

NANOCRYSTALLINE POROUS VN_x HYDROGEN STORAGE AS THE PROMISING MATERIAL FOR HYDROGEN ENERGY

НАНОКРИСТАЛЛИЧЕСКИЕ ПОРИСТЫЕ VN_x НАКОПИТЕЛИ ВОДОРОДА – ПЕРСПЕКТИВНЫЙ МАТЕРИАЛ ДЛЯ ВОДОРОДНОЙ ЭНЕРГЕТИКИ

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Abstract: The paper studies the results of investigation of VN_x thin films obtained by the ion-beam-assisted deposition (IBAD) technique in a specially designed experimental test-bench. The data on the electron microscopic examination of the nanoporous structure of the films and the measurements of their electrophysical and absorption/desorption characteristics are reported and discussed. The results make possible the application of nanoporous VN_x thin films as promising material for use as the hydrogen storage.

Keywords: NANOPOROUS FILMS, ABSORPTION, DESORPTION, HYDROGEN STORAGE, ION-BEAM-ASSISTED DEPOSITION

1. Introduction

At present, more than 50% of energy consumption is provided by irreplaceable carbon-containing products, namely, gasoline and gas. Therefore, the need is becoming clearer each day, to find additional sources, which could slow down the use of carbon energy. First of all it concerns to the motor fuel.

Over the past decades hydrogen has been regarded as the most suitable replacement for gasoline. This is because the released energy at the reaction of the hydrogen with oxygen ions is almost three times more than the energy released at the combustion of gasoline, methane or methanol. The major problem hampering the development and use of electrical plants operating on hydrogen fuel is the absence of the material that can accumulate the large quantities of hydrogen. In the early 21st century, the US Department of Energy (DOE) formulated the basic requirements for fuel systems of light duty vehicles [1]. In particular, the minimum amount of hydrogen that can be accumulated in the storage must be not less than 6 wt. % of the total mass of the storage system.

In addition to the requirements for the absorbed hydrogen mass, there are limitations on the functional parameters determining the operation of the fuel cell, namely, the temperature and pressure. The polymeric proton exchange membrane (PEM) is seen as playing a role of electrolyte in the solid fuel cell. It is its performance that determines the ranges of the operating temperatures (300-400K) and pressures (0.1-3.0 MPa), within which the hydrogen absorption/desorption processes should take place. And it is these restrictions do not allow using the traditional porous materials and hydride structures for the hydrogen storage [2]. The interaction between hydrogen molecules and the surfaces of pores in the porous materials are carrying out at the expense of the weak Van der Waals forces (physical adsorption). The heat of adsorption varies depending on the material in the range of 3 – 7 kJ/mol. As a result, the hydrogen release at room temperature is not more than 2 wt. % H_2 [3]. The hydrogen in hydrides is in atomic state and forms the chemical compounds with the atoms of the crystal lattice. The chemical adsorption heat for conventional polycrystalline structures is greater than 50 kJ/mol, which makes difficult the hydrogen desorption of from hydrides at temperatures less than 500K [4]. To ensure a hydrogen release in the temperature range of 300-400K the desorption heat should be in the range of 27-50 kJ/mol.

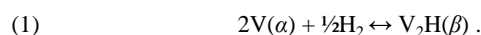
In the mid-1980s for the improving of the thermodynamic and kinetic characteristics of hydride structures the reactive mechanical milling process (RMM) was developed and implemented. With this method, the hydride phase production occurs during the grinding of the powder mixture in a hydrogen atmosphere [5]. If hydride phase formation process is to be completed the long grinding times

(hundreds of hours) and hydrogen pressure of 1.0-3.0 MPa [6] must be provided.

The entire process of hydride phase formation in metals and alloys can be divided into several stages: the physical adsorption of hydrogen molecules on solid state surface; their dissociation; overcoming the surface barrier by hydrogen atoms; their diffusion into the depth of material; and the chemical compound formation. It follows that, if the hydrogen amount absorbed by "massive" material are determined by its structure, the kinetic and thermodynamic characteristics of the absorbent largely depend on how quickly the hydrogen atoms can overcome the surface barrier of 50 nm-thickness. Therefore, it is not surprising that along with the study of "massive" solid-state hydrogen storage, the processes of hydrogen absorption by the thin film structures constantly draw great attention since the 1980s (see, e.g., [7-10]).

