Stand for Investigation of Hydrogen-Storage Materials

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Abstract – **A stand for determination of thermodynamic characteristics of hydrogen-storage materials is presented. Structure, action principle as well as a mathematical method for calculation of the quantity absorbed hydrogen, are described.**

Keywords – **hydrogen-storage materials, stand, investigation, thermodynamic characteristics, mathematical method.**

I. Introduction

During the last years at accelerated rates begins development of new branch in the industry – Hydrogen energetics and technologies [1] [2] [3] [4]. These rates are determined by the comprehensive application of the hydrogen not only like fuel but also like necessary raw material in many technological processes. The hydrogen is the perfect ecological type of fuel but because of the large interval of concentrations, which it forms with the air, arise important technical difficulties for its storage, transportation and distribution. Economical unprofitable and not safe, are the methods for storage and transportation of hydrogen in gas vessels under high pressure or in liquid state in thermal insulated vessels. Alternative way for solving these problems is the use of hydrogen-absorbing materials for storage of big quantities of hydrogen in comparatively small volumes and under low pressure, Fig.1 [5].

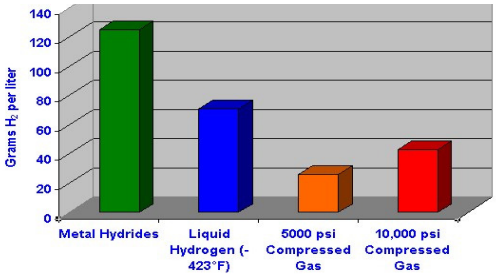

Fig.1 Storage capacity at the separate methods

The process of creating of new materials for storage of hydrogen requires development of methods for determination of their thermodynamic characteristics. In many cases, the used calorimetric and gravimetric testing methods of hydrogen-absorbing materials do not allow the determination of the real operating characteristics of the materials. Similar to the real conditions of exploitation of the reactive hydrogen tanks are the manometric testing methods of hydrogen-absorbing materials [6].

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This paper considers stand for determination of thermodynamic characteristics of materials with hydrogen – absorbing ability, created by teams of Technical University – Sofia and Technovacsystem Ltd by PHARE project [7]. The work of the stand is based on manometric method.

II. Stand for Investigation – Construction and Description

The worked our stand for investigation of hydrogen-storage materials is shown on Fig. 2. The principle scheme of the stand is shown on Fig. 3. The basic elements of the stand are: reactor; high-vacuum pump aggregate; furnace; tanks for hydrogen with different volumes (R1-R3) and referent vessel for hydrogen (Ref); sensors for temperature (T1-T5) and pressure (P1-P9); electronic calculating machine and digital microprocessor devices for reading temperature and pressure; pipe connections and seals; electro-magnetic valves (V1-V8); reducing valves V2,V3,V4; manual valves (V9-V12). The use of electro-magnetic valves gives the opportunity for subsequent automation of the control process.

Fig. 2 Stand for testing of hydrogen-storage materials

The reactor is one of the critical components of the stand, because it has to give possibility for enough rapid heat transfer to and from the test, and in that way to assure one implementation of the test near to the isotherm, despite the permanent releasing, respectively increasing of the heat from the reactions which take place in the reactor during hydriding respectively dehydriding of the test body. In order to avoid losses of hydrogen and generating a mistake during the experiment, the material from which the reactor is made must not absorb hydrogen. It is made a reactor from chromium-nickel alloy with cylindrical form and volume 6,4 cm^3. The small working volume allows decreasing the time for evacuating of the system as well as the use of small quantity of test body. When the material is used in the form of powder

is possible partial sucking of the powder from the vacuum pump during evacuating of the reactor. The detached powder from the test increases the mistakes at the measurement of the quantity of absorbed hydrogen and it causes damage in the vacuum system – vacuum pumps, sensors, valves and etc. With aim of preventing the above-described problems, it is foreseen the initial evacuating of the reactor to be done through needle valve. At the entry of the reactor is placed porous filter plate from sintered material which does not absorb/adsorb hydrogen. The plate prevents the sucking of the test from the vacuum pump, and simultaneously with that the filter assures enough good penetration and going out of hydrogen. For the most precise measurement of the temperature of the test body is implemented measurement of the temperature out of the reactor and the temperature inside of the reactor. For the calculations of the quantity of absorbed hydrogen is used the average value from the two measurements. The measurement of the temperature inside of the reactor is implemented with temperature sensor, placed in the middle of the test in chromium-nickel hood, so that the sensor to be entirely wrapped by the investigated material. The construction of the reactor allows its repeated use. The connecting of the reactor with the system is implemented through threaded connection with copper seal. The reactor is welded in its lower part.

