

STRUCTURE OF INORGANIC COMPOUNDS

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Structure of Hydrides Based on V–Cr Alloys

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Abstract—The structure of deuterides based on $V_{0.9}Cr_{0.1}$ and $V_{0.5}Cr_{0.5}$ alloys has been investigated by neutron diffraction at room and low (77 K) temperatures. It is found that $V_{0.9}Cr_{0.1}D_{2.0}$ deuteride has a CaF_2 ($Fm\bar{3}m$) crystal structure, which corresponds to vanadium dihydride. $V_{0.5}Cr_{0.5}D_{0.7}$ deuteride has a NiAs ($P\bar{6}/_3mmc$) structure type, similar to chromium hydride.

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INTRODUCTION

Vanadium-based hydrides with a high hydrogen mass content (3.8%) are promising materials for storing hydrogen. However, the conditions of hydrogenation of metallic vanadium and the values of pressure for vanadium mono- and dihydride dissociation limit the wide practical application of these compounds. The interaction of hydrogen with multicomponent vanadium alloys (among which V–Cr–Ti alloys should be selected [1–3]) was investigated in order to make progress in this field.

This study is based on the data of [4] on the influence of some elements on the hydrogen sorption ability of vanadium. According to these data, the introduction of most elements (except for Ti, Zr, and Nb) increases the dissociation pressure of the dihydride phase. The introduction of chromium also makes vanadium dihydride less stable. A study of $V_{1-x}Cr_x$ alloys ($x = 0–0.2$) [5] showed that an increase in chromium content leads to an increase in hydrogen desorption pressure and that an alloy containing 20% Cr does not interact with hydrogen at pressures up to 70 atm. The application of the high-pressure technique in investigations in this field is expected to gain new knowledge about metal–hydrogen systems. For example, the interaction of hydrogen with $V_{1-x}Cr_x$ alloys ($x = 0.1–0.5$) was studied in [6] at pressures up to 2000 atm. Hydrogen absorption and desorption isotherms were plotted, domains of existence of hydride phases were determined, and the ΔH and ΔS values were calculated. It was found that hydride formation in the $V_{1-x}Cr_x-H_2$ system with x ranging from 0.1 to 0.4 occurs in two stages and is characterized by the formation of a stable hydride phase and a hydride phase with a high dissociation pressure.

At the same time, the formation of only one hydride phase and the almost complete reversibility of the hydrogen absorption–desorption reaction were

observed in the $V_{0.5}Cr_{0.5}-H_2$ system. It was noted in [5] that, if $V_{0.9}Cr_{0.1}H_{1.9}$ is similar to vanadium dihydride, a hydride based on $V_{0.5}Cr_{0.5}$ alloy can be considered a vanadium-stabilized chromium hydride. Kajitani et al. [7] investigated the structure of deuterides based on $V_{1-x}Cr_xD_{0.5}$ and $V_{1-x}Ta_xD_{0.5-x}$ alloys ($x = 0.01–0.1$) and found that an increase in the chromium content leads to an increase in the fraction of deuterium-filled octahedral interstitial sites in the lattice.

In this paper we report the results of studying the structure of hydrides based on $V_{0.9}Cr_{0.1}$ and $V_{0.5}Cr_{0.5}$ alloys synthesized under high hydrogen pressure. The positions of deuterium atoms in the metal sublattice of the alloys are determined. It is revealed that $V_{0.9}Cr_{0.1}D_{2.0}$ deuteride has a crystal structure of CaF_2 ($Fm\bar{3}m$), which corresponds to vanadium dihydride. $V_{0.5}Cr_{0.5}D_{0.7}$ deuteride with a high chromium content has the NiAs crystal structure ($P\bar{6}/_3mmc$), corresponding to chromium hydride.

EXPERIMENTAL

Alloy samples were prepared by melting initial high-purity components in an electric-arc furnace in an inert atmosphere. After melting, the samples were weighted again to monitor the alloy composition. Alloys were hydrogenated in a Sieverts-type facility with an operating pressure range up to 3000 atm. The scheme and description of the facility can be found in [8]. Deuterium-containing samples were prepared for neutron diffraction study. Deuteride samples were passivated after synthesis. To this end, an autoclave with a sample under a high hydrogen pressure was cooled to liquid nitrogen temperature (77 K), after which the pressure was reduced to atmospheric. Then the autoclave with a sample was open and kept in air for several hours at a temperature of 77 K. Powder samples were placed in an aluminum container. Neu-

neutron diffraction measurements were performed on a DISK system ($\lambda = 1.668 \text{ \AA}$) at the National Research Centre “Kurchatov Institute.” The structural data were refined using the Fullprof software.

