hydrogen Energy 35 9060–69
[7] Lototskyy M V, Yartys V A, Pollet B G and Bowman R C Jr. 2014 Metal hydride hydrogen compressors: a review Int. J. Hydrogen Energy 39 5818–51
[8] Indeitsev D A and Semenov B N 2008 About a model of structure-phase transformations under hydrogen influence Acta Mechanica 195 295–304
[9] Zaika Yu V and Rodchenkova N I 2009 Boundary-value problem with moving bounds and dynamic boundary conditions: diffusion peak of TDS-spectrum of dehydriding Appl. Math. Modelling 33 3776–91
[10] Zaika Yu V and Bormatova E P 2011 Parametric identification of a hydrogen permeability model by delay times and conjugate equations Int. J. Hydrogen Energy 36 1295–1305
[11] Zaika Yu V and Rodchenkova N I 2013 Hydrogen-solid boundary-value problems with dynamical conditions on surface Math. Modelling (New York: Nova Sci. Publishers) 269–302
[12] Pushilina N S, Kudliarov V N, Laptev R S, Lider A M and Teresov A D 2015 Microstructure changes in Zr–1Nb alloy after pulsed electron beam surface modification and hydrogenation Surf. Coat. Technol. 284 63–68