ISSN 1070-3632, Russian Journal of General Chemistry, 2007, Vol. 77, No. 4, pp. 694–711. © Pleiades Publishing, Ltd., 2007.
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Problem of Hydrogen Storage and Prospective Uses of Hydrides for Hydrogen Accumulation

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Received September 9, 2006

Abstract—Merits and demerits of existing methods of hydrogen storage are discussed. Special attention is given a metal hydride technology based on the ability of metals, intermetallic compounds, and alloys for reversible reaction with hydrogen. It is noted that the basic advantages of metal hydrides are a high volumetric hydrogen content, operational safety, technological flexibility, and low power inputs on hydrogen absorption and desorption.

DOI: 10.1134/S1070363207040329

INTRODUCTION

One of the major problems whose successful solution will promote in many respects further progress of hydrogen energetics is to organize a technically and economically effective storage and transportation of hydrogen. Even though hydrogen is a power-intensive and ecologically clean energy carrier, it is quite inconvenient to use because of its extremely low density (~0.09 kg m^{-3}). To maintain a 62 mileage of an electromobile on fuel cells (FCs), one should have ~11 m^3 of hydrogen onboard.

For a higher density hydrogen should be compressed to hundreds atmospheres, cooled below the boiling point (20 K), or bound [1–3]. The first two approaches are realized in physical methods, when hydrogen molecules do not react with the storage medium, and the third, in chemical or physical chemical methods (adsorption, absorption, chemical reaction) when hydrogen "is compactly packed" in the storage material [4–6].

At present the manufacture of a cylinder and cryogenic liquid hydrogen has been mastered. Other methods have the status of perspective, basically being on the stages of technological development or small-scale industrial production.

Conditions for hydrogen storage define power inputs for the realization of one or another method: the higher the hydrogen pressure and the larger the energy gap between the storage and ambient temperatures, the higher the power inputs. An optimum method should combine a high hydrogen storage density with low power inputs. However, it is not always possible, as, leading in one of the parameters, one or another method of hydrogen storage, as a rule, concedes alternative in other characteristics.

Various hydrogen application areas make various demands to its storage systems. Lightweight storage systems (and, correspondingly, high weight contents of stored hydrogen) are important for motor transport and, especially, for aerospace technics, but not so essential, for example, for filling stations. A small volume of the container (high volumetric density of

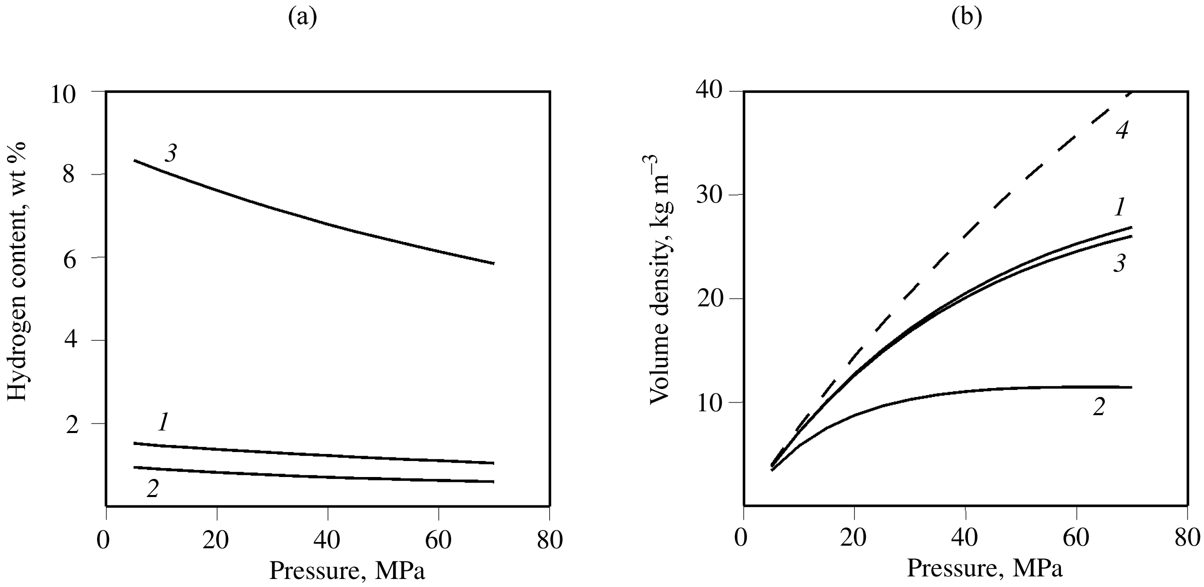

Fig. 1. (a) Weight contents and (b) volume densities of hydrogen storage in gas cylinders from various materials: (*1*) steel (σ = 469 MPa, ρ = 7800 kg m^{-3}); (*2*) aluminum (σ = 100 MPa, ρ = 2700 kg m^{-3}); (*3*) composite material (σ = 429 MPa, ρ = 1200 kg m^{-3}); and (*4*) volume density of gaseous hydrogen at room temperature.

stored hydrogen) also is critical for small vehicles (cars), but is less important for stationary conditions. Therefore, each of the above methods of hydrogen storage can in principle find its "economic niche."

The urgency of the hydrogen storage problem is also evidenced by the fact that the target parameters for mobile hydrogen storage systems envisaged by the Hydrogen Program of the US Department of Energy [7] (6 wt%, density 45 g l^{-1}) are planned to fit by 2010 in the framework of programs for development of hydrogen energy and technology, financed by the European Union [8].

PHYSICAL METHODS OF HYDROGEN STORAGE

Large volumes of gaseous hydrogen are not much more difficult to store at atmospheric and increased (up to 15 MPa) pressure than natural gas. For this purpose, gas holders, natural and artificial underground tanks, and other systems are applied. The total capacity of such systems can reach several millions cubic meters, and, therefore, they remain a unique opportunity for storing large hydrogen volumes with a long-term, for example seasonal, cycle of refuelling the storage facility and withdrawing hydrogen from it [1, 6].

Gaseous hydrogen is usually stored and transported under pressures of up to 35 MPa in cylinders from several liters to several cubic meters in capacity [9]. Such cylinders transported to consumption sites on automobiles or railway platforms.

Since a cylinder contains nothing but compressed gas, such storage system is characterized by limiting weight content (100%) and volumetric density of hydrogen. Improvement of storage parameters in real systems is limited by cylinder the dimensions and weight. The latter parameter is determined by the excess gas pressure and strength of shell material and can be calculated from strains arising in vessels under pressure. Depending on the accepted procedures for strength calculations, there are various formulas for shell thickness. As a rule, they allow to define the ratio of shell thickness to characteristic container size and give close results.

According to calculations [3, 10], increased excess pressure inside of the container entails growth of wall thickness and, correspondingly, volume and weight of the cylinder shell. This slightly decreases the volumetric hydrogen storage density and essentially decreases the weight content. This tendency is the stronger the lower the strength of the construction material. Moreover, the weight content of hydrogen will be the lower, the higher the shell material density. On the other hand, as the pressure of hydrogen increases, its volumetric density increases. Figure 1 shows the example dependences of the weight content and volumetric density of compressed hydrogen on pressure for various cylinder shell materials. Obviously, to increase the weight content of hydrogen, light high-strength materials are required, and the volumetric density is increased by increasing pressure.

Small amounts of compressed hydrogen are usually stored and transported in steel cylinders with working pressures of up to 15–20 MPa. The weight of hydrogen in such cylinders makes no more than 1.5 wt%, and the volumetric density, 10–12 kg m^{-3}.

Since the mid-1970s, the progress in materials science has inspired the development of a new generation of gas cylinders of a thin aluminum or plastic sleeve covered form the outside by a composite plastic, reinforced glass, or carbon fiber. Such cylinders allow hydrogen to be stored under pressures of up to 35–70 MPa, and, therewith, the weight density of stored hydrogen was above 6 wt% and its volumetric density, up to 30 kg m^{-3}. Now 35-MPa composite cylinders are produced on the industrial scale, and serial release of 70-MPa cylinders is planned. The leading manufacturers of cylinders are Dynetec (Canada–Germany), Quantum (USA), BOC (Great Britain), and some others [7, 10–13].