RESULTS AND DISCUSSION

The initial $V_{0.9}Cr_{0.1}$ and $V_{0.5}Cr_{0.5}$ alloys have a body-centered cubic lattice in which vanadium and chromium atoms are distributed statistically. The lattice periods are $3.021(1) \text{ \AA}$ for $V_{0.9}Cr_{0.1}$ and $2.950(2) \text{ \AA}$ for $V_{0.5}Cr_{0.5}$; these values correspond to the data obtained by studying the chromium–vanadium phase diagram in [9].

The neutron diffraction data on deuterides are presented in Figs. 1 and 2 and in Tables 1 and 2. The vertical bars (in the lower part) in the neutron diffraction patterns are the Bragg positions from the container in which the sample was placed. These experimental data confirmed the results of [6] and showed that the

$V_{0.5}Cr_{0.5}D_{0.7}$ and $V_{0.9}Cr_{0.1}D_{2.0}$ deuterides formed have different structures which also differ from their initial structures. The occupancy of the positions of metal and deuterium atoms in deuteride structures is determined and the interatomic distances are calculated as a result of the refinement of the structural parameters.

The refinement of neutron diffraction data showed that the structure of $V_{0.9}Cr_{0.1}D_{2.0}$ deuteride is similar to that of vanadium dihydride VH_2 ; it is an fcc lattice of the CaF_2 structure type (sp. gr. $Fm\bar{3}m$). In this lattice vanadium and chromium atoms are statistically distributed over $4a$ positions, while deuterium atoms occupy tetrahedral interstitial sites.

$V_{0.5}Cr_{0.5}D_{0.7}$ deuteride has a hexagonal lattice of the NiAs structure type (sp. gr. $P6_3/mmc$), similar to chromium hydride. The hydride unit cell contains two formula units. Chromium and vanadium atoms are statistically distributed over lattice sites, while deuterium atoms occupy octahedral interstitial sites.

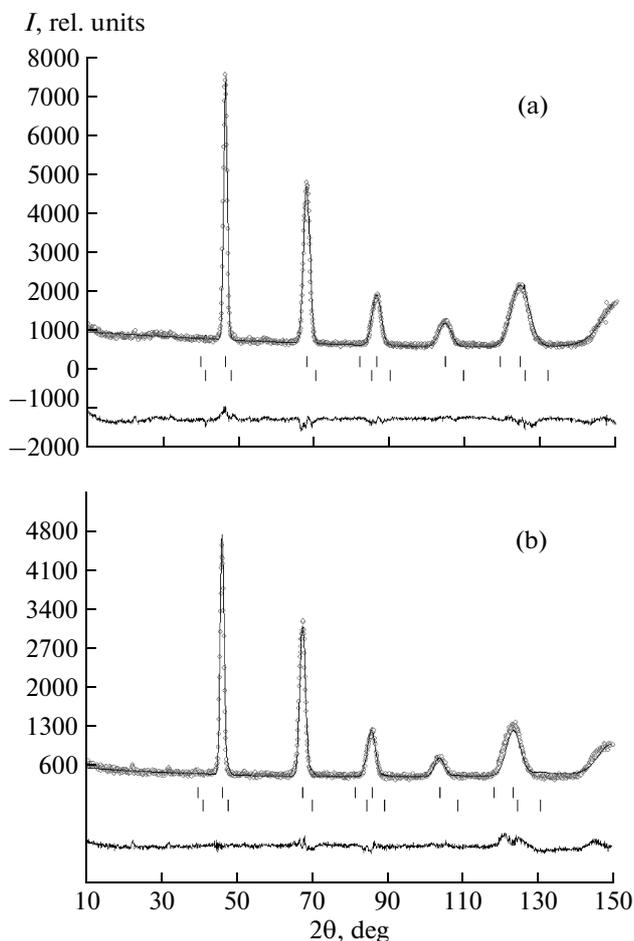


Fig. 1. Neutron diffraction pattern of a $V_{0.9}Cr_{0.1}D_{2.0}$ sample (CaF_2 structure, sp. gr. $Fm\bar{3}m$) collected (a) at a temperature of 77 K ($a = 4.196 \text{ \AA}$, $R_w = 8.2\%$) and (b) at room temperature after exposure to air for a week ($a = 4.194 \text{ \AA}$, $R_w = 7.1\%$).

