PROPAGATION OF WAVES OF METAL-HYDRIDE THERMAL CONVERSION IN BLOWN-THROUGH POROUS MEDIA

Kyu-jong Kim

UDC 536.2:546.11

A method of metal-hydride thermal conversion that is an alternative to the traditional method is proposed and investigated. The unlike poles of metal-hydride thermal converters are distributed in pairs inside parallel channels. The channels are blown through with a heat-transfer agent. Thermal conversion develops as a set of successive heat waves. By a numerical-modeling method it is shown that the maximum thermal effect is attained in synchronous motion of the heat wave and the heat source (or sink) that accompanies the phase transition in the succession of metal-hydride poles. The results are presented in a form convenient for prediction of the thermal and energy efficiency of the proposed thermal-conversion method in real devices.

The methods of sorption and chemisorption thermal conversion continue to be a serious alternative to vapor-compression methods, since they make it possible to use heat energy instead of electric or mechanical energy, including especially sources of low-potential waste heat. However because of low thermal efficiency, bulky equipment, and the difficulty of realizing the sorption cycle of thermal conversion these methods have failed to find sufficient application up to now.

Certain hopes have been pinned on metal-hydride thermal conversion, which belongs to the chemisorption type of methods and results from the discovery of intermetallic alloys such as LaNi₅, FeNi, and Mg₂Ni, capable of interacting with hydrogen rapidly and reversibly [1, 2]. For some alloys, we do not observe any restriction on the rate of the reaction with hydrogen up to -100° C [3]. The heat of the hydride-formation reaction, referred to unit mass of sorbed matter (in this case, hydrogen), exceeds the heat of phase transition for water and Freon by approximately an order of magnitude. The hydrides of these alloys contain large amounts of hydrogen. The density of the hydrogen that is distributed in the crystal lattice under normal conditions can be higher than the density of liquid hydrogen [11].

The present investigation is devoted to the development of a new thermal-conversion method in which the indicated advantages of a sorption hydride system would be realized most fully.

Metal-Hydride Pair. Thermal conversion is realized on two unlike hydrides (a metal-hydride pair) [2, 4]. Each hydride of the pair is placed in a separate vessel. A metal-hydride converter is two hydride vessels connected by a channel for a free flow of hydrogen. In what follows these vessels will be called thermal-converter poles.

The hydrides differ from one another by the equilibrium hydrogen pressure. Over each hydride, taken separately, the latter is determined by the Van't Hoff equation in the form [4]

$$\ln p = \frac{\Delta S}{R} - \frac{\Delta h}{RT}$$

or in the identical form

$$p = p_{\max} \exp\left(-\frac{\Delta h}{RT}\right). \tag{1}$$

Curves of the pressure as a function of the temperature in accordance with formula (1) are presented qualitatively in Fig. 1a. The hydride in the pair that has a higher equilibrium temperature for the same pressure

Academic Scientific Complex "A. V. Luikov Institute of Heat and Mass Transfer of the National Academy of Sciences of Belarus," Minsk, Belarus. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 71, No. 1, pp. 51-61, January-February, 1998. Original article submitted June 21, 1997.



Fig. 1. Hydrogen pressure vs. temperature for the hydrides of a metal-hydride pair (a) and schematic diagram of a traditional metal-hydride thermal converter (b): 1, 3) mean-temperature tanks; 2) high-temperature tank; 4) low-temperature tank.

TABLE 1. Equilibrium Properties of Hydrides

No. of alloy	Alloy	Δh , kJ/mol	$\Delta S, J/(mol \cdot K)$
1	MNi4.15Fe0.85	25.10	104.68
2	LaNis	31.80	110.04
3	LaNi4.9Alo.1	32.64	110.46
4	LaNi4.75Alo.25	34.73	110.46
5	LaNi4.6Alo.4	36.40	109.20
6	LaNi4.5Alo.5	38.49	111.29
7	LaNi4.25Al0.75	44.35	117.99
8	LaNi4Al	47.70	118.83

is called the high-temperature hydride and is denoted by HM. The other hydride is called low-temperature and is denoted by LM. We will call the thermal-converter poles high-temperature and low-temperature, respectively. The equilibrium pressure over the high-temperature hydride for the same temperature is lower than that over the low-temperature one (Fig. 1a). A list of hydrides, that are recommended for compositing hydride pairs and their corresponding Van't Hoff constants is given in Table 1 [5, 6].

