

Absorption of Hydrogen by V–Mo and V–Mo–Ti Alloys

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Received April 17, 2013

Abstract—We have studied the interaction of hydrogen with V–Mo and V–Mo–Ti alloys. Hydrogen absorption and desorption isotherms have been measured, the stability ranges of the forming hydride phases have been determined, and the ΔH and ΔS of the reactions involved have been calculated. X-ray diffraction results indicate the formation of three hydride phases, with FCC and BCC structures.

Keywords: hydrogen, alloys, hydrides, high pressure, hydrogen storage

DOI: 10.1134/S2075113314010134

INTRODUCTION

Vanadium and its alloys that absorb up to 3.8 wt % of hydrogen are promising materials for its storage and transportation. However, both the hydrogenation conditions of alloys and the amounts of hydrogen evolved from the hydrides in a suitable temperature range limit their practical applications. In order to improve these characteristics, the interaction of hydrogen with both the variety of compositions and multicomponent vanadium alloys is actively studied [1–4]. At the same time, the absorption of hydrogen by binary vanadium alloys, including vanadium–molybdenum alloys, is studied rather poorly [5, 6]. The published results indicate that the doping of vanadium with molybdenum increases the dissociation pressure of the hydride phase; moreover, the synthesis of a composition that is close to the dihydridic one for the $V_{0.9}Mo_{0.1}$ alloy did not succeed in [7] at room temperature and hydrogen pressure up to 100 atm. The interaction of hydrogen with the V–Mo and V–Mo–Ti alloys in a wide range of pressures is investigated in this work.

It should also be noted that the vanadium alloys with molybdenum, titanium, and chromium are advanced structural materials for nuclear power reactors. In this connection, the results of studies on the behavior of this kind of alloys in a hydrogen atmosphere are important as well for developers of novel structural materials.

EXPERIMENTAL

The alloys were prepared by arc-melting the mixtures of pure metals in a water-cooled copper sole of an electric arc furnace with a nonconsumable tungsten electrode in an atmosphere of purified argon with a pressure range from 0.1 to 0.15 MPa. Homogenizing annealing was carried out at 1250°C for two hours in the argon atmosphere, and then the container with

samples was quenched in cold water. The X-ray patterns were obtained on a DRON-3M diffractometer (CuK_{α} radiation) with a graphite monochromator on the reflected X-ray beam. The diffraction patterns were refined by the Rietveld method using the Rietan 2000 software package [8]. Hydrogen-sorption properties of the alloys were investigated in a wide temperature range from -50 to $150^{\circ}C$ and pressure range from 0.01 to 3000 atm using the setup and procedure described in [9]. In order to stabilize the hydride phases obtained at high hydrogen pressures, a series of procedures were implemented. First, an autoclave with the sample saturated with hydrogen for 1 h was cooled down to the temperature of liquid nitrogen. Next, the hydrogen pressure over the sample was reduced to 2–5 atm, and then the autoclave was unscrewed and the cooled hydride was left in contact with air for 1.5–2 h in order to inhibit hydrogen recombination centers on the sample surface. After that, the hydride was transferred from the autoclave into a metal container cooled down to the temperature of liquid nitrogen. All the studied hydrides under these conditions were stable and non-pyrophoric. The hydrides were removed from liquid nitrogen right before the X-ray diffraction analysis. The thermodynamic functions, i.e., the enthalpy and entropy changes during the reaction of the alloys with hydrogen, were calculated from the Van't Hoff equation with the fugacity values corresponding to dissociation pressures of the hydrides at different temperatures over the activated samples after two or three cycles of hydrogen absorption and desorption. Hydrogen desorption was carried out under vacuum at 300 – $350^{\circ}C$ for 2–3 h.

RESULTS AND DISCUSSION

The results of X-ray diffraction analysis of the investigated alloys showed that all of them crystallize

