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Early evaluation of hydrogen isotopes separation by V4Cr4Ti-based sorbents at low temperatures

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ABSTRACT

This paper presents the results of experiments on hydrogen isotopes sorption with V4Cr4Ti vanadium alloys from a mixture of hydrogen isotopes. The studies were carried out at temperatures of 353 K, 393 K, 423 K; and pressures of 10^3–10^4 Pa in gas mixture of hydrogen isotopes. The α-phase domain of V-H (D) system was studied, where the concentration of hydrogen isotopes atoms should not exceed 0.015H (D) atoms per metal atom. The separation parameters were derived for several saturation conditions accordingly to registered time dependences of hydrogen isotopes partial pressure drop.

The conclusion was made about the prospects of using vanadium alloys in hydrogen isotopes separation and purification systems.

1. Introduction

It looks promising to use vanadium alloys for of hydrogen isotopes separation in hydrogen systems. The fact is that vanadium has unique property with respect to hydrogen: protium atoms usually occupy the bcc lattice of vanadium octahedral interstices, while the deuterium occupies mainly tetrahedral interstices [1–3]. All that considerably affects the pattern of diffusivity and solubility of hydrogen isotopes in vanadium. It was concluded from V-H and V-D phase diagrams [1] that the temperature of vanadium deuteride decomposition is about 373 K, while for vanadium hydride it is more than 473 K (for H/V and D/V concentration ratios equal to about 0.5).

All that allows to create a system in which mainly deuterium will be absorbed from hydrogen isotopes mixture (at saturation temperatures above 393 K). It can be assumed that such systems will operate with high separation efficiency. The equilibrium solubility of hydrogen (deuterium) in vanadium hydride (deuteride) is more than 100 times higher than the equilibrium solubility of hydrogen (deuterium) in α-phase of V-H (V-D) system (for saturation temperature of 473 K and for saturation pressure of about 10^3 Pa). [4]

Today many studies on characterization of hydrogen isotopes interaction with vanadium alloys have been carried out (for example [5–8]). However, almost all these experiments were conducted with a single hydrogen isotope only, while the presence of gaseous hydrogen isotopes mixture can influence the kinetics of absorption. In the paper the sorption characteristics of V4Cr4Ti vanadium alloy were examined with various mixtures of hydrogen isotopes.

2. Experimental part

2.1. Material and methods

The samples of V4Ti4Cr vanadium alloy sized 1 × 20 × 25 mm were investigated.

Investigations were conducted on the experimental setup, which scheme is shown in Fig. 1.

The setup is designed for investigation of sorption and desorption processes within temperature range from 29 3 K to 1173 K with online mass-analysis of gas composition in the chamber with sample (sample holder). The setup consists of:

- sample holder (CV4) with a tested sample, ohmic heater and K-type thermocouple;

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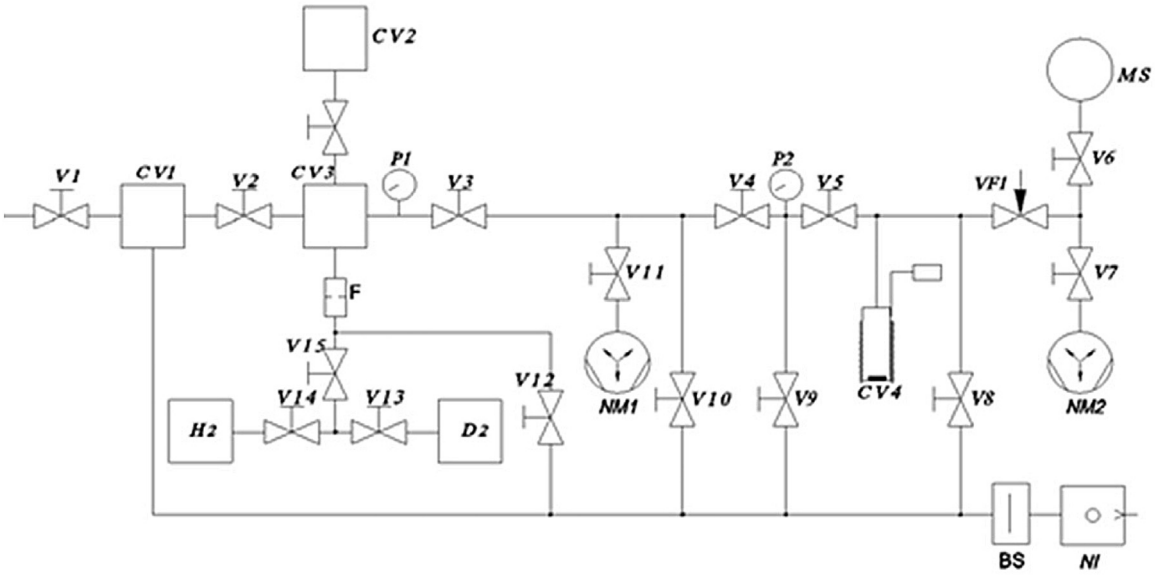