Principle of Operation for the Traditional Metal-Hydride Thermal Converter. In the general case, a metal-hydride pair operates with four heat tanks (Fig. 1b). The cycle of metal-hydride thermal conversion begins with the step of vapor charging, in which the vapor is brought to the active state. Let us assume that at the beginning of the process both poles are at the temperature of the mean-temperature tank T_{mean} . In the cooling cycle, the ambient medium usually acts as the mean-temperature tank. In Fig. 1a, this state corresponds to points 1 and 3. Then the high-temperature pole is brought in contact with the heat-transfer agent of the high-temperature tank, whose energy is used to charge the pair, while the low-temperature pole continues to be in contact with the meantemperature tank 3. When the pressure in the high-temperature pole (point 2), as a result of its heating, rises above the pressure in the low-temperature pole (point 3), the hydrogen will begin to liberate itself from the hydride phase of the high-temperature pole and shift to the adjoining low-temperature pole. The heat of sorption released in this pole is removed to the mean-temperature tank.

The quantity of heat expended on pair charging can be calculated using the formula

$$Q_{\rm H} = \Delta m_{\rm H_2} \Delta h_{\rm H} + m_{\rm hH} c_{\rm hH} \left(T_{\rm high} - T_{\rm mean} \right) + m_{\rm pH} c_{\rm pH} \left(T_{\rm high} - T_{\rm mean} \right). \tag{2}$$

According to expression (2), in the periodic process of the hydride cycle of thermal conversion, heat is expended not only on the phase transition, which is the aim of the charging, but also on heating the hydride mass and structural elements of the high-temperature pole.

The free energy of the charged pair, in particular, can be used to realize the cooling cycle, the heat-pump cycle, or the cycle of recovery of low-potential heat. When the cooling cycle is implemented, the high-temperature pole cools down in contact with the mean-temperature tank, and the heat of phase transition for hydrogen is expended not only on the production of cold in the cold tank (Q_L) but also on the cooling of the hydride mass and structural elements of the low-temperature tank; at least from the temperature of the mean-temperature tank to the temperature of the low-temperature tank:

$$Q_{\rm L} = -\Delta m_{\rm H_2} \Delta h_{\rm L} + m_{\rm hL} c_{\rm hL} \left(T_{\rm mean} - T_{\rm low} \right) + m_{\rm pL} c_{\rm pL} \left(T_{\rm mean} - T_{\rm low} \right).$$
(3)

As we can see, the metal-hydride cycle is traditionally implemented in a complex periodic process and calls for a whole system of heat tanks. One of the obvious drawbacks of this implementation is irreversible heat losses [7]. The coefficient of performance (COP) for an ideal cooling cycle will be determined by the first terms of the right-hand sides of Eqs. (2) and (3):

$$COP_{ideal} = \frac{\Delta h_{L}}{\Delta h_{H}}.$$
(4)

In an actual process, COP is calculated using the formula

$$COP = \frac{|Q_L|}{Q_H}$$
(5)

and is reduced due to irreversible heat losses in both the charging step (the denominator in (5) is increased) and the discharging step (the numerator is decreased).

The problem of the cooling capacity of metal-hydride thermal conversion is associated with the duration of the cycle, which is restricted by the transport of heat from the heat-transfer agent to the phase-transition zone in a weakly heat-conducting hydride medium rather than by the rate of reaction. Special hydride compounds with a high thermal conductivity are currently being developed. An increase in it is attained by diluting the hydride mass with an addition of inert highly heat-conducting metal. An increase in metal intensity leads to a natural additional increase in irreversible heat losses because of an increase in the corresponding terms in Eqs. (2) and (3) and, as a result, leads to an even larger decrease in the COP (5).

The temperature of the constructed hydride tank owing to the irreversible heat losses is usually only $10-30^{\circ}$ C lower than the temperature of the mean-temperature tank (the ambient medium). Thus, the goal of metal-hydride thermal conversion is limited, as a rule, by the problems of cold conditioning, while the problem of production of cold at a level that is accessible for thermal conversion (to -100° C) is not posed in the traditional cooling cycle [9]. It should be noted that loss of thermal efficiency due to expenditure of cold on precooling the mass of the accompanying components is not inevitable thermodynamically. This expenditure can be recovered in a thermodynamically reversible process.

