EXPERIMENTAL INVESTIGATION OF HYDRIDE HYDROGEN ACCUMULATOR

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The article describes an experimental hydride hydrogen accumulator. Processes of its charging and discharging were experimentally investigated. The obtained characteristics are described fairly accurately by equations. Dependences of the charging and discharging rates on the diameter of the hydride accumulator are presented.

The main difficulties hindering the extensive introduction of hydrogen in transport power plant are connected with its storage. To a certain extent these difficulties can be overcome by the use of hydride accumulators (HA) [1, 2]. In spite of the great weight of hydride storage systems, they have a number of very valuable properties from the point of power engineering, viz., lengthy storage without evaporation, great reliability, safety in operation, the possibility of liberating hydrogen at constant rate.

Hydrogen is absorbed by hydride in a certain temperature range, and the speed of the process is proportional to the pressure; also a considerable amount of heat is liberated; this has to be conducted away, and the rate of heat removal determines the intensity of hydrogen absorption.

Hydrogen is liberated from hydride at a certain temperature which is higher than the temperature of absorption at the given pressure. In that case the reaction involves the absorption of heat which has to be supplied to the hydride from outside. In both cases the amount of heat is determined by the enthalpy of hydride formation and by the weight of the hydride.

We investigated the influence of: 1) the pressure of the hydrogen on the charging characteristics of the HA; 2) the discharge pressure on the characteristics of the HA in operation in a power plant with a low-temperature electrochemical generator; 3) the discharge pressure on the characteristics of the HA when it was electrically heated; 4) the diameter of the HA on the charging and discharging characteristics.

For that purpose we built and investigated a prototype of the hydride accumulator. The hydride hydrogen accumulator (Fig. 1) consists of the two coaxial cylinders 5 and 6. Into the inner cylinder 6 six kilograms of intermetallic phase $LaNi_5$ are poured, and this forms the hydride $LaNi_5H_6$. Within the working substance there are two tubular electric heaters (TEH) 8 and the pipe for the inlet and outlet of hydrogen 14, provided with screen filters with filtering ability 0.8 μm for preventing hydride particles being entrained by the stream of hydrogen and removed from the HA. Pipe 14 is connected with the membrane valve 13. The hydrogen pressure is checked by manometer 2.

The coaxial cylinders form an annular channel in which, when necessary, water is supplied through the nozzle unions 4 and 15. The hydride can be heated either by the TEH's or by hot water fed to the annular channel; this brings about liberation of hydrogen. The pressure of the liberated hydrogen depends on the counterpressure and may attain 15 MPa.

The HA is provided with an electromagnetic pressure sensor 10 and a protective device 11 which interrupts the electric power supply to the TEH's when the permissible pressure is exceeded.

Power is supplied to the TEH's through an electronic control unit which was specially designed and made for this hydride accumulator operating on 220 V, 50 Hz. The electronic unit makes it possible to adjust the voltage supplied to the TEH's steplessly within the limits 0-210 V and to supply current to the potentiometric pressure sensor. The signals from

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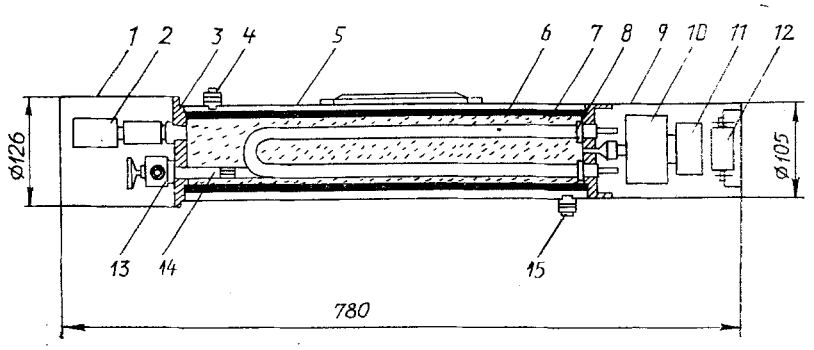

Fig. 1. Hydrogen accumulator: 1, 9) protective jackets; 2) manometer; 3) front lid; 4, 15) nozzles; 5) outer tube; 6) inner tube; 7) hydride; 8) TEH's; 10) pressure sensor; 11) contact breaker; 12) plug and socket; 13) valve; 14) pipe for hydrogen inlet and outlet.

the sensor are transmitted to the commutation device of the unit. The electronic unit contains a pointer-type milliammeter type M 265 M which registers the voltage supplied to the TEH's, the pressure in the hydride accumulator in the ranges 0.1-0.6 and 0-15.0 MPa. The controlled parameter in the range of pressure measurement is selected with the aid of a multiposition switch. The TEH's are connected to the power supply unit by the plug and socket 12.