The principal advantages of cylinder hydrogen storage are its simplicity and absence of power inputs for gas delivery. Compression of hydrogen necessitates high power inputs (10–15% of the calorific efficiency of hydrogen), but, as the pressure increases, the power consumption increases only slightly, proportionally to log compression [4].

The low volumetric density and safety problems associated with the use of explosive gases under high pressures complicate considerably the storage of gaseous hydrogen. Furthermore, to compress hydrogen to high pressures is in itself a fairly intricate engineering problem in view of the possible gas leakage through mobile seals and hydrogen corrosion of constructional materials.

Hydrogen molecules are nonpolar and fairly weakly interact with each other. As a result, condensation of gaseous hydrogen demands deep cooling. Despite of the low temperatures of liquid hydrogen storage systems, the pressure in them can only slightly be above atmospheric (critical pressure 1.3 MPa). Thereof, the requirements for the strength and material of walls of cryogenic containers for liquid hydrogen storage are not as rigid as for high-pressure vessels. This allows high weight storage densities to be attained, and the limiting volumetric density will be determined by the density of liquid hydrogen (70 kg m^{-3}).

Because of the low critical temperature (–240°C), liquid hydrogen can be stored either in open systems or in special closed tanks in which gas dumping is envisaged when the pressure increases by more than 0.2–0.3 MPa; otherwise, the pressure can increase (at room temperature) up to ~103 MPa [3, 14]. Storage of liquid hydrogen involves inevitable and rather significant losses due to evaporation: up to ~0,4% a day for 50-m^3 tanks, 0.2% a day for 100-m^3 tanks, and 0.06% a day for 20000-m^3 tanks, i.e. losses can be lowered by increasing tank volume. By employing special thermoisolation systems and additional cooling one can lower losses of hydrogen in fairly small cryogenic tanks, too.

One of the problems of long-term storage of liquid hydrogen is associated with the necessity for its *ortho–para* conversion, since the spontaneous transformation of the *ortho* modification whose fraction in an equilibrium gaseous hydrogen at room temperature makes 25%, into the *para* hydrogen, stable at the cryogenic temperatures ~20 K, is accompanied by heat release (1407 J mol^{-1}), exceeding the evaporation heat of liquid hydrogen (921 J mol^{-1}).

Now technologies of hydrogen liquefaction and liquid hydrogen storage are well developed; highly effective cryogenic tanks and their refuelling infrastructure are created, and safety measures are improved. Cryogenic tanks with screening vacuum thermoisolation allow maximum, compared to alternative methods, weight density of hydrogen (more than 15–20 wt%) for small (automobile) cryogenic tanks. As the tank size increases, this parameter increases considerably to reach 86 wt% in large aerospace cryogenic tanks [15].

The basic disadvantage of the cryogenic method of hydrogen storage is its high energy demands. According to calculations, the minimal mechanical work spent by an ideal refrigerator for transforming gaseous hydrogen with a normal *ortho–para* ratio at room temperature into a liquid *para* hydrogen at the boiling points, is ~41 J mol^{-1} or about 18% of the calorific efficiency of hydrogen. The power inputs of real devices for liquid hydrogen production make 30–50% of the calorific efficiency of hydrogen. Therefore, this method of storage is very expensive.

Along with the above-described industrial methods, there are a number of physical hydrogen storage methods which are presently at the engineering development level. One of such methods is hydrogen storage in the microcapsulated state [1, 5]. This method can be related to methods of compresses gas storage (35–65 MPa), where the role of cylinders is played glass microspheres with a diameter of 5–500 μm and a wall thickness of about 1 μm. At elevated temperatures (200–400°C), the glass walls become penetrable for hydrogen, which makes it possible to fill the system with hydrogen and to give it out to a consumer. The weight density of stored hydrogen is up to 10 wt% and its volumetric density is up to 20 kg m^{-3}, which is commensurable with parameters for composite gas cylinders. Additional energy expenses are associated with heating of microspheres on refuelling storage facility and withdrawing hydrogen. The major disadvantage of this method is that it involves high hydrogen losses due to mechanical destruction of glass microspheres on transportation [5].

Hydrogen storage in high-pressure cryogenic vessels holds promise. The essence of this method consists in the use of standard composite high-pressure tanks (aluminium sleeve covered by reinforced plastic) placed in a cryogenic thermoisolating shell. Such cylinders can be filled either with liquid and gaseous H_2 at low temperatures [16]. In the latter case, higher volumetric and weight hydrogen storage densities are attained, compared to gas cylinders at room temperature [9].

Physical methods of hydrogen storage in the form of cryogenic liquid or compressed gas are largely insufficiently economically effective, convenient, and safe. A special problem is associated with hydrogen embrittlement of metal parts of hydrogen storage systems, which forms a demand for expensive high-alloy materials, correct welding, protection against electrochemical corrosion, application inhibitors and coatings, etc.

The development of a competitive, maximally compact, and safe technology for hydrogen storage in environmental conditions (~0,1 MPa, ~300 K) will allow hydrogen to more successfully compete to natural and synthetic fuels. Such technology can be realized with bound hydrogen.

ADSORPTION HYDROGEN STORAGE METHODS

Materials capable of accumulating hydrogen can be arbitrarily classed in terms of bonding energy [17]. The weakest bonding is characteristic of physical hydrogen adsorption. Gaseous hydrogen interacts with adsorbent surface by means of van der Waals dispersion forces. This interaction relates to weak (1–10 kJ mol^{-1}), and at temperatures above critical it extends in depth by no more than one monolayer. From this it follows that materials for storage of adsorbed hydrogen should possess a high specific surface area (the calculated hydrogen weight density (wt%) to specific surface area (m^2 g^{-1}) is 2.27×10^{-3}, and essential adsorption capacities are observed only at lowered temperatures [3].

The known hydrogen-adsorbing materials are zeolites. They are characterized by low water capacities (up to 0.3 wt% at room temperature and up to 1.8 wt% at a liquid nitrogen temperature and a pressure of 1.5 MPa) [18], which casts doubt in the competitiveness of zeolites in hydrogen storage systems. Slightly better parameters are characteristic of high-porosity organometallic carcasses, such as $Zn_4O[O_2C–C_6H_4–CO_2]_3$ with a high specific surface area (up to 3000 m^2 g^{-1}), which are presently widely studied. At a hydrogen pressure of 2 MPa, they adsorb up to 1 wt% of hydrogen at room temperature and up to 4.5 wt% at 70 K [19].

Chahine et al. [20] found that mixtures of hydrogen and water crystallize at low temperatures (below 250 K) and high pressures (~220 MPa) to form an s_{II} clathrate structure with the $H_2 : H_2O$ molar ratio 1 : 2, which is preserved when the pressure is dumped to atmospheric at $T \leq 145$ K. This corresponds to a fairly high weight hydrogen capacity (up to 5.3%). Even though the formation of hydrogen clathrate hydrates demands high pressures and significant power inputs, Young [21] recently showed that hydrogen clusters in such structures can be stabilized by small tetrahydrofuran admixtures. As a result, clusters persist at a much lower pressures (5 MPa) and higher temperatures (280 K). In view of this circumstance, and well as because water which functions here as a hydrogen-storing material is present in abundance on the Earth and beyond it, this hydrogen storage technology should be considered as fairly promising.

Among hydrogen adsorbents, special researcher's attention is given to carbon materials. Even in [1] it has been reported that low-density charcoal can absorb up to 7–8 wt% of hydrogen at ~4 MPa and 65–78 K (the reversible hydrogen capacity at the pressure 0.2–4 MPa and the same temperatures is 4–5%). According to [20–24], charcoals have a high hydrogen-sorption capacity: up to 10–13 wt%, 35 kg m^{-3} at 77 K and 5.5 MPa. In late 1990th, the information on a higher capacity carbon nanotubes and nanofibers appeared [25–28]. However, these works proved to be insufficiently reliable and failed to step over the bounds of experiments and assumptions on the structure of carbon sorbents, based on general considerations. The hydrogen-sorption capacities of well-certified carbon nanomaterials, measure over the past years [29–35], testify that the initial optimism concerning their use for hydrogen storage has been insufficiently substantiated.