New Concept of Thermal Conversion. Heat can be recovered if metal-hydride conversion is performed in a blown-through porous medium. The idea of the method had its origin in analysis of superadiabatic combustion waves that develop in blown-through porous media in low-power reactions [10]. Combustion is usually characterized by its adiabatic temperature, which is determined in terms of the thermal effect of the reaction performed under adiabatic conditions, when the heat of reaction is expended on heating its products and the components inevitably accompanying the reaction. Aside from reaction products, these can be atmospheric nitrogen and excess oxygen, if the adiabatic temperature is estimated for a lean gaseous mixture, or inert components of the porous medium, if the adiabatic temperature is estimated for the porous-medium matrix, which includes sparse solid-fuel particles. This porous medium is considered to be a very low-grade ashed solid fuel.



Fig. 2. Scheme of metal-hydride thermal conversion on heat waves in porous media: 1, 2) high-temperature and low-temperature channels.

The thermal effect of a reaction of low-grade fuels can be measured in tens of degrees, but this is obviously insufficient for the reaction to be self-sustained. However, combustion is still possible in superadiabatic waves that develop in blown-through porous media with a highly developed surface for heat transfer between the blown-through heat-transfer agent and the matrix of the medium. Under these conditions, the reaction is largely freed of the heat load associated with the necessity of directly heating the accompanying components. This heat recirculates from the components that have undergone reaction transformations to the components that begin to react. Thus, in a superadiabatic process, rational utilization of the heat of reaction is attained and the temperature of the equilibrium reaction is restored to the degree required for self-sustaining the combustion.

A similar situation occurs under conditions of hydride thermal conversion, where the attainment of the equilibrium temperature is hindered by irreversible losses associated with scattering of the heat of phase transition on the components that accompany the thermal conversion. To solve the problem of recovering this heat, two porous-medium channels, into which the poles of the thermal converters are built, are constructed in the proposed method (Fig. 2). The high-temperature poles are placed in one channel. Let us call it high-temperature. The low-temperature poles are distributed in a low-temperature channel that is parallel to it. The porous media thus constructed become thermoreactive, similarly to porous media containing fuel inclusions. Under the heat action on the high-temperature channel, spontaneous charging of the pairs in the vicinity of this action begins. If the channels are blown through by the heat-transfer agent, the metal-hydride pairs will begin to interact similarly to how heat sources interact through a superadiabatic-combustion wave, having been freed of irreversible losses of heat expended on heating the accompanying ballast components. The heat of reaction is accumulated in the heat wave.

The thermal effect of adiabatic thermal conversion can be calculated using the formula

$$\Delta T_{\rm ad} = \frac{\Delta m_{\rm H_2} \Delta h}{(m_{\rm h} c_{\rm h} + m_{\rm p} c_{\rm p}) + m_{\rm s} c_{\rm s} / N_{\rm p}}.$$
(6)

The components involved in the thermal conversion are the hydride mass and the elements of the pole construction and the adjacent porous medium. In a moving thermal-conversion wave, similarly to combustion, we can expect, to one degree or another, recovery of the heat that is expended on heating and/or cooling the accompanying components and accumulation of the heat of phase transition.

It should be noted that beyond the presented energy analogy there are substantial differences between the two processes considered.

Combustion is a high-temperature process. Its equilibrium temperature is estimated in thousands of degrees. Therefore the increase in the combustion temperature in a superadiabatic process should be considered only as a tendency toward recovery of the equilibrium temperature. Conversely, in the process of metal-hydride conversion, restoration of the equilibrium temperatures is a practical goal. Furthermore, the process of combustion is thermally activated and self-propagating, while phase-transition processes are locally equilibrium owing to the fast reaction of hydrogenation even at low temperatures [3].

