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HEAT AND MASS TRANSFER IN HYDROGEN SORPTION—DESORPTION IN METAL-HYDRIDE POWER-PLANT COMPONENTS

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UDC 536.242

A mathematical model which describes the dynamics of hydride-accumulator operation, taking account of the laws of heat and mass transfer and the reaction kinetics of hydrogen sorption—desorption, is developed. Estimates of the accuracy of the approximate analytical solutions are given. A generalization of the quasi-steady method of solving the Stefan problem is obtained.

The hydrides of intermetallide compounds (IMC) — for example, $LaNi_5$, FeTi, etc. — are capable of reversible sorption and desorption of a large quantity of hydrogen. To optimize the operating conditions and construction of hydride accumulators, it is expedient to use mathematical modeling. In [1], a mathematical model of heat transfer in the hydride layer was proposed, and an approximate analytical solution was obtained under the assumption that sorption—desorption occurs at constant temperature (frontal model). In [2], a model taking account of heat and mass transfer was proposed; in [3], a model also taking account of the kinetics of hydrogen sorption—desorption was considered.

The mathematical model here outlined is obtained on the basis of the laws of mass and energy conservation in differential form [4] and the equations of reaction kinetics, and is more general than those considered previously.

The following assumptions are made in its formulation:

1) heat transfer occurs on account of heat conduction of the hydride and convection in the filtration of free hydrogen in the hydride pores;

2) the filtration of hydrogen occurs in viscous conditions;

3) the change in hydrogen content in the hydride is due to two factors: the sorption—desorption reaction and the diffusion of bound hydrogen in the hydride.

The mathematical model includes the following equations:

mass conservation of free hydrogen (continuity) taking account of the equation of state of an ideal gas for free hydrogen

$$\frac{M_{H_2}}{R_{gas}}\frac{\partial}{\partial\tau}\left(\frac{\Pi p_{H_2}}{T}\right)=hd_{me}^2\operatorname{div}\left(\frac{\Pi^3}{(1-\Pi)^2}\frac{p_{H_2}}{\mu_{H_2}T}\operatorname{grad}p_{H_2}\right)-\frac{M_{H_2}}{2}\frac{\rho_h}{M_h}\left(\frac{d\varkappa}{d\tau}-\operatorname{div}(D_H\operatorname{grad}\varkappa)\right); \quad (1)$$

energy conservation (heat transfer)

$$\left(c_h\rho_h+c_{H_2}\frac{M_{H_2}}{R_{gas}}\Pi\frac{p_{H_2}}{T}\right)\frac{\partial T}{\partial\tau}=\operatorname{div}(\lambda_h\operatorname{grad}T)+\frac{Q\rho_h}{2M_h}\left(\frac{d\varkappa}{d\tau}-\right. \quad (2)$$

$$\left.-\operatorname{div}(D_H\operatorname{grad}\varkappa)\right)+\beta hd_{me}^2\frac{M_{H_2}}{R_{gas}}c_{H_2}\frac{\Pi^3}{(1-\Pi)^2}\frac{p_{H_2}}{\mu_{H_2}T}(\operatorname{grad}p_{H_2},\ \operatorname{grad}T);$$

the kinetic equation of hydrogen sorption—desorption

$$\frac{d\varkappa}{d\tau}=K\exp\left(-\frac{e}{R_{gas}T}\right)\left[\frac{p-p_d(T,\ \varkappa)}{p_d(T,\ \varkappa)}\right](\varkappa_{max}-\varkappa). \quad (3)$$

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 60, No. 6, pp. 928-936, June, 1991. Original article submitted December 6, 1989.

0022-0841/91/6006-0707$12.50

With stronger assumptions, the model in Eqs. (1)-(3) reduces to the models proposed in [1-3].

Numerical solution of Eqs. (1)-(3) is undertaken by a purely implicit scheme with iterations [5].

For engineering applications and for estimates of the influence of various factors on the sorptional conditions of an accumulator, it is important to find analytical solutions of this problem with reasonable simplifying assumptions. Below, so as to be specific, sorptional conditions are considered (desorption conditions are considered analogously). According to [1, 2], the kinetics of the chemical reaction is not the limiting stage for $LaNi_5$; therefore, the following assumption is made below:

4) there is local equilibrium at each point between the free and bound hydrogen.

