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Applications of Zr–V hydrogen getters in vacuum-plasma devices: Phase-structural and hydrogen sorption characteristics

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Abstract

The paper considers materials science aspects of the applications of the reversible hydrogen getters in vacuum-plasma devices. The selection of hydrogen getter material, which is located in the vacuum chamber of the installation, is based on a convenience of switching of its functions from the "internal" source of hydrogen supply to the mode of control over the hydrogen pressure by chemically "pumping" hydrogen from the volume into the getter. The energy of plasma particles bombarding the surface of the material allows controlling the supply of the plasma-forming gas (hydrogen).

The arc-melted ZrV alloy modified by small amounts of oxygen was used as getter material. Hydrogen sorption characteristics of the alloy were studied in the Sieverts-type setup. The hydrides were characterised by vacuum Thermal Desorption Spectroscopy. X-ray diffraction was employed to study phase-structural composition of the getter and its hydride.

A technology of the production of the MH elements for vacuum-plasma installations has been developed. The MH elements on the basis of the H-saturated ZrV(O) alloy have shown a resistance against sputtering during their bombardment by high-energy particles in vacuum.

Keywords: Hydrogen storage materials; Gas–solid reactions; Electrode materials; X-ray diffraction; Thermal analysis

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1. Introduction

An interesting field of the applications of metal hydrides (MH) comprises vacuum-plasma technologies where hydrogen isotopes are used as working medium. MH allow not only to create the compact and technologically flexible gas supply systems, but, also, to substantially increase the efficiency of the installation in total [1,2]. This advantage is most clear for the so-called "internal" gas supply systems for hydrogen isotopes using "high-temperature" MH. They are directly placed into a vacuum chamber of the installation and provide both the evacuation of the chamber and the supply of a plasma-forming hydrogen gas. By introducing a MH material into the electrodes of the plasma-forming system, the possibility to effectively control these processes appears [3].

Reversible hydrogen getters on the basis of Zr–V alloys are now used as working materials for these systems. Their hydrogen sorption characteristics fit well into the required pressure and temperature ranges for the electro-physical installations [1–3].

Among Zr–V getter materials, the alloys containing α-Zr, C15-ZrV_2, and η-Zr_3V_3X phases are of special interest.

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The latter are formed by the modification of the alloy with non-metal component, X = O, B, N [4,5]. These alloys have improved hydrogen sorption characteristics including dynamics of sorption of low-pressure hydrogen. Recently intensive studies of these materials, especially focused on the relationship between their structure and hydrogen sorption properties, have been carried out [6–8]. However, several details, important from the application point of view, remain unclear: first of all, the issue of the reproducibility of the performances of these material used as getters, which are made in industrial conditions from materials with technical-grade purity; secondly, the issue of the characteristics of hydrogen desorption into vacuum as well as of the possible sputtering of the getter constituents, depending on the H content. The question about the stability of these performances under hard operating conditions (bombardment with high-energy particles in vacuum that usually results in sputtering, even for refractory metals, like tungsten) also remains unanswered yet.

This work is devoted to the application of the reversible hydrogen getters formed by the equiatomic ZrV alloys modified by traces of oxygen, in vacuum-plasma installations. The paper describes the experimental study of material aspects of the problem, including the preparation of starting alloy, its structure and hydrogen sorption properties, vacuum thermodesorption of hydrogen, as well as making and preliminary testing of the MH elements for vacuum-plasma installations.

2. Experimental

The as-cast equiatomic ZrV starting alloy (weight ∼ 100 g) was prepared in an arc furnace under the purified argon. An estimated content of oxygen impurity in the alloy introduced from the vanadium metal was 0.1–0.5 wt.%. The alloy and the product of its hydrogenation were studied by the XRD technique, Siemens D5000 diffractometer, Cu Kα radiation, 2θ range 10–90°, step 0.015°. The theoretical patterns of the constituent phases were simulated by Powder Cell software and analysed using the reference structural data [4,9,10].

