THE CREATION OF METAL HYDRIDE ACCUMULATORS OF HYDROGEN FOR EDUCATIONAL PROGRAMS AND LABORATORY USE


Institute for Problems of Materials Science of NAS of Ukraine, Laboratory #67, 3 Krzhyzhanovsky str., Kiev 03142, Ukraine
1 Dnepropetrovsk National University, 72 Gagarin str., Dnepropetrovsk, 49000 Ukraine

Abstract
The present work describes the investigation of alloy of AB5 type based on the commercial cerium ligature on addition of LaNi5 and V, Cu, Al, Fe. Insertion of additions makes possible the change of pressure of hydride dissociation.

The alloy composition was selected so that the equilibrium pressure of hydrogen over metal hydride was provided in the range from 0,5 to 10,0 MPa at the room temperature.

The paper presents experimental installation allowed investigations to be made of the hydrogen capacity of materials.

The developed multicomponent systems are characterised by high compactness, relatively low working temperature at the hydrogen supply under predetermined pressure and by good dynamics of process. The metal hydride accumulators cited in this paper can be used for educational programs and in research laboratories. The metal hydride torch elaborated owing to the experience on the creation of accumulators is useful in many applications.

Keywords: metal-hydride, hydrogen, sorption, volumetric measurement, hydrogen storage.

1. Introduction
As was apparent after scientific investigations of Earth ecology and energetic reserves of our planet, at present time humanity have to solve the energetic problem. It is connected with the man future and effect of his activity on the environment. The energetic revolution is to be happen. In the course of such changes the power resources, energy carriers, equipment producing and consuming the energy are bound to be substituted. Scientists are of the opinion that hydrogen is the most suitable energy carrier and source, because it is of greatest abundance and ecologically clean.

Therefore the interest in using hydrogen as universal synthetic fuel and energy carrier both for stationary and mobile applications has been intensified worldwide. Such an approach for solving problems of our civilization is conditioned by plenum sources of raw materials for hydrogen production, high energy capacity of hydrogen, technological flexibility and safe processes of energy conversion using hydrogen with respect to environment.

The chief drawback of hydrogen is too low specific energy capacity per unit volume because in the normal conditions hydrogen is in a gaseous state and has very low boiling and critical points. The development of effective methods for compact hydrogen storage is a key problem of its use [1].

Mankind has tried to use hydrogen-sorption properties of metals and alloys to solve different scientific and technical problems for over 50 years [2-10]. Many chemical elements and compounds have been studied for this period. Metal hydrides have already found a wide application owing to the peculiarities of thermodynamics of hydrogen sorption and desorption processes that depend on the chemical composition of a solid subjected to the process of hydrogen pickup.

Such compounds attract interest by their high hydrogen capacity. The amount of hydrogen stored in a vessel filled with metal hydride can be 2-3 times larger than that in the

* Corresponding author. Fax: +38-044-424-0381; E-mail: shurzag@materials.kiev.ua (D.V. Schur).
same vessel filled with liquid hydrogen. The method of hydrogen storage in metal hydrides advantageously differs from those in gas-cylinders and cryogenic. This method is safe and requires less service costs. Therefore the world-known companies have put in order the repetition work of various modifications of metal hydride storage elements with different designs.

Metal hydride storage elements can be used both for safe and compact hydrogen storage and for the solution of some other problems enumerated below.

1. Hydrogen purification - scavenging to ppm amounts.
2. Hydrogen separation - from the mixture containing from 1 to 90% non-hydrogen atoms and molecules.
3. Isotope separation - protium, deuterium and tritium.
4. Hydrogen compression - hydrogen is sorbed at low temperature and desorbed at higher temperature and creates high pressure.
5. Heat accumulation - the process is based on the use of heat efficiency (20-60 kJ/mol) of the hydrogenation/dehydrogenation reaction for heat absorption and evolution.

Laboratory 67 at the Institute for Problems of Materials Science of NASU have been developed the series of metal hydride storage elements for various applications discussed in the present paper.

2. Experimental setup for measurements of hydrogen-sorption characteristics

Traditionally, hydrogen-sorption capacity is measured volumetrically on the setups of Siverts type. This universally known method is quite precise until we operate with the samples from hydrogen-sorbing materials with certain density. If specific density is low, uncertainty of the value may contribute seriously to the error in the determination of hydrogen-sorption capacity.

The experimental setup, that was manufactured on the basis of the performed evaluative calculations and analysis of literature, is designed to investigate the hydrogen-sorption characteristics of metals, carbon materials and composites on their base with various specific density using the volumetric method in the pressure range from 0.01 to 30 MPa H$_2$ and the temperatures between the boiling point of liquid nitrogen and heating up to 1473 K (Fig.1).