Hydrides based on vanadium, relatively light transition metal, are considered promising for use as the solid hydrogen storages. Total hydrogen amount accumulated there in reaches 2.1 wt. %. At the same time, the number of hydrogen atoms absorbed by VH_2 substantially greater than, for example, in the popular hydride MgH_2 (11,2 in VH_2 compared to 2,3 in MgH_2 , atoms/cm³, $\times 10^{22}$) [11].

V-H system is characterized by the existence of following phases: α -solid solution; β -($VH_{0.45}$ - $VH_{0.95}$), and γ - VH_2 . There is the $\beta + \gamma$ phase mixture in the $VH_{1.0}$ - $VH_{2.0}$ concentration range. Due to the existence of several V-H phase varying in crystal structure, several plateau responsible for the transition from one phase to another should be observed in P-C-T diagrams. The first plateau corresponds to the transition from the α -solid solution to β -phase.



Total amount of the accumulated hydrogen reaches 0.7 wt. %. β -phase is stable at a pressure of 0.1 MPa and at room temperature. Therefore, the destruction of β -phase has never been observed at room temperature.

The second plateau corresponds to the transition from the β -phase to the γ -phase.



This γ -phase is unstable at the atmospheric pressure. P-C diagram of VH_2 hydride at 45°C is characterized by quite wide plateau corresponding to the pressure of 0.4-0.5 MPa [11]. Consequently, only about half of the possible amount of hydrogen absorbed by vanadium can be used practically.

Success in creating the appropriate hydrogen storage using the vanadium hydride primarily depends on whether it will be possible

to improve the gravimetric capacity up to 7.6 wt. % of H_2 while improving the thermodynamics of desorption processes. Solutions to this problem are displayed in Fig. 1. They are as follows: the creation of a nanocrystalline structure and the introduction of catalyst additive into grains lattice (the improvement of the thermodynamic and kinetic characteristics); stabilization of the hydride phase by means of VN_xH_y complex hydride formation and the creation of additional traps for hydrogen (gravimetric capacitance increase).

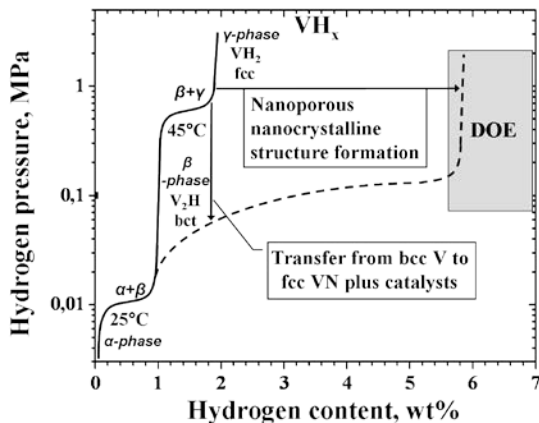


Fig.1 Pressure-concentration constitution diagram for hydride VH_x . (Summarized data from [12]). Dot line is related to the state when this hydride may be used as hydrogen storage. The receipts for this state achievement are shown.

The paper presents the results of study of the structure, electrophysical and absorption/desorption characteristics of VN_x films obtained by the ion-beam-assisted deposition technique.

2. Experiment procedure

Nanocrystalline porous VN_x thin films were obtained by evaporation of vanadium from the electron beam crucible at the simultaneous irradiation by the mixed beam of nitrogen and helium ions with an energy of 30 keV (IBAD technique). The ratio between the deposition rate of vanadium atoms and ion implantation of the gas ions was equal to 0.5 atom/ion. The film deposition was carried out on the substrates of silicon and sapphire at 200°C. The structure of the films deposited on silicon has been studied by means of transmission electron microscope JEM 100CX and scanning microscope JSM 7001F. The films deposited on sapphire were used for the examination of their electrophysical properties, absorption and desorption of hydrogen.

