A METHOD FOR APPROXIMATE CALCULATION OF THE HEAT AND MASS TRANSFER PROCESSES IN HYDROGEN ACCUMULATION IN METAL HYDRIDES AND AN ANALYSIS OF ITS RANGE OF APPLICATION

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An approximate mathematical model, allowing calculation of heat and mass transfer processes in metal-hydride hydrogen accumulators, is given. Its range of application is analyzed using an asymptotic expansion of the nonstationary problem of heat and mass transfer with phase transition in terms of a small parameter.

Presently it is believed that one of the most promising methods for storing hydrogen is its accumulation in intermetallide hydrides due to a reversible sorption-desorption reaction [1] ($LaNi_5$ is used most often). Metal hydride elements are also the basic parts of thermochemical hydrogen compressors [2].

To design the metal-hydride elements, it is important to have a simple and dependable mathematical model which allow a description, with sufficient accuracy, of the processes occurring during their operation. Studies [3, 4] propose the most complete mathematical model by taking into account the heat transfer by heat conduction and convection, the hydrogen filtration and diffusion, and the kinetics of a hydrogenation reaction. The energy equation involves rapidly oscillating coefficients since the heat transfer proceeds in a porous hydride matrix. Averaging of this equation and calculation of the effective thermal conductivity are dealt with in [5].

The processes of heat transfer and hydrogen filtration are defined by parabolic partial differential equations. The model considered is essentially nonlinear because of the presence of a sorption-desorption reaction. All this makes calculations by the complete model complicated and decreases its usefulness. At the same time, it is known [6] that for many intermetallides (including $LaNi_5$) the sorption-desorption reaction is not the limiting stage, it proceeds fast enough for the process to be assumed quasi-equilibrium. Moreover, at a specified pressure, the reaction proceeds with almost constant temperature. In practical units, the processes of heat transfer and filtration go on very slowly because of the low thermal conductivity of the hydride and the high heat of the hydrogenation reaction and, hence, they are close to stationary.

It is desirable to use these facts for simplifying the mathematical model. Studies [6, 7] suggest a frontal model of heat transfer, according to which the hydrogenation reaction occurs over the surface (front) of phase transition rather than in an intermetallide region.

To describe the heat transfer processes, use is made of a quasi-stationary approximation [8, 9], according to which the temperature profile is predicted not from the parabolic but rather from the corresponding elliptic energy equation. Adequacy of the frontal model and its applicability conditions are studied analytically in [4] and numerically in [10].

The indicated approach permits an utmost simplification of the mathematical model and an analytic description of the dynamics of thermal processes in the operation of the metal hydride element. However, it does not allow for hydrogen filtration, which has a noticeable effect on element dynamics with small porosity and particle size of the hydride. During the element operation, crushing and compaction of the metal hydrate powder occur; therefore, the filtration influence increases with time.

The current study simultaneously analyzes the heat transfer and filtration processes based on the frontal model. Both processes are described using a quasi-stationary approximation. This enables the reduction of the model to equations involving only ordinary derivatives. Finally, we obtain conditions whose fulfillment makes the employment of the quasi-stationary approximation reasonable.

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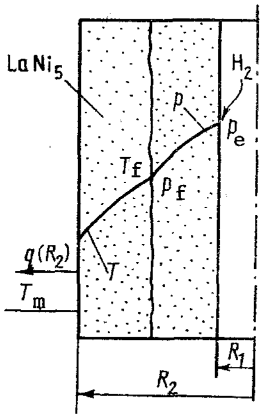

Fig. 1. Diagram of thermal and filtration fluxes and fields in the element.

1. Derivation of the Approximate Model. The calculation will be performed for the most frequently used metal-hydride elements of cylindrical shape. Let us examine in detail the calculation technique for thermodynamic elements operating in the mode of hydrogen sorption and heat transfer to the surrounding medium. Hydrogen is supplied from the inner cylindrical surface, here we use conditions of the first-kind as to pressure. Heat removal is effected from the outer cylindrical surface, with boundary conditions of the third kind. Figure 1 shows a calculational diagram.

The stationary equation of filtration in cylindrical coordinates has the form

$$\frac{\partial}{\partial r}\left(p\frac{\partial p}{\partial r}\right)+\frac{1}{r}p\frac{\partial p}{\partial r}=0,$$

whose solution is $p^2 = A_1 \ln r + A_2$.