Hydrogen sorption characteristics were measured in the Sieverts-type setup. A sample of the starting alloy (pieces 1–5 mm in size, the weight was varied within 0.5–20 g) was activated by heating to 250–300 °C in vacuum during 1 h, followed by the saturation with hydrogen at the starting pressure up to 10 bar and room temperature. The product of hydrogenation was grinded in argon atmosphere to fine powder (grain size less than 50 μ). Part of the powder ($m \sim 0.5$ g) was loaded into the setup to measure TDS ($T = 20$–850 °C, heating rate 6 °C/min) and followed by measurements of the characteristics of the consequent hydriding. Another part was used to make the metal-hydride elements to be accommodated in the vacuum plasma installations.

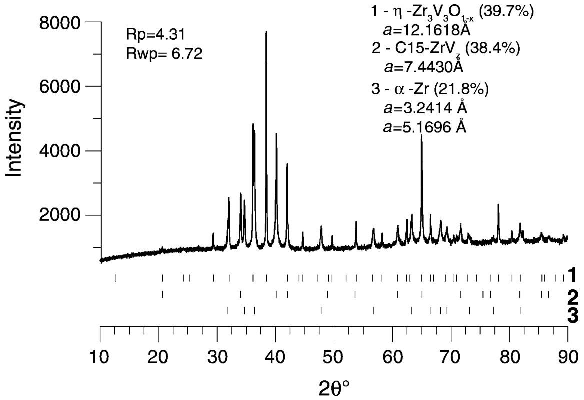

Fig. 1. XRD pattern of the dehydrogenated sample ($T_{\max} = 850\,°C$; $P = 10^{-6}$ mbar).

3. Results and discussion

3.1. Phase-structural characteristics and H sorption properties

The XRD patterns of the alloys and their hydrides are presented in Figs. 1 and 2.

The alloy contains η-$Zr_3V_3O_{1-x}$ (structure type η_1-Fe_3W_3C) and, also the C15-ZrV_2 intermetallic Laves phase (structure type $MgCu_2$) together with α-Zr. The pattern of the dehydrided sample (Fig. 1) is identical to those for the starting alloy characterizing at the same time by a decreased background because of an essential annealing of the sample.

The product of hydrogenation (Fig. 2) contains the tetragonal ε-ZrH_x, C15-ZrV_2H_x (lattice volume expansion, compared to the starting alloy, $\Delta V/V_0 = 20.1\%$), as well as two hydrides of the η-phase having the lattice periods of 13.005 ($\Delta V/V_0 = 22.3\%$) and 12.715 Å ($\Delta V/V_0 = 14.3\%$). The intensities of the (3 3 3/1 1 5) lines of the η-hydrides are related as 1:1.4, respectively. Such a behaviour is similar to one observed for deuterides formed by η -$Zr_3V_3(B_2O_3)_xD_y$($x = 0.12$–0.2, $y = 8.0$–6.4) and can be explained by the partial

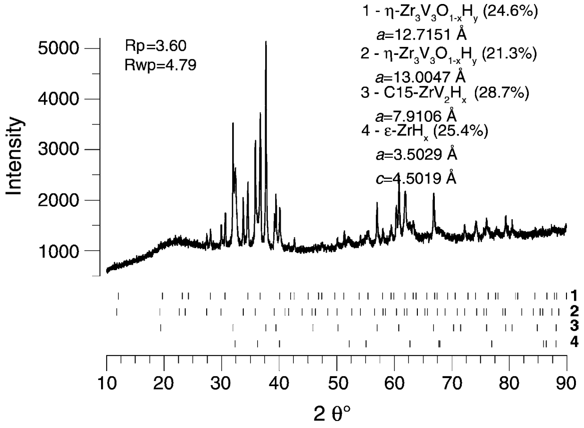

Fig. 2. XRD pattern of the hydrided sample ($T = 20\,°C$, $P = 10$ bar, $H/M = 1.49$).

redistribution of non-metallic atoms during hydrogenation that, in turn, results in the change of the set of interstitial sites available for hydrogen [7]. As it was estimated from the dependencies of lattice parameters of η -$Zr_3V_3O_xH_y$ on oxygen content (x) and H sorption capacity (y) [8], the compositions of the studied η-hydrides approximately correspond to the formulae $Zr_3V_3O_{0.7}H_{6.6}$ and $Zr_3V_3O_{0.4}H_{10.7}$.