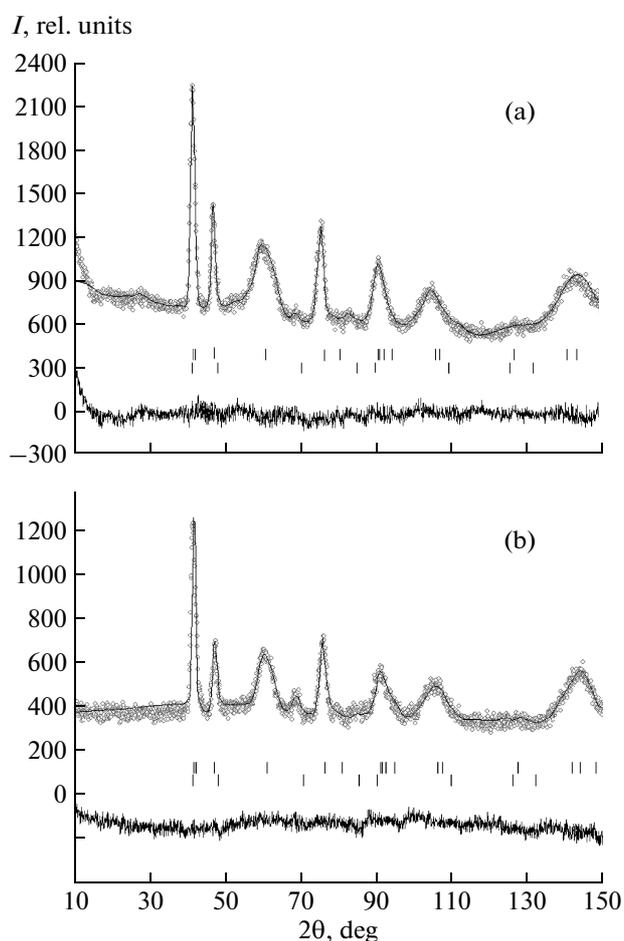


Fig. 2. Neutron diffraction pattern of a $V_{0.5}Cr_{0.5}D_{0.7}$ sample (NiAs structure, sp. gr. $P6_3/mmc$) collected (a) at 77 K ($a = 2.687 \text{ \AA}$, $c = 4.596 \text{ \AA}$, $R_w = 10.5\%$) and (b) at room temperature after exposure to air for a week ($a = 2.616 \text{ \AA}$, $c = 4.606 \text{ \AA}$, $R_w = 11.2\%$).

Table 1. Structural data on deuterides

Atoms	Position type	Occu-pancy	Atomic coordinates		
			x	y	z
$V_{0.9}Cr_{0.1}D_{2.0}$ (77 K)					
V	4a	0.9	0	0	0
Cr	4a	0.1	0	0	0
D	8c	2.0(2)	0.25	0.25	0.25
$V_{0.9}Cr_{0.1}D_{2.0}$ (293 K)					
V	4a	0.9	0	0	0
Cr	4a	0.1	0	0	0
D	8c	2.0(1)	0.25	0.25	0.25
$V_{0.5}Cr_{0.5}D_{0.7}$ (77 K)					
V	2a	0.5	0	0	0
Cr	2a	0.5	0	0	0
D	2c	0.7(1)	0.333	0.666	0.25
$V_{0.5}Cr_{0.5}D_{0.66}$ (293 K)					
V	2a	0.5	0	0	0
Cr	2a	0.5	0	0	0
D	2c	0.66(2)	0.333	0.666	0.25

A comparison of interatomic distances in deuterides showed that the introduction of chromium (atomic radii of vanadium and chromium are 1.34 and 1.27 Å, respectively) into the alloy composition significantly changes the V–V (Cr), V(Cr)–D, and D–D bond lengths (Table 2).