The mass flux density of hydrogen moving to the phase transition surface is determined according to the Darcy law by the pressure gradient on the front:

$$j_f=-\sigma\left(\frac{p}{T}\frac{\partial p}{\partial r}\right)\Big|_{r=r_f}, \tag{1}$$

where r_f is the radius of the phase transition front, and σ, in accordance with [11], is equal to

$$\sigma=h\frac{\Pi^3}{\mu}\left(\frac{d}{1-\Pi}\right)^2 M_{H_2}\frac{1}{\tilde{R}}.$$

On the other hand, this flux is governed by the sorption rate, which, in turn, depends on the velocity of the phase transition front $\dot{r}_f$

$$j_f=-\delta\dot{r}_f, \tag{2}$$

where

$$\delta=\frac{\varkappa_{\max}-\varkappa_0}{2M_h}\rho_h M_{H_2}.$$

By equating expressions (1) and (2), we arrive at the equation for $r_f(t)$

$$\frac{\sigma}{T_f}\frac{A_1}{r_f}=\delta\dot{r}_f. \tag{3}$$

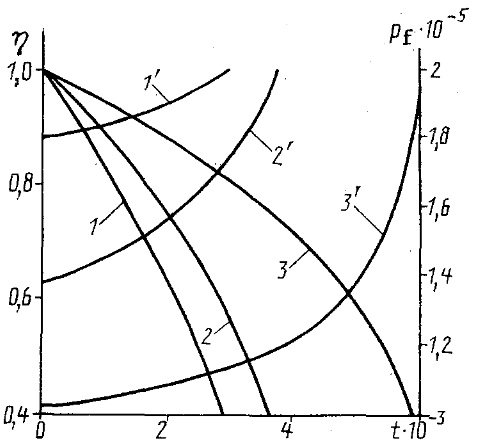

Fig. 2

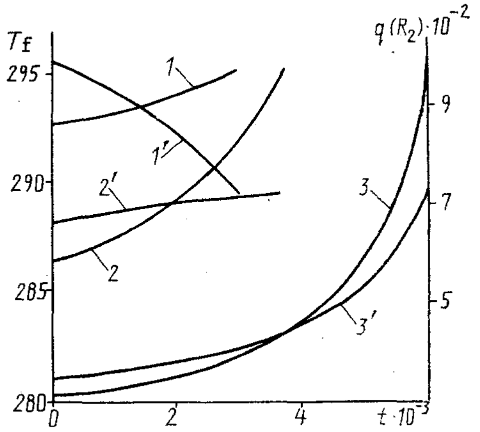

Fig. 3

Fig. 2. Relations $\eta(t)$ (curves 1, 2, and 3) and $p_f(t)$ (curves 1', 2', and 3'): 1, 1') $\Pi = 0.2$, $d = 5 \cdot 10^{-6}$ m; 2, 2') $\Pi = 0.15$, $d = 4 \cdot 10^{-6}$ m; 3, 3') $\Pi = 0.13$, $d = 3 \cdot 10^{-6}$ m.

Fig. 3. Relations $T_f(t)$ (curves 1, 2, and 3) and $q(R_2, t)$ (curves 1', 2', and 3'): 1, 1') $\Pi = 0.2$, $d = 5 \cdot 10^{-6}$ m; 2, 2') $\Pi = 0.15$, $d = 4 \cdot 10^{-6}$ m; 3, 3') $\Pi = 0.13$, $d = 3 \cdot 10^{-6}$ m.

The integration constant A_1 is obtained from the boundary conditions

$$\text{at } r = R_1 \quad A_1 \ln R_1 + A_2 = p_e^2,$$

$$\text{at } r = r_f \quad A_1 \ln r_f + A_2 = p_f^2,$$

whence

$$A_1 = -\frac{p_e^2 - p_f^2}{\ln (r_f/R_1)}. \tag{4}$$

Substituting Eq. (4) into Eq. (3) yields

$$\dot{r}_f = -\frac{\sigma}{\delta} \frac{p_e^2 - p_f^2}{T_f r_f \ln (r_f/R_1)}. \tag{5}$$

Equation (5) involves the unknown function $p_f(r_f)$. To define it, we write the equation for $\dot{r}_f$ proceeeding from the analysis of thermal processes (only filtration processes were analyzed in deriving Eq. (5)).

