CALCULATION OF THE OPERATION OF A METALLOHYDRIDE REFRIGERATOR AND OPTIMIZATION OF THE SWITCHING TIME FOR HEAT FLUXES

A. V. Kuznetsov   UDC 536.242

A mathematical model permitting the calculation of heat and mass transfer processes in a metallohydride refrigerator is proposed. An algorithm for determining the optimum switching time for the heat fluxes in the system is developed for a prescribed cycle time from the condition of producing the maximum refrigeration effect per unit heat supplied from a high-temperature source.

Numerous investigations are currently devoted to the use of metallohydrides to construct thermal pumps that convert waste heat (for example, of an automobile, an aircraft or even a spaceship) and to construct environmentally safe refrigerators not using Freons [1−5]. One of the important problems of designing these systems is optimization of the parameters of the operating cycle. Here, the requirement of optimality includes both high thermodynamic efficiency and provision of prescribed technical requirements (fixed cycle time, heat power, etc.).

In [6] an investigation of a thermal pump that incorporates two metallohydride elements is carried out, the metallohydride in them being distributed as a plane layer. Heat is supplied (removed) on one side of this layer, and hydrogen on the other. Since from structural and technological considerations metallohydride elements of cylindrical shape are more promising than plane ones, the problem of developing a calculation procedure for a thermal pump or a refrigerator that uses precisely these elements is of importance. Furthermore, in addition to solving the direct problem, i.e., calculating this metallohydride system, it is important to develop a procedure for solving the inverse problem: to find parameters of the cycle that satisfy prescribed technical requirements and ensure the optimum operating efficiency of the system.

In the present work, on the basis of results obtained in [7, 8], a calculation method for a metallohydride refrigerator incorporating two elements of cylindrical shape is proposed. Furthermore, we developed a method for solving a particular inverse problem: to find from a prescribed cycle time the switching time for the heat fluxes in a system (the choice of division of the cycle into preparatory (idle) and operating half-cycles).

A diagram of the metallohydride refrigerator and the thermal field and the pressure field in the elements for the preparatory half-cycle are given in Fig. 1. Hydrogen is supplied (removed) from the outer cylindrical surface, and boundary conditions of the first kind with respect to the pressure are used here. Heat removal (heat supply) is performed, according to boundary conditions of the third kind, from the inner cylindrical surface. We will consider the ends of the metallohydride elements to be heat-insulated and impermeable for $R_1 < r < R_2$ and the boundary conditions to be uniform along the element height.

