

Parametric Control of Diffusion Kinetics in Cylindrical Claddings

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Abstract—An algorithm for parametric control using the internal stresses of different physical nature in mathematical simulations of diffusion processes is proposed. Primary consideration is given to thermal, concentration, and residual stresses with a logarithmic coordinate dependence. This dependence allows us to obtain an exact analytical solution for diffusion kinetics in investigating the hydrogen permeability of cylindrical claddings.

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INTRODUCTION

Cylindrical claddings are one of the most frequently encountered structural elements in different technical applications, particularly the fuel elements of nuclear reactors [1, 2]. Their function is to contain fission products and interstitial impurities as the nuclear fuel burns out. The structural stability of the claddings is determined by the levels and distribution patterns of their internal stresses. The latter include temperature, concentration, and residual stresses caused by the nonuniform distribution of temperature, the concentration of doping elements, and the density of structural defects (e.g., edge dislocations). Internal stresses greatly influence the kinetics of diffusion processes, due to the elastic interaction between point defects with the first invariant of stress tensor. The interaction potential (binding energy) is generally determined by the known relationships [3]

$$V = -\frac{\sigma_{II}}{3} \delta v, \quad (1)$$

where σ_{II} is the first invariant of the internal stress tensor, and δv is the change in crystal volume caused by the introduction of impurity atoms. When $\sigma_{II} > 0$ (tensile stress) and $\delta v > 0$ (impurity atoms raise the crystal lattice parameter), potential V assumes a negative value. This corresponds to the impurity atoms being attracted to the region of tensile stress and its displacement from the region of compression stress. If $\sigma_{II} > 0$ and $\delta v < 0$ (impurity atoms lower the crystal lattice parameter), the diffusion flow of impurity atoms changes: Impurities of short atomic radius migrate to the region of compressive stress and are forced out of the region of tensile stress. The stratification of the solid solution containing doping elements with different atomic radii thus occurs.

The diffusion flow of impurity atoms through cylindrical cladding characterizes its diffusive permeability. This characteristic of the system is largely

dependent on the distribution of internal stresses of different physical natures. In the linear theory of continuous medium mechanics, the superposition principle is observed: Tensor components of different kinds of stresses allow algebraic summation. This means that internal stresses can be controlled to vary the diffusive permeability of cylindrical claddings, since the internal stresses in the cladding have different signs with identical coordinate dependence. Among interstitial impurities, hydrogen atoms dominate because of the high diffusion mobility of hydrogen atoms over a wide range of temperatures. For example, at room temperature the diffusion coefficient for hydrogen atoms is greater by several orders of magnitude than that of substitutional impurities and other interstitial impurities; we may therefore consider the hydrogen permeability of claddings in the presence of frozen nonuniform concentrations of other doping elements. The aim of this work was to study means of controlling internal stresses and thus the hydrogen permeability of cylindrical claddings. The results from theoretical analysis are used as an example of numerical (computer aided) simulation of diffusion processes. This covers systems in which the complex coordinate dependence of internal stresses does not allow us to obtain an analytical solution to diffusion kinetics equations.

FIRST INVARIANT OF THE INTERNAL STRESS TENSOR

The hydrogen permeability of a cylindrical cladding depends on the level and pattern of the distribution of internal stresses of different natures. They result in the diffusive redistribution of hydrogen atoms. The latter migrate to tensile stress regions and are forced out of the regions of compressive stress. Such behavior is due to the crystals' lattice parameter tending to grow when interstitial impurities (e.g., hydrogen atoms) are present.

Among internal stresses, temperature stresses play a leading role. In advanced technologies, structural elements operate at elevated temperatures. The diffusion of doping elements depends exponentially on this parameter. The physical mechanism of thermal stress is well understood. When the temperature is nonuniform, the hotter region expands while cooler regions resist expansion. The former are thus in a compressed state, being unable to expand according to the temperature field. Cooler regions of the material are in a different position: hot regions tend to stretch in excess of temperature expansion, so cooler regions of the material are in a state of tension. The simplicity of this physical picture is helpful in analyzing the distribution pattern of thermal stress for a particular temperature field. Diffusion processes occur much more slowly than thermal processes, so we limit our consideration of the problem of diffusion kinetics in cylindrical claddings to a case of stationary temperature distribution:

