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Crystal lattice of solid body can store simultaneously both molecules and atoms of hydrogen in quantities

A. Guglya [a,*], E. Lyubchenko [b], Yu. Marchenko [a], E. Solopikhina [a], V. Vlasov [a]

[a] National Science Center "Kharkov Institute of Physics and Technology", 1, Akademicheskaya St., Kharkov, Ukraine

[b] National Technical University "Kharkov Polytechnic Institute", 21, Frunze St., Kharkov, Ukraine

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ABSTRACT

The regularities of the effect exerted by gas molecules from the residual atmosphere in the vacuum chamber on the absorption characteristics of $V_{0.9}Ti_{0.1}N_x$ thin-film were investigated. It is shown that the open nanoporous structure actively absorbs not only the hydrogen molecules but also the larger molecules. The saturation with hydrogen at 20 °C leads to the reduction of absorption capacity of the material (no more than 3 wt.%) and the increasing of the temperature of hydrogen desorption (500 °C) are observed. High temperature (250 °C) of hydrogen saturation may reduce the temperature of desorption up to 275 °C and increase the gravimetric capacity to 7 wt.%. It is shown that the hydrogen in the porous nanocrystalline structures can be maintained both in the intergranular and interparticle pores and at grain boundaries and in not filled by nitrogen sites of $V_{0.9}Ti_{0.1}N_x$ grains. At that, the greatest amount of hydrogen is held just in the interparticle pores and vacant sites.

Introduction

At the beginning of the XXI century such issues as the conservation of fossil energy sources (oil, gas and coal) and the search for additional eco-friendly energy sources became increasingly important. Hydrogen is considered to be rather promising in this respect for a score of reasons. The world hydrogen reserves are almost limitless and its firing is non-environment damaging. Importantly that the heat amount released per unit of mass during interaction with oxygen is three and a half times the heat amount released at the organic fuel combustion. The key issue of hydrogen use is the difficulty of its uptaking in the large amounts in relatively small capacities. Presently, hydrogen used on industrial scale is accumulated either in high-pressure (up to 70 MPa) vessels or it is cooled to 20.3 K to be stored in liquid state. Over the past decades, the so-called solid-state hydrogen accumulators have been intensively developed and studied.

Hydrogen in solid-state accumulators can be storage in a large amount and it can be retained either by means of the chemical compounds formation or by physical adsorption of molecular hydrogen in micropores. The acceptable results

* Corresponding author. Tel.: +380 57 335 66 91.
E-mail address: guglya@kipt.kharkov.ua (A. Guglya).

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were often achieved at the absorbed hydrogen amount in hydride structures of 9–10 wt.%. However, the enthalpy of hydrogen chemisorption is more than 50 kJ/mol. This fact prevents the release of hydrogen from lattices at the temperature below 573 K.

Nowadays, the metal-organic frameworks (MOF) are tested for physical adsorption of molecular hydrogen. The MOF represents an organic skeleton that contains the metal atoms at the certain points. In addition, the carbon formations, in particular, nanotubes, nanofibers, fullerenes, composite nanoporous metalloid structures and activated carbon that were obtained by different vacuum deposition techniques are also studied. As of today, the frame structures demonstrate the acceptable level of hydrogen adsorption in the region of 4–10 wt.%. However, due to the low heat of physical adsorption that is within the range of 4–18 kJ/mol, hydrogen is released from them at the very low temperature (less than 77 K).

The analysis of the obtained results allows us to determine two perspective lines that lead to the noticeable increase in the absorption capacity of hydrogen accumulators and temperature drift towards the range desired by US Department of Energy (DOE range). The first line is associated with transformation of the composition and structure of simple and complex hydrides due to increase of the amount of metal components, mixing of the nitrogen- and boron-based hydrides with each other, or with the hydrides fineness decrease by milling them in ball mills. All these processes inevitably result in increase of the structure imperfection degree, decrease of the grain size, and formation of the system of intergranular nano-pores capable of adsorbing hydrogen in molecular state. This means that such structures start to storage hydrogen not only by formation of the chemical bonds but also by its physical adsorption.