In this case, Eq. (3) takes the form

$$p=p_d(T, \varkappa) \quad \text{or} \quad T=T_d(p, \varkappa). \tag{4}$$

Equation (4) specifies the isotherms (isobars) of IMC equilibrium.

The basic cases permitting analytical solution are now considered.

Problem 1

As shown in [1], the equilibrium isotherms for $LaNi_5$ may be schematized up to isobaric areas covering the whole sorptional capacity of the IMC. Under this assumption, the sorption reaction will proceed over a front and not in a zone of finite size (see problem 2). The initial temperature of the IMC layer T_0 may be assumed to be the equilibrium temperature of sorption, since with rapid stabilization of the working hydrogen pressure $p = p_0$, there is adiabatic heating of the IMC layer with partial sorption of hydrogen up to an amount κ_0 determined from the thermal balance.

The pressure difference over the cross section of the IMC layer (see problem 3) and the heat transfer in hydrogen filtration (contributing no more than 5% to the total heat transfer, according to our estimates) are neglected.

Thus, on making the following additional assumptions:

5) a frontal model;

6) the process occurs without hindrance of the hydrogen filtration;

7) convective heat transfer is small in comparison with conductive heat transfer,

the classical Stefan problem is obtained. The time of accumulator charging with boundary conditions (BC) of the first kind (constant temperature is maintained at the accumulator surface) and with BC of the third kind (heat transfer occurs in the coolant) is of interest here.

Since heat transfer in a hydride accumulator is not highly intensive [1], it is expedient to use an approximate quasi-steady method of solving the Stefan problem developed in [6, 7], according to which the temperature field is determined from the solution of the steady elliptical equation corresponding to Eq. (2). This method is developed for bodies of simple configuration: an infinite plate, infinite cylinder, and sphere. Its generalization for an IMC layer of arbitrary configuration is now obtained.

Assertion 1. The differential equation describing the steady temperature distribution may be written in the form

$$\frac{d^2T}{dv^2}\, s(v) + 2\frac{dT}{dv}\frac{ds}{dv} = 0, \tag{5}$$

where s(v) is the area of the surface bounding volume v.

Proof. With a steady temperature distribution, the heat flux passing through the surface s(v) is equal to the heat flux passing through the surface s(v + dv), where dv is the change in the volume bounded by surface s

$$\langle q(v+dv)\rangle s(v+dv)=\langle q(v)\rangle s(v).$$

Expanding q and s in Taylor series and neglecting terms of order o(dv), it follows that

$$\left(\langle q(v)\rangle + \frac{d\langle q\rangle}{dv}dv\right)\left(s(v)+\frac{ds}{dv}dv\right) = s(v)\langle q(v)\rangle,$$

or

$$\langle q(v)\rangle \frac{ds}{dv} + \frac{d\langle q\rangle}{dv}s(v) = 0. \tag{6}$$

Since the mean variation in the coordinate of a surface point over the normal to the surface s with change in volume by dv is $\langle dn\rangle = dv/s(v)$, the mean — over surface s — heat flux density is as follows according to the Fourier law

$$\langle q\rangle = -\lambda\frac{dT}{\langle dn\rangle} = -\lambda\frac{dT}{dv}s(v). \tag{7}$$

Substitution of Eq. (7) into Eq. (6) yields Eq. (5).

Assertion 2. The time of accumulator charging with BC of the first kind $T_{sur} = T_{co}$ is determined from the formula

$$\tau_{ch}^{I} = \frac{E}{\lambda_h(T_p - T_{co})}I,\ I = \int_0^V\left[\int_{v_p}^{V}\frac{dv}{s^2(v)}\right]dv_p, \tag{8}$$

where v_p is the volume of hydride bounded by the phase-transition surface.

Proof. The accumulator-charging time is determined from the thermal balance (the heat liberated in the course of chemical reaction is equal to the heat extracted)

$$\tau_{ch} = E\int_0^V\frac{dv_p}{\langle q\rangle s}. \tag{9}$$

Expansion of $\langle q\rangle$ using Eq. (7) gives

$$\tau_{ch} = -\frac{E}{\lambda_h}\int_0^V\frac{dv_p}{\frac{dT}{dv}(v_p)s^2(v_p)}. \tag{10}$$

To determine dT/dv in Eq. (10), Eq. (5) is integrated twice

$$T(v) = C_1\int_v^V\frac{dv}{s^2(v)} + C_2.$$

The constants of integration C_1 and C_2 are found from the conditions $T(v_p) = T_p$, $T(V) = T_{co}$

$$T(v) = \frac{T_p - T_{co}}{\int_{v_p}^{V}\frac{dv}{s^2(v)}}\int_v^V\frac{dv}{s^2(v)} + T_{co},$$

and hence

$$\frac{dT}{dv}(v) = -\frac{T_p - T_{co}}{\int_{v_p}^{V}\frac{dv}{s^2(v)}}\frac{1}{s^2(v)}. \tag{11}$$

Substitution of Eq. (11) into Eq. (10) gives Eq. (8).