![Fig. 1. General view of the setup for investigation of hydrogen-sorption properties.](image)

Constructively, this design is a high pressure gas system consisting of distribution pipelines, a main manifold and a low pressure manifold, two buffer capacities for gas branching fault, a reactor with a heating system and a metal-hydride unit for hydrogen storage/compression (Fig.2).
The volumes of empty reactor and of connecting systems of capillary pipe-lines have been carefully determined by hydrogen leak-in from the calibrated system volume, i.e. the standard deviation corresponding to the estimation error for the volume is less than ±0.01 cm³. The volume of empty reactor with capillary pipe-lines is 9.5 cm³. Pressure control is exerted by the high (to 16 MPa) and low (to 1.6 MPa) pressure diaphragm pickups with a view to bring the working pressure to the upper limit of the range of measurement (Fig.3). Accuracy of measurements is 0.15 %. The selected pressure pickups allow the easy integration into the control system. The temperature conditions in the reactor are assured by the furnace where the heating regime is preassigned and controlled by the precision preset temperature controller RIF-101.

The temperatures of the sample inside the reactor and of the heating element in the furnace are controlled by thermocouples with an accuracy of ±1°C. Low-temperature measurements are performed by submersion of the reactor into the Dewar flask with liquid nitrogen (T = 77 K). The vacuum system has been assembled on a basis of the universal vacuum unit VUP-5.

The readings from the pickups are processed by the interface block Agilent. The investigation program is given by a computer. Scanning and data processing are performed automatically.

The 220 l metal-hydride storage/compressor has been manufactured and used for production of high purity hydrogen. It provides the controlled gas leak-in at a pressure to 16 MPa.
3. Metal-hydride unit for hydrogen storage/compression

In designing this unit a special attention has been given to the system for feeding, purifying and compressing hydrogen in use.

The laboratory metal-hydride unit (Fig. 4) for high-pure hydrogen storage/compression that has been manufactured and tested in our institute is designed to operate as a part of the new setup. The main specification to the unit is a possibility to supply hydrogen into the gas system of the setup (volume varies between 15 and 500 cm$^3$ depending on the connected buffer vessels) under the pressure controlled in the range from 10 to 160 bar. The total required hydrogen storage capacity comprises 220 l that provides intensive experimental operation during 2 - 4 weeks without recharging the unit. The container of the hydrogen storage unit (Fig. 5) is made from the tubular stainless steel case (ø70x5 mm, $L$=306 mm) and the face flanges 10 mm in thickness.

According to the performed strength calculations (GOST 14249-89, safety margin 1.5, correction for the strength reduction by welding 0.8), the working pressure in the MH container can be as high as 300 bar at $T$=250$^\circ$C.

The weight of the assembled empty container is 5.2 kg.

4. Hydrogen accumulators of various applications

Laboratory 67 at the Institute for Problems of Materials Science of NASU has developed the series of metal hydride storage elements for various applications (Fig. 6).
Fig. 4. Position of the unit for hydrogen storage/compression in the setup.

Fig. 5. Assembly drawing (a) and general view before assembly (b) of M-H container: 1 - case, 2 - heat exchanger, 3 - filter with gas input/output fitting, 4 - point for metal-hydride loading, 5 - thermocouple shield, 6 - position for electric heater, * - welded seams.

Fig. 6. The series of metal hydride storage elements for various applications.
Intermetallic compounds used in the storage elements were selected on the basis of consumers' individual requirements concerning temperature and hydrogen pressure. Alloys of AB5 and AB types with different additives are typically used.

The vessels in which the metal hydrides are placed have been designed for pressures from 15 to 20 MPa with double margin of safety. Hydrogen from the storage elements can be yielded at room temperature under a pressure from 0.1 to 5 MPa, and in heating to 100°C from 4 to 16 MPa. Hydrogen can be produced at 20 MPa in heating to 300°C. Internal and external heat exchangers are used in the storage elements of this modification. 0.1 to 5 MPa, and in heating to 100°C from 4 to 16 MPa. Hydrogen can be produced at 20 MPa in heating to 300°C. Internal and external heat exchangers are used in the storage elements of this modification.

Capacity of storage elements can be varied from liters to several thousands of liters. Each storage element is equipped with a manometer which simultaneously used as a safety valve.

Photographs in the supplement shows three modifications of the desk hydrogen storage elements of different capacities (“Alsav”, “Viachbog”, “Dmisch”), which have been designed for operation under laboratory conditions, complete with the laboratory fuel cells (Fig. 7, 8, 9, 10). The storage elements can be used for other purposes as hydrogen sources.

![Fig. 7. The high-pressure vessels for hydrogen storage of “Viachbog” modification and hydrogen accumulators “Viachbog” of 3, 10, 15 and 75 l capacity.](image1)

![Fig. 8. The high-pressure vessels for hydrogen storage of “Alsav” modification and hydrogen accumulators “Alsav” of 3, 10, 15, 75 and 170 l capacity.](image2)
The use of metal hydrides (MH) allows the manufacture of very compact, safe and technologically flexible hydrogen storage units. Also, selectivity of the reversible hydrogen interaction with hydride forming metals and alloys makes it possible to purify hydrogen from gas admixtures in the MH units. The possibility to control the output hydrogen pressure by controlling heat influence on the MH sorbent allows the realization of controlled hydrogen supply to a consumer under the preset, and increased pressures. All the mentioned processes, storage, purification, compression / controlled supply, can be combined in a single multifunctional unit. This feature makes such applications extremely effective.