Hydrogen absorption properties of the V–Mo and V–Mo–Ti alloys

Starting alloy	Lattice period, Å	Stable hydride, lattice period, Å	High-pressure hydride, lattice period, Å	Hydrogen content, wt %/pressure, atm	Reversible hydrogen capacity, wt %	$P_{\text{abs}}/P_{\text{des}}$, 23°C, atm	ΔH , kJ/mol H ₂ /ΔS, J/(K mol H ₂)
V [11, 12]	3.030	VH _{0.9} bct: $a = 6.04$. $c = 6.72$	VH _{2.1} fcc: 4.24	3.9/100	2.2	—	41.8/142
V _{0.95} Mo _{0.05} [7]	3.035	—	—	3.4	2.0	—	—
V _{0.8} Mo _{0.2}	3.0514 (2)	V _{0.8} Mo _{0.2} H _{0.5} bcc: 3.1444 (4)	V _{0.8} Mo _{0.2} H _{1.7} fcc: 4.3041 (3)	2.7/1400	1.95	1200/400	24.4/134.5
V _{0.75} Mo _{0.25}	3.0612 (1)	V _{0.75} Mo _{0.25} H _{0.5} bcc: 3.1126 (4)	V _{0.75} Mo _{0.25} H _{1.5} fcc: 4.2746 (2)	2.4/1400 at –50°C	1.5	—	18.2/145
Ti _{0.1} V _{0.75} Mo _{0.15}	3.0671 (3)	Ti _{0.1} V _{0.75} Mo _{0.15} H _{0.5} bcc: 3.1643 (4)	Ti _{0.1} V _{0.75} Mo _{0.15} H _{1.8} fcc: 4.2944 (2)	3.1/1430	2.1	140/18	31.2/129.7
Ti _{0.1} V _{0.7} Mo _{0.2}	3.0714 (5)	Ti _{0.1} V _{0.7} Mo _{0.2} H _{0.5} bcc: 3.1686 (1)	Ti _{0.1} V _{0.7} Mo _{0.2} H _{1.7} fcc: 4.2958 (3)	2.6/2350	1.8	520/130	27.3/133.4
Ti _{0.1} V _{0.65} Mo _{0.25}	3.0736 (6)	Ti _{0.1} V _{0.65} Mo _{0.25} H _{0.5} bcc: 3.1743 (4)	Ti _{0.1} V _{0.65} Mo _{0.25} H _{1.7} fcc: 4.2885 (5)	2.5/2490	1.4	960/300	22.1/123.3

in the cubic system with the bcc lattice (table). Binary V–Mo alloys are extremely malleable, and therefore the X-ray diffraction experiments were performed in this case on the appropriately prepared metallographic sections. On the contrary, ternary V–Mo–Ti alloys are pretty fragile and easily crushed. As seen from the data in the table, replacement of vanadium with molybdenum leads to an appropriate increase in the lattice parameters of alloys, which is consistent with the data reported in [10].

Upon carrying out the activation, it is established that considerable interaction of V_{0.8}Mo_{0.2} with hydrogen in the first cycle at room temperature starts at a pressure of about 100 atm. Hydrogen desorption isotherms for this sample after the activation are shown in Fig. 1a. As seen from Fig. 1, two regions can be distinguished in the hydrogen desorption isotherms. The first one at $H/M \leq 0.5$ corresponds to the stable hydride not releasing hydrogen in this temperature range. A plateau in the isotherms indicates the formation of hydride with high dissociation pressure. The reaction of hydrogen absorption and desorption is characterized by a significant pressure hysteresis; that is, the hydrogen absorption pressure at 23°C in the plateau region is 1200 atm, while the desorption pressure is 400 atm. The maximum hydrogen uptake achieved for V_{0.8}Mo_{0.2} at room temperature and a pressure of 2800 atm is 2.7 wt %, which increases slightly to 2.8 wt % upon a decrease in temperature to –50°C. The calculated values of the enthalpy and entropy of the reaction in the plateau region are given in table.

The interaction of hydrogen with V_{0.75}Mo_{0.25} in the first activation cycle also starts at a pressure of about 100 atm, but further hydrogen absorption occurs at much higher pressures. In this connection, the following technique was used for measuring the hydrogen desorption isotherms. First, the alloy was saturated

with hydrogen at a pressure of 2000 atm and a temperature of –50°C. Then, after complete saturation of the sample with hydrogen, the autoclave was thermostated at the intended temperature of measurements. Thus, the measurements were carried out at –50.0 and 23°C (see Fig. 1b). The maximum hydrogen content achieved for V_{0.75}Mo_{0.25} does not exceed the value $H/M = 1.5$ (2.3 wt %). As in the case of V_{0.8}Mo_{0.2}, the following two hydride phases are formed in the V_{0.75}Mo_{0.25}–H₂ system: a stable hydride with the composition V_{0.75}Mo_{0.25}H_{0.5} and a high-pressure hydride with the composition V_{0.75}Mo_{0.25}H_{1.5}. The values of the enthalpy and entropy of the reaction calculated on the basis of measured data in the plateau region are given in the table. The results of X-ray diffraction analysis of the hydride phases confirm the conclusions drawn from the analysis of the hydrogen desorption isotherms. As follows from the obtained data (see table), the high-pressure hydrides, V_{0.8}Mo_{0.2}H_{1.7} and V_{0.75}Mo_{0.25}H_{1.5}, are hydrides with the fcc lattice that are similar to vanadium dihydride. However, the low-pressure hydrides, V_{0.8}Mo_{0.2}H_{0.5} and V_{0.75}Mo_{0.25}H_{0.5}, in contrast to the lower vanadium hydrides, preserve the bcc lattice of the starting alloy. Summarizing the results, we can conclude that the introduction of molybdenum reduces the region of the existence of stable hydride phases by almost a factor of two.