CHEMICAL METHODS OF HYDROGEN STORAGE

All materials for storage of chemically bound hydrogen can be divided into two groups. The first includes hydrogen-containing materials capable of liberating hydrogen in certain conditions (elevated temperatures and action of catalysts). Examples are provided by the catalytic decomposition of ammonia at 800–900°C and hydrogenation/dehydrogenation of unsaturated hydrocarbons:

$$2NH_3 \rightleftarrows N_2 + 3H_2 - 92\ \text{kJ}, \quad (1)$$

$$C_6H_{12} \rightleftarrows C_6H_6 + 3H_2 - 206.2\ \text{kJ}. \quad (2)$$

The second group includes energy-accumulating substances not necessarily containing chemically bound hydrogen but able to generate it when oxidized with water. An example is spongy iron which reacts with water vapor at 550–600°C:

$$3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2. \quad (3)$$

Others energy-accumulating substances (aluminum, silicon, and other elements) liberate hydrogen from water in milder conditions, even at room temperature. Alloys with small additives of activator metals, such as Al–Ga, hold the greatest promise. By varying the alloy structure and hydrogen generation conditions one can achieve a fairly fast and readily controllable hydrogen evolution in mild conditions. The given method is a fairly good candidate for autonomous hydrogen generators [36, 37].

Decomposition of compounds containing chemically bound hydrogen with water is also possible. Reactions of binary and complex metal hydrides with water, resulting in hydrogen evolution, most commonly occur at 100–300°C.

The principal advantage of storage and transportation of chemically bound hydrogen, specifically in the form of ammonia, methanol, or ethanol, is a high volumetric hydrogen density (~100 kg m^{-3}). The weight contents, too, is high enough: For example, 1 kg of hydrogen is generated from 5.65 kg of ammonia (17.7 wt%). The profitability of such storage and transportation systems consists not only in that they make use of ammonia pipelines instead of hydrogen, which is half-cost, but also in lower power inputs. At a compressor efficiency of 75%, to compress hydrogen requires a factor of 20–25 less installed capacity, than to compress ammonia. The cost gain reveals itself only on long-distance transportation of ammonia. The use of methanol as a raw material for production of hydrogen and reductive gases makes it possible to cut down expenses for hydrogen transportation and storage. Hydrogen production from methanol is cheaper by 20% than from natural gas. The generation of hydrogen from methanol at elevated temperatures (~400°C) in the presence of catalysts is a process similar to those with first group materials.

The principal disadvantage of hydrogen storage in the chemically bound state is that the medium for hydrogen storage is difficult to use many times. An exception is provided by unsaturated systems which can undergo reversible catalytic hydrogenation/dehydrogenation reactions, such as the catalytic hydrogenation/dehydrogenation of double bonds in fullerenes [25, 38–48]. Thus, fullerene C_{60} can reversibly bind up to 6.3 wt% of hydrogen, which corresponds to the formula $C_{60}H_{48}$. The effective catalysts of fullerene hydrogenation/dehydrogenation are hydrides of intermetallic compounds. However, hydrogenation/dehydrogenation processes can be realized only at elevated temperatures of about 400°C and hydrogen pressures of about 10 MPa, which is associated with high power inputs. In case of fullerenes, a problem is also is the side double-bond polymerization process, which adversely affects the reversible hydrogen capacity of the system on cyclic operation.

The yields of hydrogen in the reactions of metals and hydrides with water, related to the weight of the starting material, can reach 10–15 wt%. This way holds promise for hydrogen storage systems, when no restrictions are posed on the weights of the device and water used for hydrogen production.

Of practical interest are lithium hydride and its mixtures with Al or Si. Therewith, the reactor medium is alkaline and favors dissolution of aluminum and silicon hydroxides. However, the high cost of lithium compounds and poor controllability of these reactions make them scarcely feasible. Hydrogen production by hydrolysis of complex sodium boron and aluminum hydrides seems more practical, since manufacturing technologies for $NaBH_4$, $NaAlH_4$, and LiH are fairly well developed. However, hydrolysis of sodium boron hydride can be accompanied by formation of by-products, viz. toxic volatile boranes [17]:

$$2NaBH_4 + 2H_2O \rightleftarrows B_2H_6 + 2NaOH + 2H_2. \quad (4)$$

METAL HYDRIDES AS HYDROGEN STORAGE MEDIA

A serious alternative to the above-described hydrogen storage and transportation methods is the metal hydride methods, i.e. the storage of hydrogen in the form of metal hydrides or intermetallic compounds (IMCs).

The discovery in the second half of the XIX century of the ability of some metals for reversible absorption of significant amounts of hydrogen has generated a lot of technical ideas on the practical application of this phenomenon. The reason lies in a unique combination of properties of metal–hydrogen systems, possibility of creating extremely high volumetric densities of hydrogen atoms in a metal matrix, wide range of operating pressures and temperatures, selectivity of hydrogen absorption, significant changes in the physical properties of metals on their saturation with hydrogen, catalytic activity, and a lot of other features. These properties all have been the subject of extensive research. Accoring to Sandrock's review [47], almost 1500 works were published worldwide over the period 1866–1946 on the subject "Hydrogen in Metals." Later on the intensity of research in this field steadily increased and mounted up after the discovery of intermetallic compounds which reversibly react with hydrogen at moderate temperatures and pressures to form corresponding hydrides ($ZrNiH \sim 3$ [50]; $LaNi_5H \sim 6.7$ [51]). The database available via the Internet at *http://hydpark.ca.sandia.gov* contains data for 2000 metal hydrides and intermetallides from 1200 references, and this information is far from exhaustive [52].

The reversible formation of a metal hydride can be accomplished by direct reaction of a hydride-forming metal (intermetallide) with gaseous hydrogen or electrochemically [53]:

$$M(s.) + H_2 \rightleftarrows MH_x(s.) + Q, \qquad (5)$$

$$M(s.) + H_2O(l.) + e^- \rightleftarrows MH_x(s.) + OH^-(l.). \qquad (6)$$

In the majority of metal hydride applications, including hydrogen storage and transportation, the first (gas-phase) process is realized. The second process is used in electrochemical power sources with metal hydride electrodes.

The hydrogen absorption by reaction (5) includes transport of hydrogen molecules to the surface of a material, their physical adsorption, dissociation of adsorbed H_2 molecules, and transition of hydrogen atoms to the bulk of the material with formation of an addition solid solution (α-phase) and then a hydride (β-phase).

The concentration of hydrogen atoms in the α-phase is insignificant, and they are statistically distributed over voids of the metal matrix which preserves the initial structure with a slight (up to 5%) gain in volume. On the contrary, β-hydride characteristically contains much hydrogen ($H/M \sim 1$), and hydrogen atoms are ordered. Depending on the nature of the metal–hydrogen bond, the structure of the metal matrix can undergo essential changes in the relative arrangement of metal atoms or preserve the initial geometry with increases metal–metal distances.

Hydrogen directly reacts with the majority of metals, forming binary hydrides MH_x. At present binary hydrides are synthesized all metals of the Periodic System [54–58], except for some Group VI–VIII transition metals.[1]

In terms of the type of the hydrogen–metal bond, metal hydrides are subdivided into three classes with essentially different physical and chemical properties.

Ionic hydrides are salt-like compounds with an ionic bond, in which hydrogen is present in the form of the hydride anion H^- and metal, in the form of a cation. Typical representatives of ionic hydrides are alkali and alkaline-earth metal hydrides, such as KH and CaH_2. Trihydrides of rare-earth metals (REMs) of the composition RH_3 and dihydrides EuH_2 and YbH_2, too, are classed with ionic hydrides. Ionic hydrides are synthesized by the reaction of a metal with gaseous hydrogen at increased (hundreds degrees of Celsius) temperatures and pressures of up to 10 MPa [58]. Such hydrides exhibit properties typical for ionic compounds. The packing density of metal atoms in ionic hydrides is higher than in the starting metals, i.e. hydride formation is accompanied by compression of the metal matrix. Solid ionic hydrides are dielectrics, whereas in solution (in nonaqueous polar solvents) or melt they dissociate into hydride anion and metal cation, as a result of which the solution or melt acquire electric conductance. Ionic hydrides are generally Lewis bases and can form complex compounds with other, acid (commonly covalent) hydrides, such as $Li[AlH_4]$ and $Na[BH_4]$.