During the preparatory (idle) half-cycle (segment AB in Fig. 2) element 1 is heated by the heat-transfer agent with the high temperature T_h (i.e., it operates as a refrigerating element) and it desorbs hydrogen, and element 2 gives heat to the heat-transfer agent with the intermediate temperature T_m (i.e., it operates as a heating element) and it sorbs hydrogen. During the operating half-cycle (segment CD in Fig. 2) element 1 gives heat to the heat-transfer agent with the intermediate temperature T_m (i.e., it operates as a heating element) and it sorbs hydrogen, and element 2 takes heat from the heat-transfer agent with the low temperature T_{low} (i.e., it operates as a refrigerating element) and it desorbs hydrogen.
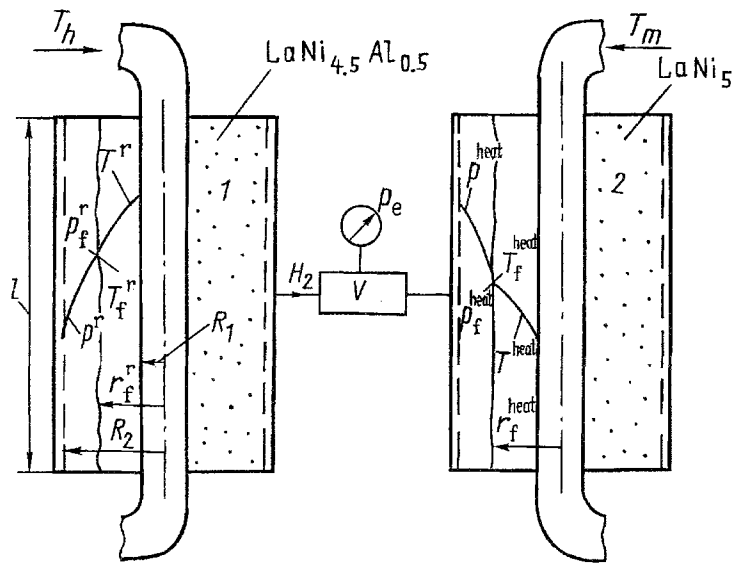
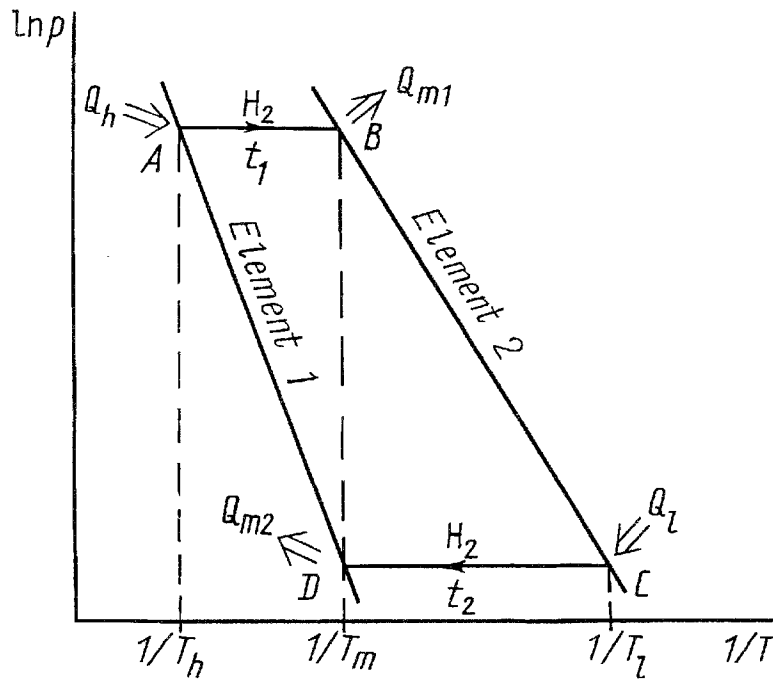---

Fig. 1. Diagram of the metallohydride refrigerator.

Fig. 2. Refrigerating cycle of the metallohydride system.

The intermetallide pair in the metallohydride refrigerator is usually selected so that T_m corresponds to the ambient temperature, i.e. the quantities of heat Q_{m1} and Q_{m2} are removed to the ambient medium. Thus, in order to remove the quantity of heat Q_{low} from the low-temperature heat-transfer agent during the operating half-cycle, energy equal to the quantity of heat Q_h is spent, which goes to the heating (for example, by electric heaters) of the high-temperature heat-transfer agent during the preparatory half-cycle. This gives rise to the problem of determining the time of switching the system from the preparatory half-cycle to the operating one so that the ratio Q_{low}/Q_h attains a maximum, i.e., the maximum refrigerating effect is attained per unit heat supplied from the high-temperature source.

