THIN FILM NANOPORES (V, 10Ti)N_xH_v HYDROGEN STORAGES

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This scientific paper delves into the findings of the investigation carried out to determine the adsorption and electrophysical characteristics of nanoporous (V, 10 at.% Ti)N_x films obtained using the ion beam-assisted deposition technique (IBAD). It has been shown that these films can accumulate more than 7 wt.% hydrogen at a relatively low pressure of 0,5 MPa. One part of it is accumulated in the grain boundaries and pores but another one forms the hydride phase. A complete release of hydrogen occurs at a temperature of 250 °C. During the hydrogen desorption the specific resistivity of (V, 10Ti)N_xH_y films is roughly increased by a factor of 10⁷.

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INTRODUCTION

Development of storage devices for the fuel cells of battery-driven vehicles requires the use of compact and lightweight materials with high hydrogen capacity. Therefore, single-component and complex hydrides based on lightweight metals (Mg, Ca, Na, Al, Be) provoke interest not only because of their tendency to accumulate a considerable amount of hydrogen but also because of substantial weight percentage of hydrogen contained in hydrides of these metals. It is also known that vanadium is a relatively light transition metal and the vanadiumbased hydride can also be used for the fabrication of hydrogen storage devices. It has low hydrogen desorption temperature (~ 40 °C) and accumulates it in amounts comparable with those accumulated by porous and metal-organic structures. In addition, it is very important that the amount of absorbed hydrogen atoms (in the unit of volume) in VH₂ is considerably higher than, for example, in MgH₂.

The V-H system is characterized by availability of the following phases: α , $\dot{\alpha}$ is the solid solution, β -(VH_{0.45}-VH_{0.95}) and γ -VH₂. In the region of the VH_{1,0}-VH_{2,0} concentrations there is a mixture of β + γ -phases. In the homogeneity region of β -phase the ordered structures of V₂H, V₃H₂, and V₄H₃ have been revealed. The VH₂-phase is less stable than the β -phase. The hydrogen adsorption/desorption reaction VH + 1/2H₂ \leftrightarrow VH₂ occurs at moderate temperature and pressure. As a result only half of hydrogen adsorbed by vanadium can roughly be used for the reverse adsorption/desorption process.

A diffusion mobility of hydrogen in metals with the bcc lattice is much higher than in metals with fcc and face-centered close-packed lattices. Moreover, the hydrogen mobility is higher in vanadium than in niobium and tantalum with the fcc lattice. According to the data given in the paper [1] diffusion activation energy in $\dot{\alpha}$ -VH_x at x = 0.17-0.38 varies in the range of 0.087...0.132 eV/at. (10...15.2 kJ/mole). In the 0.486<x<0.736 range, where the β -phase exists energy remains virtually unchanged, i.e. 0.230...0,240 eV/at. [2].

The data given above refer only to traditional polycrystalline materials. Orimo S. et al. [3] showed in what way the absorption kinetics of hydrogen in vanadium can be improved for nanocrystalline films.

Vanadium was milled in the ball mill in the hydrogen atmosphere during 5, 10 and 60 min. As a result were obtained specimens with the grain size of 80, 30 and 10 nm, respectively. Mass-spectrometry and nuclear magnetic resonance data showed that a decrease in the grain size results in the cardinal enthalpy reduction of diffusion processes.

The situation can still be improved if the VH_x hydride is altered to the nitrogen – containing VN_xH_y hydride through the addition of nitrogen in the amount required for the formation of such a chemical compound as VN_x. Vanadium nitride has the fcc lattice which is more close-packed in comparison with the bcc lattice, and this would improve nitride phase stability. The paper [4] showed that the bonding energy between the vanadium atoms and the NH₂ compound was equal to 142 kJ/mole, which is sufficient to provide the nitride phase stability.

However, the complex hydride of a stochiometric composition won't be able to provide accumulation of the required amount of hydrogen alone and release it at low temperatures. Using the Ti-C compound as an example, the authors of the paper [5] showed that the TiC_{0.6} ceramics has the highest gravimetric capacity (up to 2.9 wt.%) and acceptable kinetics of hydrogen desorption. The lattice sites that were not occupied by carbon atoms create the required vacancy super saturation, which provides a high hydrogen diffusion coefficient. In addition, such "carbon" vacancies are capable of retaining up to 4 hydrogen atoms [6], which permits to accumulate a large quantity of hydrogen at room temperature.

