Hydrogen Sorption Properties of $V_{1-x}Cr_x$ ($x = 0.1-0.5$) Alloys

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Abstract—We have studied the interaction of hydrogen with vanadium−chromium alloys. Hydrogen absorption and desorption isotherms have been constructed, the stability ranges of the forming hydride phases have been determined, and the ΔH and ΔS of the reactions involved have been evaluated. X-ray diffraction characterization results indicate the formation of three hydride phases, with fcc, bcc, and hcp structures.

INTRODUCTION

It is known that vanadium and its alloys react with hydrogen to form hydrogen-rich hydride phases [1−3] and are potentially attractive hydrogen storage and transport materials. The amount of sorbed hydrogen and the thermal stability of such hydrides depend significantly on the composition of the alloy. It is worth pointing out that most studies addressed the interaction of hydrogen with Ti−V−Cr alloys [4−6]. At the same time, few studies have been concerned with the general relationships in the interaction of hydrogen with vanadium−chromium alloys, which are used as a base in engineering multicomponent alloys. The influence of chromium on the hydrogen sorption properties of vanadium was first reported by Reilly and Wiswall [7]. Lynch et al. [8] studied the interaction of hydrogen with $V_{1-x}Cr_x$ ($x = 0-0.2$) alloys and showed that the addition of chromium increased the hydrogen desorption pressure and that the alloy containing 20% chromium did not react with hydrogen at pressures of up to 7 MPa.

The purpose of this work was to study the interaction of hydrogen with vanadium−chromium alloys at higher pressures.

EXPERIMENTAL

The alloys for this investigation were prepared in an electric arc furnace under an argon atmosphere.

The alloys were characterized by X-ray diffraction (XRD) on a DRON-3M diffractometer (CuK_α radiation, diffracted-beam graphite monochromator). Diffraction line profiles were refined by the Rietveld method with RIETAN-2000 [9].

The hydrogen sorption properties of the alloys were studied at temperatures from −50 to 200°C and pressures from 1 kPa to 200 MPa using the apparatus and procedure described elsewhere [10]. The thermodynamic functions (enthalpy and entropy) of the reac-

tion of the intermetallic phase with hydrogen were evaluated using the van't Hoff equation and the corresponding temperature-dependent hydride dissociation pressure after two or three hydrogen absorption−desorption cycles.

XRD examination of the hydriding products included characterization of so-called stable phases (hydrides stable at room temperature and low hydrogen pressures) and high-pressure phases (hydrides forming at hydrogen pressures above 0.1 MPa). In the former case, a sample for XRD characterization was withdrawn from the autoclave at room temperature and passivated with octane. In the case of high-pressure phases, a number of measures were taken, described elsewhere [10, 11], which included cooling of the autoclave to liquid-nitrogen temperature under a hydrogen pressure, pressure release, and obligatory passivation of the sample with air at liquid-nitrogen temperature.

RESULTS AND DISCUSSION

According to XRD data, the $V_{1-x}Cr_x$ ($x = 0.1-0.5$) alloys have a body-centered cubic (bcc) lattice. Their lattice parameter decreases linearly with increasing chromium content (table), in good agreement with previous results [12]. As to our results on the interaction of hydrogen with V−Cr alloys, it is worth noting first of all that, in contrast to pure vanadium, all of the alloys studied reacted with hydrogen at room temperature. Figure 1 shows the hydrogen absorption and desorption isotherms of our samples.

Significant interaction of the $V_{1-x}Cr_x$ alloys with hydrogen in the first hydriding cycle at room temperature begins at different hydrogen pressures. In particular, the $V_{0.9}Cr_{0.1}$ alloy reacts with hydrogen starting at a pressure below 5 MPa, whereas the hydriding of the $V_{1-x}Cr_x$ alloys with $x = 0.2$, 0.3, and 0.4 requires pressures of at least 15 MPa. At the same time, the $V_{0.5}Cr_{0.5}$ alloy reacts with hydrogen starting at a pressure near