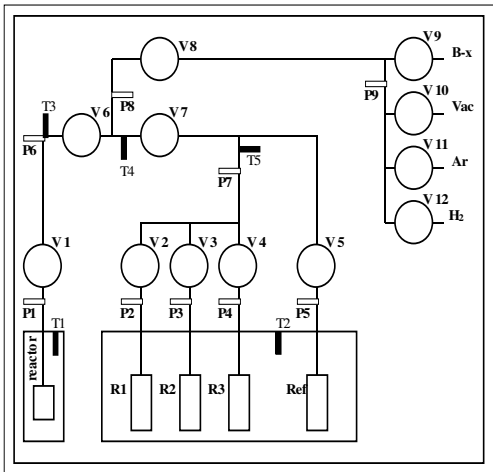

Fig. 3 Scheme of stand for determination of PCT diagrams of metal hydrides

The high-vacuum pump aggregate is consisted of three pumps: rotary pump, roots pump and diffusion pump, and it reaches limit vacuum in the range from 10^{-5} – 10^{-6} Pa. In the conditions of high vacuum and appropriate temperature depending on the material of the test, the oxides are decomposed and active metal surfaces are created, and the kinetics of the absorbing and desorbing process is improved [8].

The referent vessel (Ref) is made of chromium-nickel steel and it has volume 0,3 dm^3.

Depending on the type of the material which will be investigated and with aim of implementing economic profitable experiments, it is necessary in the system to be provided enough quantity of hydrogen. This is done through combination of the vessels for hydrogen (R1-R3) having different volumes 0,3, 0,5 and 1dm^3. The vessels are placed in water bath, in order to minimize the temperature gradient, and also the temporary temperature changes in them during the experiments. The temperatures of the hydrogen in Ref, R1, R2 and R3 are measured with heat-sensitive element placed inside of the relevant tank. During the experiment is obtained information about the temperature of the water bath. The average value of the two measurements is taken at the determination of the hydrogen-absorbing capacity of the test. Although the undertaken measures, at the time of the experiment are obtained minimum changes in the temperature and the pressure of the gas in vessels Ref, R1, R2 and R3 leading to mistakes at calculating of the final quantity of hydrogen, absorbed by the test body. This imposes the introducing of correction coefficient at calculating of the absorbed by the test body hydrogen.

The pipelines of the system are made of stainless steel. The connecting of the separate sections is done through VCR threaded connections. For sealing the connections pipeline – pipeline, pipeline – sensors, pipeline – valves, are used copper seals which prevent the flowing of gas from the system under high pressures - 160 bar.

Sensors Pt100, class B, working temperature to 100^{o}C are used for reading of the temperature. The pressures in each part of the system are measured by sensors for absolutely pressure having the following characteristics – body from stainless steel, working pressure 0-160 Bar, output current 4 -20 mA, exactness 0,25%, working temperature to 85^{o}C. The use of this type of sensors allows specifying the quantity of hydrogen for unit of volume with maximum mistake 0,02 %. The total maximum mistake which is obtained at neglecting the mutual compensating of the mistakes is 0,18 % hydrogen for the whole stand. The information from the sensors is visualized and processed by programmable microcontrollers type TC800. It is foreseen processing and graphic visualization of the results by personal computer, and deducing the results on a paper through printing device. For this aim is used interface type RS485 assuring the communication between the microcontrollers and the electronic calculating machine (ECM). The processing of the information received from the sensors is implemented through software POLIMONITOR. The use of ECM allows the storage of the results of the implemented experiment, which can be used during subsequent experiments. There is a possibility for forming of data base from the results and the methods of implementation of the experiment facilitating the operator's work at subsequent experiment, as well as for analysis of the results.

The used furnace is vertical type. It can maintain temperature up to 700°C and gives opportunity to be investigated high-temperature hydrogen-storage materials. The characteristic of the furnace allows uniformity heating of the reactor and eliminating mistakes as a result of temperature gradient in the test. Its temperature is controlled by microcomputer type RT290.

The system is divided into separate parts which volumes are preliminary determined by using the methods – on the base of isothermal extension of one, accepted for ideal, gas at room temperature and low pressures (< 0.3MPa) from one known referent volume in volume which will be determined. It is specified the volume of the not filled with test body reactor's part, as well as the volume of the valves, the vessels for

hydrogen and the referent vessel. The determination of the volume of the referent vessel is done by weighing it in empty state and after filling it with water.