Assertion 3. The accumulator-charging time with BC of the third kind $q_{sur} = \alpha(T_{sur} - T_{co})$ is determined from the formula

$$\tau_{ch}^{III} = \tau_{ch}^{I} + \tau'_{ch}, \tag{12}$$

where τ_{ch}^{I} is determined from Eq. (8) and τ'_{ch} is the charging time with convective heat transfer from the surface under the assumption that the temperature difference over the hydride layer is negligibly small (physically, this is realized when α is small; in this case, $T_{sur} \approx T_p$) and the heat flux density from the accumulator surface is constant: $q'_{sur} = \alpha(T_p - T_{co})$. In this case

$$\tau'_{ch} = \frac{E}{\alpha(T_p - T_{co})}\,\frac{V}{S}. \tag{13}$$

Proof. It follows from Eq. (9) for the accumulator charging time, since the integral is additive, that, to prove Eq. (12), it is sufficient to prove that

$$\frac{1}{\langle q^{III} \rangle} = \frac{1}{\langle q^{I} \rangle} + \frac{1}{\langle q' \rangle}, \tag{14}$$

but

$$\langle q^{I} \rangle = \lambda \left\langle \left| \frac{\partial T_{I}}{\partial n} \right| \right\rangle = \lambda \left\langle \left| \frac{\partial \theta}{\partial n} \right| \right\rangle (T_p - T_{co}), \tag{15}$$

where $\theta = T/(T_p - T_{sur})$ is the dimensionless temperature; and

$$\langle q' \rangle = \alpha(T_p - T_{co}); \tag{16}$$

$$\langle q^{III} \rangle = \alpha(T_{sur} - T_{co}). \tag{17}$$

On the other hand

$$\langle q^{III} \rangle = \lambda \left\langle \left| \frac{\partial T_{III}}{\partial n} \right| \right\rangle = \lambda \left\langle \left| \frac{\partial \theta}{\partial n} \right| \right\rangle (T_p - T_{sur}). \tag{17'}$$

Here, the similarity of the temperature fields of problems with boundary conditions of the first and third kind is taken into account

$$\theta = \frac{T_{I}}{T_p - T_{co}} = \frac{T_{III}}{T_p - T_{sur}},$$

which follows from the fact that T_I and T_{III} satisfy the Laplace equation $\Delta T = 0$, which remains valid on multiplying T by a constant.

Eliminating T_{sur} from Eqs. (17) and (17'), it is found that

$$\langle q^{III} \rangle = \frac{\alpha \lambda_h \left\langle \left| \frac{\partial \theta}{\partial n} \right| \right\rangle (T_p - T_{co})}{\alpha + \lambda_h \left\langle \left| \frac{\partial \theta}{\partial n} \right| \right\rangle}. \tag{18}$$

Substitution of Eqs. (15), (16), and (18) into Eq. (14) completes the proof.

In calculating an infinite plate, infinite cylinder, and sphere on the basis of Eqs. (8) and (12), the well-known formulas are obtained, confirming that this method is a generalization of the ordinary calculations using the quasi-steady method.