The second class include *covalent hydrides* in which the metal and hydrogen atoms are linked by a covalent bond. All hydrogen compounds of nonmetals, viz. CH_4, NH_3, H_2O, etc., are formally classed with covalent hydrides. With few exceptions (AlH_3 whose direct synthesis was performed hydrogen pressures higher than 3000 MPa [61] and also by bombardment of aluminum with a beam of hydrogen ions [62]), covalent hydrides are not formed by direct reaction of

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[1] Over the past years, hydrides of all 3*d* and 4*d* transition metals have been synthesized at the Institute of Solid State Physics RAS, except for ruthenium. The synthesis was performed at high (up to 90 kbar) hydrogen pressures and temperatures (up to 1000°C) after which the products were quenched under high hydrogen pressure at the liquid nitrogen temperature [59, 60].

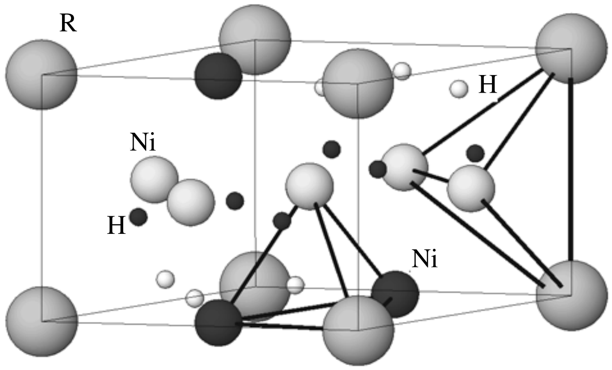

Fig. 2. Structure of intermetallic hydride RNi_5H_6.

hydrogen with metal and are synthesized by methods of preparative chemistry. For example, beryllium hydride is obtained by the reaction of dimethylberyllium with lithium aluminum hydride in diethyl ether [58]:

$$Be(CH_3)\ 2+\ 2LiAlH_4 \rightleftarrows BeH_2 + 2LiAlH_3CH_3. \quad (7)$$

Covalent hydrides are generally fairly unstable. Many of them tend to polymerize to form three-center bridging bonds M···H···M.

An abundant and a practically important class of metal hydrides is formed by *metallic hydrides* in which hydrogen donates its electron to the metal conductivity zone, thus realizing a metallic bond. Differently, metallic hydrides can formally be considered as alloys of metallic hydrogen. Evidence in favor of this approach is provided by the preserved metallic properties of such hydrides, in particular their high thermo- and electroconductivities. Almost all transition metals capable of reversibly reacting with hydro gen form metallic hydrides. The composition of metallic hydrides is, as a rule, nonstoichiometric. Depending on the nature of the metal, their stability widely varies.

The above classification reflects the general regularities of the physical chemistry of metal hydrides. At the same time, it is quite idealized, since real hydrides frequently feature a mixed type of the hydrogen–metal bond. A typical example of an ionic–covalent hydride is provided by magnesium hydride. In transition metal hydrides, an ionic–metallic bond is often realized. Thus, dihydrides and trihydrides P3M (nontoichiometric) are typical representatives of compounds with a metallic bond, whereas, with approach to the MH3 stiochiometry, the M–H bonds gets ionic.

The change of the bond type causes reversibly changes the electrical, optical, and other properties of the hydride in the order metal semiconductor dielectic [63, 64].

The formationof stable binary hydrides is accompanied by essential structural changes. This takes place with hydrides of alkali and alkaline-earth metals, REMs and actinides, titanium subgroup metals, etc. With these metals, reaction (5) is only reversible at high temperatures and, as a rule, proceeds very slowly. Another extreme case is formation unstable binary hydrides of transition metals, such as nickel, with weak elements of M–H bonds. Such hydrides can be synthesized either by reaction (5) at high (hundreds MPa) pressures or electrochemically by reaction (6) at high overvoltages.

Hydrides of IMCs of the general formula $A_mB_nH_x$, where A_mB_n is a compound of two or more metals (IMCs), one of which (A) forms a stable binary hydride and others (B) do not react with hydrogen under usual conditions. Hydride-forming intermetallides are commonly classified on the basis of their component ratio *m/n*. Of a great number of families of hydride-forming IMCs, the most practically valuable are AB_5 (structural type $CaCu_5$), AB_2 (Lawess phases), AB (structural type CsCl), and A_2B (structural type B_2Al). In AB_5 compounds, REM and/or calcium are used as component A, in AB_2 and AB, titanium subgroup elements, and in A_2B, largely magnesium. The most common components B in all the families are transition metals (Fe, Co, Ni, V, Mn, Cr, etc.) [53].

The formation of IMC hydrides is accompanied by insertion of hydrogen atoms in interstitials of the metal matrix and significant expansion of the crystal lattice. A typical example are hydrides RNi_5H_6 (R is REM), where H atoms occupy tetrahedral R_2Ni_2 and REM voids of the structure of the parent intermetallide (Fig. 2).[2] Such behavior is typical of binary hydrides with a metallic bond type. The basic difference is that the number of various types of interstitials in the structures of hydride-forming IMCs is generally much larger of the corresponding types of interstitials in binary hydrides.

The principles of formation of the most probable structures of IMC hydrides can be formulated as follows [65].

Positions in the metal sublattice of the starting compound, preferably occupied by hydrogen atoms on hydride formation, represent tetrahedral voids with radii larger than 0.4 Å.

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[2] Recent neutron and synchrotron X-ray diffraction revealed a certain deformation of the metal matrix (transition from the structural type *P6/mmm* to *P321*) in hydrides (deuterides) RNi_5H_6, accompanied by displacement of H atoms in R_2Ni_2 voids to the triangular facet RNi_2.

Interatomic distances M–H in IMC hydrides are close to those in binary hydrides, not exceeding the corresponding radius of metal M by 0.2–0.3 Å. Interatomic distances H–H should be much smaller than 1.8–2.0 Å.

Voids having in their facets the major part of metal atoms A with a high hydrogen affinity, are filled first.

The larger the distance between adjacent M atoms in void facets, compared with the sum of their atomic (metal) radii, the more probably H atoms will insert in these voids.

The unit cell volume typically gains from 10–15 to 25–30% on IMC hydride formation. As a rule, the symmetry of the metal matrix is not strongly affected by hydrogenation. However, as the contents of component A increases, the hydrogenation of IMCs is accompanied by more appreciable changes in the mutual position of metal atoms, which leads to an essential reorganization of the metal matrix (examples: TiFe and Mg_2Ni) or to its hydrogenolysis producing a mixture of a stable binary hydride of component A and an intermetallide enriched with component B (example: Mg_2Cu).

The kinetics of hydrogen absorption/desorption in mild conditions, characteristic of intermetallic hydrides is suitable for practical applications and makes these compounds the most appropriate materials for hydrogen storage systems [66, 67].

Absorption of hydrogen by metals and IMCs is accompanied by embrittlement of the starting material and formation of finely powered metal hydride phases, which slightly complicates the design of metal hydride hydrogen accumulators: a need in gas filters or dustless metal hydride composites. At the same time, this feature can be useful for some adjacent applications, where crushed metal materials are required, say in constant magnet production [68].

One more class of metal hydrides is formed by coordination compounds at which hydrogen is present as a ligand. Such compounds are called *complex hydrides*. They can be synthesized in no other way than by methods of preparative chemistry and are unsuitable for reversible hydrogen storage. An exception are systems on the basis of $NaAlH_4$, in which reversible hydrogen sorption/desorption can be achieved with the aid of catalysts (transition metals and their compounds) [69].[3]

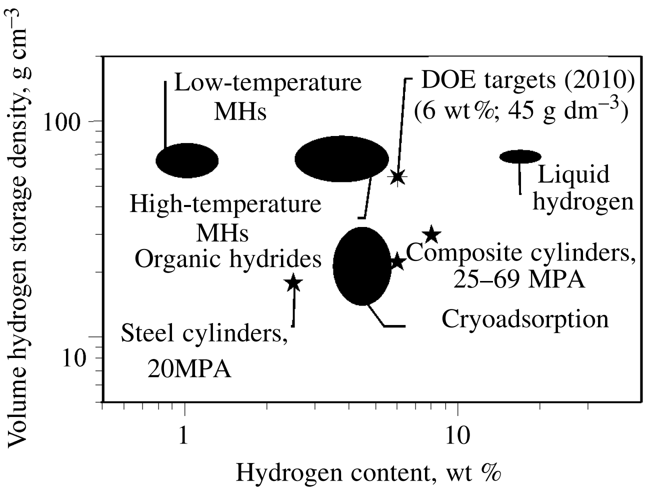

Fig. 3. Capacitance characteristics of various methods of hydrogen storage.