Although chromium and molybdenum are elements of the same subgroup of the periodic system, their influence on the interaction of their vanadium alloys with hydrogen is notably different. First of all, despite the fact that the radius of molybdenum atoms is larger than the radius of chromium atoms, hydride phases with molybdenum are characterized by much higher dissociation pressures [13]. On the other hand, as noted in [14], molybdenum hydride is even less stable than chromium hydride, which correlates with the

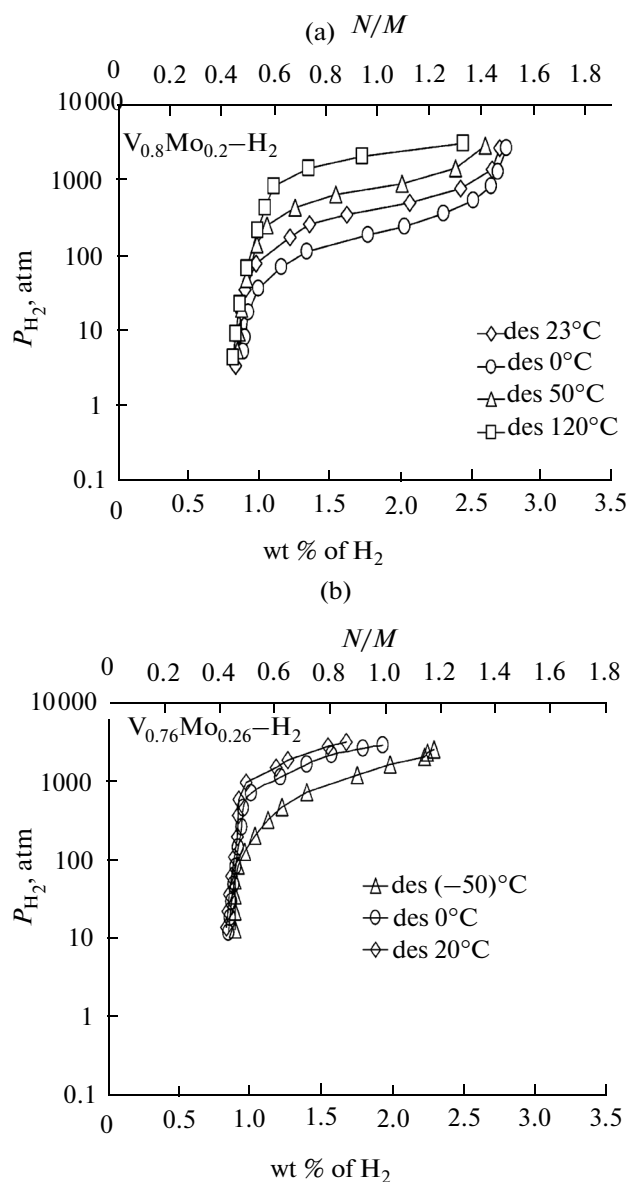


Fig. 1. Hydrogen desorption isotherms in the V–Mo–H₂ system: (a) for the V_{0.8}Mo_{0.2}–H₂ system; (b) for the V_{0.75}Mo_{0.25}–H₂ system.

results obtained in the present studies. In addition, while the stable hydrides V_{0.9}Cr_{0.1}H_{0.7}, V_{0.8}Cr_{0.2}H_{0.6}, and V_{0.7}Cr_{0.3}H_{0.5} show the body-centered tetragonal (bct) structure similar to the lowest vanadium hydride with the composition V₂H [13], the stable hydrides V_{0.8}Mo_{0.2}H_{0.5} and V_{0.75}Mo_{0.25}H_{0.5} have the bcc lattice.

As expected, the introduction of titanium into the composition of the vanadium–molybdenum alloys leads to the formation of more stable hydrides. The Ti_{0.1}V_{0.9-x}Mo_x alloys in the first activation cycle at pressures up to 50 atm react with hydrogen, forming stable hydrides with $H/M \sim 0.5$. Further absorption of hydrogen occurs at higher pressures. As seen from Fig. 2, two areas of the existence of hydride phases can be distinguished also for the Ti_{0.1}V_{0.9-x}Mo_x–H₂ sys-

tem; that is, stable hydrides with an H/M ratio up to 0.5 and hydrides with high dissociation pressure at higher hydrogen content. As seen from the results of X-ray diffraction analysis of the hydrogenation products (see table), the introduction of a small amount of the third component, titanium, in the alloy's composition does not change the nature of transformations occurring in the system upon hydrogen absorption. The stable Ti_{0.1}V_{0.9-x}Mo_xH_{0.5} hydrides are characterized by the bcc lattice, and the structure of high-pressure hydrides is similar to that for vanadium dihydride.

