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Interaction of Vanadium Alloys with Hydrogen at High Pressures

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Abstract—The interaction of the $V_{0.95}Cu_{0.05}$, $V_{0.94}Co_{0.06}$, and $V_{0.9}W_{0.1}$ alloys with hydrogen has been studied at hydrogen pressures of up to 250 MPa. We have constructed hydrogen absorption/desorption isotherms at different temperatures and determined the thermodynamic parameters of the systems. According to X-ray diffraction data, the high-pressure hydride phases $V_{0.94}Co_{0.06}H_{1.4}$ and $V_{0.9}W_{0.1}H_{1.2}$ consist of a face-centered cubic phase similar in structure to the γ-phase of vanadium dihydride. In the case of the vanadium–copper alloy, the maximum composition of the hydride is $V_{0.95}Cu_{0.05}H_{0.5}$.

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INTRODUCTION

Hydrogen-rich (3.8 wt %) vanadium hydride is a promising hydrogen-storage material. At the same time, the hydriding conditions of metallic vanadium and the dissociation pressures of vanadium mono- and dihydrides limit its potential applications. To improve these characteristics, intense research effort has focused on the interaction of hydrogen with vanadium alloys and the influence of various elements on the hydrogen sorption properties of vanadium.

As shown in one of the first studies concerned with doping of vanadium [1], most elements raise the equilibrium dissociation pressure of vanadium dihydride, with the strongest effect produced by Si, Ge, W, Fe, Mo, and Ni. Yukawa et al. [2–5] investigated in greater detail the interaction of hydrogen with vanadium alloys doped with other metals (Ti, Cr, Mn, Fe, Co, Ni, and Cu) to 1, 3, and 6 at %. For the vanadium alloys containing 1% another metal, they measured hydrogen absorption/desorption isotherms at a temperature of 313 K and pressures of up to 4 MPa [2]. For the $V_{0.99}Co_{0.01}$ alloy, the formation of β- and γ- hydride phases was demonstrated, like in the vanadium–hydrogen system. The stability range of the dihydride phase extends from 0.8 H/M to 1.8 H/M, and the dissociation pressure of this phase exceeds that of vanadium. Doping of vanadium with a large amount of cobalt (3 and 6 at %) leads to further destabilization of the β-hydride phase, and the γ-phase does not form under such experimental conditions [3–5]. According to Verbetsky and Zontov [6], the VCo and V_3Co compounds do not interact with hydrogen at pressures below 10 MPa.

Similar hydride phases were identified for the vanadium–copper alloy $V_{0.99}Cu_{0.01}$, and the dissociation pressure of the corresponding dihydride phase was shown to be essentially identical to that of vanadium [2]. The interaction of hydrogen with copper-rich alloys has not been studied. Yukawa et al. [2] related the pressure change to the atomic radius and electronegativity of the constituent elements: the elements with a small atomic radius or high electronegativity raise the pressure of hydrogen desorption from vanadium dihydride.

The hydrogen sorption properties of vanadium–chromium, vanadium–molybdenum, and vanadium–tungsten alloys have been the subject of extensive studies [7–12]. As shown by Xiaoxi et al. [7] and Lynch et al. [8], the pressure of hydrogen desorption from vanadium dihydride rises with increasing chromium content. Using high hydrogen pressures, Verbetsky et al. [9] were able to synthesize hydrides of $V_{1-x}Cr_x$ alloys with x from 0.2 to 0.5, which do not form hydride phases at low pressures. The major phase in the hydriding products of $V_{0.9}Cr_{0.1}$ and $V_{0.8}Cr_{0.2}$ samples at high hydrogen pressures was an fcc phase similar to vanadium dihydride VH_2. High-pressure hydrides with an approximate composition $V_{0.6}Cr_{0.4}H_{1.0}$ and $V_{0.5}Cr_{0.5}H_{0.9}$ have an hcp lattice similar to the lattice of the chromium hydride CrH.