A stationary heat conduction equation in cylindrical coordinates is of the form

$$\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} = 0,$$

and its solution is

$$T = B_1 \ln r + B_2.$$

The density of the heat flux from the phase transition surface is equal, by the Fourier law, to

$$q_f = -\lambda \frac{\partial T}{\partial r} (r_f) = -\lambda \frac{B_1}{r_f}.$$

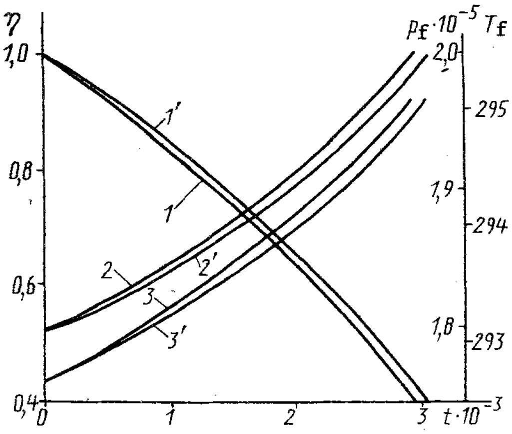

Fig. 4. Relations $\eta(t)$ (curves 1 and 1′), $p_f(t)$ (curves 2 and 2′), and $T_f(t)$ (curves 3 and 3′) calculated from the approximate (1, 2, and 3) and complete (1′ , 2′, and 3′) models for Ste = 3.7×10^{-2} and $\varepsilon = 8.9 \times 10^{-5}$.

The integration constant B_1 is found from the boundary conditions

$$\text{at } r = R_2 \qquad -\lambda \frac{B_1}{R_2} = \alpha\left(B_1 \ln R_2 + B_2 - T_m\right),$$

$$\text{at } r = r_f \qquad B_1 \ln r_f + B_2 = T_f .$$

We obtain

$$q_f = \frac{\lambda\alpha\left(T_f - T_m\right)}{r_f\left(\alpha \ln(R_2/r_f) + \lambda/R_2\right)}. \tag{6}$$

Alternatively, q_f is defined by the hydrogen desorption rate, which leads to the expression

$$q_f = -E\dot{r}_f. \tag{7}$$

By equating expressions (6) and (7), we obtain the equation for $r_f(t)$

$$\dot{r}_f = -\frac{\lambda}{E}\,\frac{\alpha\left(T_f - T_m\right)}{r_f\left(\alpha \ln(R_2/r_f) + \lambda/R_2\right)}. \tag{8}$$

Equation (8) involves the unknown function $T_f(r_f)$.

Equating expressions (5) and (8) gives the functional relation $p_f = f(T_f)$

$$p_f^2 = p_e^2 - \frac{\delta\lambda}{\sigma E} T_f \ln\left(r_f/R_1\right)\frac{\alpha\left(T_f - T_m\right)}{\left(\alpha \ln(R_2/r_f) + \lambda/R_2\right)}. \tag{9}$$

On the other hand, it is known [12] that the relation $p_f(T_f)$ for equilibrium sorption appears as

$$p_f = 10^5 \exp\left(A - B/T_f\right), \tag{10}$$

where A = 12.94 and B = 3615 for $LaNi_5$.

By equating the expressions for p_f from Eqs. (9) and (10), we derive a transcendental equation to define the relation $T_f(r_f)$

$$10^5 \exp(A - B/T_f) = \left[p_e^2 - \frac{\delta\lambda}{\sigma E} T_f \ln(r_f/R_1) \frac{\alpha (T_f - T_m)}{(\alpha \ln(R_2/r_f) + \lambda/R_2)} \right]^{1/2}. \tag{11}$$

The system (8) and (11) represents the approximate mathematical model of a metal-hydride element and allows the calculation of its operation dynamics, given the external pressure, which may be a function of time: $p_e = p_e(t)$. Indeed, with the function $r_f(t)$ found, the hydrogen and heat flux densities on the hydrogenation front are determined by Eqs. (2) and (7). Since the pressure and temperature fields are assumed to correspond to the stationary distribution at each time instant, densities of these fluxes at the inner and outer cylindrical boundaries of the element are determined by a simple conversion:

$$j(R_1) = j_f r_f / R_1, \quad q(R_2) = q_f r_f / R_2.$$

Unlike the complete model, the approximate one does not incorporate partial differential equations and is much more simple to use for analysis and solution. To expedite the calculation, it is reasonable to differentiate the transcendental equation (11) with respect to time and to express the derivative T_f in explicit form. The resulting system of two ordinary differential equations of the first order is convenient to solve by the Runge–Kutta method. To determine the initial value of T_f, the transcendental equation (11) must be solved once at $r_f = R_2$.

Figures 2 and 3 show calculated results for the dynamics of processes occurring in charging the metal hydride element with $LaNi_5$. The calculations were conducted for $R_2 = 0.01$ m, $R_1 = 0.4R_2$, $T_m = 273$ K, $\alpha = 50$ W/(m^2·K), and $p_e = 2 \cdot 10^5$ Pa.