Therefore, in order to get a material capable of adsorbing at least 6 wt.% H_2 it is insufficient to design nitride or carbide ceramics with under saturated nitrogen or carbon bonds. It is necessary to form such a nanocrystalline structure whose intergranular space would contain additional pore-like traps that would adsorb hydrogen in its molecular state. The intergranular boundaries should provide a reasonable hydrogen adsorption and desorption kinetics.

1. EXPERIMENT STATEMENT

Traditional equilibrium methods used for the creation of nitrogen-containing complex hydrides include the production of material powders or their hydrides with their further milling in hydrogen or ammonia atmospheres for many hours. Such materials consist of crystallites that originate, in their turn, from grains whose size varies in the range of several microns to 10 nm. The intergranular boundaries have a width of approximately 1nm.

The previous papers [7, 8] showed that using IBAD we can produce VN_xH_v and $(V, Ti)N_xH_v$ nanoporous films that can adsorb up to 7.4 wt.% hydrogen. In addition, the methods of neutron spectroscopy showed that most pores have relatively large size of 7 to 14 nm. These pores are not of vacuum type and have been partially filled with nitrogen. It has been established that the kinetics and thermodynamics of hydrogen desorption from such pores still require improvement. Thus, the size of 7 to 14 nm characterizes not so much hydrogen capacity of nanoporous complex vanadium hydrides as the amount of the excess nitrogen in the material. During the adsorption of hydrogen in such a structure a certain portion of it fills free space inside the pores occupied by nitrogen. A certain portion dissociates on the pore surface and forms the hydride VN_xH_y-phase. Naturally, if the pores having such a size were of a vacuum type we could hardly expect the



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retention of such an amount of hydrogen from them at room temperature.

In order to improve kinetic and thermodynamic characteristics of hydrogen desorption we deposited (V, 10 at.%Ti)N_x films of 1 μ m thick with the grain size of 15 to 20 nm in ion bombardment conditions. The plates made of polished sapphire monocrystal of 1 mm thick were used as the substrates.

The pore size was determined using the data of transmission electron microscopy. Fig. 1 gives the images of $(V, 10Ti)N_x$ films at the initial growth stage (a) and at the final growth stage (b). In the latter case the film was thinned to a required thickness using the ion beam. The estimated size of pores did not exceed 6 nm. The pores are mainly located at intergranular junctions. They mainly have a shape elongated along the boundaries, as a result the width of most boundaries is increased (see Fig. 1,a). The grain boundary structure of the formed film is slightly different. However, the boundary width is virtually the same across the grain perimeter. Notably, we can assert that the porous zone envelops almost the entire space around the grains.



Fig. 1. (V, 10Ti) N_x film structure: a - at the initial deposition stage (estimated film thickness of 20 nm), b - at the final stage (of 1 μ m thick)

It is known [9-11] that the definition of the adsorption capacity of materials with a bcc lattice that can capture oxygen-containing molecules requires their obligatory preliminary activation. Usually this is realized through the heating of a specimen in a vacuum up to a temperature of 400 to 450 °C during 1 to 2 hours, with injection of hydrogen into the chamber and subsequent cooling. Such a procedure is repeated until the specimen starts to intensively adsorb hydrogen, which is controlled by a change in pressure inside the specimen-containing chamber.

This method is used in the case when the volume of the test material allows for the accumulation of hydrogen in amounts sufficient for the measurement by available sensors. The volume of films studied by us is rather low; therefore ordinary manometers fail to reliably register a change in pressure caused by hydrogen adsorption. Therefore, in order to control the activation process we measured the resistivity value of $(V, 10Ti)N_x$ films during their annealing and hydrogen saturation. In nanocrystalline films whose intergranular boundaries contain pores the resistivity value depends not only on the size of grains and pores, but also on the amount of gas captured by the pores during their formation or saturation. In our case the main gas component in non activated films is nitrogen [7]. Therefore, the change of this value during annealing and exposure to hydrogen environment can be used as a parameter that defines the degree of activation of this material. The availability of interrelation between the change in the resistivity of thin "dense" films and hydrogen adsorption kinetics was repeatedly noticed earlier [12, 13].

