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SOLIDS

Thermal Diffusion of Hydrogen in Zirconium with Allowance for Thermal Stresses

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Abstract—The thermal diffusion of hydrogen atoms in zirconium is studied with allowance for thermal stresses. As a mathematical model, a steady-state temperature in a hollow cylinder is considered. The logarithmic coordinate dependence of this temperature allows an exact analytical solution to be obtained for a diffusion kinetics problem. The results of a theoretical analysis can serve as a test example for studying mass transfer in systems with a more complex coordinate dependence of temperature.

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Internal stresses of various physical origins (thermal, residual, defect-induced stresses) substantially affect the kinetics of diffusion processes [1–4]. For example, substitutional impurities with a large atomic radius (with respect to the base metal) and interstitial impurities migrate to the zone of tensile stresses and the corresponding impurities having a small atomic radius migrate to the zone of compressive stresses. As a result, a solid solution consisting of impurities of different kinds becomes separated. If the concentration of the latter impurities exceeds the solubility limit at a given temperature, new-phase precipitates form. The appearance of thermal stresses is caused by a nonuniform temperature, which affects diffusion by itself (thermal diffusion) [5, 6].

Thermal diffusion in solids differs from the corresponding process in gas mixtures, which is caused by the appearance of thermal stresses due to a nonuniform temperature. A light impurity in gases (e.g., hydrogen) is known to diffusionally migrate to a region with an elevated temperature [7, 8]. A temperature gradient in solids creates thermal stresses, namely, tensile stresses in a cold region and compressive stresses in a hot region. The lattice parameter under these conditions corresponds to a certain average temperature. Therefore, the characteristic sizes of tetrahedral and octahedral interstices intended for the accommodation of interstitial impurities seem to be approximately the same in hot and cold regions in a solid body. Actually, they are substantially different.

The material in a cold region is tensioned, and interstitial impurities (e.g., hydrogen atoms) can easily penetrate into interstices. In contrast, they can hardly penetrate into them in a hot region because of compressive stresses. These stresses eject interstitial impurities, and a diffusion flux is directed opposite to the temperature gradient (to a region with a low temperature).

The purpose of this work is to analyze the thermal diffusion of hydrogen atoms in zirconium with allowance for thermal stresses. Zirconium is used in nuclear power (e.g., in fuel-element cans in nuclear reactors), which is caused by a proper combination of its physicomechanical properties and small low thermal-neutron capture cross section. As a mathematical model, we consider a stationary temperature distribution in a hollow cylinder. We have chosen a long hollow cylinder because of the following factors. First, long hollow cylinders are used as a model for zirconium fuel-element cans in nuclear reactors. Second, when describing the temperature distribution and thermal stresses in them, we can use the state of plane deformation. Finally, the logarithmic coordinate dependence of the temperature and the corresponding thermal stresses allow us to obtain an exact analytical solution to the problem of diffusion kinetics. The results of theoretical analysis in combination with exact analytical dependences can serve as a test example for studying the mass transfer in systems with a more complex coordinate dependence of temperature.

In terms of the thermodynamics of irreversible processes, the diffusion flux of hydrogen atoms with allowance for concentration, temperature, and thermal-stress gradients has the form [9]

$$j = -D\left(\nabla C + \frac{C\nabla V}{kT} + \frac{CQ\nabla T}{kT^2}\right), \quad (1)$$

where D is the diffusion coefficient of hydrogen atoms, k is the Boltzmann constant, T is the absolute temperature, V is the potential of interaction (binding energy) of a hydrogen atom with the field of thermal stresses, and