$$T = T_1 + \frac{(T_2 - T_1)}{\ln R/r_0} \ln r/r_0, \quad (2)$$

where r_0 and R are the internal and external radii of the cylindrical cladding, and T_1 and T_2 are the temperatures of the internal and external surfaces ($T_1 > T_2$). The temperature distribution has a logarithmic dependence on the radial coordinate. A similar coordinate dependence holds for temperature stresses as well. The first tensor invariant takes the form (state of plane deformation) [4]

$$\sigma'_{\parallel\parallel} = \frac{2\alpha\mu(1+\nu)(T_1 - T_2)}{(1-\nu)\ln R/r_0} \times \left[1 + 2 \ln r/R + \frac{2(r_0/R)^2}{1 - (r_0/R)^2} \ln r_0/R \right], \quad (3)$$

where α is the thermal expansion coefficient; μ is the shear modulus; and ν is the Poisson ratio. Other symbols correspond to those used earlier. The diffusion of hydrogen atoms depends on the gradient of $\sigma'_{\parallel\parallel}$ ($\nabla \sigma'_{\parallel\parallel}$), so constant relationships (3) vanish upon differentiation. However, the constants in expression (3) must be considered when determining the equilibrium concentrations of hydrogen atoms at area boundaries.

A nonuniform distribution of impurity atoms gives rise to concentration stresses. These are determined in a manner similar to the one for temperature stresses. The coefficient of thermal expansion is set to correspond to the variation in the crystals lattice parameter per unit concentration of impurity atoms. Renormalization of the constants in thermoelasticity equations makes it easy to write the first invariant of the concentration stress tensor:

$$\sigma''_{\parallel\parallel} = \frac{2\beta\mu(1+\nu)(C_1 - C_2)}{(1-\nu)\ln R/r_0} \times \left[1 + 2 \ln r/R + \frac{2(r_0/R)^2}{1 - (r_0/R)^2} \ln r_0/R \right], \quad (4)$$

where $\beta(C_1 - C_2)$ is the concentration deformation similar to temperature deformation $\alpha(T_1 - T_2)$, C_1 , C_2 are concentrations of impurity atoms on the internal and external cladding surfaces ($C_1 > C_2$). Other symbols have the earlier meanings. Concentration stresses affect the diffusion kinetics of hydrogen atoms. This is important at intermediate temperatures, where the nonuniform concentration of substitutional impurities remains unchanged. At elevated temperatures, the nonuniform concentration diffuses and the stresses disappear.

Residual stresses arise during the fabrication and operation of products. If the magnitude of shear stress under an external load (force or temperature) exceeds the material's yield strength, a plastic flow begins in a local region. When the external load is relieved, the material remains in a stressed state. Such internal stresses are now known as residual stresses. In cylindrical cladding, these stresses are created in the following way: A doubly connected region is converted to a singly connected region through the formation of a radial gap. The two surfaces of the gap acquire a slight angular disorientation. The gap in the cladding is filled by additional material. The system again becomes doubly connected, but this time with internal stresses. The internal surface is in a stretched state, and the external surface is in a compressed state. The first invariant of the residual stress tensor also has a logarithmic dependence on the radial coordinate [4]:

$$\sigma''_{\parallel\parallel} = \frac{\omega\mu(1+\nu)}{2\pi(1-\nu)} \times \left[1 + 2 \ln r/R + \frac{2(r_0/R)^2}{1 - (r_0/R)^2} \ln r_0/R \right], \quad (5)$$

where ω is the turning angle of the cladding gap's edges (measured in radians). Other symbols are identical to those used above. Note that relation (5) is identical to the first invariant of the stress tensor of wedge disclinations (ω being the Frank vector module) [5].

Analysis of relations (3), (4), and (5) shows that they have identical logarithmic dependences on the radial coordinate. This difference is characteristic only of constants that characterize the nature of internal stresses. The hydrogen permeability of the cylindrical cladding depends on all types of internal stress. They are described by a second order tensor and are included in diffusion kinetics equations with different signs. The laws of tensor algebra in a linear space allow us to control the internal stresses in a cylindrical cladding in order to change its hydrogen permeability.