Thus, for a plate

$$I = \int_0^L \left[\int_{l_p}^{L} dl \right] dl_p = \frac{L^2}{2}; \tag{19}$$

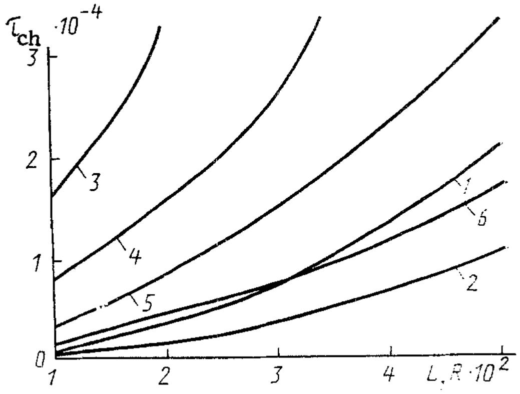

Fig. 1. Dependence of the charging time of an accumulator with LaNi$_5$ on the characteristic dimensions ($p = 12\cdot10^5$ Pa, T_{co} = 288 K): 1) plate; 2) cylinder, BC of the first kind; 3) plate; 4) cylinder, BC of the third kind, α = 10 W/m^2·K; 5) plate; 6) cylinder, BC of the third kind, α = 60 W/m^2·K.

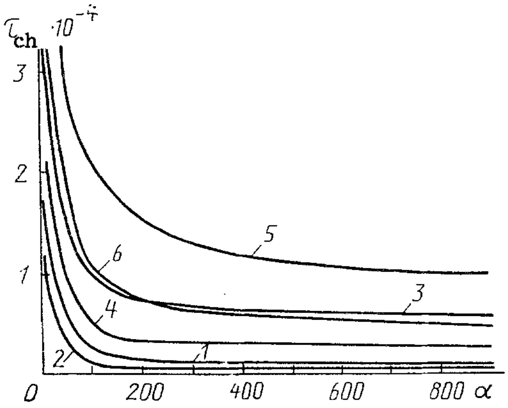

Fig. 2. Dependence of the charging time of an accumulator with LaNi$_5$ on the heat-transfer coefficient in coolant ($p = 12\cdot10^5$ Pa, T_{co} = 288 K): 1) plate; 2) cylinder, L = R = 0.01 m; 3) plate; 4) cylinder, L = R = 0.025 m; 5) plate; 6) cylinder, L = R = 0.05 m.

for a cylinder

$$I=\int\limits_0^R\left[\int\limits_{r_p}^R\frac{d(\pi r^2)}{(2\pi r)^2}\right]d[\pi r_p^2]=\frac{R^2}{4};$$

for a sphere

$$I=\int\limits_0^R\left[\int\limits_{r_p}^R\frac{d\left(\frac{4}{3}\pi r^3\right)}{(4\pi r^2)^2}\right]d\left(\frac{4}{3}\pi r_p^3\right)=\frac{R^2}{6}.$$

Note that this method is also applicable for the calculation of ingot solidification times and in other cases where the approximate solution of the Stefan problem with BC of the first or third kind by a quasi-steady method is undertaken.

The dependence of the accumulator charging time on the characteristic dimension — for a plate, half its thickness; for a cylinder, the radius — is a clearly expressed quadratic parabola (Fig. 1). The charging time of a cylindrical accumulator is half that of an accumulator in the form of a plate with R = L.

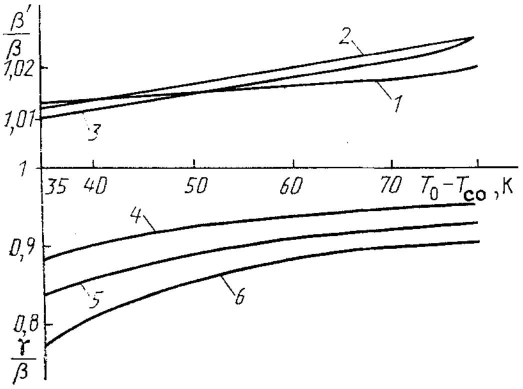

Fig. 3. Dependence of the ratios β'/β and γ/β on the temperature difference for $LaNi_5$ when $p = 5\cdot10^5$ (1, 4), $12\cdot10^5$ (2, 5), and $20\cdot10^5$ (3, 6) Pa.

The dependence of the accumulator charging time on the heat-transfer coefficient with BC of the third kind is shown in Fig. 2. It is evident that, at small α (for example, cooling by a gas flow), τ_{ch} increases strongly. At large α (cooling by a liquid flow), the solution of the problem tends to the solution of a problem with BC of the first kind when $T_{sur} = T_{co}$ and further decrease in τ_{ch} cannot occur.