In our experiments the start time of the activation of nonporous $(V, 10Ti)N_xH_y$ films was recorded by a change in their resistivity after their heating up to 400 °C and hydrogen injection up to 0.8 MPa. The purpose of this experiment was to remove nitrogen (oxygen) molecules from the intergranular boundaries and replace them with hydrogen molecules.

Fig. 2 shows the change in the value of specific resistivity of $(V, 10Ti)N_xH_y$ films during their annealing and injection of hydrogen into the chamber. It can be seen that an increase in the annealing temperature results in a slight decrease in the specific resistivity (negative temperature coefficient of resistance). During the injection of hydrogen at 400 °C up to the pressure of 0.8 MPa an insignificant increase in resistance is

observed. At a pressure of 0.8 MPa a stepwise more than 10^2 times increase in resistance is observed. During further cooling of the sample its resistance is reduced to the initial value. At the repeated annealing a decrease in resistance occurs only up to a temperature of 50 °C. Starting from this temperature value a sequential increase in resistance is observed. At a temperature of 300 °C the specific resistance in films exceeds its initial value 10^5 times (not show on the Fig. 2).



Fig. 2. The changing in the value of specific resistivity of $(V, 10Ti)N_xH_y$ films during their annealing and injection of hydrogen into the chamber

After the activation (V, 10Ti)N_x films were saturated by hydrogen in the chamber preliminary evacuated to the pressure of $\sim 10^{-5}$ mm Hg, at 200 °C and a pressure of 0.5 MPa (1 hour).

2. RESEARCH RESULTS 2.1. HYDROGEN DESORPTION

To study the hydrogen desorption we fabricated special stand that represents a system of two vacuum chambers separated from each other by the valve whose volumes are correlated as 1:10. The chamber of a smaller size was used for the saturation of specimens with hydrogen, and also for annealing and resistivity measurement. While studying the hydrogen desorption the valve between the chambers was opened and both of them were evacuated to the pressure not worse than 10⁻⁴ mm Hg. After that the valve connecting both chambers with the high-vacuum pump was closed and the specimens were exposed to annealing. The amount of hydrogen released during the annealing was recorded with a change in pressure, which, in its turn, was measured by the vacuum sensor. A total volume of chambers and film mass were selected so as to ensure the harmony of the entire pressure range measured by the sensor, in terms of the number of hydrogen molecules, with the hydrogen weight percentage range of 0.5 to 10.

Fig. 3 (curve 1) gives the released hydrogen amount versus annealing temperature curve. It is seen that the hydrogen desorption starts already at 30 °C. At 200 °C the number of the molecules of the desorbed hydrogen reaches $1.5 \cdot 10^{19}$ H₂ (3.5 wt.%). A further increase in temperature results in the marked increase in hydrogen release rate (3.5 wt.%). On reaching 250 °C the total mass of the released hydrogen exceeds 7 wt.%.

While cooling the specimen (curve 2) a decrease in pressure inside the working chamber is observed starting from 130 °C, which is indicative of that the portion of released hydrogen is readsorbed by the (V, 10Ti)N_x film. Total decrease in pressure inside the chamber during cooling to 20 °C corresponds to the absorption of $8 \cdot 10^{18}$ hydrogen molecules, which corresponds to 2 wt.% H₂.



Fig. 3. The relationship of the change in the amount of hydrogen in the annealing chamber during heating (1) and cooling (2) of the (V, 10Ti)N_xH_y film. The repeated heating (3) and cooling (4)

To prove this statement we exposed the films to repeated annealing. Fig. 3 (curve 3, 4) shows the change in the pressure in the annealing chamber during the repeated heating and cooling of the films. It can be seen that the amount of released hydrogen is close to the value of 2 wt.%. During the cooling the film reabsorbs hydrogen.