Mathematical Formulation of the Problem. Propagation of thermal-conversion waves in thermally active porous media was investigated by a numerical-modeling method. The equations of heat transfer for gas filtration in each channel of the porous medium were integrated:

$$(\rho c)_{\rm sH} \frac{\partial T_{\rm H}}{\partial \tau} = \lambda \frac{\partial^2 T_{\rm H}}{\partial x^2} - (w \rho c)_{\rm gH} \frac{\partial T_{\rm H}}{\partial x} + w_{\rm H}, \qquad (7)$$

$$(\rho c)_{\rm sL} \frac{\partial T_{\rm L}}{\partial \tau} = \lambda \frac{\partial^2 T_{\rm L}}{\partial x^2} - (\nu \rho c)_{\rm gL} \frac{\partial T_{\rm L}}{\partial x} + w_{\rm L}.$$
(8)

The heat-wave velocity in the porous media, if there were no heat sources in them $(w_H = 0, w_L = 0)$, according to Eqs. (7) and (8), is determined by the formulas

$$u_{\rm H} = \frac{(\wp c)_{\rm gH}}{(\rho c)_{\rm sH}} , \quad u_{\rm L} = \frac{(\wp c)_{\rm gL}}{(\rho c)_{\rm sL}}.$$
(9)

Heat waves whose velocity is calculated by means of formulas (9) will be called free. System of equations (7) and (8) was made consistent through the magnitudes of the acting internal heat sources associated with the phase transition in the poles of the metal-hydride pairs:

$$w_{\rm H} = -\left(\rho c\right)_{\rm sH} \Delta T_{\rm adH} \frac{d\eta}{d\tau} = \alpha_{\rm vH} \left(T_{\rm hH} - T_{\rm H}\right), \tag{10}$$

$$w_{\rm L} = (\rho c)_{\rm sL} \Delta T_{\rm adL} \frac{d\eta}{d\tau} = \alpha_{\rm vL} \left(T_{\rm hL} - T_{\rm L} \right). \tag{11}$$

In determining sources (10) and (11) we employed the adiabatic temperatures in each channel (6) as well as the degree of hydrogenation of the poles in the low-temperature channel η . The degree of hydrogenation in the high-temperature channel is accordingly equal to $1-\eta$. The quantity η varies from 0 to 1 if the thermal converter goes from the ground to the active state, and it characterizes the degree of charge for the pair.

The function of the heat source in (7) and (8) was determined in the following manner. For the instantaneous temperatures of the porous media in the vicinity of the high- and low-temperature poles of the pair $T_{\rm H}$ and $L_{\rm L}$, the temperatures of the phase transition in the poles $T_{\rm hH}$ and $T_{\rm hL}$ are adjusted inertialessly to these temperatures in accordance with the thermal resistances between the phase-transition zones and the porous medium in the vicinity of the pole:

$$\frac{\alpha_{\rm vL} \left(T_{\rm L} - T_{\rm hL}\right)}{\alpha_{\rm vH} \left(T_{\rm H} - T_{\rm hH}\right)} = -\frac{\Delta h_{\rm L}}{\Delta h_{\rm H}}.$$
(12)

The hydrogen pressure in the poles of one pair was assumed to be the same:

$$p_{\rm L} = p_{\rm H} = p , \qquad (13)$$

......

and the phase-transition temperatures were determined in accordance with the Van't Hoff equation (1):

$$T_{\rm hH} = \frac{\Delta h_{\rm H}}{R \ln \left(\frac{p_{\rm sH}}{p_{\rm H}}\right)},\tag{14}$$

$$T_{\rm hL} = \frac{\Delta h_{\rm L}}{R \ln \left(\frac{P_{\rm sL}}{P_{\rm L}}\right)}.$$
(15)



Thus, the function of the internal heat source was determined by solving system of the nonlinear equations (10)-(15). The heat source associated with the thermal conversion was considered to be quasihomogeneous, which is in agreement with the idea of a thermally active quasihomogeneous porous medium.

Results of Numerical Modeling and Their Discussion. Numerical analysis is performed by variation in the vicinity of the following basic relation of the parameters: the length of the thermal-converter channels L = 0.5 m; the initial temperature of the porous media and the heat-transfer agents $T_{\text{mean}} = 293$ K; the velocity of propagation for a free heat wave in the high-temperature channel $u_{\text{H}} = 5$ cm/min, in the low-temperature channel $u_{\text{L}} = 3$ cm/min; the temperature of the heat-transfer agent that initiates the thermal conversion $T_{\text{high}} = 593$ K; the time in which the high-temperature heat-transfer agent is pumped through, $\tau_{\text{high}} = 7.5$ min; the thermal conductivity of the porous medium $\lambda = 1$ W/(m·deg); the density and heat capacity of the porous medium $\rho_s = 1500$ kg/m³ and $c_s = 1000$ J/(kg·deg); the hydride pair: the low-temperature pole is No. 6, and the high-temperature pole is No. 1 (see Table 1); the adiabatic temperature of the thermal conversion in the high-temperature channel $\Delta T_{\text{adH}} = 40^{\circ}$, and in the low-temperature channel $\Delta T_{\text{adL}} = 26^{\circ}$; the volumetric coefficient of heat transfer between the porous medium and the phase-transition zone for each channel $\alpha_{\text{NL}} = \alpha_{\text{VH}} = 10,000$ W/(m³·deg).