Q is the heat of transfer. The last two parameters are to be explained. Interaction potential V is determined from the expression [10]

$$V = -\frac{\sigma_{ll}}{3}\delta v, \tag{2}$$

where σ_{ll} is the first invariant of the thermal-stress tensor and δv is the change in the metal volume upon the accommodation of hydrogen atoms. This quantity has the same value for all metals (3×10^{-30} m^3) [11]. At $\sigma_{ll} > 0$ (positive dilatation) and $\delta v > 0$ (hydrogen atom increases the lattice parameter), potential V is negative, which corresponds to the attraction of a hydrogen atom to a region with tensile stresses. Physically, this means that the diffusion flux of hydrogen atoms is directed opposite to the temperature gradient, since tensile stresses are inherent in a cold region. Parameter Q is the coefficient of proportionality between a heat flow and the concentration gradient of hydrogen atoms by analogy with thermal conductivity when a heat flow is described with a temperature gradient. The numerical value and sign of Q are found experimentally. For zirconium and its alloys (e.g., zircaloy-2), the coefficient of the heat of transfer is positive and lies in the range 0.056–0.500 eV for the temperature range 500–1000 K [12]. Physically, the positive sign of Q means that the diffusion flux of hydrogen atoms is directed opposite to the temperature gradient, i.e., to a cold region in the material. Thus, the temperature and the related thermal stresses transfer hydrogen atoms in the same direction.

We now consider the diffusion redistribution of hydrogen atoms in a hollow cylinder in the presence of a temperature gradient and thermal stresses. With the continuity condition of a diffusion flux

$$\frac{\partial C}{\partial t} + \operatorname{div} j = 0$$

we obtain the following equation for determining the concentration of hydrogen atoms:

$$\begin{gathered}\frac{1}{D}\frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r} + \frac{\nabla(C\nabla V)}{kT} + \frac{Q\nabla(c\nabla T)}{kT^2}, \\ r_0 < r < R, \\ C = C_0 \text{ at } t = 0, \quad C = C_p^1 \text{ at } r = r_0, \\ C = C_p^2 \text{ at } r = R,\end{gathered} \tag{3}$$

where t is the time; r_0 and R are the inside and outside radii of the hollow cylinder, respectively; C_0 is the initial concentration of hydrogen atoms; and C_p^1 and C_p^2 are the equilibrium concentrations of hydrogen atoms at the hollow-cylinder boundaries. The other designations correspond to those accepted earlier.

The physical meaning of the initial and boundary conditions of problem (3) is obvious. At the initial time, the concentration of hydrogen atoms is equal to the initial value. The conditions at the region boundaries mean that an equilibrium concentration is immediately reached there (according to the heat of transfer and the field of thermal stresses) and then remains constant during diffusion. In the general case, problem (3) contains significant mathematical difficulties. However, we can introduce some simplifications using physical considerations and mathematical formalism. Let us dwell on them.

The stationary temperature in a hollow cylinder is found by solving the problem

$$\begin{gathered}\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} = 0, \quad r_0 < r < R, \\ T = T_1 \text{ at } r = r_0, \quad T = T_2 \text{ at } r = R\end{gathered} \tag{4}$$

and has the form

$$T = T_1 + \frac{T_2 - T_1}{\ln\frac{R}{r_0}}\ln\frac{r}{r_0}, \tag{5}$$

where T_1 and T_2 are the temperatures at the boundaries of the hollow cylinder ($T_1 > T_2$).

A logarithmic function is a harmonic function, and its gradient is inversely proportional to the radius in the polar coordinate system. As applied to Eq. (5), this means that $\Delta T = 0$ and $\Delta T \sim r^{-1}$. This specific feature in the temperature distribution substantially changes initial Eq. (3), since σ_{ll} also has a logarithmic coordinate dependence [13],

$$\begin{gathered}\sigma_{ll} = \frac{2\alpha\mu(T_1 - T_2)(1+\nu)}{(1-\nu)\ln\frac{R}{r_0}} \\ \times\left\{1 + 2\ln\frac{r}{R} + \frac{2\left(\frac{r_0}{R}\right)^2}{1-\left(\frac{r_0}{R}\right)^2}\ln\frac{r_0}{R}\right\},\end{gathered} \tag{6}$$

where α is the linear thermal expansion coefficient, μ is the shear modulus, and ν is the Poisson ratio. The other designations correspond to those accepted earlier.