It should be noted that during the repeated cooling of the films (without previous hydrogen saturation) hydrogen absorption in amount of 2 wt.% takes place at a total pressure in the chamber not more than $2 \cdot 10^{-1}$ mm Hg. The adsorption of hydrogen in such amount at such a low pressure can be indicative of that the film surface and the system of intergranular channels and pores have not been "poisoned" by oxygen-containing molecules. At such conditions the absorption of molecular hydrogen by open intergranular porosity can occur at partial hydrogen pressures lower than $2 \cdot 10^{-1}$ mm Hg.

2.2. RESISTIVITY

Taking into consideration uncommon structure state of hydrogen storages based on complex vanadium hydride the change of such parameter as the resistivity value during heating can provide additional information about the gas release kinetics. For the multicomponent materials the polycrystalline-to-nanocrystalline state transition is usually accompanied by a decrease in the value of the temperature coefficient of resistance (TCR). The availability of intergranular pores in such a structure results in the origination of a tunneling conduction mechanism and as a consequence TCR changes its positive sign for negative. In nanocrystalline VN_xH_y materials interganular boundaries and nanopores absorb and release hydrogen in large amounts. The resistivity value of such a material can be a function not only of the grain size and pores but also of the amount of gas adsorbed by the pores.

The resistance of the complex hydrides studied in the paper [7] was within $(4 \cdot 10^3 \pm 200) \mu\Omega \cdot cm$, which is much higher in comparison with that of a powder material (85 $\mu\Omega \cdot cm$). TCR has a negative value equal to $-(2...3) \cdot 10^{-4}$ degrees⁻¹ in the temperature range up to 600 °C. During the hydrogen saturation of the material the resistance increased to $(6.5...7.0) \cdot 10^3 \mu\Omega \cdot cm$, and during the annealing at a temperature of up to 500 °C a decrease in resistance ([7], Fig. 5) was observed. The authors arrived at a conclusion that hydrogen is absorbed by the pores and it also forms a hydride phase. During the annealing hydrogen is released only from the pores. The occupancy of the pores with nitrogen is not changed.

A decrease in the grain size and pore diameter in the $(V, 10Ti)N_x$ films that were investigated in this paper the resulted in resistivity increase up to $(5...6) \cdot 10^4 \,\mu\Omega \cdot cm$ and TCR decreased to $(3...4) \cdot 10^{-5}$ degrees⁻¹. In addition, the film resistance versus annealing temperature curve of hydrogen absorbed (200 °C, 0.5 MPa, 1 hour) films has also changed (Fig. 4). (Resistivity and hydrogen pressure were measured simultaneously during the annealing).



Fig. 4. The change in the $(V, 10Ti)N_xH_y$ film resistivity during its heating and cooling

The Figure shows that the negative sign of TCR exists only until the temperature of ~40 °C. In the temperature range of 40 to 150 °C approximately a two-fold increase in resistivity is observed. A further increase in temperature resulted in giant resistivity jumps. At 300 °C the resistivity of the (V, 10Ti)N_xH_y film exceeded the value of $10^5 \Omega$ ·cm. During the specimen cooling the resistance practically acquires its initial value. We can explain this by the adsorption of hydrogen from the chamber volume.

The increasing of the resistivity of the $(V, 10Ti)N_xH_y$ film is correlated with increasing of hydrogen desorption (see Fig. 3). From our point of view it is indicated that an increase in the annealing temperature results in the complete evacuation of hydrogen from the intergranular boundaries and pores. As a result, the space between the grains becomes practically impassable for conductivity electrons, which results in the giant increase in the resistivity. During the cooling the conduction of the (V, 10Ti)N_xH_y film is virtually restored due to the reverse hydrogen absorption from the chamber.

3. DISCUSSING OF THE RESULTS

Thin-film structures based on vanadium complex hydrides are not just porous or "bulk". In spite of the fact that heir density is very close to that of the bulk vanadium nitride $(4.5...5.0 \text{ g/cm}^3)$ the level of porosity reaches 30% and the specific area of the pore surface reaches $15...2 \text{ m}^2/\text{g}$. This is possible due to the fact that the materials used by us combine small grain size with a high density of intergranular pores. The density of such pores exceeds 10^{18} cm^{-3} . Actually all intergranular joints contain pores.