The only case in which problem 1 has an accurate analytical solution is the case of an infinite plate with a BC of the first kind. According to [6], it is found that the time dependence of front motion is given by the formula

$$x_p(\tau)=\beta\sqrt{\tau}, \tag{20}$$

where β is found from the transcendental equation

$$\lambda_h(T_0-T_{co})\exp\left(-\frac{\beta^2}{4a_h}\right)=\frac{\varkappa_{max}-\varkappa_0}{2M_h}\rho_h Q\frac{\sqrt{\pi}\beta}{2}\sqrt{a_h}\operatorname{erf}\left(\frac{\beta}{2\sqrt{a_h}}\right).$$

Hence, the oscillator charging time in this case is

$$\tau_{ch}=L^2/\beta^2. \tag{21}$$

The quasi-steady method gives the same formulas for $x_p(\tau)$ and τ_{ch}, but according to Eqs. (8) and (19)

$$\beta'=\left(\frac{2\lambda_h}{E}(T_0-T_{co})\right)^{\frac{1}{2}}.$$

The dependence of β'/β on the temperature difference T_0-T_{co} (in the frontal model, $T_0 = T_p$) is shown in Fig. 3. The error of this approximate method is less with small temperature differences, when the temperature field is able to relax to the steady state; with increase in the temperature difference, the error of the method increases. As is evident, the error of the method is no more than 3% for the given temperature differences.

Problem 2

Assumption 5 is weakened here:

5') the equilibrium isotherm (isobar) is approximated not by a constant function, as in the frontal model but by a piecewise linear model.

In this case, the sorption reaction occurs not over the front but in the IMC layer: in the region $0 < x < x_p$, sorption ends; in the region $x_p < x < L$, it proceeds. The accumulator charging ends when $x_p(\tau)$ reaches L. To obtain an approximate analytical solution of this problem for an infinite plate with BC of the first kind, the accurate solution for a semiinfinite body is used [8].

$$x_p(\tau)=\gamma\sqrt{\tau}, \tag{22}$$

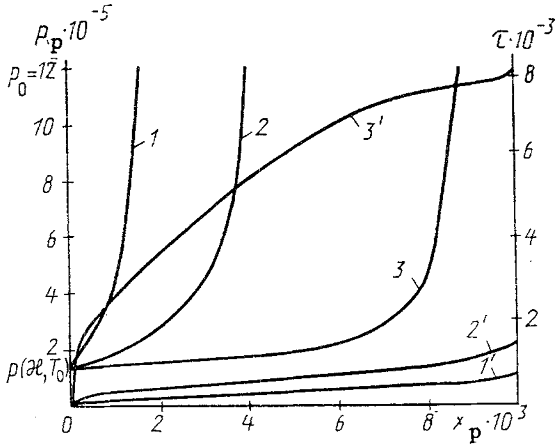

Fig. 4. Dependence of the pressure at the phase-transition front on the coordinate of the front (1-3) and dynamics of front motion (1'-3') for LaNi₅, $T_{co} = 288$ K, $d_{me} = 4 \cdot 10^{-6}$ m: 1, 1') $\Pi = 0.15$; 2, 2') 0.1; 3, 3') 0.05; p_p, Pa; x_p, m.

where $\gamma = 2k\sqrt{a_h}$, and k is found from the transcendental equation

$$\frac{\exp(-k^2)}{\operatorname{erf} k} \frac{c\,(T^*(p_0) - T_{co})}{c_{ef}(T(\varkappa_0, p_0) - T^*(p_0))} = \left(\frac{c_h}{c_{ef}}\right)^{\frac{1}{2}} \frac{\exp\left(-k^2 \frac{c_{ef}}{c_h}\right)}{\operatorname{erfc}\left(k \frac{c_{ef}^{1/2}}{c_h^{1/2}}\right)}.$$

Equation (22) is of the same form as Eq. (20), but γ and β are found from different transcendental equations. The charging time may be found from Eq. (21) if β is replaced by γ.

The ratio γ/β (the dependence of γ/β on the temperature difference is shown in Fig. 3) characterizes the influence of nonzero width of the sorption zone on the dynamics of accumulator charging. If it is close to unity, the sorption zone may be neglected and the frontal model of problem 1 is considered. It is evident that γ/β is closer to unity for large differences since intense processes are closer to frontal. For the given conditions, the maximum deviation of γ/β from unity is no more than 25%.

Note that the results of analyzing problem 2 agree with those of [9], where the influence of the nonzero sorption zone is investigated by numerical solution of the problem.