We also assume that the temperature drop $T_1 - T_2$ is significantly smaller than the absolute value of average temperature T_0, i.e., $\frac{T_1 - T_2}{T_0} \ll 1$. As a result, we arrive at the following mathematical formulation of problem (3):

$$\begin{gathered}\frac{1}{D}\frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial r^2} + \frac{1-\beta_1-\beta_2}{r}\frac{\partial C}{\partial r}, \quad r_0 < r < R, \\ C = C_0 \text{ at } t = 0, \quad C = C_p^1 \text{ at } r = r_0, \\ C = C_p^2 \text{ at } r = R,\end{gathered} \tag{7}$$

where dimensionless parameters β_1 and β_2 have the form

$$\beta_1 = \frac{4\alpha(T_1 - T_2)\mu(1+\nu)\delta v}{3kT_0(1-\nu)\ln\frac{R}{r_0}},$$
$$\beta_2 = \frac{Q(T_1 - T_2)}{kT_0^2\ln\frac{R}{R_0}}. \quad (8)$$

The former parameter takes into account the effect of thermal stresses, and the latter, thermal diffusion. Their ratio determines the contribution of the material characteristics to the mass-transfer kinetics with allowance for thermal diffusion and thermal stresses, all other things being equal,

$$\frac{\beta_1}{\beta_2} = \frac{4\alpha T_0\mu(1+\nu)\delta v}{3(1-\nu)Q}. \quad (9)$$

As a rule, all components of this ratio are determined experimentally. Without loss of generality, we take the following values of the constants: $\alpha = 10^{-5}$ K, $\mu = 4 \times 10^{10}$ Pa, $\nu = 0.3$, $\delta v = 10^{-30}$ m^3, $T_0 = 10^3$ K, and $Q = 0.4$ eV (0.64×10^{-19} J) (β is zirconium phase). For these values, we obtain $\frac{\beta_1}{\beta_2} = 0.05$. Physically, this means that, under the given conditions, thermal diffusion prevails over the effect of thermal stresses. At $\frac{R}{r_0} = 1.6$ and $T_1 - T_2 = 10^2$ K, we have $\beta_1 + \beta_2 = 1$. Problem (7) can now be formulated rather simply,

$$\frac{1}{D}\frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial r^2}, \quad r_0 < r < R,$$
$$C = C_0 \text{ at } t = 0, \quad C = C_p^1 \text{ at } r = r_0, \quad (10)$$
$$C = C_p^2 \text{ at } r = R.$$

Since the solution to this problem is well known, we can write the temperature variation of the concentration of hydrogen atoms as

$$C - C_0 = \frac{R(C_p^1 - C_0) - r_0(C_p^2 - C_0) + r(C_p^2 - C_p^1)}{R - r_0}$$
$$+ \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{1}{n}[(-1)^n(C_p^2 - C_0) - (C_p^1 - C_0)] \quad (11)$$
$$\times \sin\frac{\pi n(r - r_0)}{R - r_0}\exp\left(-\frac{\pi^2 n^2 Dt}{(R - r_0)^2}\right).$$

This expression contains the equilibrium concentrations of hydrogen atoms at the inner and outer surfaces of the hollow cylinder,

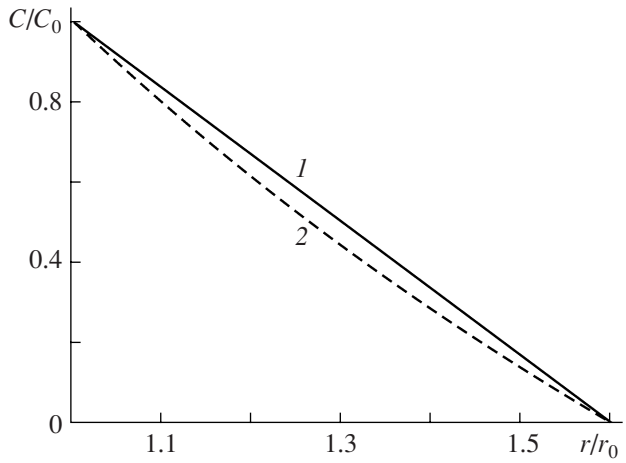
$$C_p^1 = C_0\exp\left(-\frac{Q}{kT_1}\right), \quad C_p^2 = C_0\exp\left(\frac{Q}{kT_2}\right), \quad (12)$$

