

Nano crystalline porous thin film hydrogen storages

Abstract

The results of high-resolution transmission electron microscopy revealed that TiN_x and VN_x films consist of 150-200 nm particles, which boundaries contain nano-pores of 10-15 nm diameters. Particles themselves consist from randomly oriented 10-20 nm nano-grains. Examination of the absorption characteristics of VN_x and TiN_x films showed that the amount of absorbed hydrogen depends very little on the chemical composition of films, but it is determined by pore structure. The amount of absorbed hydrogen at 0.3 MPa and 20°C is 6-7 wt.%, whereas, the bulk of the hydrogen is accumulated in the grain boundaries and pores.

Keywords: Nano grains, Hydrogen, Equilibrium, Nitrogen

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Introduction

Vanadium and titanium hydrides are deemed to be promising as solid state hydrogen storages. V-H system includes the following phases: α - solid solution; β -($VH_{0.45}$ - $VH_{0.95}$) with body-centered tetragonal lattice (bct) and γ - VH_2 with fcc lattice. There are three phases in Ti-H system also: α -solid solution; β -($TiH_{0.5}$ - $TiH_{0.9}$) with bcc-lattice and δ - TiH_2 with fcc-lattice. The total mass of stored hydrogen in γ - VH_2 approaches value of 2.1 wt.%. δ - TiH_2 absorbs 4.0 wt.% H_2 . Therefore, the amount of absorbed hydrogen atoms comes to be 11.2 in VH_2 is and 9.1 in TiH_2 (at/cm³, x10²²). In order to meet the U.S. Department of Energy (DOE) requirements .¹ (gravimetric capacitance: >5.4wt%; hydrogen release temperature range: < 85°C; the time period required to achieve the maximum hydrogen flux: 4 seconds; the equilibrium pressure: < 0.4 MPa), it is necessary to solve several challenging problems:

- To increase the thermodynamic stability of γ - VH_2 (to reduce the thermodynamic stability of δ - TiH_2). Decision: to form more "dense" VN fcc-lattice instead of "loose" bcc-vanadium lattice, and TiN fcc-lattice instead of hcp-titanium lattice.
- To develop such vanadium and titanium hydride structures that would ensure high diffusion mobility of hydrogen at its accumulation and, in particular, its release. Decision: to create nanocrystalline VN and TiN nitrides.
- To increase the gravimetric capacity by forming additional traps in VH_2 and TiH_2 hydrides to retain hydrogen at low pressure and temperature. Decision: to create a nanocrystalline structure, which will have the opportunity to store hydrogen not only in atomic but in molecular state - nanocrystalline porous structure.

Nanocrystalline TiN_x and VN_x porous thin films were obtained by evaporation of titanium and vanadium (99, 98%) at the simultaneous irradiation by a mixed beam of helium and nitrogen ions ($N_2^+/He^+=1$) with energy of 30 keV (research facility Argo-1 .²). A total pressure of nitrogen and helium in the chamber of Argo-1 equals to $1.5 - 2.0 \cdot 10^{-3}$ Pa. Under the same pressure, the nitrogen molecules and helium atoms are absorbed by the substrate surface continuously and simultaneously with the metal vapor deposition. When ion bombardment has occurred, the partial dissociation of nitrogen molecules on the film surface took place. The ion source and electron-beam evaporators in the Argo-1 are located on the lower flange of the camera. With this configuration, the gas ions beam and the flux of evaporated metal atoms are combined in space during the entire

IBAD process. We assume that the partial dissociation of accelerated nitrogen molecules directly in the chamber volume is possible during their collisions with vanadium atoms also. There would be continuous chemisorption of the nitrogen atoms and vanadium/titanium nitride formation on the substrate surface.

It is known that the path depth of ions with an energy of several tens keV in the solid body crystal lattice is 50-100 nm. This means that during the film growth there is a change of the crystal structure of material at a depth of 50-100 nm as compared to the structure that formed in its infancy. In particular, there is an increase in the concentration of interstitial gas impurities. Part of gas molecules will condense at the grain boundaries forming the system of gas-filled pores that are preventing the grain boundaries densification. Such pores combined by the grain boundaries create an open pore structure, which can be used for storing hydrogen in large quantities.