To measure the total amount of absorbed hydrogen special test-bench consisting of two vacuum chambers, separated by a valve, whose volumes correspond as 1:10, was designed [13, fig.2]. For the saturation by hydrogen the film was placed in a small chamber that was pumped out to a high vacuum. The film on the substrate was heated to 200°C. Then the chamber was filled with hydrogen to a pressure of 0.1 MPa, the heating was turned off, and the film was maintained at 20°C during 1 hour. During the hydrogen desorption investigation a valve between the chambers was opened, and the chambers were pumped out up to the pressure not worse than 10^{-3} Pa. Then the valve connecting two chambers with the high-vacuum pump was closed and annealing took place. The amount of hydrogen released at annealing process was determined from the vacuum transducer readings. Measured pressure was recalculated to the amount of hydrogen molecules as well as the number of hydrogen weight percents relatively to the mass of the film.

3. Results and discussion

In contrast to the PVD, CVD and MS techniques the surface layer of the film at the ion-beam-assisted deposition contains

inhomogeneous zone in which the number of generated defects and the concentration of implanted gas increases successively from the film surface into the depth of the zone. The length of this zone is determined by the depth of the ion path in the substance that is used for the bombardment of the deposited material. For nitrogen ions with energy of 30 keV the length of the inhomogeneous zone is about 60-70 nm [14]. Due to the presence of such zone the process of film structure formation in IBAD technique is not limited by the generation stage only. The final structure is formed at a film thickness more than 70 nm.

Fig. 2 a, b shows the transmission and scanning electron microscopy data for VN_x films, respectively. It is seen that the films consist of grains of irregular shape distributed in the space in arbitrary way (Fig. 2, a). The grains with a diameter of 15-30 nm dominated. Also the cylinder-shaped grains with the height less than 80 nm and diameter of 20-25 nm are observed. The Fig. 2, b shows that the grain boundaries contain a large number of nano-pores with size that varies in the range of 3-5 nm. This result confirms our data on the structure of nano-porous hydrogen storages reported and published earlier [13, 15, 16].

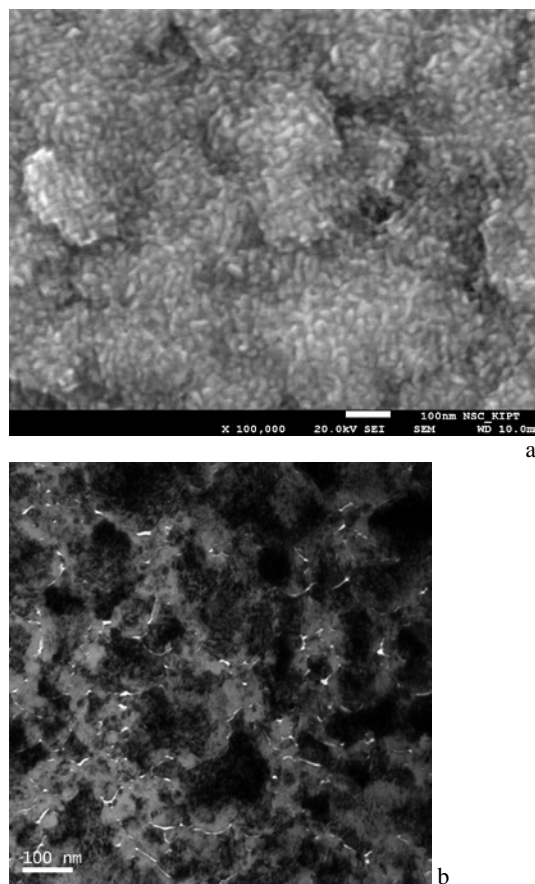


Fig.2 Scanning (a) and transmission (b) electron microscopic images of VN_x films

Taking into account the structural irregularity of VN_x films, the change of resistivity in the absorption and desorption processes can provide the important information about the pores state and kinetics of the hydrogen release from them. For multicomponent materials the presence of gas-containing pores in such structure leads to the appearance of additional conduction mechanism which is either in the occurrence of thermionic conduction electrons due to emission from the gaseous impurities (nitrogen, oxygen) located on the pore surfaces and/or in their volume, or due to the tunneling effect. Consequently, the resistivity of material, which pores in whole or in part are filled with gas, will be less than that for the material with vacuum pores. For this occasion the electrical resistivity of material will be determined by the scattering of electrons by phonons, and boundaries of the nano-grain and nano-pores.