According to Asano et al. [10], who investigated the interaction of hydrogen with $V_{1-x}Mo_x$ ($0 \le x \le 0.1$) alloys, the dissociation pressure of the hydride phases in this system increases with increasing molybdenum content. For example, they were able to synthesize the hydride with the composition $V_{0.9}Mo_{0.1}H_{1.74}$ only when the reaction temperature was reduced to – 30°C.

Verbetsky et al. [11] studied the high-pressure interaction of hydrogen with a number of binary ($V_{0.8}Mo_{0.2}$ and $V_{0.75}Mo_{0.25}$) and ternary (Ti–V–Mo) vanadium-based alloys. They constructed hydrogen absorption and desorption isotherms in the systems studied and used the results to assess the thermodynamic parameters of decomposition of the hydride phases. As shown by X-ray diffraction, stable hydride phases based on all of the alloys studied have the bcc

Hydrogen sorption properties of the $V_{0.94}Co_{0.06}$ and $V_{0.9}W_{0.1}$ alloys

Alloy	Lattice parameter of the alloy, nm	Lattice parameter of hydride phases, nm	Maximum hydrogen content H/M at 20°C	ΔH, kJ/mol H_2	ΔS, J/(mol H_2 K)
V [1]	0.303	$VH_{0.9}$ (bct): $a = 0.604$, $c = 0.672$ $VH_{2.1}$ (fcc): $a = 0.424$	2.1 (1 MPa)	41	142
$V_{0.94}Co_{0.06}$	0.3000(2)	$V_{0.94}Co_{0.06}H_{1.4}$ (fcc): $a = 0.4268(3)$	1.4 (170 MPa)	34.23(2)	130.86(2)
$V_{0.9}W_{0.1}$	0.3055(1)	$V_{0.9}W_{0.1}H_{0.6}$ (bct): $a = 0.6077(2)$ $a = 0.6630(1)$ $V_{0.9}W_{0.1}H_{1.2}$ (fcc): $a = 0.4282(3)$	1.2 (160 MPa)	32.47(2)	150.15(2)

lattice, in contrast to the bct lattice of vanadium monohydride. The high-pressure hydride phases of all the compounds have the fcc lattice, like vanadium dihydride. With increasing molybdenum concentration in both the binary and ternary alloys, the maximum hydrogen content of the hydride phases decreases and the hydrogen desorption pressure rises. The effect of tungsten on the interaction of vanadium with hydrogen is essentially unexplored. According to Yukawa et al. [12], the hydrogen permeability of the $V_{0.95}W_{0.05}$ alloy decreases even with increasing temperature. In the temperature range from 400 to 500°C, the maximum hydrogen content corresponded to the composition 0.5–0.6H/ $V_{0.95}W_{0.05}$.

The purpose of this work was to study the interaction of hydrogen with vanadium–cobalt, vanadium–copper, and vanadium–tungsten alloys at high pressures. It is also worth pointing out that vanadium alloys are attractive structural materials for nuclear power reactors. In connection with this, results on hydrogen-induced phase transitions in such alloys are obviously of importance for designers of new structural materials.

EXPERIMENTAL

Alloy samples for this investigation were prepared by reacting pure metals in an electric arc furnace under an inert atmosphere. The alloys were then vacuum-annealed in silica ampules at a temperature of 800°C for 240 h. Before hydriding, “buttons” of the alloys were crushed into pieces in an anvil in order to accommodate the samples in a hydriding reactor. The synthesis of hydrides and investigation of alloy–hydrogen equilibrium were performed at hydrogen pressures of up to 250 MPa in an apparatus described elsewhere [13]. To determine the molar volume of the hydrogen used for hydriding, we relied on the van der Waals equation for real gases. The composition of the hydride phases formed at high hydrogen pressures was determined with an accuracy of 0.1 H/FU. Before X-ray diffraction characterization, samples of the hydrides synthesized at high pressures were first passivated in air. To this end, the autoclave containing the sample was cooled to liquid-nitrogen temperature (77 K) under a high hydrogen pressure and then the pressure was released. After that, the autoclave containing the sample was held open in air for 1 h at liquid-nitrogen temperature (77 K).