We use the calculation procedure for cylindrical metallohydride elements proposed in [8]. This procedure makes use of a frontal model of transfer processes in the metallohydride layer [9]: the assumption that the

hydrogenation (dehydrogenation) reaction proceeds over the surface (front) of the phase transition, which in our case is a cylindrical surface whose radius $r_f(t)$ changes with the course of the process. In [8] by using a quasistationary approximation a system of equations is obtained that connects the hydration front radius, the temperature on the hydration front, and the external hydrogen pressure, i.e., the pressure at which hydrogen is supplied to the metallohydride element or removed from it. By using these results we find that the metallohydride refrigerator in Fig. 1 is described by the following mathematical model. For the heating element (element 2 during the preparatory half-cycle and element 1 during the operating one) the following equations are valid:

$$\dot{r}_f^{heat} = \frac{\lambda}{E} \frac{\alpha^{heat} (T_f^{heat} - T_w^{heat})}{r_f^{heat} (\alpha^{heat} \ln (r_f^{heat}/R_1) + \lambda/R_1)}, \tag{1}$$

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

where

$$\sigma = \frac{h}{2} \frac{\Pi^2}{\mu} \left(\frac{d}{1 - \Pi} \right)^2 M_{H_2} \frac{1}{\tilde{R}}, \quad \delta = \frac{\kappa_{max} - \kappa_0}{2M_{hyd}} \rho_{hyd} M_{H_2}.$$

Since the heating element in the case of both the operating and preparatory half-cycles gives heat to the heat-transfer agent with the ambient temperature, $T_w^{heat} = T_m$.

For the refrigerating element (element 1 during the preparatory half-cycle and element 2 during the operating cycle) the following equations are valid:

$$\dot{r}_f^r = \frac{\lambda}{E} \frac{\alpha^r (T_w^r - T_f^r)}{r_f^r (\alpha^r \ln (r_f^r/R_1) + \lambda/R_1)}, \tag{3}$$

$$10^5 \exp (A^r - B^r/T_f^r) = \left[p_e^2 + \frac{\delta\lambda}{\delta E} (T_f^r \ln (R_2/r_f^r) \frac{\alpha^r (T_w^r - T_f^r)}{\alpha^r \ln (r_f^r/R_1) + \lambda/R_1} \right]^{1/2}. \tag{4}$$

During the preparatory half-cycle the refrigerating element is heated by the high-temperature source, and therefore $T_w^r = T_h$, and during the operating one it takes heat from the cold heat-transfer agent, i.e., $T_w^r = T_{low}$.

To close the system (1)-(4), an equation is required that describes the change in the external hydrogen pressure, i.e., the pressure in the tube connecting the metallohydride elements. This equation follows from the balance of the flow rates of the hydrogen sorbed by the heating element and desorbed by the refrigerating element, with account for the equation of state of an ideal gas for the hydrogen:

$$\dot{p}_e = \frac{1}{V} \frac{\tilde{R}T_{H_2}}{M_{H^2}} 2\pi\delta l (\dot{r}_f^r r_f^r - \dot{r}_f^{heat} r_f^{heat}). \tag{5}$$