Fig. 1. Diagram of set-up for studying of hydrogen sorption properties. CV1-CV3 vacuum chambers for gas mixturing; CV4 sample holder with tested sample; P1, P2 deformation type pressure gages; MS quadrupole mass spectrometer; F hydrogen Pd-Ag filter; NM1, NM2 ion high-vacuum pump; BS liquid nitrogen trap; NI vacuum fore pump, V1-V15 vacuum valves.

- vacuum chamber of quadrupole mass-analyzer (MS), connected with CV4 via leak valve (VF1);
- pumping system (NM1, NM2, BS, II), where ion pumps provide a high vacuum in sample holder and in the measuring part of experimental setup, while the mechanical fore-pump provides initial vacuum;
- pressure monitoring systems (P1, P2) based on two pressure gauges of deformation type;
- hydrogen gas purification system based on palladium-silver filter (F);
- gas mixture preparation systems (CM1, CM2, CM3).

The analog signals of mass spectrometer and pressure sensors are digitized and pathed to PC for processing and storage. Computer also controls the temperature and rate of sample heating using a high-precision temperature controller.

Experiments were carried out after the sample surface cleaning by oxidizing and reducing oxides on surface. The applied technique of samples cleaning was elaborated experimentally and performed as follows:

- sample in sample holder was annealed at temperature of 973 K in oil-free vacuum using ohmic heater;
- system was cooled down to room temperature;
- the sample holder was filled with 400 Pa of oxygen and heated up to T = 873 K with 2 h exposure;
- oxygen was pumped out from sample holder, holder and sample were annealed 2 h at T = 973 K;
- the sample holder was filled with hydrogen at T = 973 K (P = 260 Pa) and kept in such condition for next 2 h;
- the gaseous content was pumped out from sample holder and it was refilled with fresh portion of hydrogen (at T = 973 K, P = 260 Pa);
- sample was cooled down in hydrogen till the T = 293 K, when hydrogen was pumped out from sample holder;
- the sample was degassed from hydrogen at 973 K and cooled down.

Experiments on vanadium alloy saturation with hydrogen were carried out using so-called integral method: the sample inside sample holder was set to needed temperature of saturation and then the holder was filled with controlled amount of hydrogen-deuterium mixture so starting the saturation process. During the sample saturation the pressure change and gas composition were monitored by computer software.

The sample saturations were carried out sequentially at gradually increasing pressures of hydrogen-deuterium gas mixture. Upon completion of a series of experiments of sample charging at one temperature, the mixture was pumped out and sample degassed several hours at 973 K under continuous pump-out of sample holder. Then a new series of experiments was conducted at other saturation temperature.

The main conditions and parameters of conducted studies were:

The saturation pressures of hydrogen and deuterium in mixture: 10^2-10^4 Pa;

Saturation temperatures: 353 K, 393 K, 423 K;

Number of saturation cycles at one temperature: 3–5;

2.2. Results and discussion

Fig. 2 shows the typical sorption dependences of pressure change in chamber with samples of vanadium alloy: the overall view of experiment diagram and reduced dependences of pressure change in sample holder with V4Ti4Cr sample at a temperature of 423 K are shown.

In a series of experiments it was found that:

- the absorption rate is different for different hydrogen isotopes; for each certain level of pressure the following inequality is fulfilled: $dP_{H2}/dt > dP_{HD}/dt > dP_{D2}/dt$;
- dependences of hydrogen isotopes pressure drop in chamber can be well-described by a second order polynomial: $P(t)=at^2 + bt + c$;
- dependences of gas release from a sample while it is degassed after saturation show a fast release of hydrogen, then the yield of HD molecules follows and then follows the latest yield of deuterium molecules (see Fig. 3).

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