The configuration of intergranular pores in our film structures is not just a system of voids that directly traverse each other (it is peculiar for metal-&-organic and carbon film structures). In our case the pores are relatively long (~ 10 nm) interconnected by intergranular boundaries, whose width does not exceed 1 nm. This value is very closely related to the most optimal (0.6 nm) design size at which hydrogen will be retained in its molecular state [14]. The availability of such branched pore system connected by narrow and long channels provides fast delivery of molecular hydrogen to the film volume and its retention at room temperature.

The next stage, i.e. when the pores and intergranular boundaries turn out to be filled with molecular hydrogen, originates the second step of hydrogen adsorption. The dissociation of hydrogen molecules, the diffusion of atomic hydrogen and the formation of hydride phase VN_xH_y occur at the pore-grain boundaries. Thanks to the small grain size this process passes rather quickly and at low pressures.

It is known [4] that the stability of such complex hydrides as VNH₂ and TiNH₂ is rather high (142 and 121 kJ/mole) therefore the hydrogen desorption can hardly be expected in that temperature range, in which it occurs in our experiments. In addition the coefficient of hydrogen diffusion in such nitrides of stochiometric composition is very low. However, these statements are related to polycrystalline structures. When the grain size is 20 to 25 nm the thermodynamically balanced concentration of vacancies in the major portion of the volume of grains is much higher than that in "bulk" materials [15]. Therefore, the structures of such nanocrystalline films are far from being stochiometric. The availability of a large amount of vacancies that are not filled with nitrogen atoms provides a high coefficient of hydrogen diffusion at relatively low temperatures; this can explain a good kinetics of its adsorption and desorption.

In addition some scientific papers show that vacant positions in nitrides/carbides on sites that contain no nitrogen/carbon atoms can retain up to 4 hydrogen atoms. That is, a high equilibrium concentration of vacancies in the nanocrystalline grains of vanadium/titanium nitrides provides not only an optimal kinetics of hydrogen adsorption, but also high gravimetric characteristics of such film structures.

Thus, the combination of the developed system of open intergranular nanoporosity with nanocrystalline grains of nonstoichiometric vanadium/titanium nitrides should provide acceptable thermodynamic, kinetic and gravimetric characteristics for the materials of such a kind. Hydrogen will be retained both in the form of molecules and in hydride phase.

CONCLUSIONS

The results given in this paper show that the use of IBAD allows not only for the controlled formation of nanoporosity with prescribed parameters but also for the embedment of this nanoporosity into the nanocrystalline structure of a matrix. The material produced in such a way is capable of accumulating hydrogen at low pressures and room temperature in amounts required for practical use. The availability of narrow channels in the form of grain boundaries provides high diffusion mobility, which allows hydrogen to accumulate and release from the material within a short period of time and also creates conditions for the retention of molecular hydrogen in the pores at room temperature. Varying the basic parameters of the ion beam-assisted process and first of all its radiation component it is possible to produce nanocrystalline porous structures in which the grain size can be both higher and lower than the pore diameter. Just the wanted relationship between the sizes of these elements of the crystalline structure will allow for the fabrication of solid-state hydrogen storages with appropriate characteristics.

REFERENCES

1. J. Kleiner, E. Sevilla, R. Cotts. Diffusion of hydrogen in α -VH_x // *Phys. Rev. B.* 1986, v. 33, p. 6662.

2. Y. Fukai, S. Kasama. Nmr studies of anomalous diffusion of hydrogen and phase transition in vanadium-hydrogen alloys // *Acta Metall*. 1977, v. 25, p. 59-70.

3. S. Orimo, F. Kimmerle, G. Majer. Hydrogen in nanosrtuctured vanadium-hydrogen systems // *Phys. Rev. B.* 2001, v. 63, p. 094307-10.

4. S. Kapellos, A. Mavridis, J. Harrison. Electronic structure of transition-metal amide ions ⁺TiNH₂, ⁺VNH₂, ⁺CrNH₂, and ⁺MnNH₂ // *J. Phys. Chem.* 1991, v. 95, p. 6860-6865.

5. A. Gringoz, N. Glandut, S. Valette. Electrochemical hydrogen storage in $TiC_{0.6}$ not in $TiC_{0.9}$ // *Electrochemistry Communications.* 2009, v. 11, issue 10, p. 2044-2047.