Equations (1)-(5) form a closed mathematical model that fully describes the system under study (in practical calculations it is convenient to differentiate Eqs. (2) and (4) with respect to time, having expressed explicitly the derivative $\dot{T}_f$, and to solve the obtained system by the Runge–Kutta method). Indeed, as follows from [8], all the basic parameters that determine heat and mass transfer in the metallohydride refrigerator are expressed unambiguously in terms of the functions $r_f^{heat}(t)$, $r_f^r(t)$, $T_f^{heat}(t)$, $T_f^r(t)$, and $p_e(t)$:
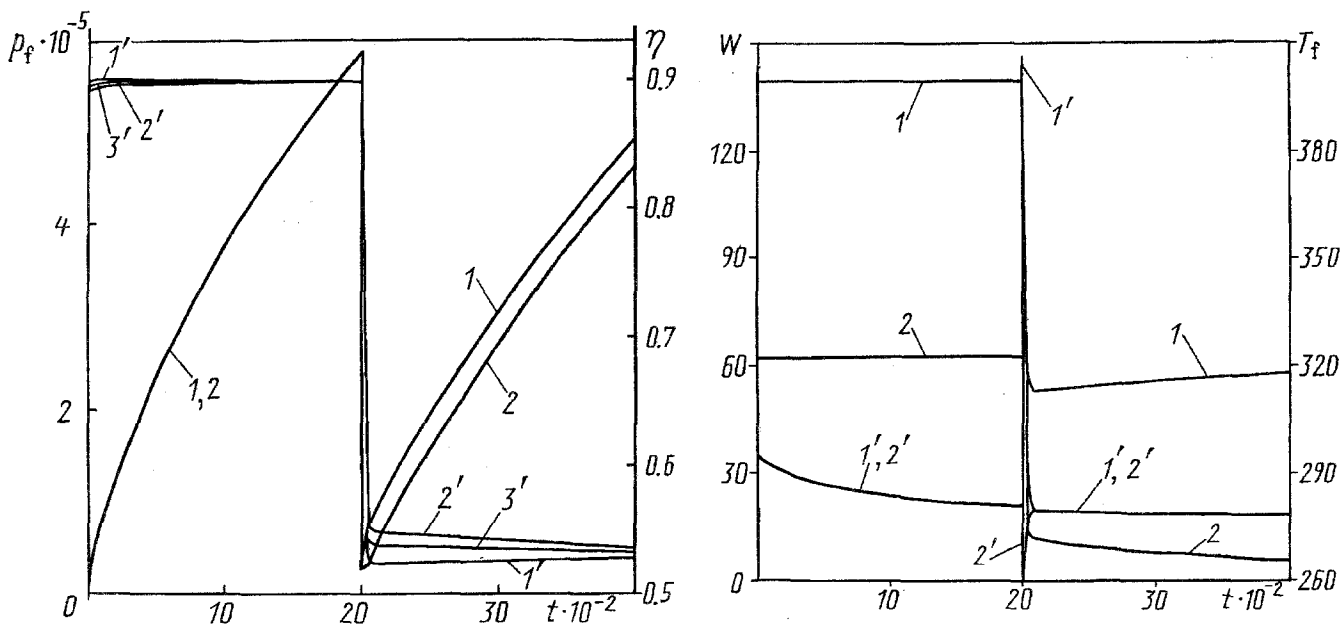
the pressure on the hydrogenation front

Fig. 3. Relative hydrogenation front radius η (1, 2) and hydrogenation front pressure p_f, Pa (1', 2') vs time t, sec: 1, 1') for element 1; 2, 2') for element 2; 3') external pressure $p_e(t)$, Pa.

Fig. 4. Hydrogenation front temperature T_f, K (1, 2) and heat (refrigerating) power of the elements W, W (1', 2') vs time t, sec: 1, 1') for element 1; 2, 2') for element 2.

$$p_f = 10^5 \exp (A - B/T_f) ;$$ (6)

the flow rate of the hydrogen sorbed (desorbed) by the metallohydride element:

$$J = 2\pi r_f l \delta \dot{r}_f ;$$

the heat flux supplied to (removed from) the element (heat or refrigerating power):

$$W = 2\pi r_f l E \dot{r}_f .$$

Figures 3 and 4 give results of calculating the metallohydride refrigerator for the following initial data: $\Pi = 0.3$; $d = 7 \cdot 10^{-6}$ m; $V = 5 \cdot 10^{-4}$ m^3; $R_2 = 0.015$ m; $R_1 = 0.518 R_2$; $l = 0.2$ m; $T_{low} = 285$ K; $T_m = 298$ K; $T_h = 423$ K; $\alpha^{heat} = 150$ W/(m$^2 \cdot$ K); $\alpha^r = 150$ W/(m$^2 \cdot$K); in element 1, LaNi$_{4.5}$Al$_{0.5}$ served as the metallohydride, and in element 2, LaNi$_5$. The total cycle time is equal to $t_\Sigma = 4 \cdot 10^3$ sec, and the heat flux switching time is chosen in the middle of the cycle time $t_1 = t_\Sigma/2 = 2 \cdot 10^3$ sec.