The V–D interatomic distances (1.84 Å) for vanadium dideuteride were taken from [10]. The interatomic distances for chromium hydride (Cr–H = 1.92 Å) were calculated from the data of [11]. The interatomic distances for β_2 -vanadium deuteride (V–D = 1.58 Å) were taken from [12, 13]. In addition, the interatomic distances for VH_2 were calculated based on the structural data obtained in [14].

An analysis of interatomic distances showed that the V(Cr)–D distances (1.93 Å) in the deuteride sample with a structure of chromium hydride $V_{0.5}Cr_{0.5}D_{0.7}$ are larger than the V–D distances for β_2 -deuteride (1.58 Å) and are almost equal to the Cr–H distances (1.92 Å). Thus, when compared with chromium hydride, the introduction of a metal with a larger atomic radius barely changes the metal–hydrogen distance.

In the $V_{0.9}Cr_{0.1}D_{2.0}$ deuteride with a CaF_2 structure, which contains a small amount of metal with a smaller atomic radius, the interatomic distances V(Cr)–D (1.88 Å) are close to the V–D interatomic distances in dideuteride (1.84 Å).

Studies of the structure of *d*-metal hydrides were analyzed in [10, 12]. It was concluded that in hydrides of metals with an atomic radius larger than the vanadium atomic radius (Ti, Zr, Nb, Ta), hydrogen fills tet-

Table 2. Interatomic distances in $V_{0.9}Cr_{0.1}D_{2.0}$ and $V_{0.5}Cr_{0.5}D_{0.7}$ deuterides

	$V_{0.9}Cr_{0.1}D_{2.0}$		$V_{0.5}Cr_{0.5}D_{0.7}$
V–V(Cr)	2.97(2)	V–V(Cr)	2.69(2); 2.30(1)
V(Cr)–D	1.88(2)	V(Cr)–D	1.93(2)
D–D	2.10(1)	D–D	2.77(2)

rahedral interstitial sites. In hydrides of metals with an atomic radius smaller than the vanadium radius (Cr, Mn, Fe, Co, Ni), hydrogen occupies octahedral interstitial sites in the metal lattice. Thus, a decrease in the radius of metal atoms and the corresponding decrease in the lattice period lead to a change in the coordination number of hydrogen atoms. Vanadium is at the boundary between the metals characterized by the tetrahedral and octahedral filling of interstitial sites in metal hydrides. Therefore, in this case, one should expect that an increase in the chromium content in a vanadium-based alloy may lead to the more likely filling of octahedral interstitial sites with hydrogen because of the decrease in the lattice period. This in turn will change the lattice type from cubic to hexagonal.

The data obtained confirm this suggestion. With an increase in chromium concentration, the formation of a dihydride phase becomes impossible even at hydrogen pressures of up to 3000 atm. At the same time, a transition from a bcc lattice for $V_{0.9}Cr_{0.1}D_{2.0}$ (Fig. 1a) to an hcp lattice for $V_{0.5}Cr_{0.5}D_{0.7}$ (Fig. 2a) is observed.

A neutron diffraction analysis performed after the exposure of $V_{0.9}Cr_{0.1}D_{2.0}$ and $V_{0.5}Cr_{0.5}D_{0.7}$ deuteride samples in air at room temperature for a week (Figs. 1b, 2b) demonstrated only a slight decrease in the lattice parameters. This fact indicates the high stability of deuteride samples after passivation in air. We can also conclude that the structure of synthesized hydrides does not change at 77 K.

CONCLUSIONS

The structure of deuterides based on $V_{0.9}Cr_{0.1}$ and $V_{0.5}Cr_{0.5}$ alloys was investigated by neutron diffraction. The positions of metal and deuterium atoms in the deuteride lattice are refined. It is established that $V_{0.9}Cr_{0.1}D_{2.0}$ deuteride has a CaF_2 -type crystal structure (sp. gr. $Fm\bar{3}m$) and is similar to vanadium dihydride. $V_{0.5}Cr_{0.5}D_{0.7}$ deuteride is crystallized into the NiAs structure type (sp. gr. $P6_3/mmc$), similarly to chromium hydride.

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