Structure and hydrogen sorption properties of V–Cr alloys

Parent alloy	Lattice parameter, Å	Stable hydride; lattice parameter, Å	High-pressure hydride; lattice parameter, Å	wt % hydrogen (pressure, MPa)	Reversible hydrogen capacity, wt %	$p_{abs/des}$, MPa (20°C)	ΔH, kJ/mol $H_2/\Delta S$, J/(K mol H_2)
V [13,14]	3.030	$VH_{0.9}$ bct: $a = 6.04$, $c = 6.72$	$VH_{2.1}$ fcc: $a = 4.24$	3.9 (10)	2.2		41/142
$V_{0.9}Cr_{0.1}$	3.0211(1)	$V_{0.9}Cr_{0.1}H_{0.7}$ bct: $a = 6.0335(2)$, $c = 6.7026(4)$	$V_{0.9}Cr_{0.1}H_{1.9}$ fcc: $a = 4.2585(4)$	3.6 (56)	2.3	2.9/1.55	33.6/137
$V_{0.8}Cr_{0.2}$	3.0055(2)	$V_{0.8}Cr_{0.2}H_{0.6}$ bct: $a = 5.9627(6)$, $c = 6.622(2)$	$V_{0.8}Cr_{0.2}H_{1.0}$ fcc: $a = 3.9519(9)$	1.9 (90)	0.7	12.0/3.5	26.3/120
$V_{0.7}Cr_{0.3}$	2.9928(2)	$V_{0.7}Cr_{0.3}H_{0.5}$ bct: $a = 5.9758(6)$, $c = 6.340(1)$	$V_{0.7}Cr_{0.3}H_{1.0}$ hcp: $a = 2.736(1)$, $c = 4.721(3)$; fcc: $a = 3.933(2)$	1.9 (70)	0.9	17.0/2.13	33.3/134
$V_{0.6}Cr_{0.4}$	2.9677(1)	$V_{0.6}Cr_{0.4}H_{0.3}$ bct: $a = 5.9494(6)$, $c = 6.223(1)$	$V_{0.6}Cr_{0.4}H_{0.95}$ hcp: $a = 2.735(1)$, $c = 4.674(2)$	1.8 (70)	1.2	13.0/3.26	29.5/129
$V_{0.5}Cr_{0.5}$	2.9504(2)		$V_{0.5}Cr_{0.5}H_{0.9}$ hcp: $a = 2.731(1)$, $c = 4.630(3)$	1.8 (200)	1.7	34.0/6.6	25.4/122

10 MPa. Thus, it is clear why the $V_{1-x}Cr_x$ alloys with $x > 0.15$ studied by Lynch et al. [8] at pressures no higher than 7 MPa did not react with hydrogen.

Hydriding in the $V_{1-x}Cr_x$–H_2 system (Fig. 1) at x from 0.1 to 0.4 involves two steps and leads to the formation of a stable hydride phase and a hydride phase with a high dissociation pressure. The composition range of the stable hydride phase decreases from H/M = 0.7 at $x = 0.7$ to H/M = 0.3 at $x = 0.4$. At the same time, in the $V_{0.5}Cr_{0.5}$–H_2 system only one hydride phase exists and the hydrogen absorption–desorption process is almost fully reversible.

The alloys differ markedly in hydrogen capacity (Fig. 1, table). The $V_{0.9}Cr_{0.1}$ alloy has the highest hydrogen capacity, comparable to that of VH_2, whereas the hydrogen capacity of the alloys containing more chromium does not exceed 1 H/M. The hydrogen capacity drops most sharply in going from the $V_{0.9}Cr_{0.1}$ alloy to $V_{0.8}Cr_{0.2}$.

Figure 2 shows the composition dependences of the equilibrium hydrogen absorption and desorption pressures in the region of the high-pressure plateau. The dependences are nonlinear and, at first glance, contradictory, primarily because the decrease in equilibrium hydrogen desorption pressure with an increase in the content of the hydride non-forming component (with an increase in chromium content from 20 to 30%) is an unusual fact.