As Fig. 3 shows, the relative radii of the hydrogenation front for both elements $\eta^{heat} = r_f^{heat}/R_2$ and $\eta^r = r_f^r/R_2$ decrease monotonically with time from R_1/R_2 at the initial instant, when the reaction proceeds on the inner cylindrical surface of the element, to some value $r_f(t_1)/R_2$, when there is a change in the heat fluxes in the system at the instant $t = t_1$. The reaction of the intermetallide with hydrogen changes its direction (if there was desorption, sorption commences, and vice versa), and the reaction commences again from the inner surface of the element (since it is precisely from there that the cooling or heating is performed). The difference $p_e - p_f^{heat}$ shows hindered filtration in the heating element (sorber), while the difference $p_f^r - p_e$ shows hindered filtration in the refrigerating element (desorber). As is evident, the operating half-cycle occurs with much more hindered filtration than the preparatory one. This is associated with the fact that the pressure in the preparatory half-cycle is approximately 11 times higher than that in the operating one but the intensity of the thermal and filtration processes

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is approximately equal (which is evident from the similar heat powers of the elements in Fig. 4). This means that the mass fluxes of hydrogen for both half-cycles are similar; however, to attain this flux in the operating half-cycle, a pressure gradient approximately 11 times larger is required because of the lower pressure and hence the lower hydrogen density. Hindrance of the filtration is maximum at $t = t_1$, after which it decreases since as the phase transition front moves, the filtration length decreases.

As Fig. 4 shows, the refrigerating power of the system is practically constant in time in the operating half-cycle. This occurs because at the beginning the process proceeds with strongly hindered filtration and at the end with strongly hindered heat transfer (as indicated by the increase in the temperature on the phase transition front of the heating element and the decrease in the temperature on the phase transition front of the refrigerating element during the operating half-cycle) and these phenomena compensate each other as it were. A short-term power peak of the element 1 at $t = t_1$ is associated with a heat shock in heat flux switching.

By analyzing Figs. 3 and 4 we can notice easily that the switching time for the system heat fluxes t_1 is not chosen in an optimum manner: not the entire heat Q_h transferred to element 1 by the high-temperature heat-transfer agent (with the temperature T_h) during the preparatory half-cycle is taken by element 2 from the low-temperature heat-transfer agent (with the temperature T_{low}) during the operating half-cycle; we denote the quantity of removed heat by Q_{low}. For the calculated case, when t_1 is chosen equal to $t_\Sigma/2$, the ratio $Q_{low}/Q_h = 0.744$.

We consider the problem of choosing the time t_1 for a prescribed cycle time t_Σ so that the Q_{low}/Q_h (see Fig. 2) ratio is maximum. We will solve this problem for the case where the volume of the tube that connects the elements can be assumed to be a small parameter. With this assumption Eq. (5) becomes

$$\dot{r}_f^r r_f^r = \dot{r}_f^{heat} r_f^{heat},$$

which in connection with the same initial conditions for Eqs. (1) and (3) leads to the requirement of equality of the right-hand sides of these equations:

$$\frac{\alpha^{heat} (T_f^{heat} - T_w^{heat})}{r_f (\alpha^{heat} \ln (r_f/R_1) + \lambda/R_1)} = \frac{\alpha^r (T_w^r - T_f^r)}{r_f (\alpha^r \ln (r_f/R_1) + \lambda/R_1)}. \tag{7}$$

At small V Eqs. (1) and (3) thereby coincide and the temperatures on the phase transition front for the heating and refrigerating elements T_f^{heat} and T_f^r are related by relation (7) (by virtue of the equivalence of Eqs. (1) and (3) at small V the superscripts on r_f can be omitted).