DIFFUSION KINETICS AND HYDROGEN PERMEABILITY

Allowing for internal stresses of different physical natures, the diffusion kinetics of hydrogen atoms is

described by parabolic-type equations under the appropriate initial and boundary conditions [3]:

$$\frac{1}{D} \frac{\partial C}{\partial t} = \Delta C + \frac{\nabla(C\nabla V)}{kT}, \quad r_0 < r < R,$$

$$C(r, 0) = 0, \quad C(r_0, t) = C_p, \quad C(R, t) = 0, \quad (6)$$

$$\Delta = \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r}, \quad \nabla = \frac{\partial}{\partial r},$$

where D is the coefficient of hydrogen atom diffusion; k is the Boltzmann constant; T is the absolute temperature; V is the bonding energy of hydrogen atoms under different types of internal stresses; and C_p is the equilibrium concentration of hydrogen atoms on the cladding's internal surface. Other symbols remain the same as above. The physical sense of the initial and boundary conditions of problem (6) is fairly obvious. At the initial moment in time, the concentration of hydrogen atoms in the cylindrical cladding is zero. The same concentration is observed on the external surface of the considered system. Physically, this means that hydrogen atoms leave the external surface the moment they arrive on it. This condition allows us get to the heart of the cladding's hydrogen permeability. On the internal surface, an equilibrium concentration of hydrogen atoms is maintained that generally depends on the magnitude of $\sigma_{ii}^{t,c,r}$ in the near-surface region. Below, we use relations (3), (4), and (5) and simplify problem (6)

$$\frac{1}{D} \frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial r^2} + \frac{1 - \alpha_1 - \alpha_2 - \alpha_3}{r} \frac{\partial C}{\partial r}, \quad r_0 < r < R, \quad (7)$$

$$C(r, 0) = 0, \quad C(r_0, t) = C_p, \quad C(R, t) = 0.$$

Constants α_1 , α_2 , and α_3 characterize the ratio of the bonding energy between hydrogen atoms under internal stresses to the energy of thermal motion

$$\alpha_1 = \frac{4\alpha(T_1 - T_2)\mu(1 + \nu)\delta v}{3kT(1 - \nu)\ln R/r_0},$$

$$\alpha_2 = \frac{4\beta(C_1 - C_2)\mu(1 + \nu)\delta v}{3kT(1 - \nu)\ln R/r_0}, \quad (8)$$

$$\alpha_3 = \frac{\omega\mu(1 + \nu)\delta v}{3kT\pi(1 - \nu)}.$$

All designations are the same as the ones used above.

The effect of internal stresses of different physical natures can be considered by introducing a dimensionless constant that can easily be calculated. Most important: they can be summed algebraically within the linear theory of solid media mechanics if we employ the superposition principle. This allows us to control the internal stresses when studying the hydrogen permeability of cylindrical claddings. If the sum of the dimensionless constants in the problem is much less than unity, the internal stresses act as weak perturbations of the main diffusive flow of hydrogen atoms.

An alternative case corresponds to the dominant role of internal stresses. Estimates show that values of the dimensionless constants are close to unity with slight deviations in one direction or another. By way of illustration, let us consider a cylindrical cladding based on Zr-Sn: $R/r_0 = 1.1$; $\alpha = 10^{-5} \text{ K}^{-1}$; $(T_1 - T_2) = 10^2 \text{ K}$; $\mu = 4 \times 10^{10} \text{ Pa}$; $\nu = 0.3$; $kT = 4.1 \times 10^{-21} \text{ J}$; $\delta v = 3 \times 10^{-30} \text{ m}^3$; $\beta = 0.1$; $\omega = 0.16 \text{ rad}$; $(C_1 - C_2) = 1.3 \times 10^{-2} \text{ (at)}$.