The present XRD characterization results for the low- and high-pressure hydrides (table) enable this contradiction to be overcome. XRD examination showed that all of the hydrides formed at low hydrogen pressures ($V_{0.9}Cr_{0.1}H_{0.7}$, $V_{0.8}Cr_{0.2}H_{0.6}$, $V_{0.7}Cr_{0.3}H_{0.5}$, and $V_{0.6}Cr_{0.4}H_{0.3}$) had a body-centered tetragonal (bct) structure, similar to the structure of the vanadium hydride with the composition V_2H. The major phase in the products of $V_{0.9}Cr_{0.1}$ and $V_{0.8}Cr_{0.2}$ hydriding at high hydrogen pressures is a phase with a face-centered cubic (fcc) structure, similar to vanadium dihydride (VH_2). The high-pressure hydrides with the approximate compositions $V_{0.6}Cr_{0.4}H$ and $V_{0.5}Cr_{0.5}H_{0.9}$ have a hexagonal close-packed (hcp) crystal lattice similar to that of the chromium hydride CrH [15]. XRD examination of the products of high-pressure $V_{0.7}Cr_{0.3}$ hydriding indicated the presence of two phases: hcp (70%) and fcc (30%). The presence of the fcc phase in this material can be accounted for by the fact that high pressures and low temperatures lead to the formation of an fcc hydride, like in the Cr–H_2 system: the chromium hydride CrH_x has an hcp lattice for $x < 0.5$, whereas for $x > 0.55$ a solid solution forms between an fcc and an hcp phase. Thus, the high-pressure hydride with the approximate composition $V_{0.7}Cr_{0.3}H$ is an intermediate phase between the high-pressure hydrides $V_{0.8}Cr_{0.2}H$ and $V_{0.6}Cr_{0.4}H$ [15]. The XRD characterization results for the hydrides allow us to adequately interpret the data in Fig. 2: the nonlinear

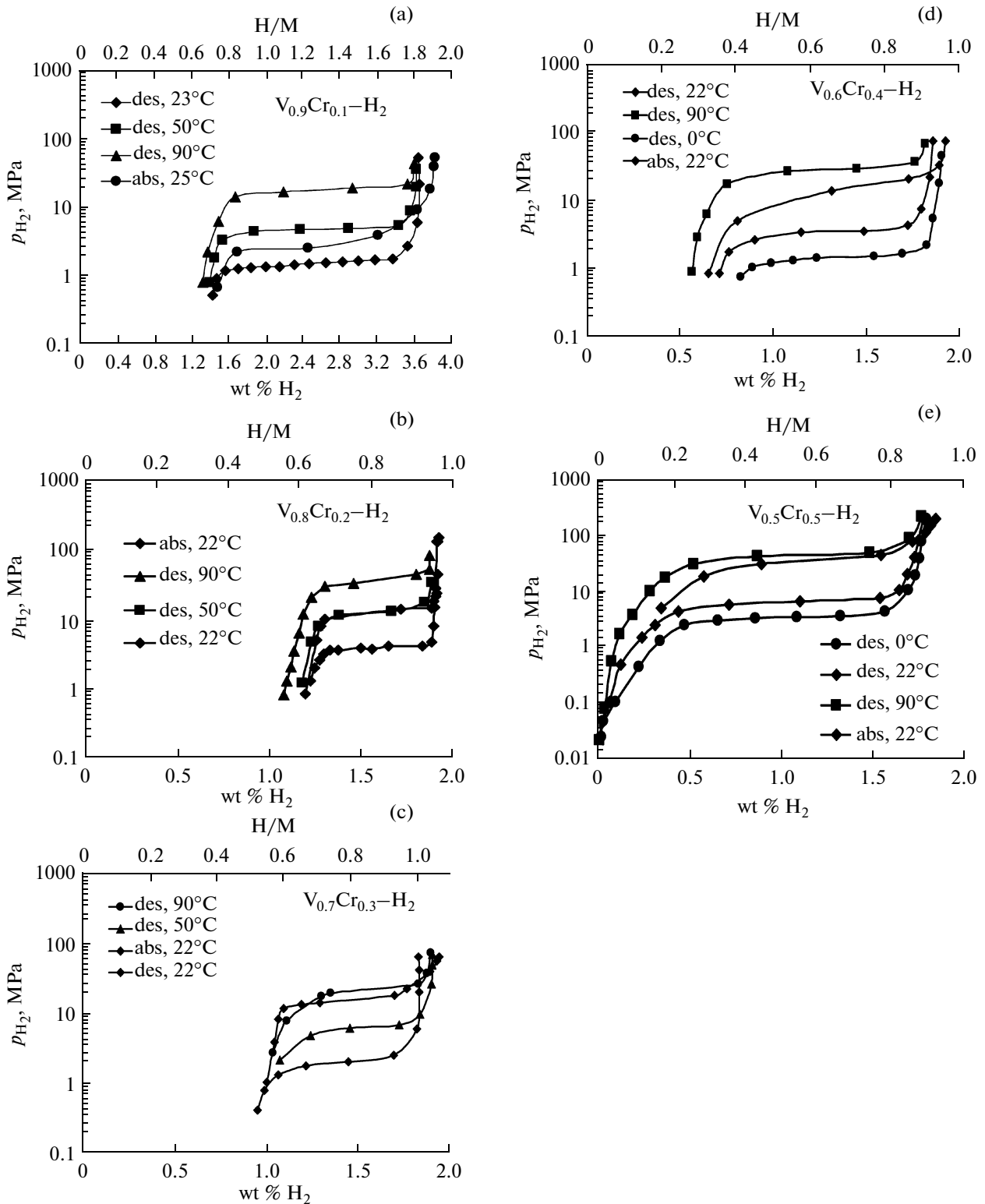**Fig. 1.** Hydrogen absorption and desorption isotherms in the V$_{1-x}$Cr$_x$–H$_2$ ($x = 0.1-0.5$) system.