The elements of the hydride accumulator are made of steel marques 12Kh18N9T and 12Kh18N10T and joined together by argon-arc welding.

The technical characteristics of the HA are the following:

Length of HA, m	0.78
Diameter of HA, m	0.126
Weight of HA, kg	23.4
Intermetallic phase	$LaNi_5$
Length of hydride cartridge, m	0.48
Diameter (inner) of hydride cartridge, m	0.08
Weight of intermetallic phase, kg	6.0
Weight of stored hydrogen, kg	0.081
Total power of TEH's, kW	0-0.96
Working pressure, MPa	Up to 15.0

The intermetallic phase $LaNi_5$ was preliminarily activated. For that it was placed in a thick-walled stainless-steel cylinder which was evacuated, heated to 550°C, and held under 4.0 MPa hydrogen pressure for 5 h. Then the hydrogen was removed and the vacuum pump was switched on for 2 h.

This procedure was repeated four times, and then the intermetallic phase was poured in an argon atmosphere into the accumulator. To stabilize the kinetic characteristics, the HA passed through eight cycles of charging-discharging. In the experiment we used hydrogen marque A in cylinders.

In the investigation of the charging process water at 293°K was pumped through the water jacket of the HA. The flow rate of the water was 0.1 kg/sec, the charging pressure was between 0.59 and 2.85 MPa with fluctuations of no more than ±0.05 MPa.

Figure 2a shows the characteristics of charging. The reaction proceeds with the greatest intensity during the first two minutes, the flow rate of hydrogen at that time is as much as 10-23 g/min. During that time the inter-metallic phase absorbs between 0.21 and 0.65 wt.% hydrogen. Then the speed of the reaction drops abruptly, and for most of the time it remains approximately constant. The surge of the flow-rate characteristic at the initial instant is due to the property of hydrides to absorb and liberate initial portions of hydrogen at high rates. Besides, the speed of hydrogenation depends largely on the intensity of removal of the reaction heat. At the initial instant the heat of hydrogenation is absorbed directly by the intermetallic phase itself, and that also speeds up the process. It can be seen from

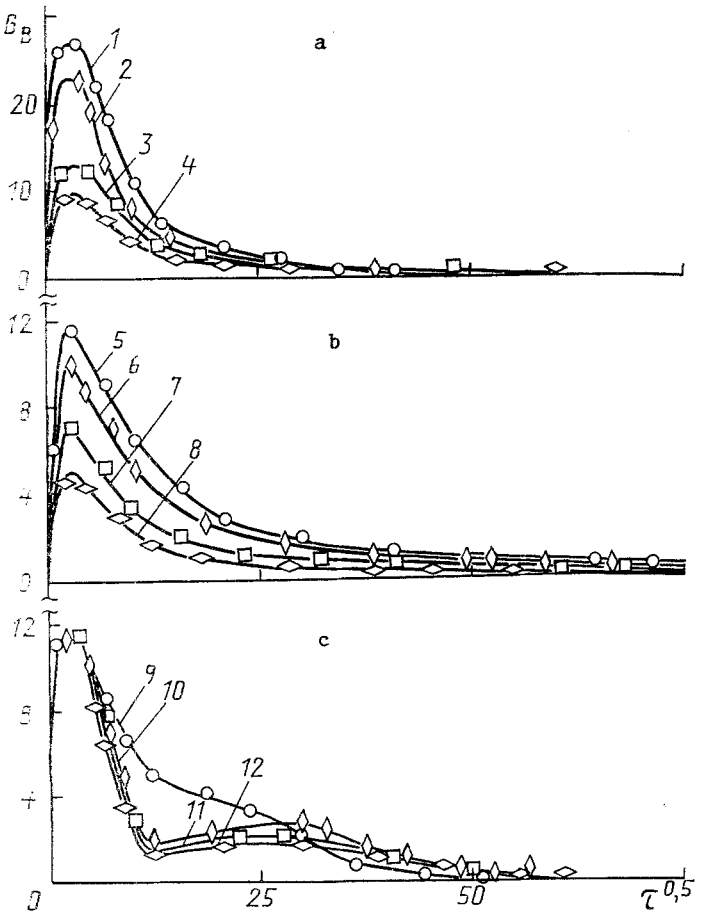

Fig. 2. Characteristics of charging (a) and discharging (b, c) the HA: 1) P_c = 2.85 MPa; 2) 1.62; 3) 1.08; 4) 0.59; 5) P_d = 0.116 MPa; 6) 0.356; 7) 0.61; 8) 0.82; 9) 0.12 MPa; 10) 0.47; 11) 1.05; 12) 1.63 MPa. $\tau^{0.5}$, sec; G_B, g/min.