RESULTS AND DISCUSSION

According to X-ray diffraction data, the synthesized materials were single-phase and had the bcc lattice. The lattice parameter of the as-prepared $V_{0.95}Cu_{0.05}$ alloy was determined by X-ray diffraction to be 0.3021(3) nm. Data on the hydrogen sorption properties of the alloys and X-ray diffraction data for the synthesized high- and low-pressure hydrides are summarized in the table.

Interaction of the $V_{0.94}Co_{0.06}$ alloy with hydrogen. The addition of cobalt to vanadium reduced the amount of reversibly stored hydrogen and the maximum hydrogen content (Fig. 1). As seen in Fig. 1, the hydrogen desorption isotherms comprise two distinct portions. One portion, up to a composition near 0.6 H/M at 20°C, corresponds to the formation of a stable hydride phase, which releases little hydrogen at the measurement temperatures in this study. At higher hydrogen concentrations, we observe a plateau corresponding to the formation of a high-pressure hydride phase up to a composition of 1.3 H/M. At 170 MPa, the maximum hydrogen content of the high-pressure hydride phase corresponds to the composition $V_{0.94}Co_{0.06}H_{1.4}$. The table presents the enthalpy and entropy of hydrogen desorption reaction evaluated from the equilibrium pressures measured in the plateau region.

Interaction of the $V_{0.95}Cu_{0.05}$ alloy with hydrogen. The hydriding of a sample of this alloy first led to the formation of a stable hydride phase with the highest hydrogen content near 0.3 H/M. When the pressure

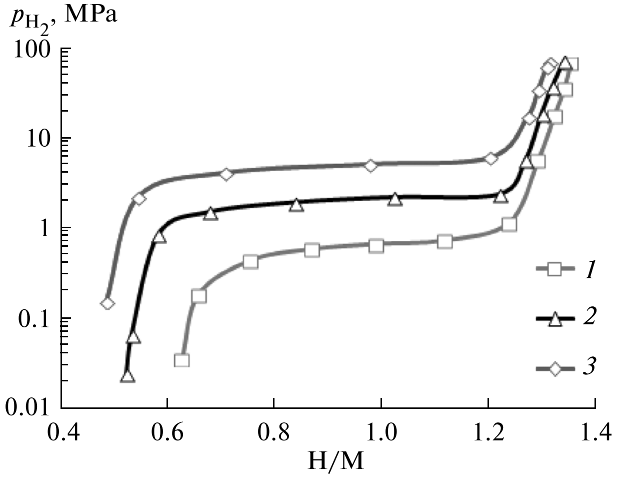

Fig. 1. Hydrogen desorption isotherms in the $V_{0.94}Co_{0.06}$–H_2 system at (*1*) 20, (*2*) 50, and (*3*) 70°C [1].

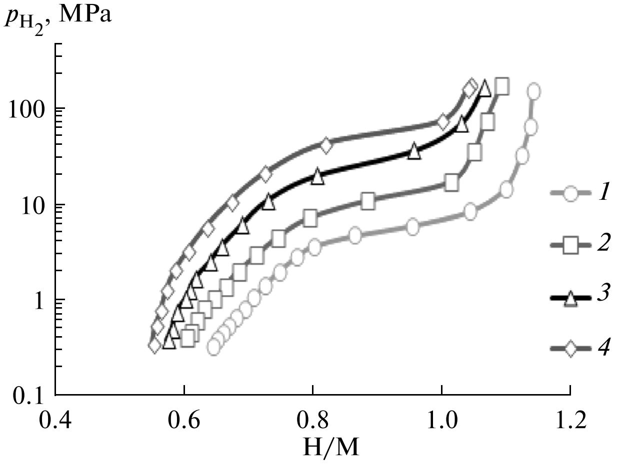

Fig. 2. Hydrogen desorption isotherms in the $V_{0.9}W_{0.1}$–H_2 system at (*1*) 0, (*2*) 20, (*3*) 40, and (*4*) 60°C [1].

was raised further, to 200 MPa, we observed only slight hydrogen absorption, and the maximum composition of the hydride corresponded to 0.5 H/M at 200 MPa and room temperature.