Structure of TiN_x and VN_x films.

Figure 1 shows SEM images of TiN_x and VN_x films deposited on sapphire substrates.. It can be seen that film structure consists of particles with a diameter of 150-250 nm. TEM investigation showed .³ that the particles are not homogeneous formations and consist of nano grains. The boundaries are loose; and the connections of 3-4 particles contain pores of 5-10 nm in size.

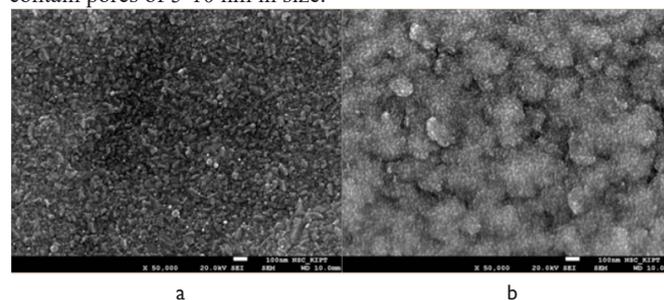


Figure 1 The structure of the surface TiN_x (a) and VN_x (b) film.

Hydrogen absorption

Figure 2 shows the results of hydrogen absorption for VN_x and TiN_x films. The data on hydrogen absorption by vanadium and titanium taken from .⁴⁻⁶ are also presented in this figure to compare. The values of hydrogen absorption are very high in spite of a small specific film surface. The specific surface measured according to the BET method was 12.4 m²/g for TiN_x and 13.2 m²/g for VN_x .

The shapes of the hydrogen absorption isotherms are similar for all samples. For both films at pressures of 0.1-0.15 MPa, bends in the curves are observed; they are more visible for TiN_x films while the temperature increases. This may be due to the successive filling of traps of various activities by hydrogen and penetration of hydrogen into the grains.

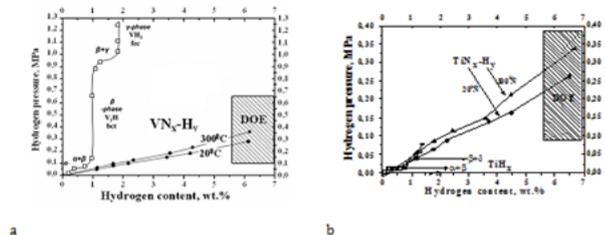


Figure 2 Pressure-concentration dependences for (a) $\text{VN}_x\text{-H}_2$ and (b) $\text{TiN}_x\text{-H}_2$ films.

Pressure-concentration diagrams for hydride VH_x ⁴ and TiH_x ^{5,6} DOE requirements are shown for comparisons.

Discussion

The interpretation of obtained results is difficult because the physical and chemical adsorptions can be involved in the process of hydrogen uptaking by $(\text{V}, \text{Ti})\text{N}_x$ films. Physical adsorption is related to uptake of hydrogen by porous structure and it decreases usually with an increase in temperature. This dependence is typical for all films; and this fact makes it possible to state that the hydrogen capture occurs mainly in pores. Chemical adsorption can be related to formation of hydrides and amides MeNH and must become more intense with temperature increase. Vanadium hydride decomposes at 200°C, and titanium hydride TiH_2 is stable in the interval of experimental temperatures.⁷ Nevertheless, the isotherms for VN_x and TiN_x films are almost the same confirming the insignificant role of metal-nitrogen hydrides in hydrogen uptaking.

Conclusion

The results of our studies have shown that V and Ti deposition at bombardment by high-energy N and He ions leads to formation of nanostructured nitrides, the intergrain spaces in which are occupied by

pores. The presence of two components in the ion beam, the difference between the distributions of ion energy losses, and the implantation of gas atoms during the process of metal deposition are factors that determine the formation mechanism for material structure and pores. Unlike plasma and thermal deposition, the process of grain nucleation is not finished after the metal condensation and nitride formation; it has the stage of partial destruction of the primary structure with nucleation of the next population of grains, growth of the grains, and formation of a solid film. The progressive filling process of substrate surface leads to formation of cavities in the film volume; they have different hydrogen adsorption capacities and different heats of their adsorption.

Acknowledgments

None.

Conflicts of interest

None.

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