Results of the numerical modeling are presented in Figs. 3-5.

Figure 3b presents typical profiles of developing thermal-conversion waves for the basic relation of the parameters. Thermal conversion in a two-channel system was initiated by the action of a flow with a temperature of 320° C on the high-temperature channel for 7.5 min. In the same period, the heat-transfer agent was blown in the low-temperature channel in the direction opposite to the blowing in the parallel channel. The heat-transfer agent temperature at the inlet to the channel was assumed to be equal to the ambient temperature channel with the velocity $u_{\rm L} = -15$ cm/min. After the indicated period of heat-wave initiation, pumping of the heat-transfer agent in the high-temperature channel continued, but now at the ambient temperature. In the low-temperature channel, the pumping was switched to that codirected with the flow of the heat-transfer agent in the high-temperature channel the flow of the heat-transfer agent in the high-temperature channel the flow of the heat-transfer agent in the high-temperature channel continued, but now at the ambient temperature. In the low-temperature channel, the pumping was switched to that codirected with the flow of the heat-transfer agent in the high-temperature channel the flow of the heat-transfer agent in the high-temperature channel the flow of the heat-transfer agent in the high-temperature channel the flow of the heat-transfer agent in the high-temperature channel. The velocities of the free heat waves in both channels were prescribed in accordance with the values for the basic variant.

The heat wave of the source in direct contact with the high-temperature poles charged the pairs. As the heat wave left the charged space of the porous medium behind, discharging accompanied by "pumping" of heat from the low-temperature channel to the high-temperature channel was spontaneously initiated in it. A positive thermal-conversion wave adjacent to the charge wave was induced in the high-temperature channel, and a negative cold wave was induced in the low-temperature channel.



Fig. 4. Cooling capacity (W) vs. thermal effect of adiabatic thermal conversion (a), polarity of metal-hydride pairs (b) (along the horizontal – HM hydride No. from Table 1), ratio of the velocities of free heat waves in high- and low-temperature channels (c), and channel length (d). The isolines refer to the thermal effect of cold thermal conversion

Comparing the traditional thermal-conversion method (Fig. 1a) and the method realized in heat waves (Figs. 2 and 3), we can see basic differences concerning their practical implementation. In the traditional method, the accumulators of thermal-conversion energy are heat tanks through which the heat-transfer agent, usually in liquid form, is pumped. The tanks are located beyond the thermal-converting elements.

When thermal-conversion waves are realized, the energy is accumulated in the heat waves inside the porous medium directly adjacent to the poles. As a heat-transfer agent, we can use a gas flow since heat-transfer efficiency, even for a gas of low heat capacity and low thermal conductivity, is ensured on the developed surface of the porous medium. This opens up the possibility of performing thermal conversion using high-temperature heat sources.

A heat wave as a heat tank is nonisothermal. This permits temperature selection of the heat energy removed from the wave through the outlet cross section of the porous medium x = L (Figs. 2 and 3). If the objective of thermal conversion is to produce cold with a temperature T_{low} , the heat-transfer agent from the heat wave of the low-temperature channel should be selected in a time interval when the heat-transfer agent temperature is no higher than T_{low} . The thermal-conversion energy, referred to this temperature, can be calculated by means of the formula

$$Q_{T_{\text{low}}} = \int_{\tau_1}^{\tau_2} (\rho v c)_g (T_{x=L} - T_{\text{mean}}) d\tau , \qquad (16)$$

where τ_1 is the instant starting from which the temperature of the heat-transfer agent that flows out of the porous medium turns out to be lower than T_{low} ; τ_2 is the instant after which the temperature of the emergent wave returns to a level above T_{low} .