Problem 3

Retaining assumption 5, assumption 6 is discarded: the pressure difference over the cross section of the IMC layer is not neglected. The mathematical formulation of the problem will include two coupled equations: the heat-conduction and continuity (hydrogen-filtration) equations. The case which is most unfavorable for filtration is considered: heat extraction and hydrogen supply occur on different sides of the infinite plane hydride layer. Solving the resulting system with BC of the first kind by the quasi-steady method considered here, an ordinary differential equation is obtained for the coordinate of the hydriding front $x_p(\tau)$

$$\frac{dx_p}{d\tau} = \frac{\lambda_h}{E}[T(p_p(x_p), \varkappa_{max}) - T_{co}]\frac{1}{x_p}$$

with the initial condition $x_p(0) = +0$, where the pressure at the hydriding front p_p is determined from the transcendental equation

$$\frac{T_{\mathrm{co}} + (T_{\mathrm{co}}^2 + 4\varphi)^{1/2}}{2} = T(p_{\mathrm{p}},\ \varkappa_{\max}),$$

and

$$\varphi = h\frac{\Pi^3}{\mu}\left(\frac{d_{\mathrm{me}}}{1-\Pi}\right)^2 \frac{Q}{\lambda_{\Gamma} R_{\mathrm{gas}}} \frac{x_{\mathrm{p}}(p_0^2 - p_{\mathrm{p}}^2)}{2(l - x_{\mathrm{p}})}.$$

The dependence of the pressure at the sorption front p_p (minimum pressure in the IMC layer) on the front coordinate x_p and the dynamics of $x_p(\tau)$ are shown in Fig. 4. It is evident that, at high porosity (curve 1), the process occurs practically without hindrance of the filtration; the accumulator charging time here is practically the same as the time calculated from Eq. (8). At small porosity (curve 3), the hindrance of filtration is significant; the accumulator charging time is increased severalfold. The curve of $x_p(\tau)$ has a point of inflection on passing from conditions with hindrance of the filtration $p_p < p_0$ to conditions with no hindrance $p_p \approx p_0$. Note that the dispersity of the hydride d_{me} also has a strong influence on the filtration.

Thus, a generalization of the quasi-steady method for approximate solution of Eqs. (1), (2), and (4) (problem 1) has been developed and tested. The solution of problems 2 and 3 permits the evaluation, for specific accumulator parameters, of the applicability of assumptions 5 and 6, i.e., the possibility of using the frontal model without taking account of hindrance of hydrogen filtration.

NOTATION

M, molecular mass, kg/kmole; Π, porosity, vol. fraction; p, pressure; Pa; T, temperature, K; $\langle q \rangle$, surface-mean heat flux density, W/m^2; τ, time, sec; ρ, density, kg/m^3; μ, dynamic viscosity, Pa.sec; D, diffusion coefficient, m^2/sec; λ, thermal conductivity, W/m.K; $\underline{a} = \lambda/c\rho$, thermal diffusivity, m^2/sec; $\varkappa$, content of bound hydrogen in hydride, katom H/kmole IMC; Q, specific heat of hydriding, J/kmole H_2; $E = Q\rho_g(\varkappa_{max} - \varkappa_0)/2M_g$, heat liberated per m^3 hyride as a result of hydriding, J/m^3; R_{gas} = 8314 J/kmole·K, universal gas constant; h, empirical filtration coefficient ($h = 2.37 \cdot 10^{-3}$ for $LaNi_5$ [10]); β, coefficient taking account of the deviation from thermal equilibrium in convective heat transfer between free hydrogen and hydride (at equilibrium, $\beta = 1$); α, heat-transfer coefficient in coolant, W/m^2·K; $T^*(p_0) = T(p_0, \kappa_{max})$, temperature of upper discontinuity in isobar in piecewise-linear approximation, K; K, rate constant, sec^{-1}; e, activation energy, J/kmole; (,), scalar product; x, Cartesian coordinate, m; r, current radius in cylindrical or spherical coordinates, m; L, half the plate thickness, m; R, radius of cylinder of sphere, m; V, hydride volume in accumulator, m^3; d_{me}, mean diameter of hydride particle, m. Subscripts: H_2, free hydrogen in hydride pores; H, chemically bound hydrogen; h, hydride; 0, initial value ($\tau = 0$); co, coolant; p, phase, transition boundary; sur, value at accumulator surface; max, maximum value; d, value at equilibrium dissociation.

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