where C_0 is the initial concentration of hydrogen atoms. These relationships only take into account the heat of transfer, since the contribution of thermal stresses is an order of magnitude smaller under these conditions. As follows from physical considerations, the equilibrium concentration of hydrogen atoms at the inner surface is lower than the initial concentration. This is caused by the fact that the diffusion flux is directed from the inner surface and that an equilibrium concentration is immediately reached at the boundary. At the outer surface of the hollow cylinder, the equilibrium concentration of hydrogen atoms exceeds the initial concentration, since the diffusion flux is directed toward the outer surface. An equilibrium concentration is also immediately reached at its boundary. Hydrogen atoms then undergo diffusion redistribution according to Eq. (11). In a steady state, this flux is compensated for by the flux induced by a concentration gradient via thermal diffusion (dynamic equilibrium).

A comparison of problems (7) and (10) demonstrates that thermal diffusion in combination with thermal stresses changes the symmetry of the diffusion equations. The diffusion redistribution of hydrogen atoms in a hollow cylinder occurs according to the law typical of a strip. As a result, the formation of the concentration of hydrogen atoms is accelerated. The physical essence of the acceleration of the process kinetics is caused by the effect of thermal diffusion and the related thermal stresses.

Our analysis demonstrates that thermal diffusion plays a key role in the formation of a concentration profile. Nevertheless, we cannot rule out a significant effect of thermal stresses, which is associated with the fact that the heat of transfer is determined experimentally and exhibits a rather large scattering of its values. Therefore, cases in which the contribution of thermal stresses to the process kinetics is comparable with that of thermal diffusion are possible. It is interesting that the available experimental data on the thermal diffusion of hydrogen in zirconium indicate a positive effect of the heat of transfer. This means that thermal diffusion and thermal stresses act in the same direction: the diffusion flux of hydrogen atoms is directed opposite to the temperature gradient (to a cold region in the material).

A nonuniform temperature also affects the hydrogen permeability of a hollow cylinder. The mathematical formulation of the corresponding problem is similar to problem (3) except for the initial and boundary conditions. We take into account the simplified version of problem (3) and have



Concentration profile of hydrogen atoms in a hollow cylinder (*1*) with and (*2*) without regard for thermal diffusion and thermal stresses.

$$\frac{1}{D}\frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial r^2} + \frac{1-\beta_1-\beta_2}{r}\frac{\partial C}{\partial r}, \quad r_0 < r < R,$$
$$C = 0 \text{ at } t = 0, \quad C = C_0 \text{ at } r = r_0, \tag{13}$$
$$C = 0 \text{ at } r = R,$$

where C_0 is the concentration of hydrogen atoms at the inner surface of the hollow cylinder. The other designations are identical to those accepted earlier. The physical meaning of the initial and boundary conditions is clear. A zero hydrogen concentration is also retained at the outer surface. This means that hydrogen atoms immediately leave the outer surface as soon as they reach it. A constant concentration of hydrogen atoms is maintained at the inner surface of the hollow cylinder due to external conditions: the motion of hydrogen into the volume is immediately compensated for by the supply (removal) of hydrogen for a constant concentration to be maintained. These conditions allow us to reveal the effect of thermal diffusion and thermal stresses on the hydrogen permeability of a hollow zirconium cylinder. We now analyze two cases of temperature distribution. For the first case ($T_1 > T_2$, $\beta_1 + \beta_2 = 1$), we have

$$\frac{1}{D}\frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial r^2}, \quad r_0 < r < R,$$
$$C = 0 \text{ at } t = 0, \quad C = C_0 \text{ at } r = r_0, \tag{14}$$
$$C = 0 \text{ at } r = R.$$