The action principle of the stand with the above-described construction is on the base of the law for storage of the mass in closed isochoric system. The work with the stand is done in the following sequence:

- The test is weighed and it is charged in the reactor;
- The volume of the reactor unoccupied by the test body is determined;
- The test is activated;
- Evacuating of the whole system is done, as the heating of the test begins before reaching vacuum 10^{-5} Pa, until the test is completely desorbed;
- The type of the experiment is determined and the defining of specific for experiment parameters, for example what gas tank to be used (R1-R3), the number of the steps during implementation of the experiment and etc.;
- The desired end pressure in the reactor is determined;
- The tanks are filled with hydrogen;
- The temperature in the furnace is increased to the desired one, depending on the material which is investigated after beginning of each experiment;
- A static absorption (desorption) is implemented - it consists of leading in (leading out) hydrogen by steps: mostly at the beginning of every step one constant volume is filled (emptied) to an exact pressure and depending on the test, so that to absorb (desorb) the relevant quantity of hydrogen. At every step it has to be awaited until reaching approximately thermodynamic equilibrium to which the system approaches asymmetrically. This operation is repeated till the completely hydriding (dehydriding) of the test. The values of the pressure and the temperature are recorded, as well as the quantity of absorbed hydrogen in the beginning and in the end of every step;
- The experiment is stopped after reaching the end assigned pressure and all valves are closed.

The quantity of hydrogen absorbed by the test is calculated on the base of the hydrogen balance of the accepted closed isochoric equipment: when neglecting the losses of hydrogen the value of the quantity of hydrogen in the equipment during each experiment remains constant. This means that the changes of the quantity of absorbed hydrogen by the test, cause relevant precise defined changes in the hydrogen pressure. With known working volumes of the equipment and through measuring of relevant temperatures and pressures, and also by using an appropriate equation for the state of the hydrogen gas, is possible to calculate the quantity of hydrogen absorbed by the test at any time. The quantity of hydrogen absorbed by the test is calculated by reckoning the hydrogen content in every separate section of the system before and after each step of the absorption or desorption. For this purpose is used the equation:

$$p \cdot V = n \cdot R \cdot T \qquad (1)$$

where:

p is the pressure of the gas in the respective module of the system, Pa;

V – volume of the respective module of the system, m^3;

n – quantity gas, mol;

R – gas constant

T – temperature, K

The total quantity of gas in the system in definite moment is:

$$n_{\Sigma} = \sum_{i=1}^{k} n_i = \sum_{i=1}^{k} \frac{p_i(t) \cdot V_i}{R \cdot T_i(t)} \qquad (2)$$

where k is the number of the working sections of the system.

The total quantity of hydrogen absorbed by the test for one step is:

$$n_x = (n_{\Sigma 1} - n_{\Sigma 2}) - n_{korr} \qquad (3)$$

where:

$n_{\Sigma 1}$ – the quantity of hydrogen in the working sections in the beginning of every step;

$n_{\Sigma 2}$ – the quantity of hydrogen in the working sections at the end of every step;

n_{korr} – coefficient of mistake;

n_x – is the difference between the quantity of gas before and after the absorption, i.e. in the beginning and at the end of every step. It determines the quantity of hydrogen which is absorbed by the test.

The total quantity of hydrogen which is absorbed by the alloy is an amount of the quantity of hydrogen absorbed during each step at absorption. In analogous way is calculated the quantity of deabsorbed hydrogen at static deabsorption.

The correction coefficient n_{korr} is introduced at calculating of n_x eliminating the mistakes as a result of reading the change of the pressures and the temperatures in the separate parts of the system during the experiment, and also in consequence of inaccurate measuring of the relevant quantities.

III. Conclusion

With the created stand can be investigated hydrogen-absorbing materials with enough for the research work exactness. The presented stand assures a possibility of refueling hydrogen reservoirs on the base of hydrogen-absorbing materials. Thus the presented installation gives an opportunity for static trial the tests in conditions of absorption and desorption but it is foreseen a possibility for additional building in of regulator for the flow – allowing dynamic investigation of the experimental model. The construction of the stand allows automation of the control.

References

[1] E. Tzimas, C. Filiou, S.D. Peteves, *Hydrogen Storage:state of art and future perspective*, Petten The Netherlands, 2003.

[2] HILTech, *Hydrogen and storing hydrogen*, 2005.

[3] M. Dorheim, T. Klassen, R. Bormann, *Hydrogen storage materials*, Hamburg, Technical University Hambur –Harburg, 2004.

[4] www.whitehouse.gov/infocus/energy/

[5] www.ovonic-hydrogen.com/solutions/technology.htm

[6] Jurgen U. Keller, Erich Robens, *Thermogravimetric and sorption measurement techniques/instruments.*

[7] Dimitar Trifonov, project PHARE, *Technologies for obtaining new materials with hydrogen-storage capacity*, BG 0102.02.02.043, 2003-2005.

[8] Gerardo Friedlmeier, *Charakterisierung von hochtemperatur-metall-hydriden auf magnesium-basis*, 1997.