6. H. Ding, X. Fan, X. Li, et al. First-principles study of hydrogen storage in non-stoichiometric TiC_x // J. of Alloys & Comp. 2013, v. 551, p. 67-71.

7. V. Bryk, R. Vasylenko, A. Goncharov, et al. Formation Mechanism, Structural and Adsorption Characteristics of Microporous Nonacrystalline (V,Ti)-N-He Thin Film Composites // Surface: X-ray, Synchrotron and Neutron Investigations. 2011, v. 6, p. 66-75.

8. A. Goncharov, A. Guglya, E. Melnikova. On the feasibility of developing hydrogen storages capable of adsorption hydrogen both in its molecular and atomic states // *J. of Hydrogen Energy*. 2012, v. 37, p. 18061-18073.

9. J.J. Reilly, R.H. Wiswall. The higher hydrides of vanadium and niobium // *Inorganic Chemistry*. 1970, v. 9, N 7, p. 1678-1682.

10. J.F. Lynch, J.J. Reilly, F. Millot. The absorption of hydrogen by binary vanadium-chromium alloys // J. *Phys. Chem. Solids.* 1978, v. 39, p. 883-890.

11. D. Plante, C. Raufast, S. Miraglia, et al. Improvement of hydrogen sorption properties of compounds based on vanadium "bcc" alloys by mean of intergranular phase development // J. of Alloys& Compounds. 2013, v. 580, p. S192-S196.

12. A. Kagawa. Absorption of hydrogen by vanadium-titanium alloys // *Reports of the faculty of engineering, Nagasaki University.* 1995, v. 25, N 45, p. 233-239.

13. G. Andersson, K. Aits, B. Hjorvarsson. Hydrogen uptake of thin epitaxial vanadium (001) films // J. of Alloys & Compounds. 2002, v. 334, p. 14-19.

14. I. Carbia, M. Lopez, J. Alonso. The optimum average nanopore size hygrogen storage in carbon nanoporous materials // *Carbon*. 2007, v. 45, p. 2649.

15. N. Gladkikh, S. Durakov, A. Kryshtal, et al. *Poverhnostnie yavleniya i fazoviye prevratsheniya v kondensirovannih plenkah*. Kharkov: V.N. Karazin Kharkiv National University, 2004. 286 p. (in Russian).

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ТОНКОПЛЕНОЧНЫЕ НАНОПОРИСТЫЕ (V, 10Ті)N_xH_y-НАКОПИТЕЛИ ВОДОРОДА А.Г. Гугля, Ю.А. Марченко, Е.С. Мельникова, В.В. Власов, Е.Н. Зубарев

Приведены результаты исследований адсорбционных и электрофизических характеристик нанопористых пленок (V, 10 ат.% Ti)N_x, полученных с применением технологии ионно-стимулированного осаждения. Использование данной технологии позволило получить нанокристаллическую структуру, межзеренное пространство в которой заполнено порами размером менее 6 нм. Показано, что при относительно низком давлении (0,5 МПа) такие объекты могут аккумулировать более 7 вес.% водорода. Одна часть его накапливается в межзеренных границах и порах, другая часть – в виде гидридной фазы. Полное выделение водорода происходит при температуре 250 °C. В процессе десорбции водорода удельное электросопротивление (V, 10Ti)N_xH_y-пленок увеличивается примерно в 10⁷ раз.

ТОНКОПЛІВКОВІ НАНОПОРОВІ (V, 10Ті)N_xH_y-накопичувателі водню

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Приведено дані досліджень адсорбційних та електрофізичних характеристик (V, 10 ат.% Ti)N_x нанопорових плівок, здобутих за допомогою технології іонно-стимульованого осадження. Використання даної технології дозволило створити нанокристалічну структуру, міжзеренних простір в якій заповнений порами розміром не більше 6 нм. Виявлено, що при відносно низькому тиску (0,5 МПа) такі об'єкти можуть акумулювати більш ніж 7 ваг.% водню. Одна його частина накопичується у міжзеренному просторі, а інша – у вигляді гідридної фази. Повне виділення водню має місце при температурі 250 °C. У процесі десорбції водню питомий електроопір (V, 10Ti)N_xH_y-плівок збільшується приблизно у 10⁷ разів.