Fig. 3 shows the corresponding dependences of VN_x film resistance on annealing temperature. It is seen that resistance decrease in the temperature range of 20-60°C is observed. It is typical for the films having a negative temperature coefficient of resistance. Further temperature increase causes an intense increase in resistance.

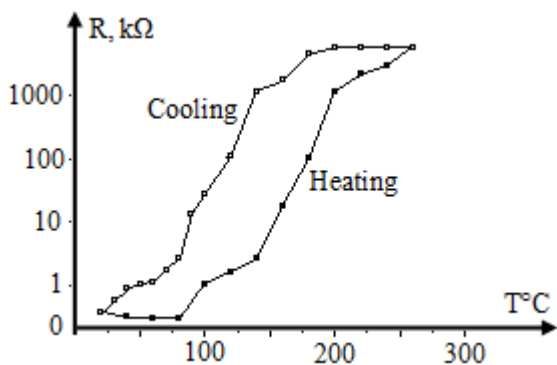


Fig. 3 Changes in electrical resistance of VN_x films saturated with hydrogen during heating and cooling

At a temperature of 260°C the resistance of VN_x films is more than 10^4 times greater than the resistance of the hydrogen-saturated samples. In the cooling process resistance remains unchanged up to 180°C, and then decreases. The final value of resistance is by 15-20% less than the resistance of the films saturated with hydrogen.

Fig. 4 shows the hydrogen desorption curves indicating that the change in resistance of the films during annealing is uniquely related to the amount of hydrogen absorbed by them.

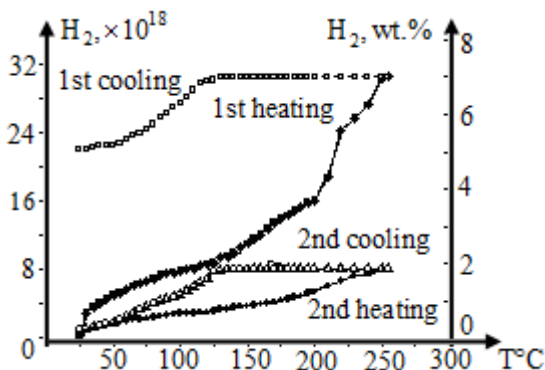


Fig. 4 Dependences of the hydrogen amount in the annealing chamber during the initial annealing and reheating of VN_x-H_x film. Reheating was performed after evacuation from the chamber of hydrogen remaining after the primary heating and cooling.

It was observed that the inflections of the primary annealing curve are correlated with the inflections in the dependence of the film resistance on the heating temperature (Fig. 3). Therefore, as the hydrogen release occurred, an increasing number of pores appears in the film; and the scattering of electrons on them leads to the gradual increase in resistance of the film. Reduce of $(V, Ti)N_x$ film resistance during cooling corresponds to the received data on hydrogen absorption from the atmosphere inside the chamber and filling the open pores by hydrogen.

4. Conclusion

The results of this study indicate that use of IBA technique ensures not only the controlled formation of nanoporosity with prescribed characteristics but also embedding this nanoporosity into the nanocrystalline structure of matrix. The material produced by this technique is capable to accumulate hydrogen at low pressures and room temperature in amounts required for real-works application. The availability of narrow channels in form of grain boundaries provides high diffusion mobility that allows

accumulating the hydrogen and releasing it from material within a short period of time, and also creates conditions for the retention of molecular hydrogen in pores at room temperature.

5. References

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