To determine the phase transition front temperatures of the heating T_f^{heat} and refrigerating T_f^r elements as functions of the position of the hydrogenation front r_f, we need one more equation that relates these quantities in addition to Eq. (7). We obtain this equation by eliminating p_e^2 from Eqs. (2) and (4):

$$10^{10} \exp^2 (A^{heat} - B^{heat}/T_f^{heat}) + \frac{\delta\lambda}{\sigma E} T_f^{heat} \ln (R_2/r_f) \frac{\alpha^{heat} (T_f^{heat} - T_w^{heat})}{\alpha^{heat} \ln (r_f/R_1) + \lambda/R_1} =$$

$$= 10^{10} \exp^2 (A^r - B^r/T_f^r) - \frac{\delta\lambda}{\sigma E} T_f^r \ln (R_2/r_f) \frac{\alpha^r (T_f^{heat} - T_w^{heat})}{\alpha^r \ln (r_f/R_1) + \lambda/R_1}. \tag{8}$$

By expressing the function $T_f^{heat}(r_f)$ from Eq. (7) and substituting it into Eq. (8) we obtain a transcendental equation for determining the dependence $T_f^r(r_f)$. Similarly, such an equation is obtained for determining the dependence $T_f^{heat}(r_f)$.

The optimality condition $Q_{low}/Q_h \to$ max will obviously be fulfilled when the amount of hydrogen desorbed by element 1 (by virtue of the smallness of V this hydrogen is completely sorbed by element 2) during the preparatory half-cycle is equal to the amount of hydrogen desorbed by element 2 during the operating half-cycle
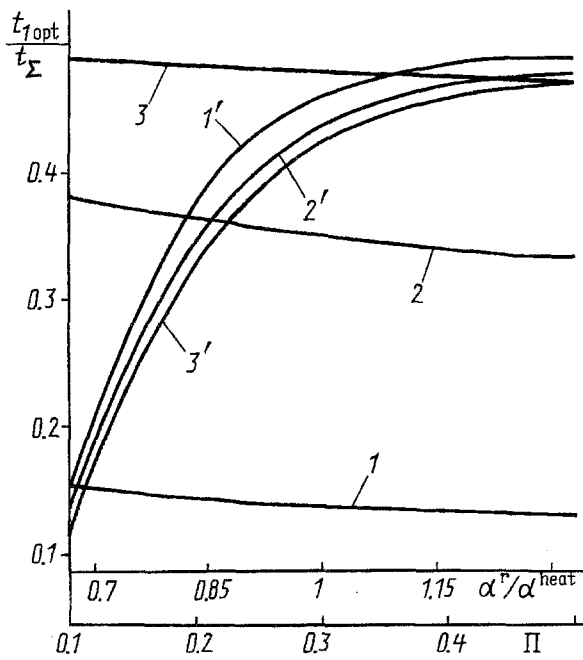
Fig. 5. Ratio of the switching time for the heat fluxes to the total cycle time $t_{1\,opt}/t_\Sigma$ vs ratio of the heat-transfer coefficients in cooling and heating α^r/α^{heat} for various values of the porosity: 1) $\Pi = 0.1$; 2) 0.2; 3) 0.5 and the ratio $t_{1\,opt}/t_\Sigma$ vs the metallohydride porosity Π for various values of α^r: 1') $\alpha^r = 100$; 2')150; 3'3') 200 W/(m²·K).
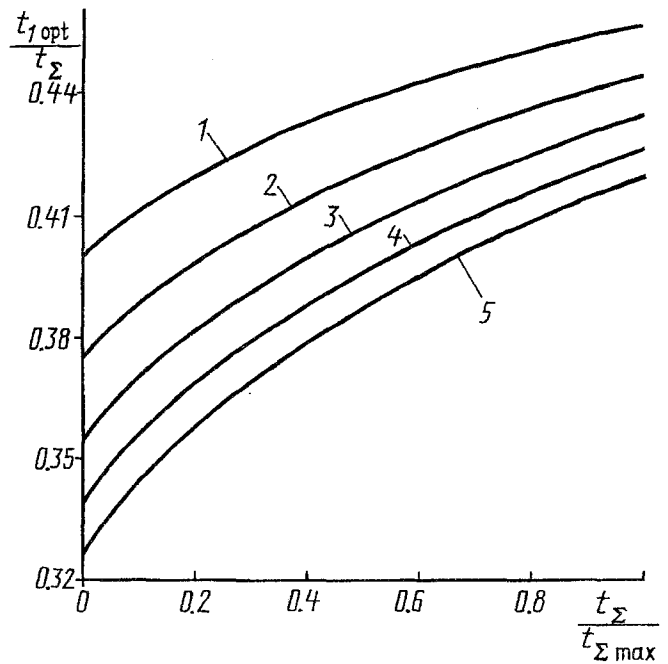
Fig. 6. Ratio $t_{1\,opt}/t_\Sigma$ vs ratio of the total and maximum cycle times $t_\Sigma/t_{\Sigma max}$ for various heat-transfer coefficients of the refrigerating element: 1) $\alpha^r = 100$; 2) 125; 3) 150; 4) 175; 5) $\alpha^r = 200$ W/(m²·K).