The alloy intensively absorbs hydrogen gas already on the first hydrogenation cycle. It was completely saturated with H in 10–15 min. The repeated hydrogenation of the dehydrided sample completes for 90–95% in 1–2 min.

Hydrogen sorption capacity of the alloy at room temperature slightly depends on a final hydrogen pressure decreasing from $H/M = 1.49$ (234.5 cm^3/g) at $P = 10$ bar to $H/M = 1.33$ (209.5 cm^3/g) at $P < 1$ bar.

The hydride having the maximum H concentration can be stabilised by exposition on air. The decomposition of air-exposed hydride begins at $T = 100\,^\circ C$ (Fig. 3a), while for the hydride prepared in situ hydrogen desorption occurs already at room temperature (Fig. 3b). Thermal decomposition of the H-saturated ZrV(O) alloy proceeds continuously between 20 and 650 °C and involves two stages. Below 400 °C (stage 1) approximately uniform gas evolution takes place leading to release of $\sim$ 40–50% of the total of absorbed hydrogen. The more intensive decomposition takes place at higher temperatures (stage 2) being characterised by linear increase of desorption rate with temperature, until a peak at $T = 590\,^\circ C$. Thermal desorption is completed at $T = 650\,^\circ C$. Reduction of the initial H content in the hydride increases the temperature of the start of gas evolution. The low-temperature stage vanishes at $(H/M)_0 < 0.65$ (Fig. 3d and e).

The observed TDS behaviour correlates with one observed for the hydrogenated η-oxyboride Zr_3V_3(B,O) [6]. As it has been shown [6], the amount of non-metallic additives in the η-phase strongly influences the thermal stability of its hydride, especially for the high-temperature peak. A comparison of our data (Fig. 3) with the dependence of high-temperature peak on (B,O) content in the η-phase presented in [6] allows to estimate that the amount of oxygen in η-phase in the studied ZrV(O) equiatomic alloy corresponds to the formula $Zr_3V_3O_{<0.5}$. It agrees well both with the estimated total oxygen content in the alloy, and with results of XRD studies (see above).

3.2. Development of the MH elements

The MH elements for vacuum-plasma installations were made of the composite material containing the hydrogen-saturated ZrV(O) alloy and 40–50% (as to the hydride weight) of copper powder (200 mesh). The hydride-copper powders were mixed and compacted, at room temperature and the pressure of 3–5 t/cm^2, into cylindrical pellets 20 mm in diameter and 4 mm in height. The total amount of hydrogen stored in the element was about 2.5 l H_2 STP. After complete hydrogen discharge, the elements could be completely saturated again, at room temperature and $P = 1$–4 bar H_2 during several hours. The working life of the MH element, without deterioration of its mechanical properties (destruction or cracking) depends on the number of recharges with hydrogen (not less than 10).

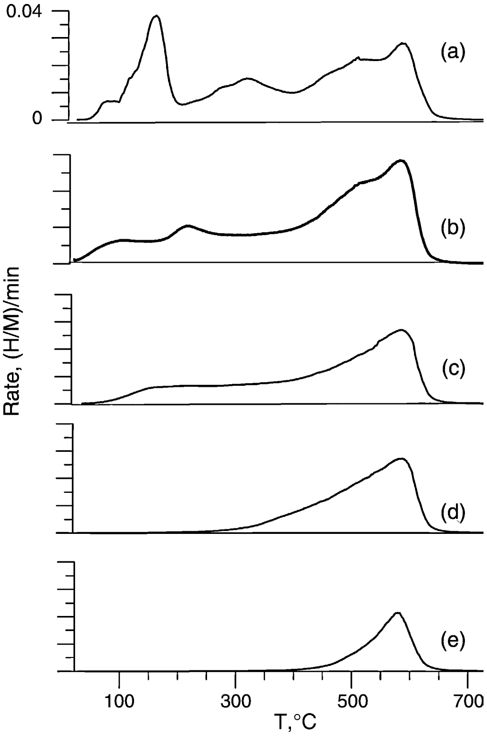

Fig. 3. Hydrogen thermodesorption curves: (a) $(H/M)_0 = 1.49$ (air-exposed hydride); (b) $(H/M)_0 = 1.33$; (c) $(H/M)_0 = 1.00$; (d) $(H/M)_0 = 0.65$; (e) $(H/M)_0 = 0.32$.