The majority of metal hydrides have high hydrogen contents: The hydrogen/metal ratio varies from 0.7–1.1 for intermetallic hydrides up to 3.75 for Th_4H_{15}, and even 4.5 for the complex hydride $BaReH_9$ [64].

Figure 3 shows typical ratios between the volumetric and weight hydrogen storage densities for various methods. Corresponding parameters for the cryogenic storage of liquid and gaseous hydrogen under pressure in contemporary composite cylinders are presented. As seen from Fig. 3, the metal hydride method can successfully compete with traditional in terms of the compactness of hydrogen storage, but concedes to them in weight parameters. The weight parameter is much higher for high-temperature hydrides of light elements, but their use is generally problematic, as some of such hydrides (BeH_2, $LiBH_4$) decompose irreversibly, whereas others (MgH_2) require too high temperatures and too much energy to form and decompose.

Along with hydrogen capacity, a practically important characteristic of metal–hydrogen systems is their thermodynamic properties. They define conditions (temperature, hydrogen pressure, power inputs) at which hydrogen absorption/evolution processes are practically feasible.

As mentioned above, hydride formation is preceded by the formation of the α-phase and solid solution of hydrogen in the metal or IMC matrix. The equilibrium concentration of hydrogen in metal (c = H/M) is defined by the pressure of gaseous hydrogen (P) and

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[3] Complex hydrides also include hydrides of the basis of A_2B composition ($Mg_2[NiH_4]$, $Mg_2[FeH_6]$, etc.) which can be arbitrarily related to intermetallic.

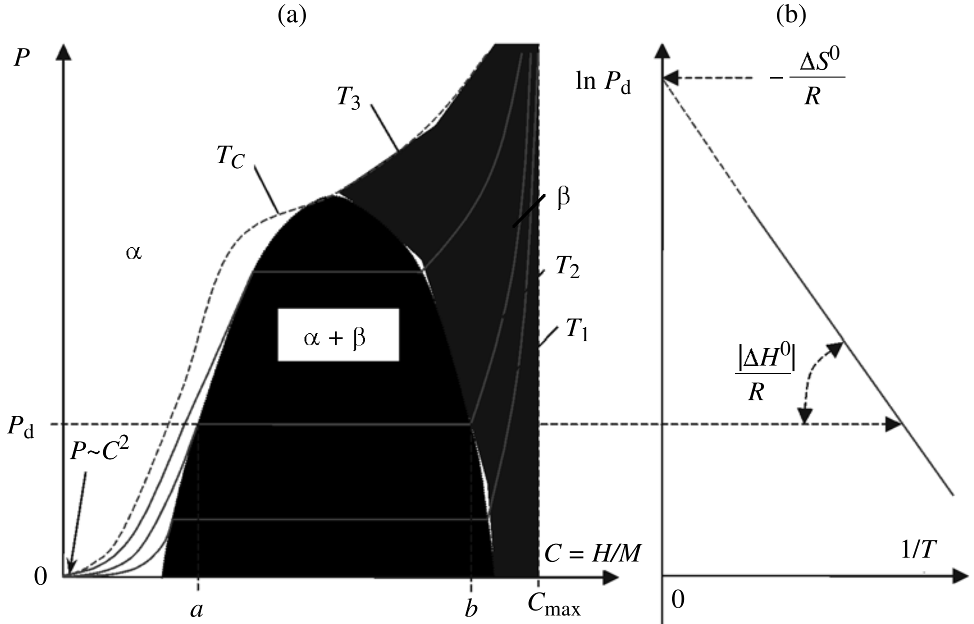

Fig. 4. Idealized *PCT* diagram of a metal–hydrogen system: (a) pressure–concentration isotherm at $T_1 < T_2 < T_3 < T_{cr}$; and (b) temperature dependence of desorption pressure.

temperature (T). According to the Henry–Sievert law, at $C \to 0$:

$$c = T_0 K_0 P_{1/2}, \tag{8}$$

where K_0 is a factor depending on temperature T.

Once some upper limit of the hydrogen concentration in the saturated solid solution (α-phase) has been attained, further hydrogen absorption is accompanied by hydride (β-phase) formation with the hydrogen concentration b ($b > a$), and the stoichiometry of reaction (5) can be rewritten as

$$1/(b - a)\mathrm{MH}_a(\mathrm{s.}) + 1/2\mathrm{H}_2(\mathrm{g.}) \rightleftarrows 1/(b - a)\mathrm{MH}_b(\mathrm{s.}). \tag{9}$$

According to the Gibbs phase rule, process (9) is equilibrium at a constant hydrogen desorption pressure (P_d), which corresponds to the appearance of a plateau on the pressure–concentration isotherm (Fig. 4a). Once the solid solution has completely transformed into hydride, further hydrogen absorption occurs via formation of its solid solution in the β-phase; therewith, the equilibrium concentration of hydrogen again increases with increasing pressure, asymptotically approaching C_{max} determined by the hydrogen capacity of the metal, i.e. by the number of voids in the metal matrix available for hydrogen insertion, related to the number of metal atoms.

Proceeding from the condition of equilibrium in the plateau region (equality of the chemical potentials of hydrogen in the gas and two solid phases), a known van't Hoff relation for the temperature dependence of the plateau pressure was deduced:

$$\ln P_d = -\frac{\Delta S^0}{R} + \frac{\Delta H^0}{RT}, \tag{10}$$

where ΔS^0 and ΔH^0 are the standard entropy and enthalpy of hydride formation, respectively, per 1 mol of gaseous hydrogen.

The $\ln P_d$ ($1/T$) dependence looks like a straight line whose slope is proportional to ΔH^0 and y-intersept (at $1/T = 0$) is proportional to ΔS^0 (Fig. 4b).

The concentration limits (a, b) of the existence of the two-phase (α + βb) pressure plateau area are temperature-dependent. They approach each other as the temperature increases and are pulled together in one point at some critical temperature T_{cr}. Therewith, the plateau degenerates into a inflection on the isotherm, and above T_{cr} hydrogen exists in metal as the α-solution exclusively (Fig. 4a).

The dependence of the equilibrium pressure and concentration of hydrogen on temperature (*PCT* diagram) is the most practically important characteristic of hydride-forming metals and intermetallides. As a rule, reference books contain the principal characteristics of the *PCT* diagram: hydrogen capacity of a hydride and standard enthalpy and entropy of hydride formation which determine the temperature dependence of P_d. The enthalpy ΔH^0 is accepted roughly