The second perspective line is associated with the efforts to transform the porous structure of metal-organic skeleton and carbon nano-structures by alloying components addition. On the one hand, this approach results in decrease of the pores average size, on the other hand, it promotes the dissociation of the part of hydrogen molecules, and retention of its atoms by formation of the chemical bonds with nitrogen, oxygen or metal. These two processes result in the drift of the hydrogen storage heat to more optimal values.

For foregoing reasons, the material with acceptable gravimetric, thermodynamic and kinetic properties must storage hydrogen both in molecular and in hydride forms.

The entire process of hydrogen uptaking in the hydride phase can be divided into several stages, such as the physical adsorption of hydrogen molecules on the surface of the solid state; their dissociation; overcoming of the surface barrier by hydrogen atoms; the diffusion deep into the material; and chemical compound formation. If the system of micro/nanoporous structure is inside dense crystalline structure, the reverse process of association of the part of hydrogen atoms may take place. The molecules that have been formed at this process will be accumulated in the intergranular pores.

Initially, at the accumulation of hydrogen by porous MOF or by the carbon structures activated by metal inclusions, hydrogen molecules fill the pores. Then a part of molecules dissociates, not on the metal surface but in the close vicinity to metal atoms; whereupon the formation of stable hydride phases occurs.

Hydrides on the base of vanadium, the respectively light transition metal, are considered to be perspective for usage as the solid state hydrogen storages. The total mass of stored hydrogen in them reaches the value of 2.1 wt.%. At that the amount of absorbed hydrogen atoms in VH_2 is essentially more than, for example, in MgH_2 hydride (11.2 in VH_2 vs. 2.5 wt.% in MgH_2, at/cm^3, x10^{22}) [1].

V–H system includes the following phases: α – solid solution; β – ($VH_{0.45}$–$VH_{0.95}$) and γ – VH_2. The $\beta+\gamma$ phase mixture is in the $VH_{1.0}$–$VH_{2.0}$ concentration range. The V_2H, V_3H_2 and V_4H_3 ordered structures are revealed in the homogeneity range of the β-phase. The β-phase has the body-centered tetragonal lattice (bct), the $VH_{1.77}$ non-stoichiometric phase has fcc lattice.

Due to the existence of several V–H phases with different crystal structures several plateaus related to the phase transitions have to appear on the P-C-T diagram (Fig. 1). The figure also shows the possible ways of the improvement of the absorptive properties of vanadium hydride, such as nanoporous structure formation (increasing of the gravimetric capacity); hydride phase stabilization by means of complex VN_xH_y hydride formation and formation of the additional hydrogen traps (the improvement of the thermodynamic and kinetic properties).

In addition to the above, it should be appreciated that the influence of the grain boundaries on hydrogen concentration essentially increases at the transition to the nano-structured thin films. Orimo S. et al. [3] showed that the grain size reduction leads to the fundamental decrease of the enthalpy of the diffusion processes. Diffusion of hydrogen in the films with the grain size less than 10 nm occurs only along the grain boundaries. The volume of the grain boundaries in this case becomes comparable with the volume of the main part of material. The diffusive mobility along the grain boundaries is by two-orders of magnitude greater than in the grain.

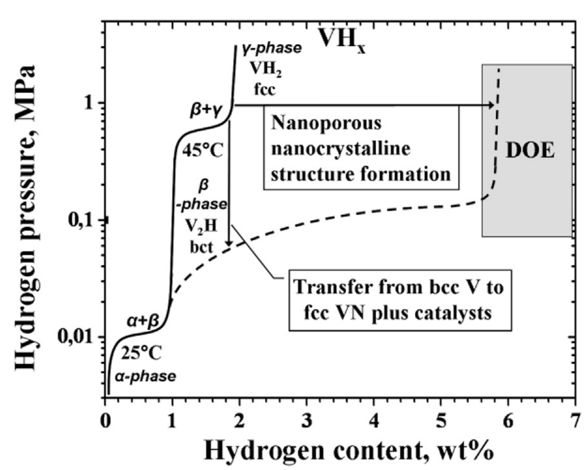

Fig. 1 – Pressure-concentration constitution diagram for hydride VH_x. (Summarized data from Ref. [2]). Dot line is related to the state when this hydride may be used as hydrogen storage. The receipts for this state achievement are shown.