variation of the hydride dissociation pressure with composition is attributable to the formation of hydrides with different structures in the V$_{1-x}$Cr$_x$–H$_2$ system at high pressures. This conclusion is supported

by the data in Fig. 3, which shows the composition dependence of the ΔH of hydrogen desorption from the fcc and hcp hydrides in the region of the high-pressure plateau. For $x < 0.2$, ΔH decreases systematically
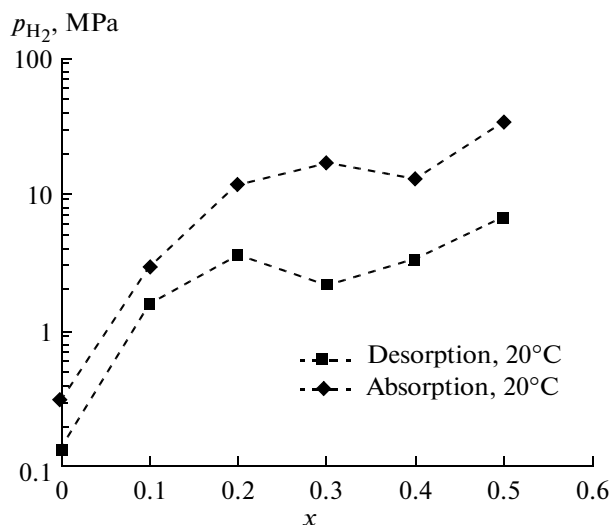
p_{H_2}, MPa

Fig. 2. Composition dependences of the equilibrium hydrogen absorption and desorption pressures in the $V_{1-x}Cr_x-H_2$ system.
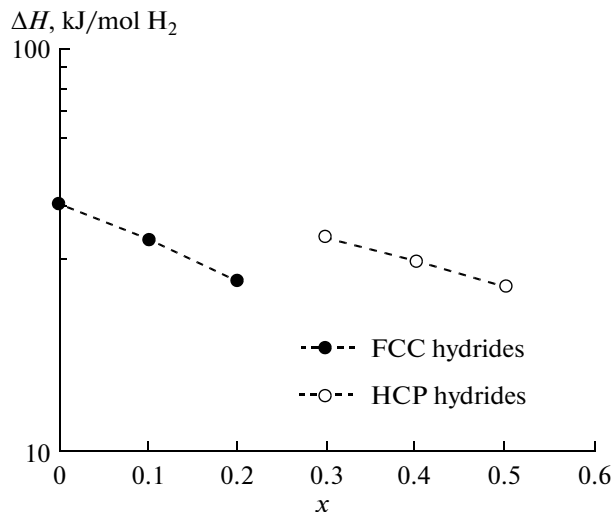
ΔH, kJ/mol H_2

Fig. 3. Composition dependence of the enthalpy of hydrogen desorption in the $V_{1-x}Cr_x-H_2$ system.

with increasing chromium content, whereas the hcp hydrides with $x > 0.2$ are closer in properties to vanadium-stabilized chromium hydrides.