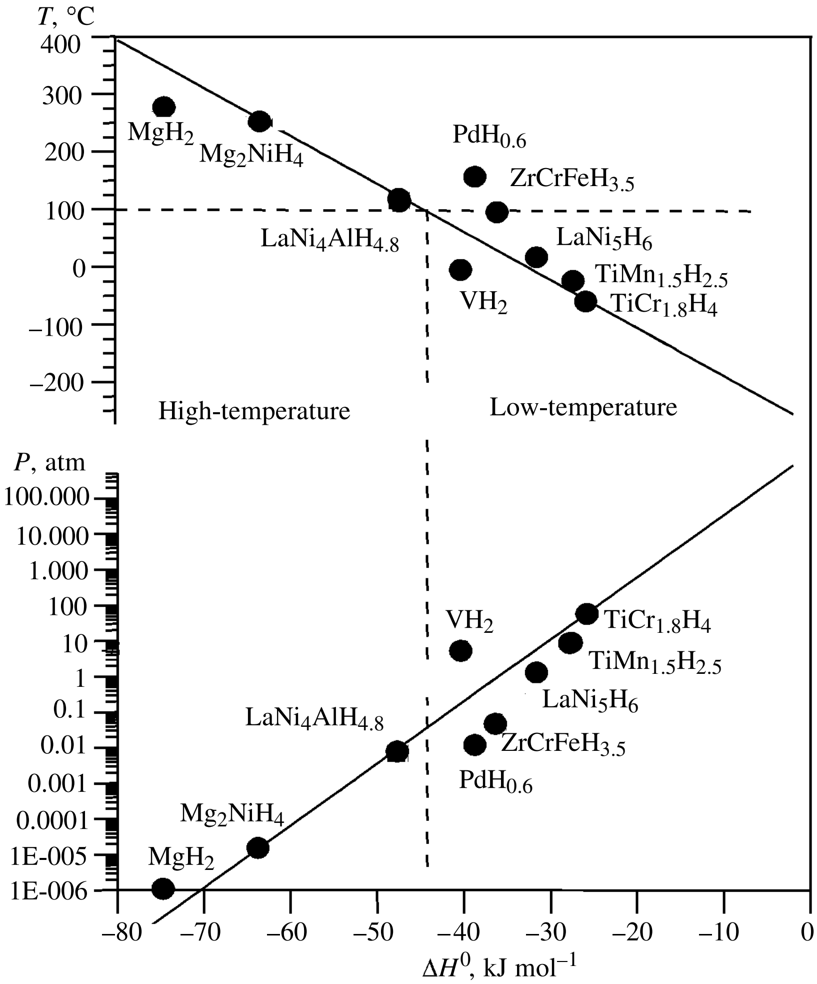

Fig. 5. Equilibrium dissociation temperatures and pressures of certain binary and intermetallic hydrides vs. standard enthalpies of their formation Solid lines show values calculated by Eq. (10) at $\Delta S = -120$ J mol^{-1} K^{-1}.

equal to the heat effect Q of reaction (5), taken with opposite sign. The ΔS^0 values for all metal–hydrogen systems are close to each other and roughly equal to the entropy of the transition of 1 mol of gaseous hydrogen to the solid phase (~120 J mol^{-1} K^{-1}).

Depending on the nature the hydride-forming metal or IMC, reversible hydrogen sorption can be realized in very wide pressure and temperatures ranges. This statement is illustrated more emphatically in Fig. 5 which shows temperatures corresponding to P_d = 0.1 MPa, calculated by Eq. (10), and P_d at room temperature. From the applied point of view, metal hydrides are convenient to divide into two groups: low-temperature and high-temperature. Such division is based on the requirements of consumers to operational parameters of hydrogen storage systems and is fairly conditional. At the same time, this classification is expedient to adhere, since features and characteristics of metal hydride systems for hydrogen storage, as a rule, primarily depend on the type of the hydride [70].

Metal hydrides whose equilibrium hydrogen pressure is above atmospheric at temperatures of up to 100°C are classed with low-temperature. This group includes several classes of IMC hydrides (AB_5, AB_2, and AB), as well as pseudobinary hydrides of certain body-centered cubic alloys on the basis of vanadium and Ti–Cr system. These materials feature low (<45 kJ mol^{-1} H_2) heat effects of reaction (5) and high hydrogen sorption/desorption rates at moderate pressures and temperatures. These materials are suitable for compact and safe hydrogen storage systems which are characterized by simplicity in operation, technologic flexibility, and low power inputs. At the same time, low-temperature metal hydrides have too low hydrogen capacities (1.5–2 wt%), and their potential maximum (for new Ti–Cr body-centered cubic alloys [71]) is 2.5–3 wt%.

High-temperature metal hydrides include first of all magnesium alloys and IMCs. They have higher, than low-temperature metal hydrides, hydrogen capacities: up to 7.6 wt% for MgH_2 [72] and low hydrogen absorption/desorption rates. Hydrogen absorption and desorption can proceed only at elevated (250–350°C) temperatures, and, therefore, these materials demand high power inputs both because of the higher (approximately double that for low-temperature hydrides) heat effect of reaction (5) and because of the necessity to maintain high temperatures.

Since late 1960s reversible reactions of hydrogen with hydride-forming metals and IMCs are in the center of research on compact hydrogen storage devices. This is primarily explained by the high volumetric density of hydrogen packing in metal hydrides (0.09–0.1 $g\,cm^{-3}$), exceeding the density of liquid hydrogen (0.07 $g\,cm^{-3}$) and comparing with the density of hydrogen nuclei in water (0.11 $g\,cm^{-3}$). The maximal density of hydrogen in metal hydrides 0.15 $g\,cm^{-3}$ for TiH_2 and 0.19 $g\,cm^{-3}$ for VH_2. The recently discovered intermetallic hydrides with abnormally short H–H distances have the local hydrogen density of 0.56 $g\,cm^{-3}$, which is 8 times the density of liquid hydrogen [73].

Compactness is the basic advantage of the hydride method of hydrogen storage. A metal hydride contains more hydrogen than the same volume of liquid hydrogen, and, therewith, a hydride accumulator can be of any shape, which facilitates its application in power devices with a deficiency of free volume.

Depending on the type of the hydride-forming metal (intermetallide) and external conditions, hydrogen absorption/desorption can be realized in wide ranges of working pressures and temperatures, and significant heat effects of reaction (5) (20–40 $kJ\,mol^{-1}$) result in that hydrogen sorption is accompanied by heating and desorption, by cooling of the metal hydride material. This circumstance underlies a lot of applications of metal hydrides, associated with energy conversion and management of heat flows.

The direction of reaction (5) is determined by hydrogen pressure and sorbent temperature. This allows the process of low-pressure hydrogen absorption to be preformed at a lowered temperature and, once the corresponding heat has been delivered to metal hydride, to desorb high-pressure hydrogen. This technique is called thermosorptive (or thermochemical) hydrogen compression and its realizing devices, metal hydride thermosorption compressors (MH TSC).

Since in the majority hydride-forming metals and IMCs small temperature changes produce significant changes in equilibrium hydrogen pressures, fairly little heat should be delivered to produce considerable hydrogen pressures. With $LaNi_5$, for example, to provide a hydrogen pressure of 15 MPa, a temperature of below 200°C will suffice. Therefore, MH TSC can serve for solving the problem of recycling low-potential (waste) heat of various industries, by converting it into the highly organized energy of compressed gas. Thus compressed hydrogen can be used in expansion machines, for example for power generation.

The management of hydrogen sorption/desorption processes and heat transfer in hydrogen–metal hydride systems allows, along with thermosorption hydrogen compressors, creation of heat machines with a closed cycle of circulation of a gaseous working body [74], including heat engines and pneumatic drives, refrigerators, heat transformers, systems for long-distance heat transfer, etc.

The selectivity of reaction (5) with respect to hydrogen allow practical application of metal hydrides in processes of hydrogen purification from gaseous impurities and hydrogen extraction from gas mixes [74–80] without use of expensive equipment like palladium or palladium–silver filters.

The possibility of controlling the pressure of desorbed hydrogen by directed heat treatment of metal hydrides allows the latter to be employed in systems for precision controlled hydrogen delivery to consumers [70]. Certain metal hydrides with fast absorption of lowpressure hydrogen (hydrogen getters) have formed the basis for effective systems of pumping and controlled supply of low-pressure hydrogen to vacuum plasma devices [81].

Thus, the use of metal hydrides, along with compact hydrogen storage, opens up wide additional possibilities. In a number of works [82–90], the expediency of combining several of the above-listed (or other) functions in integrated metal hydride devices was mentioned. Thus the advantages of the metal hydride technology over alternative hydrogen storage and processing methods are best demonstrated. Metal hydrides can find application in energetics, metallurgy, chemical industry, oil refining, etc. (Fig. 6).