(i.e., element 2 desorbs during the operating half-cycle all the hydrogen that it has sorbed during the operating half-cycle). The following equation should thereby be fulfilled:

$$r_f\,(t_1) = r_f\,(t_2) = R^* , \tag{9}$$

where $t_2 = t_\Sigma - t_1$.

To obtain the equation for determining the sought switching time for the heat fluxes in the metallohydride system t_1 for which the optimality condition (9) is fulfilled, we integrate (3) from R_1 to R^* for the preparatory and operating half-cycles:

$$\int_{R_1}^{R^*}\left[\frac{E}{\lambda}\,\frac{r_f^r\,(\alpha^r\ln\,(r_f/R_1) + \lambda/R_1)}{\alpha^r\,(T_w^r - T_f^r)}\right]_{0<t<t_1} + \int_{R_1}^{R^*}\left[\frac{E}{\lambda}\,\frac{r_f^r\,(\alpha^r\ln\,(r_f/R_1) + \lambda/R_1)}{\alpha^r\,(T_w^r - T_f^r)}\right]_{t_1<t<t_\Sigma} = t_\Sigma , \tag{10}$$

where the dependence $T_f^r(r_f)$ is determined by Eqs. (7) and (8).

Once R^* has been determined from (11), we calculate $t_{1\,opt}$ by the formula

$$t_{0\,opt} = \int_{R_1}^{R^*}\left[\frac{E}{\lambda}\,\frac{r_f^r\,(\alpha^r\ln\,(r_f/R_1) + \lambda/R_1)}{\alpha^r\,(T_w^r - T_f^r)}\right]_{0<t<t_1} . \tag{11}$$

Calculations by formulas (10) and (11) yield that the optimum time for switching the heat fluxes for the initial data for which Figs. 3 and 4 are calculated is equal to $t_{1\,opt} = 1667$ sec. A calculation by the model (1)-(5) for this value of t_1 leads to the result $Q_{low}/Q_h = 0.949$. The deviation of Q_{low}/Q_h from unity even at $t_1 = t_{1\,opt}$ is caused by the fact that the volume of the tube connecting the elements, small as it is, differs from zero (we took $V = 5 \cdot 10^{-4}$ m^3 in the calculation). As Fig. 3 shows, the processes proceed during the preparatory half-cycle at high hydrogen pressure ($p_e \approx 5.5 \cdot 10^5$ Pa) and during the operating half-cycle at low pressure ($p_e \approx 0.5 \cdot 10^5$ Pa). Therefore a portion of the hydrogen that is in the volume V during the preparatory half-cycle is sorbed in the operating half-cycle by element 1, which leads to different positions r_f^{heat} and r_f^r in the operating half-cycle. However, element 1 cannot sorb more hydrogen in the operating half-cycle than it desorbed in the preparatory half-cycle, and therefore element 2 desorbs somewhat less hydrogen in the operating half-cycle than it sorbed in the preparatory one, which leads to $Q_{low}/Q_h < 1$.