Fig. 2a that an increase of the hydrogen pressure speeds up the charging of the HA; this is in complete agreement with available data [2]. At a pressure of 2.85 MPa the intermetallic phase absorbed 1.35 wt.% of hydrogen within approximately 45 min. At a pressure of 0.59 MPa no more than 0.59 wt.% hydrogen was absorbed within the same time.

Figure 3a shows the dependences of the degree of charging the HA on the time and the hydrogen pressure. The value of W_c is characterized by the ratio of the weight of the hydrogen absorbed by the intermetallic phase by the given instant to the weight of this intermetallic phase. The presented dependences are described with an error not exceeding 10% by the following equation:

$$W_c = 1{,}35 - (1{,}35 - (5{,}465P_c + 3{,}383) \cdot 10^{-3}\ \tau^{0,5})^3.$$

When HA are used as part of low-temperature hydrogen–oxygen electrochemical generators, the heat carrier can be the electrolyte of the heating elements whose mean temperature is 355°K. Here the hydrogen pressure usually does not exceed 1.0 MPa. In our experiment the heat carrier was water 355°K hot whose flow rate was 0.18 kg/sec. The water temperature was maintained constant with an accuracy of ±1°K, the flow rate ±0.01 kg/sec. The initial hydrogen pressure in the HA was 2.5 MPa.

Figure 2b presents the obtained characteristics of discharging. Increased desorption pressure leads to lower rate and amount of hydrogen liberated from the HA (Fig. 3b) which apparently is connected with the low thermal conductivity of hydride and the course of the isothermal curves of pressure vs. composition. For instance, at a pressure of 0.82 MPa only 53% of the stored hydrogen were liberated from the HA. Obviously, if the remaining hydrogen is to be released, it is necessary either to raise the temperature of the heat carrier or to reduce the discharging pressure.

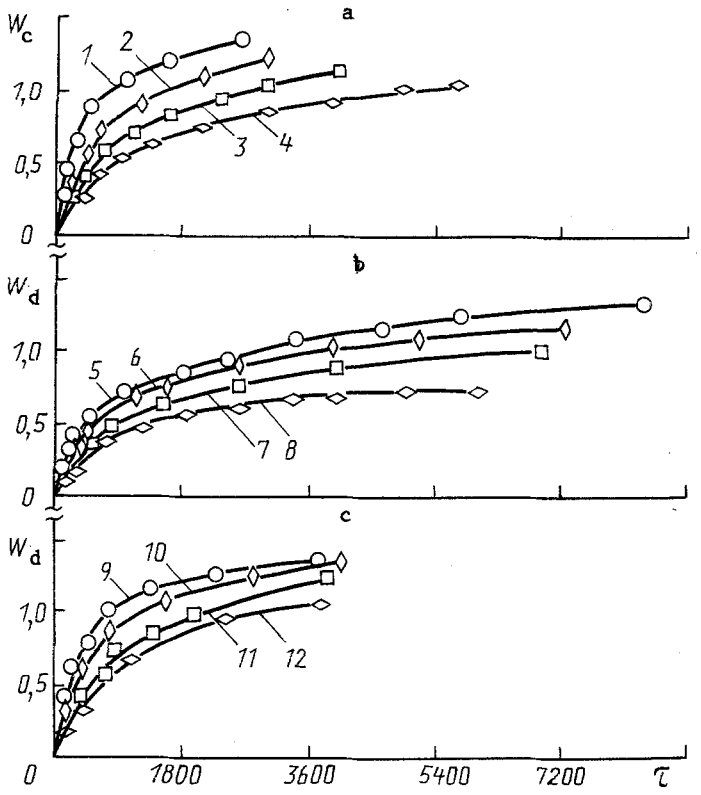

Fig. 3. Dependences of hydrogen capacity of HA on the time in charging (a) and discharging (b, c); the values of 1-12 are the same as in Fig. 2. W_c, W_d, %.