An important advantage of the metal hydride method of hydrogen storage is its high safety. Actually, the pressure of gaseous hydrogen over the majority metal hydrides at at room temperature seldom exceeds several atmospheres. This feature, alongside with the multifunctionality of metal hydride systems, makes them irreplaceable in laboratory practice. Small- (tens liters of H_2) and large-scale (up to several tens cubic meters) metal hydride hydrogen

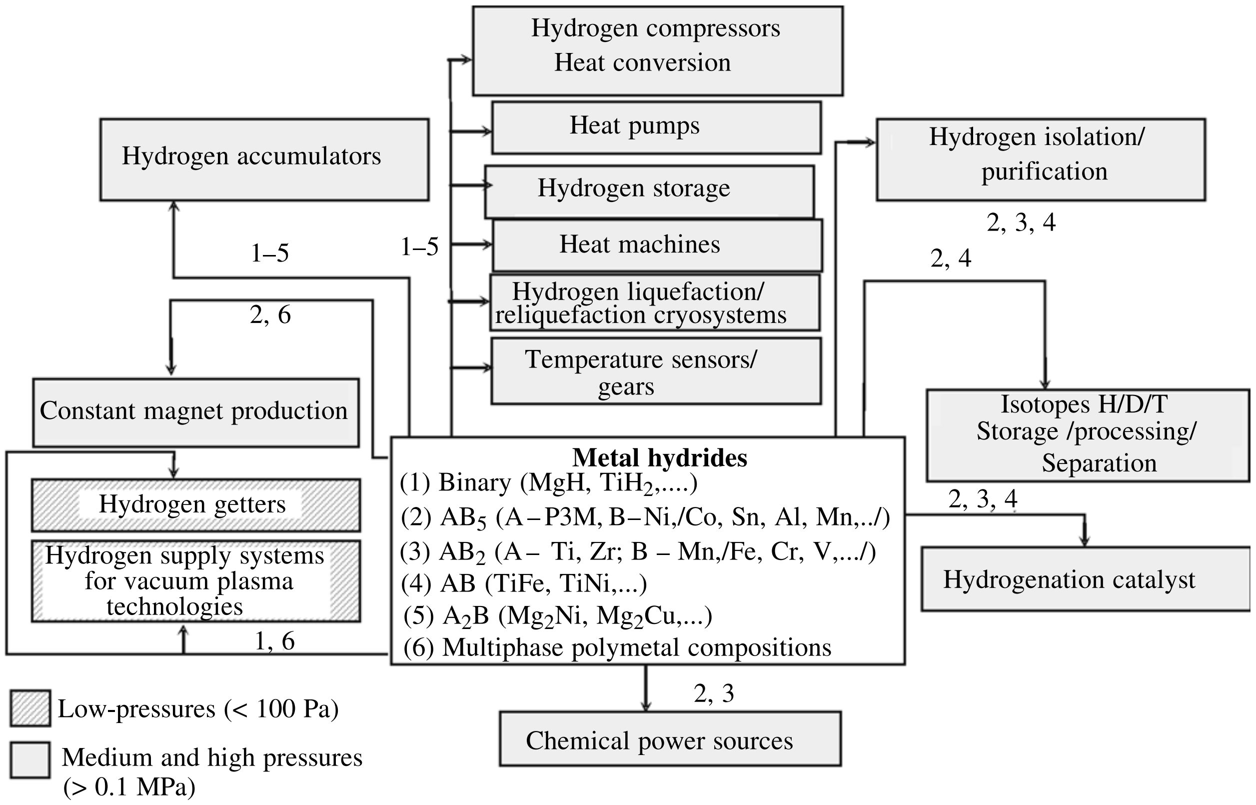

Fig. 6. Applications of metal hydrides.

storage systems are presently industrially produced, and demand for them slowly but steadily grows.

Commercial hydrogen accumulators on the basis of low-temperature metal hydrides are mainly intended for laboratory use [91–94]. They provide safe and compact hydrogen storage of high-purity hydrogen (capacity from 30–40 1 up to several cubic meters, hydrogen supply pressure 0.1–1 MPa). Commercially available systems are often offered in several options which are readily adaptable for concrete consumer requirements.

The authors of the present review, too, have accumulated some experience in the development of laboratory metal hydride hydrogen accumulators [70, 88, 89, 95]. Some of them were developed in the framework of international collaborative programs. These works characteristically involved “fit” of both the structure of the metal hydride material and the design of the accumulator to technical requirements of the end user, and also, whenever possible, use of standard constitutive elements (Fig. 7).

A metal hydride container generally represents a tubular housing having inside a heat exchanged for intensification of heat transfer in the metal hydride powder located in the tube space. The need in the heat exchanger is associated with the fairly low thermoconductivity of metal hydride materials (up to 1–2 Wm K^{-1}), and heat transfers limits the hydrogen sorption/desorption dynamics [96]. For drive the hydrogenation and dehydrogenation processes (characteristic time less than 10–15 min), the space for metal hydride powder should have the size of no more than 5–6 mm [74]. For larger hydride layers, porous matrices of highly thermoconductive metals, inferior heat exchanges, or combinations of that and another are used [96, 97]. The effective thermoconductivity of the layer can be increased, provided composite materials on the basis of metal hydrides and highly thermoconductive binders will be created.

Usually the face flange of the container has sleeves for input and output of gaseous hydrogen and loading of metal hydride powder. The sleeve is most commonly combined with a tubular filter of a porous stainless steel or a ceramic material (pore size <1 μm). In a low-temperature accumulator (on the basis of AB_5, AB_2 and AB alloys), heating and cooling are performed by external airflowing of the housing or by pumping of a liquid heat carrier. In high-temperature accumulators on the basis of magnesium alloys, a cartridge tubular electric heater is used.

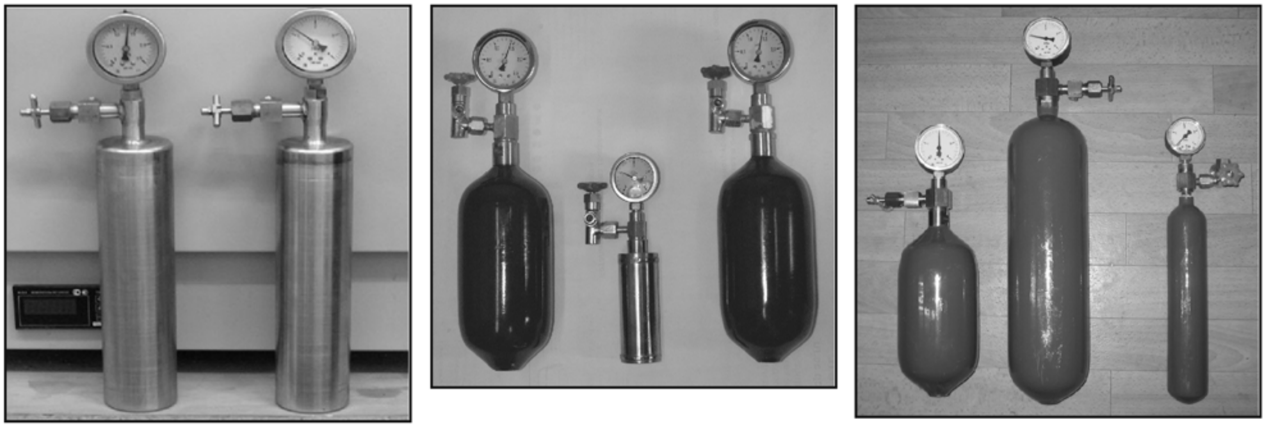

Fig. 7. Metal hydride hydrogen accumulators designed at IPCP RAS.

The filling density of metal hydride powders is 40–50% of the true intermetallide density. At higher filling densities density, the material, gaining volume due to hydride formation, can cause deformation and even destruction of the container housing [98].

Of known large metal hydride hydrogen storage systems, the largest was produces by a HERA Hydrogen Storage Systems Company (Germany) [92]) for U-212 submarine. The system was intended for storage of ~15 000 m^3 of hydrogen (100 tons of a hydride-forming material on the basis of type AB_2 intermetallides) and feeding a FC engine for a 30-day subaqua. Later the German Navy made this system over to the Munich airport for a demonstration hydrogen filling station.