If temperature changes its sign ($T_1 < T_2$), for $\beta_1 + \beta_2 = -1$ we obtain

$$\frac{1}{D}\frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}, \quad r_0 < r < R,$$
$$C = 0 \text{ at } t = 0, \quad C = C_0 \text{ at } r = r_0, \tag{15}$$
$$C = 0 \text{ at } r = R.$$

The solutions to problems (14) and (15) are well known. For convenience, we write them in the form

$$C = C_0 f(r, t), \tag{15'}$$

$$C = C_0 \frac{r_0}{r} f(r, t), \tag{15''}$$

where

$$f(r, t) = \frac{\frac{R}{r_0} - \frac{r}{r_0}}{\frac{R}{r_0} - 1} - \frac{2}{\pi}\sum_{n=1}^{\infty} \frac{\sin\frac{\pi n\left(\frac{r}{r_0} - 1\right)}{R/r_0 - 1}}{n} \times \exp\left[-\frac{\pi^2 n^2 Dt}{r_0^2\left(\frac{R}{r_0} - 1\right)^2}\right]. \tag{16}$$

According to Eqs. (15') and (15''), the concentration of hydrogen atoms forms in time identically, since Eq. (15) is reduced to Eq. (14) by a simple change of variables.

We now determine the diffusion fluxes of hydrogen atoms through the outer surface of the hollow cylinder for the following two cases of temperature distribution: $T_2 > T_1$, and $T_2 < T_1$. We use the obvious equality $f(R, t) = 0$ and obtain

$$|j_1| = DC_0 \frac{\partial f(r, t)}{\partial r}\bigg|_{r=R}, \quad |j_2| = DC_0 \frac{r_0}{R}\frac{\partial f(r, t)}{\partial r}\bigg|_{r=R},$$

$|j_1|$ and $|j_2|$ are the diffusion fluxes for $\beta_1 + \beta_2 = 1$ and $\beta_1 + \beta_2 = -1$, respectively. Their ratio characterizes the hydrogen permeability of the hollow cylinder as a function of the temperature-gradient direction,

$$\frac{|j_1|}{|j_2|} = \frac{R}{r_0}.$$

Thus, with our model, we showed that the ratio of the fluxes of hydrogen atoms as the sign of temperature changes depends only on the ratio of the characteristic hollow-cylinder sizes. The simplicity of this expression results from the following accepted condition: the sum of the dimensionless parameters is unity ($|\beta_1 + \beta_2| = 1$). Other values of these parameters do not change the qualitative picture of the hydrogen permeability of the hollow cylinder; they are only reduced to refining the numerical values of the ratio of the diffusion fluxes.

Finally, we consider the hydrogen permeability of the hollow cylinder for a steady-state diffusion process with and without regard for a temperature gradient and thermal stresses. The figure shows the concentration profiles of hydrogen atoms calculated by the relationships

$$(1)\ \frac{C}{C_0} = \frac{\frac{R}{r_0} - \frac{r}{r_0}}{\frac{R}{r_0} - 1},$$

$$(2)\ \frac{C}{C_0} = \frac{\ln\frac{R}{r}}{\ln\frac{R}{r_0}}$$

for $\beta_1 + \beta_2 = 1$ (curve *1*) and $\beta_1 + \beta_2 = 0$ (curve *2*). The temperature gradient and thermal stresses are seen to increase the supply of hydrogen atoms to the hollow cylinder. The corresponding diffusion fluxes through the outer surface have the form

$$(1)\ |j_1| = \frac{DC_0}{r_0\left(\frac{R}{r_0} - 1\right)},$$

$$(2)\ |j_2| = \frac{DC_0}{R\ln\frac{R}{r_0}}.$$

Their ratio characterizes the effect of thermal diffusion and thermal stresses on the hydrogen permeability of the hollow cylinder under the model conditions

$$\frac{|j_1|}{|j_2|} = \frac{R}{r_0}\frac{\ln\frac{R}{r_0}}{\left(\frac{R}{r_0} - 1\right)} > 1.$$

This inequality holds true at arbitrary values of $\frac{R}{r_0}$. Physically, this means that thermal diffusion and thermal stresses increase the hydrogen permeability of the hollow cylinder.

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