Calculations show that under the given conditions, the numerical values of the dimensionless constants are close to unity. This means that the effects of the concentration gradient and the internal stresses on the hydrogen permeability of a cylindrical cladding are comparable. The energy of the thermal motion of hydrogen atoms correlates to the average cladding temperature. It can exceed the difference in temperature between surfaces. All other conditions being equal, the numerical value and the sign of dimensionless relations (8) depend on $(T_1 - T_2)$, $(C_1 - C_2)$; and ω . Combining these quantities allows us to vary the second term in the right-hand side of Eq. (7) and thus control the diffusion kinetics and hydrogen permeability of the cladding. Solving Eq. (7) for arbitrary constants poses no mathematical problems. To clarify the physics of the processes in question, however, let us consider two cases of the distribution of internal stresses in a cylindrical cladding. The first of these corresponds to the resulting compression stresses on the internal surface, which change smoothly into tensile stresses at the external boundary; in our mathematical formalism, this is equivalent to altering Eq. (7) when $(\alpha_1 + \alpha_2 + \alpha_3) = 1$:

$$\frac{1}{D} \frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial r^2}, \quad r_0 < r < R, \quad (9)$$

$$C(r, 0) = 0, \quad C(r_0, t) = C_p, \quad C(R, t) = 0.$$

The internal stresses affect the formation of the field of hydrogen atom concentration: the concentration profile in the cladding is formed according to relationship for a band. This behavior has a simple physical explanation: When $\frac{\partial C}{\partial r} < 0$, term $\frac{(\alpha_1 + \alpha_2 + \alpha_3)\partial C}{r \partial r}$ corresponds to the source of hydrogen atoms. The latter are expelled from the internal near-surface region and are drawn to the external region. When $\frac{\partial C}{\partial r} < 0$, the rate of variation in hydrogen atom concentration $\frac{\partial C}{\partial t}$ under identical conditions is indeed higher for $(\alpha_1 + \alpha_2 + \alpha_3) = 1$, relative to their zero value (ignoring internal stresses). The second case describes the opposite situation: stretching on the internal surface changes to compression on the external surface; i.e., $(\alpha_1 + \alpha_2 + \alpha_3) = -1$.

The mathematical formulation of problem (7) becomes

$$\frac{1}{D} \frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r}, \quad r_0 < r < R, \quad (10)$$

$$C(r, 0) = 0, \quad C(r_0, t) = C_p, \quad C(R, t) = 0.$$

Again, internal stresses affect the formation of the field of hydrogen atom concentration: the concentration profile in the cylindrical cladding obeys the same law as in a spherical cladding. When $\frac{\partial C}{\partial r} < 0$, term $\frac{(\alpha_1 + \alpha_2 + \alpha_3) \partial C}{r \partial r}$ corresponds to a sink for hydrogen atoms. The rate of concentration profile formation slows, as follows directly from (7). When $\frac{\partial C}{\partial t} < 0$, the rate of change in hydrogen atom concentration $\frac{\partial C}{\partial t}$ for $(\alpha_1 + \alpha_2 + \alpha_3) = -1$ is indeed slower than with the zero sum of dimensionless constants.

We write the known solutions to Eqs. (9) and (10) in the form

$$C = C_p^1 f(r, t) \quad (a), \quad C = C_p^2 \frac{r_0}{r} f(r, t) \quad (b),$$

$$f(r, t) = \frac{R/r_0 - r/r_0}{R/r_0 - 1} \quad (11)$$

$$- \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{\sin \frac{\pi n (r/r_0 - 1)}{R/r_0 - 1}}{n} \exp \left[- \frac{\pi^2 n^2 D t}{r_0^2 (R/r_0 - 1)^2} \right],$$

where C_p^1 and C_p^2 are the equilibrium concentrations of hydrogen atoms at the cladding's internal boundary. They depend exponentially on interaction potential V and under the given conditions have the form

$$C_p^1 = C_0 \exp \left[\frac{1}{2} - \frac{(R/r_0)^2 \ln R/r_0}{(R/r_0)^2 - 1} \right]$$

for $\alpha_1 + \alpha_2 + \alpha_3 = 1$,

$$C_p^2 = C_0 \exp \left[\frac{(R/r_0)^2 \ln R/r_0}{(R/r_0)^2 - 1} - \frac{1}{2} \right]$$

for $\alpha_1 + \alpha_2 + \alpha_3 = -1$,

where C_0 is the average concentration of hydrogen atoms. Internal stresses with different signs alter the equilibrium concentration of hydrogen atoms. When $(\alpha_1 + \alpha_2 + \alpha_3) = 1$, dilatation on the internal surface is negative (compression stress) and so $C_p^1 < C_0$, i.e., the equilibrium concentration is less than the corresponding value when there is no stress. Physically, this means that the surface effect (the drop in equilibrium concentration) competes in forming the concentration profile according to Eq. (9). When $(\alpha_1 + \alpha_2 + \alpha_3) = -1$, positive dilatation (tensile stress) makes the equilib-

rium concentration C_p^2 higher than C_0 ; i.e., $C_p^2 > C_0$. This means that the slowing of the rate of concentration profile formation according to (10) is compensated for by an increase in C_p^2 .