Stationary systems of hydrogen storage in the form of hydrides have no strict restrictions in terms of weight and volume, and, therefore, the limiting factor in choosing one or another hydride will be, first of all, its cost. Now the prices for commercial hydride-forming alloys only slightly depend on their type and vary in a fairly wide range: from \$50–60/kg alloy (manufacturers China, CIS countries, and East Europe) up to \$300–400 (USA, Japan, and West European countries). This corresponds to primary expenses for hydrogen storage from 50 Cent to \$2–4 for 1 m^3 of hydrogen. These expenses are associated not only with purchase of a hydride-forming material and are artificially overestimated. Evidence for this statement comes from the fact that the initial raw material contributes into the total price of a material (prices for components of metal hydride materials in 1999 [53]) no more than 2.5–3%. According to our estimates, at a stable demand for metal hydrides materials, their price can fall up to \$10–15/kg. Depending on the material price/hydrogen capacity ratio, this will correspond to primary expenses of 5–25 Cent for storage of 1 m^3 of hydrogen.

Along with laboratory and stationary systems, the metal hydride method of hydrogen storage can be used for special motor transport which is demanding in terms of safety and compactness but undemanding in terms of storage density. This is a technological transport with zero harmful ehxausts, for example, mini-tractors or auto-loaders.

Figure 8 shows our estimates for various systems of hydrogen storage as a motor, including improved composite high-pressure cylinders (CGH2), cryogenic tanks for liquid hydrogen storage (LH2), as well as some bound hydrogen storage systems on the basis of the best low-temperature metal hydrides (LTMH), sodium aluminum hydride ($NaAlH_4$), and aluminum hydride (AlH_3). The weights and volumes of the systems correspond to storage of 5 kg of hydrogen on a car on fuel cells, which provide the same run as at a car with a gasoline internal combustion engine [99–100]. Provisional sizes of containers for hydrogen storage are compared to the sizes of a BMW 750hL hydrogen-powered vehicle [101]. Unlike the illustration in [64], which is often reproduced in reviews and presentations, we take account of the reduction of the hydrogen capacity of a hydrogen-storing material due to the limited density of its packing in the container, and also the contribution of the weight and volume of the container shell into the total weight (volume) of the storage system [102].

As seen from Fig. 8, the metal hydride hydrogen storage method provides the maximal compactness and surpasses cryogenic tanks in this parameter. However, low-temperature metal hydride systems have a much heavier than traditional, which makes them hardly feasible (with the mentioned exceptions) for motor transport which potentially is the basic consumer of hydrogen storage systems.

The competitiveness of the metal hydride method of hydrogen storage might be radically enhanced by

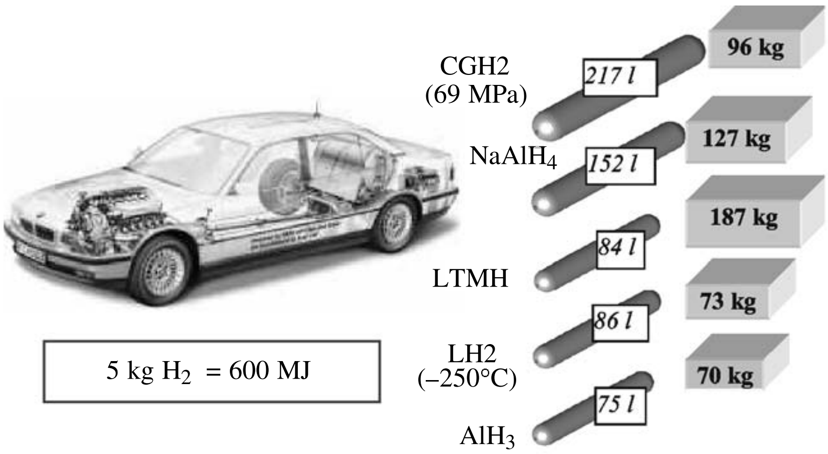

Fig. 8. Volume and weight characteristics of various storages methods of hydrogen as motor fuel.

the development of new hydrogen absorbents with a hydrogen capacity of about ~10 wt%. One such promising hydrogen absorbents might be aluminum hydride modified so that reversible hydrogen absorption/desorption occurs in practically acceptable conditions. To find out whether such modification is possible in principle, detailed physical and chemical research is necessary.

Another interesting and perspective approach to increasing the weight density of bound hydrogen is the use of complex hydrides of light metals, as well as amides. Lithium or sodium aluminum hydrides reversibly absorb and desorb hydrogen in two stages:

$$3MAlH_4 \rightleftarrows M_3AlH_6 + 2Al + 3H_2, \qquad (11)$$

$$3ALH_6 \rightleftarrows 3MH + Al + 3/2H_2.$$

The calculated hydrogen contents of Li and Na aluminum hydrides are 8.0 and 5.6 wt%, respectively [69, 103]. However, the rates of these reactions at moderate temperatures and pressure are too low, and aluminum hydrides are too sensitive to oxygen and moisture. Therefore, their practical use in hydrogen storage systems is questionable.

Some authors [104–107] consider as a possible hydrogen storage media complex lithium–beryllium hydrides synthesized in a ball mill:

$$n\mathrm{LiH} + m\mathrm{Be} + m\mathrm{H}_2 \rightleftarrows \mathrm{Li}_n\mathrm{Be}_m\mathrm{H}_{n+2m}. \qquad (12)$$

The reversible hydrogen content of such complex hydrides is almost 9 wt%. Their formation enthalpy is 40 kJ mol^{-1} H_2, and the equilibrium hydrogen pressure of 0.1 MPa is attained at 250°C. The basic obstacle for practical application of lithium–beryllium hydrides consists in their very low hydrogenation and dehydrogenation rates: The reaction time is several hours even above 300°C.

Over the past years much researcher's attention has been given to hydrogen storage systems on the basis of lithium amide and imide [108–110]. It is known that the reaction of lithium nitride with hydrogen can be reversible (ΔH = –96.3 kJ mol^{-1} H_2) and proceed in two stages:

$$Li_3N + H_2 \rightleftarrows Li_2NH + LiH, \quad (\Delta H = -165 \text{ kJ mol}^{-1} H_2), \qquad (13a)$$

$$Li_2NH + H_2 \rightleftarrows LiNH_2 + LiH, \quad (\Delta H = -44.5 \text{ kJ mol}^{-1} H_2). \qquad (13b)$$

By reaction (13), 6.5 wt% of hydrogen can be reversibly sorbed/desorbed. Hydrogen is evolved at 180–400°C; therewith, in the absence of catalysts, ammonia can be formed as a by-product by decomposition of lithium amide. Small amounts (1 mol%) of catalysts (Ni, Fe, Co, $TiCl_3$) suppresses this side reaction and improve the reaction kinetics. It is experimentally established that at the reversible reaction (14) provides desorption and absorption of about 4.5 wt% of hydrogen, which is of interest for hydrogen accumulation [108].

$$2LiNH_2 + MgH_2 \rightleftarrows Li_2Mg(NH)_2 + 2H_2. \qquad (14)$$

However, there is still insufficient evidence for the high efficiency of amide-containing systems. Apparently, their wide use will be complicated because of the problems of mechanochemical activation, ammonia impurities, and sensitivity a moisture.

CONCLUSION

In the present review we compared the capacitance characteristics of principal hydrogen storage methods.

Analysis of available literature shows that the above methods all have intrinsic advantages and disadvantages, and an ideal hydrogen storage method is still to be found. Only one of known methods, storage of liquid hydrogen in cryogenic vessels, has capacitance parameters completely meeting requirements for transport. At the same time, this method demands too high power inputs and working costs to be practical. Less power-intensive methods are characterized by insufficient volumetric densities (gas cylinders, cryoadsorption) or low weight contents (hydrides).

As mentioned above, the metal hydride method of hydrogen storage features high compactness, safety, reasonable power inputs. In view of the technological flexibility, the metal hydride method can be considered to have good prospects for creation of effective combined hydrogen storage systems.

Further research into metal hydrides can extend the range of reliable, accessible, and fairly inexpensive reversible hydrogen absorbents which meet concrete technical requirements. Furthermore, search for optimal combinations of hydrogen-absorbing materials, device designs, and technical requirements of consumers is necessary.

Search for new technical decisions on the basis of a combination of various methods of hydrogen storage holds great promise. One of examples of successful realization of this approach is the use of metal hydrides for trapping evaporated hydrogen and its subsequent liquefying in cryogenic storage systems. This system is presently applied in aerospace technics [109].

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