The cooling capacity of the thermal converter, referred to the temperature T_{low} , was calculated as the average power since the beginning of the thermal-conversion cycle (the beginning of the pumping of the hot heat-transfer agent):



Fig. 5. COP vs. the parameters indicated in the caption to Fig. 4.

$$W_{T_{\text{low}}} = \frac{Q_{T_{\text{low}}}}{\tau_2}.$$
(17)

The COP was calculated in accordance with its universally accepted definition as the ratio of the produced cold with a temperature T_{low} (16) to the source heat expended on the thermal conversion in the high-temperature channel of the thermal converter:

$$\operatorname{COP}_{T_{\text{low}}} = \frac{Q_{T_{\text{low}}}}{(\rho vc)_{g} (T_{\text{high}} - T_{\text{mean}}) \tau_{\text{high}} - \int_{0}^{\infty} (\rho vc)_{g} (T_{x=L} - T_{\text{mean}}) d\tau}.$$
(18)

Figures 4 and 5 plot the cooling capacity W and the COP of thermal conversion in a cooling cycle for a two-channel thermal converter versus the thermal effect of adiabatic thermal conversion ΔT_{adH} (a), the pair polarity, varied by choosing the high-temperature hydride, from No. 2 to No. 8 (Table 1), paired with low-temperature hydride No. 1, whose equilibrium properties are determined (b), the ratio of the heat-wave velocities in the low-temperature and high-temperature channels u_L/u_H (c), and the channel length L(r).

The numbers on the plots of the cooling capacity W(17) or the COP (18) refer to the thermal cooling effect of thermal conversion $T_{\text{low}} - T_{\text{mean}}$. In constructing the plots of Figs. 4 and 5 we employed results of numerical experiments of the type presented in Fig. 3.

As Figs. 4 and 5 show, the thermal-conversion indices, power W and energy COP, behave similarly with respect to the varied parameters. It should be noted that the cooling effect of thermal conversion exceeds -70° C. This means that the attained temperature in a cold heat wave is more than 70° C lower than the ambient temperature. The thermal effect exceeds by almost threefold the effect of adiabatic thermal conversion in the low-temperature channel. Similarly to filtration combustion, this cold wave can be defined as a superadiabatic wave. Both thermal-conversion characteristics W and COP are obviously extremal in character as functions of the adiabatic thermal-conversion effect, the pair polarity, and the velocity of a free heat wave in the low-temperature

channel. In all cases, there is the common cause of the extremal dependence. Figure 3 provides the possibility of elucidating this cause in the example of variation of the heat-wave velocity in the low-temperature channel.

As Fig. 3b shows, for the ratio $u_L/u_H = 0.6$, which is close to the optimum of the thermal effect (Figs. 4c and 5c), we observe almost synchronous motion of the cold wave and the zone of the cold-inducing phase transition. Conversely, for $u_L/u_H = 0.1$ (Fig. 3a), the phase-transition zone leads the heat wave in the low-temperature channel, but in the case of $u_L/u_H = 1.1$ (Fig. 3c), on the contrary, it lags behind it. Thus, any mismatch in the velocities of motion of the heat wave and the negative heat source associated with the phase transition leads to a reduction in the thermal-conversion efficiency.

In analyzing the effect of energy saturation of a thermal-converting porous medium (ΔT_{ad} , Figs. 4a and 5a), the ratio between the thermal effects in the thermal-converter channels was assumed to be proportional to the thermal effects of the phase transition in these channels, i.e., $\Delta T_{adH}/\Delta T_{adL} = \Delta h_H/\Delta h_L$. As follows from Figs. 4 and 5, synchronization of heat transfer and propagation of the phase-transition zone occurs at $\Delta T_{adH} = 55^{\circ}C$ ($\Delta T_{adL} = 36^{\circ}C$). In a more energy-saturated porous medium (for larger ΔT_{adL}), the discharge zone lags behind the heat wave. In a poorer medium in terms of energy (for smaller ΔT_{adL}), the discharge zone leads the heat wave. In both cases, the thermal efficiency of thermal conversion is decreased.

It is evident that more polar pairs will be discharged more intensely. The velocity of motion of the phasetransition zone for them is, naturally, higher. As Figs. 4b and 5b show, synchronization conditions correspond to pair No. 1-No. 5 most completely. For more polar pairs the discharge zone will forge ahead, while for weaker pairs it will lag behind.