Interaction of the $V_{0.9}W_{0.1}$ alloy with hydrogen. The addition of tungsten to vanadium considerably reduces the amount of reversibly stored hydrogen (Fig. 2). The isotherms obtained in this case can be divided into two distinct portions. One portion extends to 0.6 H/FU and corresponds to the formation of a stable hydride phase, which desorbs a negligible amount of hydrogen at room temperature. With increasing hydrogen pressure in the system, the isotherm shows the other portion, with a sloping plateau in the composition range from about 0.8 to 1.0 H/M at room temperature. With increasing temperature, the composition range of the high-pressure hydride phase becomes narrower, whereas that of the stable hydride phase becomes broader. The maximum hydrogen content of the hydride phase corresponds to 1.2 H/M at a pressure of 160 MPa and a temperature of 20°C. From the experimentally determined equilibrium pressures, we evaluated the enthalpy and entropy of decomposition of the high-pressure hydride phase. The results are presented in the table.

Comparison of the present results with the data in the literature indicates that the use of high hydrogen pressures makes it possible to produce hydrides of vanadium alloys with high dopant contents. For example, at high hydrogen pressures, a hydride of the $V_{0.9}W_{0.1}$ alloy was obtained at room temperature, whereas the $V_{0.9}W_{0.05}$ alloy, studied by Yukawa et al. [12], could only be hydrided at a high temperature. Taking into account data in the literature, we conclude that the stability of the $V_{0.9}M_{0.1}$ (M = Cr, Mo, W) alloys has a tendency to decrease in the order Cr < Mo < W. The data for the vanadium–chromium and vanadium–molybdenum alloys were taken from the literature [8, 11], and those for the vanadium–tungsten alloy were obtained experimentally. In this study, we synthesized the $V_{0.94}Co_{0.06}H_{1.4}$ hydride at high hydrogen pressures. As can be seen from the isotherms presented in Fig. 1, the dissociation pressure of this hydride is near 0.7 MPa at a temperature of 20°C. Thus, taking into account previous data [2–5], we conclude that cobalt doping of vanadium does not drastically increase the dissociation pressure of the dihydride phase but markedly reduces the hydrogen cobalt of the alloy. Cooper doping of vanadium has a more significant effect. In the case of the $V_{0.95}Cu_{0.05}$ alloy, no dihydride phase was obtained even at high pressures.

The reduced stability of the hydride phases based on vanadium–dopant alloys is also evidenced by the experimentally determined thermodynamic parameters of their decomposition. The data in the table demonstrate that the hydrides of the $V_{0.94}Co_{0.06}$ and $V_{0.9}W_{0.1}$ alloys are less stable than vanadium dihydride. The ΔH values of the hydrides of $V_{0.94}Co_{0.06}$ and $V_{0.9}W_{0.1}$ are 34.23(2) and 32.47(2) kJ/mol H_2, against 41 kJ/mol H_2 for vanadium dihydride. Analysis of the present X-ray diffraction data for the synthesized hydrides indicates that the stable hydride phase with the bct lattice corresponds to the β_2-phase of vanadium hydride with disordered hydrogen in its lattice. The hydride phase with the fcc lattice, which formed at high hydrogen pressures, is similar to the γ-phase of vanadium dihydride with ordered hydrogen in its crystal lattice.

CONCLUSIONS

We have studied the interaction of hydrogen with the $V_{0.95}Cu_{0.05}$, $V_{0.94}Co_{0.06}$, and $V_{0.9}W_{0.1}$ alloys at high pressures and detected the formation of high-pressure hydride phases in the case of the $V_{0.94}Co_{0.06}$ and $V_{0.9}W_{0.1}$

alloys. Using experimentally determined hydrogen desorption isotherms, we evaluated the thermodynamic parameters of decomposition of the hydride phases of the $V_{0.94}Co_{0.06}$ and $V_{0.9}W_{0.1}$ alloys. Doping of vanadium with copper, cobalt, and tungsten increases the dissociation pressure of the dihydride phase in comparison with hydrogen desorption from vanadium dihydride. All of the alloys studied absorb a smaller amount of hydrogen.

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