One can also note that the ternary alloys absorb slightly larger amounts of hydrogen in comparison with the binary vanadium–molybdenum alloys. The values of enthalpy and entropy changes in the hydro-

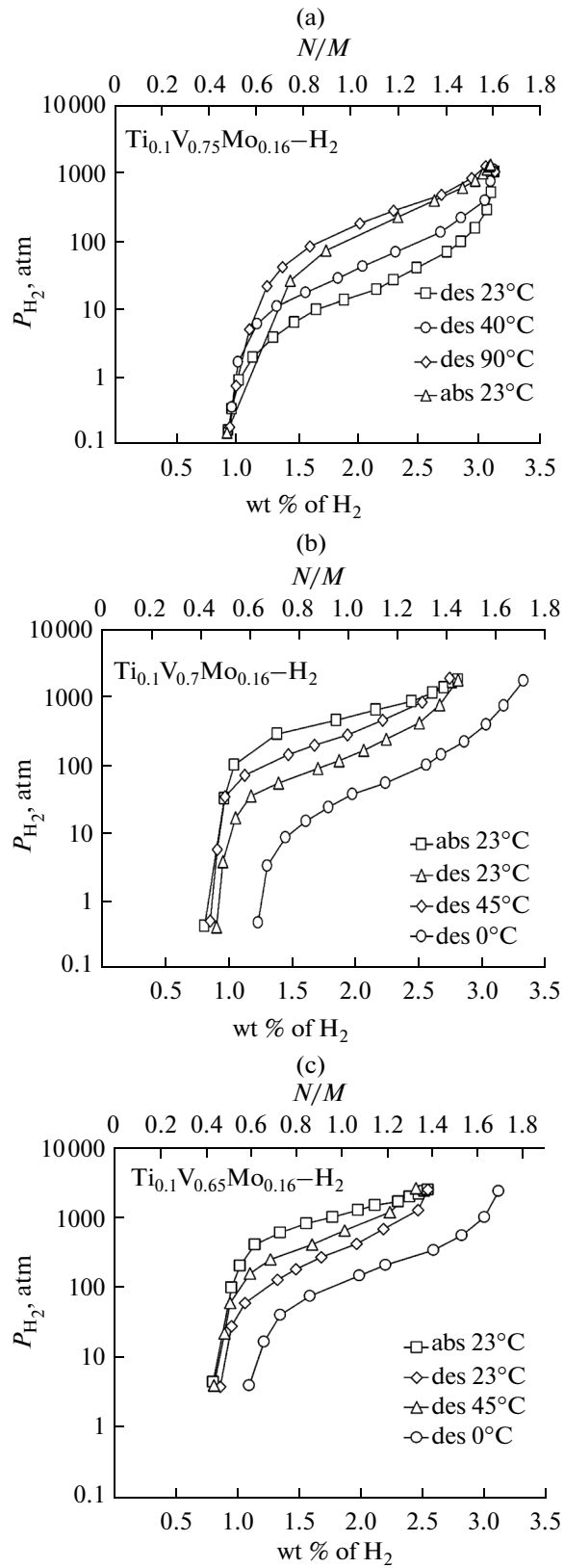


Fig. 2. Hydrogen absorption and desorption isotherms in the V–Mo–Ti–H₂ system: (a) for the Ti_{0.1}V_{0.75}Mo_{0.15}–H₂ system; (b) for the Ti_{0.1}V_{0.7}Mo_{0.2}–H₂ system; (c) for the Ti_{0.1}V_{0.65}Mo_{0.25}–H₂.

gen desorption reaction are given in table, and they also point to the greater stability of hydrides based on ternary alloys.

CONCLUSIONS

Thus, the studies show that the introduction of molybdenum into vanadium leads to an increase in the hydrogen absorption and desorption pressure and a decrease in the maximum hydrogen uptake. In contrast to the V–H₂ system, in which a number of intermediate hydride phases are present, the formation of high-pressure hydrides in the investigated samples proceeds via the stage of formation of hydrides with the bcc lattice. The alloys containing molybdenum can be used for the development of a high-pressure metal hydride compressor.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (grant no. 13-03-00459 A).

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Translated by O. Kadkin