In investigating the extrema for energy saturation and pair polarity it should be borne in mind that in energy-saturated and very polar thermal-converting porous media metal-hydride pairs can turn out to be undercharged at a fixed temperature and energy of the heat source which initiates thermal conversion. It can also be seen that the position of the extrema for a separately chosen parameter depends on the relation of the other parameters.

Analysis of W and COP as functions of the channel length L provides important information on the development and energy structure of a thermal-conversion heat wave. It should be noted that with change in the length of the channels the heat-action time τ_{high} varied simultaneously in proportion to them. The neighborhood of the hot discharging wave that precedes the cold wave that is induced in the charged (active) porous medium of the low-temperature channel can lead to partial or complete reduction of the thermal-conversion efficiency if these waves in the low-temperature channel begin to interact directly, as was noted in [10]. Irreversible losses of the energy resource of the phase transition are the analog of this situation in the traditional process if discharging is started without waiting for complete cooling of the low-temperature pole to T_{mean} in the charging step. The fact that, for the lowest thermal effect of -5° C, we attained a COP similar to the limiting value for a metal-hydride pair (the limiting quantity COP_{ideal} (4) is determined by the ratio $\Delta h_L / \Delta h_H = 0.65$) indicates the virtual absence of irreversible losses of cold of this kind in the considered example of thermal conversion on heat waves. This, in particular, is a consequence of the artificial technique employed in the charging step, owing to which there was the possibility of spatially separating the hot and cold discharging waves in the low-temperature channel (Fig. 3).

In varying the pair polarity we note a decrease in the COP when a more polar pair is chosen (Fig. 5b). In all cases, the COP corrresponds to the ideal value COP_{ideal} (4) for the considered pair.

It should be noted that in the example considered the process of thermal conversion on heat waves is nonstationary in two repects. This concerns the periodic cycle for each pair, on the one hand, as is the case when traditional thermal conversion is performed, and, on the other hand, development of a heat wave among multiple pairs, i.e., in the field of a charged (thermoactivated) porous medium. On small porous-medium lengths, a cold wave only begins to be initiated. A phase transition in this step bears a large energy load and is expended on initiating the heat wave. It is evident that there are considerable irreversible losses associated with direct cooling of all the heat-intensive ballast elements that accompany the thermal conversion. In this step, the development of the heat wave is most similar to the initial development of a superadiabatic wave with synchronous motion of the phase-transition zone and a free heat wave. This development of the heat wave naturally leads to the attainment of the maximum-in-magnitude temperature governed by equilibrium conditions. The equilibrium temperature of cold thermal conversion is rigidly linked to the temperature of the heat wave induced in the high-temperature channel in the discharging step. The lower the temperature of the heat wave in the high-temperature channel, the deeper the cold that can be produced in the low-temperature channel. This relation is controlled by choosing the basic parameters.

When the temperatures in both channels are set in the equilibrium relation a natural mismatch of the velocities of motion for the phase-transition zone v_d and the free heat wave u_L begins that will make it impossible for the process to go beyond the thermal limits determined by the equilibrium. The intrinsic velocity of an asymptotic discharging wave v_d can be calculated in a system of five equations, three of which (13)-(15) govern the equilibrium, while the other two relate the requirement of conservation of energy to the equilibrium temperatures:

$$\frac{T_{\rm H} - T_{\rm min}}{\Delta T_{\rm adH}} = \frac{v_{\rm d}}{u_{\rm H} - v_{\rm d}}, \quad \frac{T_{\rm L} - T_{\rm 0}}{\Delta T_{\rm adL}} = \frac{v_{\rm d}}{u_{\rm L} - v_{\rm d}}.$$
(19)

We note that limitation of the temperature of thermal conversion by the equilibrium makes it substantially different from the analog in the area of filtration combustion. Combustion is a high-temperature process, and the limitation on temperature is due to heat transfer and the reaction kinetics rather than the requirements of equilibrium (the latter is simply not attained).

Solving the system of equations (13)-(15) and (19) for the basic relation of the parameters yields the following magnitudes for the asymptotic discharging wave: the discharging rate $u_d = 2.182$ cm/min, the temperature in the high-temperature channel $T_H = 51.0^{\circ}$ C, and the temperature in the low-temperature channel $T_L = -49.6^{\circ}$ C. The obtained velocity of the discharging wave is similar to the velocity of the free heat wave in the low-temperature channel, which predetermines the thermal efficiency of the cooling cycle.