Fig. 4a presents the SEM image of the surface of the MH element. It has a porous structure (average pore size is 3.5–3.8 μ) where the particles of the H-saturated ZrV(O) alloy are distributed within the copper matrix.

One of the most specific features of the MH elements is their extremely high stability against sputtering under intensive bombardment with high-energy plasma particles. There was not observed a noticeable sputtering of MH cathodes made according to the procedure described above and operated for a long time in the Penning-like discharge cell. On the contrary, the cathodes made of copper or stainless steel and exposed to Penning discharge at similar conditions exhibited the sputtering, which could be easily detected as the deposition of cathode material onto a glass plate placed near the cathode. Moreover, even bombardment of the MH element with very intensive plasma flows resulting in surface melting of the sample (Fig. 4b) does not cause the significant sputtering of the sample and does not significantly change its phase composition [11].

Such a behaviour can be explained if one assumes that the energy of bombarding particles is mainly transferred to interstitial H atoms in the MH which are more light and mobile than the atoms of the metal matrix. This, in turn, causes hydrogen diffusion through the matrix to solid–gas interface where

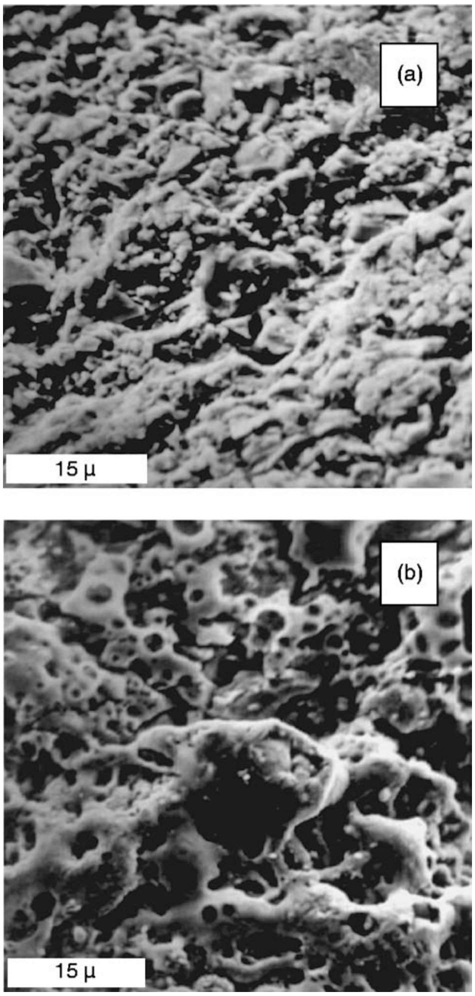

Fig. 4. SEM images of the surface of the MH element: (a) initial sample; (b) sample after plasma irradiation (2 keV N^+ ions, plasma density $2 \times 10^{14}\,cm^{-3}$, pulse duration 5 μs, and the incident energy flux up to $10\,MW/cm^2$).

hydrogen desorption occurs. As a result, instead of sputtering of metal atoms, the hydrogen desorption from the MH stimulated by ion bombardment takes place. More detailed consideration of this effect will be given elsewhere [12,13].

4. Conclusions

The phase composition, structure and hydrogen sorption properties of the equiatomic ZrV alloy modified by traces of oxygen and made at the semi-industrial conditions have been studied.

The thermal decomposition of the H-saturated ZrV(O) alloy in vacuum involves the uniform gas evolution at $T < 400\,^{\circ}C$ followed by the peak at $T = 400$–$650\,^{\circ}C$, maximum at $T = 590\,^{\circ}C$.

The technology of making functional MH elements for vacuum-plasma installations – compacted mixture of the powders of the hydrided alloy and copper – has been developed.

The MH elements on the basis of the H-saturated ZrV(O) alloy have shown to be stable against sputtering in the course of their bombarding with high-energy particles in vacuum.

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