As follows from the figures, the relative radius of the hydrogenation front $\eta = r_f/R_2$ decreases monotonically in time from 1 at the initial time instant when the reaction proceeds on the outer cylindric surface of the accumulator, $r_f = R_2$, to 0.4 when the reaction terminates on the inner surface, $r_f = R_1$. The hydrogenation front pressure in the beginning of the process is minimal, since hydrogen has to filter throughout the intermetallide layer. At the final time instant, the front pressure is equal to the external pressure p_e because the filtration length at $r_f = R_1$ is zero. The hydrogenation front temperature rises during the process, causing an increase in the temperature drop between the front and the cooling medium. This compensates for increasing distance between the front and the surface $r = R_2$, wherefrom the heat flux is removed to the medium.

Interestingly, for the modes corresponding to curves 2′ and 3′ (Fig. 3), the density of the heat flux removed to the medium $q(R_2)$ does not decrease, as would be the case if the calculation were carried out without taking account of the filtration, but rather increases in time. This indicates that the limiting stage for the calculated modes is exactly the filtration rather than the heat transfer. The conditions, for which curves in Figs. 2 and 3 are plotted, differ by the intermetallide porosity and mean particle diameter. As is evident from the figures, a decrease in Π and d by as little as 20-25% prolonges the charging by 1.5-2 times. All this points to a marked effect of the filtration processes on the element operation and the importance of their consideration in the mathematical model.

2. Applicability Conditions of the Mathematical Model. To produce the conditions, under which the quasi-stationary approximation is correct to apply for simplifying the model, let us use the fact that the appropriate solution is a zeroth-order approximation in the expansion of the solution for the relevant problem in terms of a small parameter. Studies [13, 14] obtained the expansion of the solution to the problem of heat conduction with phase transition in terms of a small parameter, which is the Stefan number Ste. The zeroth-order approximation is close to the problem solution if the small parameter to the first power is much smaller than unity. Therefore, applying the quasi-stationary approximation to the energy equation is justifiable, if the following condition is fulfilled:

$$\mathrm{Ste} = \frac{C \Delta T}{E} \ll 1. \tag{12}$$

As a characteristic temperature drop ΔT, it is convenient to choose the evaluation of the maximal temperature drop in the element $(T_f - T_m)_{max}$.

Physically, the Stefan number is the ratio of the hydride heat retentivity to the heat of the hydrogen sorption-desorption reaction. If the heat retentivity is negligible relative to the reaction heat, it may be assumed that a stationary temperature distribution is established at each time instant, i.e., the quasi-stationary distribution may be utilized.

An analog of the Stefan number for the filtration equation is the quantity ε, having the physical meaning of the ratio of the gaseous hydrogen mass, which can be accumulated in hydride pores, to the hydrogen mass, which can be isolated as a result of the reaction. Accordingly, applying the quasi-stationary approximation to the analysis of filtration processes has grounds if the amount of hydrogen, which can be accumulated in pores, is negligible as compared with the amount of hydrogen, which can be isolated in desorption, i.e., the following condition is satisfied

$$\varepsilon = \frac{2Mh}{\rho_h(\varkappa_{\max} - \varkappa_0)} \frac{\Pi \Delta p}{\tilde{R}T} \ll 1. \tag{13}$$

As Δp, we take the evaluation of the maximal pressure drop in the element $(p_e - p_f)_{\max}$.

With condition (13) fulfilled, it may be assumed that the pressure field at each time instant has managed to relax to a steady state.

Hence, the approximate model is valid when the following conditions are satisfied: the process is quasi-stationary, the frontal model is suitable, and the quasi-stationary approximation is applicable, i.e., conditions (12) and (13) are fulfilled.

When these conditions are fulfilled, the operation dynamics of the metal-hydride element is defined by Eqs. (8) and (11). As the analysis in [4, 6, 7, 10] reveals, the first two conditions are satisfied for the elements with $LaNi_5$. The fulfillment of the third condition for a specific operation mode of the element is checked readily using Eqs. (12) and (13).

3. Comparison of Predictions from the Approximate and Complete Models. To solve equations of the complete model (assuming that the sorption-desorption reaction proceeds over the front), use was made of a finite difference scheme of the predictor-corrector type [5, 15, 16], permitting the consideration of the phase transition through the solution correction at each time step rather than through iterations. The application of this scheme instead of traditional iteration reduced the calculation time by severalfold.