Laboratory # 67 at the Institute for Problems of Materials Science (IPMS) has developed a series of laboratory MH sources of high-pure hydrogen with hydrogen output under controlled increased pressure (up to 200 bar). The sources use MH placed in a pressure container equipped with an internal heat exchanger on the basis of a finned tube. The development is characterized by fitting both the MH material composition and the container design according to the end-user's specifications. The container is manufactured, whatever possible, from the standard component parts.

The laboratory metal hydride storage of high-pure hydrogen is designed for operation in the laboratory setups.

The RE(Ni,Fe,Al,V,Cu)5 hydrogen storage alloy made on the basis of the commercial cerium ligature (Ce /83%/ La Pr Nd Fe Al), lanthanum and nickel (technical purity grade
both) was used in the unit. The composition of the alloy was selected to provide hydrogen equilibrium pressure over the MH of ~3-5 bar at room temperature.

The laboratory metal hydride storage/compressor of high-pure hydrogen is designed for operation in the laboratory setups Fig. 11, 12.

Fig. 11. “Svetzag - 2000”
Overall dimensions:
Length….1410 mm
Flange diameter …….180 mm
Diameter of a working reactor 70 mm
Mass of a storage element 25.5 kg
Mass of metal hydride 7.5 kg
Hydrogen capacity 2000 l
Working pressure 30 MPa (300℃)
Working pressure 0.3 0.5 MPa (30℃)
Chemical composition of metal hydride
AB5 + Mg alloys

Fig. 12. “Vezayf - 7000”
Overall dimensions:
Length 480 mm
Height 440 mm
Width 300 mm
Number of modules 6 pieces
Mass of a module 9.8 kg
Mass of metal hydride in a module 8 kg
Hydrogen capacity of a module 1200 l
General hydrogen capacity of a storage element 7000 l
Lump of a storage element 63 kg
Lump of metal hydride 48 kg
Working pressure 0.3 0.5 MPa (T = 30℃)

The performed strength calculations (GOST 14249-89, margin of safety of 1.5 and correction for strength reduction by welding of 0.8) have shown that the allowed working pressure in the MH container can be as high as 400 bar at 300℃. All containers have been tested at test bed of high pressure allowed investigation to be made at the pressure up to 60 MPa (Fig. 13).
The developed metal hydride unit for hydrogen storage and compression is characterized by high compactness and relatively low reheat temperature of MH with the delivery of sufficiently high hydrogen pressure and good dynamic performance. The desk is designed to conduct strength and leakage tests of the high-pressure vessels used in manufacture of hydride storage units.

5. Metal hydride torch

Metal hydride torch is dedicated both to the brazing, smelting of tiny details from high-temperature materials and for the cutting of parts from foil and in the realization of another specialized works associated with the high-temperature local heating.

This torch was developed owing to the experience on the creation of accumulators with capacity of $1\div100$ litre of hydrogen. Figure 14 shows the general arrangement of the torch. This torch consist of cylindrical container filled with metal hydride, locking valve, filter element, nozzle and manometer.

The container of side 1.5 mm thick was produced from stainless steel. The filter element was made up of pipe frame fabricated from stainless steel with external diameter 8 mm and 5 μm filter micron-insert from porous fluoroplastic.

The locking valve has the centreline channel for hydrogen emission up to the nozzle.
Fig. 14. Metal hydride torch “Viachbog”

The torch is supplied with interchangeable nozzles with 0.3÷0.8 mm holes which provide the necessary flow of hydrogen in pursuance of specific works.

The main technical characteristics of torch are
- inner volume of container – 60 cm³;
- mass of metal hydride – 0.18 kg;
- hydrogen capacity – 30 l;
- total mass – 0.45 kg;
- working pressure at room temperature – 0.2÷0.5 MPa;
- maximum working pressure – 1MPa;
- length – 240 mm;
- diameter – 29 mm.

6. Conclusions

The setup designed at Institute for Problems of Materials Science of NAS of Ukraine for investigations of hydrogen-sorption properties completely meets the modern requirements for the experimental equipment of this class. The setup makes it possible to investigate hydrogen-sorption characteristics of different materials including nanocarbon structures and composites on their base with low specific density by the volumetric method in the pressure and temperature range from 0.01 to 30 MPa H₂ and between 77 and 1473 K, respectively. The setup provides the sufficient degree of accuracy.

The series of metal hydride storage elements have been developed for various applications. The metal hydride torch has been also developed and produced and its allows to operate off-line.

The present work has been performed under financial support of Science and Technology Centre in Ukraine (STCU), Project # Az-02.

References