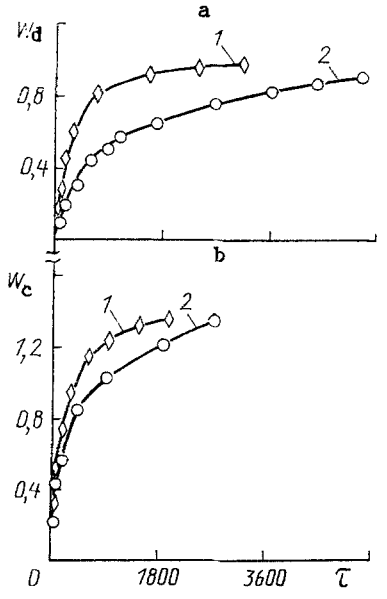

Fig. 4. Dependence of the hydrogen capacity of hydride catridges with different diameters on the time in charging (a) and discharging (b): 1) d = 0.045 m; 2) 0.08.

The value of W_d in Fig. 3b is characterized by the ratio of the weight of the hydrogen liberated from the hydride by the given instant to the weight of the intermetallic phase.

With an error not exceeding 11.5% the dependence $W_d(\tau)$ is described by the equation

$$W_d = 1{,}35 - (1{,}35 - (7{,}462 - 4{,}615P_d) \cdot 10^{-3}\tau^{0,5})^3.$$

The equation applies to P_d = 0.1-1.0 MPa, and the mentioned error does not increase if τ does not exceed $9 \cdot 10^3$ and $6 \cdot 10^3$, respectively.

The flow-rate characteristics of discharging the HA due to the heat of the TEH's are shown in Fig. 2c. The initial hydrogen pressure in the HA was 2.5 MPa, and the temperature 288°K.

At the initial instant the discharging flow rate attains 11.8 g/min, after that it abruptly drops to 1.5-4.5 g/min within 2.0-2.5 min. With 0.12 MPa hydrogen pressure the rate continues to drop; after 30 min it amounts to 0.25 g/min, and then it becomes stabilized.

With 0.47, 1.05, 1.63 MPa hydrogen pressure the drop in the rate of hydrogen liberation ceases after 2-2.5 min of operation of the HA, then it increases again, attaining 1.75-2.6 g/min by the sixth minute. Within the subsequent 9-12 min the discharging rate remains constant, and then it drops noticeably. From the fortieth minute onward it becomes stabilized and amounts to 0.1-0.2 g/min.

The dip in the characteristics in the time interval 2-2.5 min is obviously due to the fact that the liberation of hydrogen from the hydride on account of the heat of the hydride itself comes to an end, and the TEH's did not manage yet to heat it to the necessary extent. With the hydride being increasingly heated the rate of liberation increases until equilibrium is established between the heat emitted by the TEH's and the heat required by the hydride in the process of desorption. The subsequent drop of the rate is obviously due to the fact that the hydride adjacent to the TEH's has already liberated all the hydrogen.

A lowering of the heat for liberating hydrogen leads to the heating of the HA. At the end of the discharging process the temperature of the outer wall attains 395-400°K.

When the desorption pressure increases, the rate of desorption drops. The reason is that the increase of pressure is attained by the temperature rise. Thereby the temperature head between the surface of the TEH's and the hydride is reduced. Besides, an increase of the discharging pressure leads to a reduction of the amount of liberated hydrogen by 2-20% (Fig. 3c).

The dependences $W_d(\tau)$ (Fig. 3c) are described with an error not exceeding 12% by the equation

$$W_d = 1{,}35 - 1{,}35 \exp\left(\left(-2{,}474 \cdot 10^{-3} P_d + 0{,}113 \cdot 10^{-2} P_d - 0{,}173 \cdot 10^{-2} P_d + 0{,}159 \cdot 10^{-2}\right)\tau\right).$$

One way of increasing the flow rate and the amount of hydrogen from the HA is making the diameter of the hydride cartridge smaller. With equal amounts of stored hydrogen, a hydride accumulator with smaller diameter of the hydride cartridges has a larger heat exchange area, thinner layers of hydride, and consequently a higher discharging rate [3]. Figure 4 shows the charging and discharging characteristics of HA with different diameters of the hydride cartridges. The charging pressure was 2.85 MPa, the temperature of the cooling water was 288°K. In discharging the water temperature was 355°K, the discharging pressure was 0.61 MPa, the initial hydrogen pressure was 2.5 MPa. It can be seen from the figure that the hydride cartridge with 0.045 m inner diameter operates more efficiently. The amount of liberated hydrogen increased approximately by 10%, the time of discharging was reduced by about 40%, and the time of charging by about 30%.

CONCLUSIONS

1. An experimental prototype of a hydride hydrogen accumulator was built and tested. With a pressure of 2.85 MPa the charging time was 45 min.

2. With increasing discharging pressure the flow rate of hydrogen and its amount decrease by 2-50%.

3. A smaller diameter of the hydride cartridge enhances the efficiency of operation of HA.

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