The propagation of the thermal-conversion zone leads to a natural reconstruction of the thermal structure of the heat wave toward building up of extremely low-temperature portion. The low-temperature zone increases with the velocity $v_d - u_L$. The reconstruction of the discharging-wave structure can be controlled by means of the tendency for W and the COP to approach the asymptotic values as the length of the thermal-converter channels increases (Figs. 4d and 5d).

We can note that for a channel length of 0.5 m, which is quite acceptable in many practical applications, the thermal-conversion wave is sufficiently developed already. In it, the equilibrium temperature is attained. On converter channels with a 1-dm² cross section, we can attain a cooling capacity of 80 W at a temperature of -20° C and 45 W at a temperature of -40° C, which is sufficient to solve a number of practical problems.

In the present work, we considered a variant of implementation of a new concept of metal-hydride thermal conversion. We can note substantial differences in effecting the traditional and proposed methods and the high thermal efficiency of the latter. The proposed method allows for optimization of the thermal-conversion regime, which is attained by varying the parameters that govern the interaction between the thermal-converter poles in the moving heat wave.

NOTATION

c, specific heat, J/(kg·deg); COP, energy coefficient of performance; Δh , change in enthalpy when hydrogen changes to the hydride form, J/mol; L, channel length, m; m, mass, kg; $\Delta m_{\rm H_2}$, number of moles of hydrogen involved in the phase transition in the thermal-conversion cycles, mol; N_p , number of poles in the thermalconverter channel; p, hydrogen pressure, Pa; $p_{\rm max}$, constant in Eq. (1), Pa ($p_{\rm max} = \exp(\Delta S/R)$); R, universal gas constant, J/(mol·deg); ΔS , change in enthalpy when hydrogen changes to the hydride form, J/(mol·deg); T, temperature, K; $T_{\rm high}$, temperature of the high-temperature tank, K; $T_{\rm mean}$, temperature of the mean-temperature tank, K; $T_{\rm low}$, temperature of the low-temperature tank, K; ν , velocity of the gas flow, m/sec; u, velocity of the free heat wave, m/sec; w, power of the internal heat source, W/m³; W, cooling capacity, W/m²; x, coordinate, m; α_v , volumetric coefficient of heat transfer between the phase-transition zone in the hydride and the porous medium, W/(m³·deg); η , degree of hydrogenation for the alloy in the low-temperature pole; λ , thermal conductivity of the porous medium, W/($m \cdot deg$); ρ , density, k/ m^3 ; τ , time, sec; τ_{high} , action time for the hot heat-transfer agent. Subscripts: d, step of discharging of the metal-hydride pair; g, gas medium in the pore space; h, hydride; H, high-temperature hydride; L, low-temperature hydride; p, pole; s, porous-medium matrix; low, low; mean, mean; high, high.

REFERENCES

- 1. J. H. N. Van Vught, F. A. Kuijperg, and H. C. A. M. Bruning, Phillips Res. Repts., 25, 133-140 (1970).
- 2. F. E. Lynch, J. Less-Common Metals, 172-174, 945-958 (1991).
- 3. T. Domschke, T. Nietsch, and E. Schutt, Int. J. Hydrogen Energy, 16, 255-265 (1991).
- 4. M. Gambini, Int. J. Hydrogen Energy, 19, 81-97 (1994).
- 5. P. Dantzer and E. Orgaz, Int. J. Hydrogen Energy, 11, 797-806 (1986).
- 6. E. L. Huston and G. D. Sandrock, J. Less-Common Metals, 74, 435-443 (1980).
- 7. A. Nonnenmacher and M. Groll, Metal-Hydrogen Systems (ed. by T. N. Verziroglu), Pergamon Press (1981), pp. 657-665.
- 8. M. Ron, E. Bershadsky, and Y. Josephy, J. Less-Common Metals, 172-174, 1138-1148 (1991).
- 9. S. Suda, Int. J. Hydrogen Energy, 10, 757-765 (1985).
- 10. G. A. Fateev and O. S. Rabinovich, Int. J. Hydrogen Energy, 22, 915-924 (1997).