In accordance with expressions (11a) and (11b), the formation of hydrogen atom concentration fields proceeds in an identical manner over time. This follows from the theory of equations of mathematical physics, since Eq. (10) can be reduced to Eq. (9) simply by changing the variables [5]. However, the coordinate dependence of the hydrogen atom concentration and its corresponding rate of change are lower for (11b) than for (11a). We then determine the diffusion flows of hydrogen atoms through the external surface that characterize the hydrogen permeability of a cylindrical cladding:

$$|J|_1 = DC_p^1 \frac{\partial f(r, t)}{\partial r} \Big|_{r=R},$$

$$|J|_2 = DC_p^2 \frac{r_0}{R} \frac{\partial f(r, t)}{\partial r} \Big|_{r=R}. \quad (13)$$

The ratio of these flows characterizes the hydrogen permeability of a cylindrical cladding, depending on the sign of internal stresses:

$$\frac{|J|_1}{|J|_2} = R/r_0 \frac{C_p^1}{C_p^2} = R/r_0 \exp \left[1 - \frac{2(R/r_0)^2}{(R/r_0)^2 - 1} \right]. \quad (14)$$

For thin cylindrical claddings ($R/r_0 \rightarrow 1$), this ratio takes the simple form

$$\frac{|J|_1}{|J|_2} = R/r_0. \quad (15)$$

This follows directly from the limiting transition

$$\lim_{x \rightarrow 1} \frac{2 \ln x}{x^2 - 1} = 1, \quad x = \frac{R}{r_0}.$$

The ratio of diffusion flows changes when ($R/r_0 \gg 1$) (a hollow cylinder):

$$\frac{|J|_1}{|J|_2} = e(r_0/R), \quad (16)$$

where e is the base of our natural logarithms. Compression stress on the internal surface of a hollow cylinder reduces its hydrogen permeability.

In thin claddings, the main contribution to the change in hydrogen permeability comes from the change in the diffusion equation due to internal stresses. With thicker claddings, surface effects (i.e., changes in the equilibrium concentration of hydrogen atoms due to compressive or tensile stress) assume the dominant role. Compressive stresses in the near-surface internal region reduce the equilibrium concentration of hydrogen atoms while tensile stresses increase it.

The mathematical simplicity of the obtained relations is explained by our model. The change in the sign

of the sum of internal stresses for the same coordinate dependence results in differential equations in partial derivatives for the two correlated coordinate systems. The logarithmic dependence on the radial coordinates of the tensor components for stresses of different physical natures should be especially noted. In the system of cylindrical coordinates, the logarithmic function is harmonic and its gradient corresponds to one of the terms of Laplace operator. With a more complicated physical model, it is of course nearly impossible to get an exact analytical solution to the diffusion kinetics equations. Note that every type of internal stress has its own characteristic features.

CONCLUSIONS

The process of controlling internal stresses of different physical natures was studied using mathematical simulations of the hydrogen permeability of cylindrical claddings. The corresponding algorithm includes the following operations: Determining the first invariant of internal stress tensor; solving the diffusion kinetics equation; and deriving relations for the flow of hydrogen atom diffusion through the external surface of the cladding. By way of illustration, temperature, concentration, and residual stresses were considered. All of these have a logarithmic dependence on the radial coordinate. An exact analytical solution of the diffusion kinetics equations is thus obtained. Mathematically, the internal stresses are described by a second order tensor. In a linear space, tensor algebra rules apply. These allow us to use the superposition principle in linear theory and add together the tensor

components of the corresponding stresses algebraically. The physical model and its mathematical description can easily be used in developing computer algorithms to simulate diffusion processes for complex coordinate dependences of internal stresses.

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