REFERENCES

1. Sandrock, G., A Panoramic Overview of Hydrogen Storage Alloys from a Gas Reaction Point of View, *J. Alloys Compd.*, 1999, vols. 293–295, pp. 877–888.

2. Verbetsky, V.N. and Zontov, V.S., Interaction of Hydrogen with Titanium–Vanadium–Nickel Alloys, *Zh. Neorg. Khim.*, 1985, vol. 30, no. 3, pp. 589–592.

3. Sirotina, R.A. and Verbetsky, V.N., Interaction of $Ti_{0.2}V_{0.8}$ with Hydrogen Studied by Calorimetry, *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1995, vol. 36, no. 1, pp. 70–73.

4. Sung-Wook Cho, Chang-Suck Han, Choong-Nueon Park, and Etsuo Akiba, The Hydrogen Storage Characteristics of Ti–Cr–V Alloys, *J. Alloys Compd.*, 1999, vol. 288, pp. 294–298.

5. Takuya Tamura, Takashi Kazumi, Atsunori Kamegawa, et al., Protium Absorption Properties and Protide Formations of Ti–Cr–V Alloys, *J. Alloys Compd.*, 2003, vols. 356–357, pp. 505–509.

6. Takahiro Kuriiwa, Takahiro Maruyama, Atsunori Kamegawa, and Masuo Okada, Effects of V Content on Hydrogen Storage Properties of V–Ti–Cr Alloys with High Desorption Pressure, *Int. J. Hydrogen Energy,* 2010, vol. 35, pp. 9082–9087.

7. Reilly, J.J. and Wiswall, R.H., The Effect of Minor Constituents on the Properties of Vanadium and Niobium, *Hydrogen in Metals Int. Meet.*, Julich, 1972, vol. 1, pp. 39–64.

8. Lynch, J.F., Reilly, J.J., and Millot, F., The Absorption of Hydrogen by Binary Vanadium–Chromium Alloys, *J. Phys. Chem. Solids*, 1978, vol. 39, pp. 883–890.

9. Izumi, F., Rietveld Analysis and MEM-Based Whole-Pattern Fitting under Partial Profile Relaxation, *J. Rigaku*, 2000, vol. 17-1, pp. 34–45.

10. Mitrokhin, S., Zotov, T., Movlaev, E., and Verbetsky, V., Synthesis and Properties of AB_5-Type Hydrides at Elevated Pressures, *J. Alloys Compd.*, 2007, vols. 446–447, pp. 603–605.

11. Sivov, R.B., Zotov, T.A., Verbetsky, V.N., et al., Synthesis, Properties and Mössbauer Study of $ZrFe_{2-x}Ni_x$ Hydrides ($x = 0.2$–0.8), *J. Alloys Compd.*, 2011, vol. 509S, pp. S763–S769.

12. Smith, J.F., Bailey, D.M., and Carlson, O.N., The Chromium–Vanadium System, *Bull. Alloy Phase Diagrams*, 1982, vol. 2, no. 4, pp. 469–473.

13. Maeland, A.J., Investigation of the Vanadium–Hydrogen System by X-Ray Diffraction Techniques, *J. Phys. Chem.*, 1964, vol. 68, no. 8, pp. 2197–2200.

14. Reilly, G.G. and Wiswall, R.H., The Higher Hydrides of Vanadium and Niobium, *Inorg. Chem.,* 1970, vol. 9, no. 7, pp. 1678–1682.

15. Venkatraman, M. and Neumann, J.P., The Cr–H (Chromium–Hydrogen) System, *J. Phase Equilib.*, 1991, vol. 12, no. 6, pp. 672–677.