Figure 4 shows the dynamics of charging the cylindrical thermodynamic element with $LaNi_5$ at $R_2 = 0.01$ m, $R_1 = 0.4R_2$, $T_m = 273$ K, $\alpha = 50$ W/(m^2·K), $p_e = 2 \cdot 10^5$ Pa, $\Pi = 0.2$, and $d = 5 \cdot 10^{-6}$ m. Since the criteria Ste and ε are much smaller than unity in this case, the process is described well by the approximate model, which is clear from proximity of the curves derived by calculations using the complete and approximate models. The distance between the curves grows slightly with time. However, the relative error is not greater than 5%.

Thus, we have proposed the approximate mathematical model, which makes it possible to predict the heat and mass transfer in metal-hydride elements. Its range of application is limited by small values of the criteria Ste and ε. We have compared predictions from complete and approximate models.

We would like to note that the solution for the approximate model equations may be regarded as a zeroth-order approximation in the asymptotic expansion of the solution for the complete model equations (with no account of the kinetics) in terms of small parameters Ste and ε. If necessary, higher-order terms of the expansion may be derived using a perturbation method [13, 14].

NOTATION

p, pressure, Pa; T, temperature, K; t, time, sec; r, running radius, m; R_1, inner radius of the element, m; R_2, outer radius of the element, m; q, heat flux density, W/m^2; j, mass flux density of hydrogen, kg/(m^2·sec); M, molecular mass, kg/kmole; Π, porosity, vol. frac.; ρ, density, kg/m^3; μ, dynamic viscosity of hydrogen, Pa·sec; λ, thermal conductivity, W/(m·K); $\varkappa$, bound hydrogen content of the hydride, katom H/kmole $LaNi_5$; E, specific volume heat of the hydrogenation reaction, J/m^3; $\tilde{R} = 8314$ J/(kmole·K), universal gas constant; h, empirical filtration coefficient, $h = 2.37 \times 10^{-3}$ for $LaNi_5$; α, coefficient of heat transfer to the medium, W/(m^2·K); d, mean diameter of the hydride particles, m; Ste and ε, small parameters. Indexes: H_2, gaseous hydrogen in the hydride pores; h, hydride; m, medium; f, hydrogenation front; 0, initial value; max, maximal value; e, external pressure.

REFERENCES

1. S. Suda, Int. J. Hydrogen Energy, **12**, No. 5, 323-331 (1987).
2. V. A. Popovich, A. I. Ivanovskii, V. V. Solovei, and A. A. Makarov, Voprosy Atomn. Nauki Tekhn., Ser. Atomno-Vodorodn. Énerg. Tekhnol., Issue 3 (1987), pp. 56-58.
3. H. Choi and A. Mills, Int. J. Heat Mass Transfer, **33**, No. 6, 1281-1288 (1990).
4. V. M. Liventsov and A. V. Kuznetsov, Inzh.-fiz. Zh., **60**, No. 6, 928-936 (1991).
5. V. M. Liventsov and A. V. Kuznetsov, Izv. Akad. Nauk SSSR, Énerg. Trans., **37**, No. 2, 148-158 (1991).
6. G. A. Fateev, in: Physicochemical Processes in Power Units [in Russian], Minsk (1983), pp. 52-83.
7. G. A. Fateev, A. I. Cheklina, and V. K. Shchitnikov, Izv. Akad. Nauk SSSR, Ser. Fiz.-Énerg. Nauk, No. 3, 26-30 (1981).
8. R. Viskanta, Solar Heat Storage: Latent Heat Materials, **1**, 153-218 (1983).
9. A. V. Lykov, Heat Conduction Theory [in Russian], Moscow (1967).
10. G. A. Fateev, in: Heat and Mass Transfer in Electrochemical Power Generators [in Russian], Minsk (1981), pp. 22-23.
11. A. N. Artemenko and V. Yu. Stepanov, Vopr. Atomn. Nauki Tekh., Ser. Atomno-Vodorodn. Énerg. Tekhnol., Issue 1 (1987), pp. 85-87.
12. I. L. Varshavskii and V. V. Solovei, Dokl. Akad. Nauk Ukr. SSR, Ser. A, No. 4, 80-83 (1980).
13. M. Prud'homme and Nguyen T. Hung, Int. J. Heat and Mass Transfer, **32**, No. 8, 1501-1515 (1989).
14. M. Prud'homme, Nguyen T. Hung, and Nguyen D. Long, Trans. ASME, J. Heat Transfer, **111**, No. 3, 699-705 (1989).
15. Q. T. Pham, Int. J. Heat Mass Transfer, **8**, No. 11, 2079-2084 (1985).
16. V. M. Liventsov and A. V. Kuznetsov, Probl. Mashinostr. Avtom., No. 3(33), 55-58 (1990).