The dependences in Figs. 5 and 6 are calculated for the same initial data as in Figs. 3 and 4; only one of the quantities given below was varied.

Figure 5 gives the ratio of the heat flux switching time to the total cycle time $t_{1\,opt}/t_\Sigma$ as a function of the ratio of the heat-transfer coefficients in cooling and heating α^r/α^{heat} as well as the ratio $t_{1\,opt}/t_\Sigma$ as a function of the metallohydride porosity Π. As is evident, this ratio depends strongly on the porosity (with a change in it from 0.1 to 0.5 the ratio $t_{1\,opt}/t_\Sigma$ increases by approximately a factor of 4). This is caused by the fact that, as has been noted in analyzing Fig. 3, the operating half-cycle occurs with stronger hindered filtration than the preparatory one. The increase in porosity decreases sharply the duration of the operating half-cycle t_2 while the duration of the preparatory half-cycle t_1 changes but little. Consequently, since $t_\Sigma = t_1 + t_2$, an increase in the porosity leads to an increase in the relative duration of the preparatory half-cycle t_1/t_Σ and, hence, to rapid growth of the curves $t_1/t_\Sigma(\Pi)$.

The dependence of $t_{1\,opt}/t_\Sigma$ on the heat-transfer coefficients is weaker: with a twofold (from 100 to 200 W/(m$^2 \cdot$K)) change in α^r, $t_{1\,opt}/t_\Sigma$ changes by approximately 30%. The hydrogen filtration has, thereby, a strong effect on the dynamics of the processes in the element, and calculating these processes with no account taken of filtration can indeed lead to incorrect results.

Figure 6 gives the ratio $t_{1\,opt}/t_\Sigma$ as a function of the ratio of the total and maximum cycle times (when $R^* = R_2$) $t_\Sigma/t_{\Sigma max}$. As is evident, the ratio $t_{1\,opt}/t_\Sigma$ changes but little as t_Σ changes from 0 to $t_{\Sigma max}$ (within 15–30%, and this change increases with increase in α^r). This indicates that the optimum switching time depends to a greater extent on the permeability and the heat-transfer coefficients than on the cycle duration prescribed by the technical requirements.

Thus, a method for calculating heat and mass transfer processes in a metallohydride refrigerator has been developed. An algorithm that permits the calculation of the optimum switching time for the heat fluxes is proposed.

NOTATION

p, pressure, Pa; T, temperature, K; t, time, sec; t_Σ, duration of the operating cycle for the metallohydride refrigerator, sec; t_1, preparatory half-cycle duration, sec; r, current radius, m; R_1, R_2, internal and external radii of the element; $\eta = r_f/R_2$, relative radius of the hydration front; V, volume of the tube connecting metallohydride elements, m^3; W, heat power, W; Q, quantity of hear, J; J, mass flow rate of hydrogen, kg/sec; M, molecular weight, kg/mole; Π, porosity, vol. fractions; ρ, density, kg/m^3; μ, dynamic viscosity coefficient of hydrogen, Pa$\cdot$sec; λ, thermal conductivity coefficient, W/(m$\cdot$K); κ, bound hydrogen content in hydride, katom H/kmole of hydride; E, specific volume heat of hydrogenation reaction, J/m^3; $\widetilde{R} = 8314$ J/(kmole$\cdot$K), universal gas constant; h, empirical coefficient of filtration, for LaNi$_5$ $h = 2.37 \cdot 10^{-3}$; α, coefficient of heat transfer to the medium, W/(m$^2 \cdot$K); d, average diameter of hydride particle, m. Subscripts and superscripts: H$_2$, gaseous hydrogen in

hydride pores; hyd, hydride; f, hydrogenation front; 0, initial value; max, maximum value; opt, optimum value; e, external pressure, w, heat-transfer agent (coolant); heat, heating element; r, refrigerating element.

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