

STRUCTURE OF INORGANIC COMPOUNDS

Structure of Hydride Phases Based on Intermetallic Compounds ZrMoV and ZrMo_{1.5}V_{0.5} of C15 Laves Phases

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Abstract—Hydride phases have been synthesized based on ZrMoV and ZrMo_{1.5}V_{0.5} pseudobinary intermetallic compounds with a cubic structure of C15 Laves phases (sp. gr. *Fd3m* (no. 227), $Z = 8$). The ZrMoVH_{3.3} and ZrMo_{1.5}V_{0.5}H_{3.5} hydride phases are formed during hydrogen absorption. The structures of synthesized hydrides have been investigated by X-ray diffraction (XRD) and neutron diffraction analyses. It is established that the hydrogen atomic ordering in the cubic lattice of ZrMoV and ZrMo_{1.5}V_{0.5} leads to the formation of a superstructure with a tetragonal lattice (sp. gr. *I4₁/a* (no. 88), $Z = 4$). In contrast to the hydride in ZrMoV-based deuteride, a partially ordered superstructure (sp. gr. *I4₁/amd* (no. 141), $Z = 4$) is formed. The positional parameters of the metal and hydrogen atoms are determined by neutron diffraction analysis.

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INTRODUCTION

Hydride phases, containing up to six hydrogen atoms per formula unit, are formed as a result of interaction of intermetallic compounds of Laves phases with hydrogen. After a decrease in temperature or an increase in concentration, hydrogen atoms become ordered, and various superstructures are formed. For cubic C15 Laves phases, some types of superstructures can be calculated theoretically [1, 2]. The structures and thermodynamic characteristics of the previously investigated hydrides of ZrV₂ and ZrMo₂ compounds differ to a great extent. For example, in dependence of the hydrogen content, hydrides with two lattice types are formed based on ZrV₂ compound [3]. At a hydrogen content of up to 4.3 H/IC (4.3 hydrogen atoms per formula unit of an intermetallic compound (IC)), the hydride lattice is cubic; at a concentration of 4.3 H/IC, the lattice is orthorhombic; and, at 5 H/IC, the lattice is cubic. If deuterium is used instead of hydrogen, the lattice types become even more diverse [4]. For deuteride in the concentration range of up to 2 D/IC (2 deuterium atoms per formula unit of IC), the lattice is monoclinic; at 2 D/IC, the lattice is cubic; at 2.2 D/IC, the lattice is monoclinic or tetragonal; at 2.3 D/IC, the lattice is cubic; at 2.7 D/IC, the lattice is monoclinic; at 3.6 D/IC, the lattice is tetragonal; and, at 4.9 D/IC, the lattice is cubic. The interaction between ZrMo₂ and hydrogen was investigated in [5, 6]. The structural analysis of a deuteride phase containing about 4 D/IC showed that the ZrMo₂ lattice is transformed from cubic into tetragonal. The purpose of this

work was to investigate the interaction of the vanadium-containing ZrMo₂ compound with hydrogen. Depending on the vanadium content, the hydride phases whose structural types were calculated in [1, 2] can be formed.

EXPERIMENTAL

The initial samples of ZrMoV and ZrMo_{1.5}V_{0.5} intermetallic compounds were prepared from pure components in an electric-arc furnace under inert atmosphere conditions. For better homogenization, the samples were annealed at a temperature of 1500°C in vacuum for 50 h. The hydrogenation was carried out on a Sieverts system with an operating pressure range of up to 100 atm. To improve the quality of diffraction spectra, neutron diffraction analysis was performed on deuterium-containing samples. The neutron diffraction data were obtained on a DISK diffractometer ($\lambda = 1.66 \text{ \AA}$) of the IR-8 reactor at the National Research Center “Kurchatov Institute.”

RESULTS AND DISCUSSION

According to the XRD and electron microscopy data, the samples contained only traces of compounds based on the molybdenum–vanadium–zirconium solid solution. The lattice parameters a of ZrMoV and ZrMo_{1.5}V_{0.5} are 7.502(3) and 7.549(4) Å, respectively. The decrease in the lattice parameter in the intermetallic compound with a higher vanadium content is

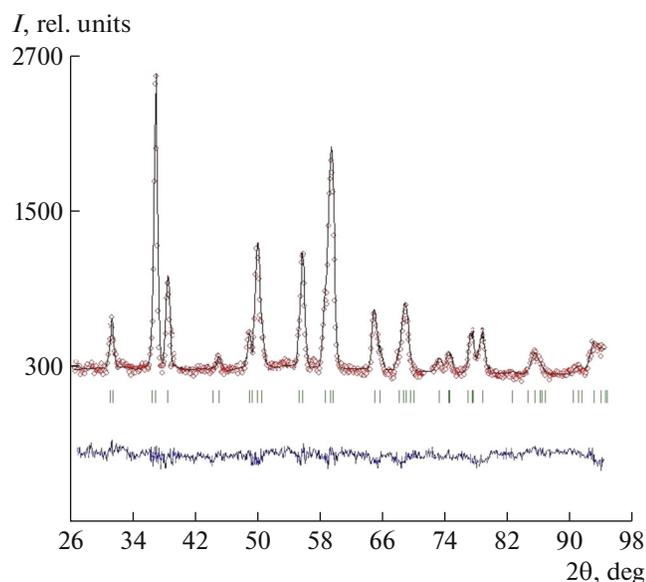


Fig. 1. Neutron diffraction pattern of a $\text{ZrMo}_{1.5}\text{V}_{0.5}\text{D}_{3.5}$ deuteride sample. Hereinafter, circles are experimental data, solid lines are calculated values, the difference curve is given in the bottom, and the positions of Bragg reflections are indicated by vertical bars.

systematic; it is explained by the fact that the atomic radius of vanadium is smaller than that of molybdenum. The hydride phases containing of about 3.1–3.5 H/IC were formed as a result of the reaction of synthesized ZrMoV and $\text{ZrMo}_{1.5}\text{V}_{0.5}$ samples with hydrogen. An increase in the vanadium content in an intermetallic compound decreases significantly the hydrogen pressure during absorption. The ZrMoV sample absorbed hydrogen at a pressure of about 2 atm, whereas hydrogen absorption in the $\text{ZrMo}_{1.5}\text{V}_{0.5}$ sample occurred at a pressure of about 30 atm.

The XRD data of the $\text{ZrMo}_{1.5}\text{V}_{0.5}$ -based hydride and deuteride samples showed that they have tetragonal lattices and identical structures (sp. gr. $I4_1/a$ (no. 88), $Z = 4$). The neutron diffraction data of $\text{ZrMo}_{1.5}\text{V}_{0.5}\text{D}_{3.5}$ deuteride revealed that all deuterium atoms occupy the site $16f$ with an environment $\text{Zr}_2(\text{Mo}, \text{V})_2$. The deuteride lattice periods were found to be $a = 5.556(3) \text{ \AA}$ and $c = 7.968(2) \text{ \AA}$ (Fig. 1, Table 1).

Table 1. Structural parameters of the $\text{ZrMo}_{1.5}\text{V}_{0.5}\text{D}_{3.5}$ sample

Atom	Site	Atomic coordinates			Occupancy
		x/a	y/b	z/c	p
Zr	$4a$	0	0.25	0.125	1.0
Mo(V)	$8d$	0.25	0.25	0.75	1.0
D	$16f$	0.186(3)	-0.070(2)	0.060(3)	0.88(2)
$R_w = 7.8\%$					

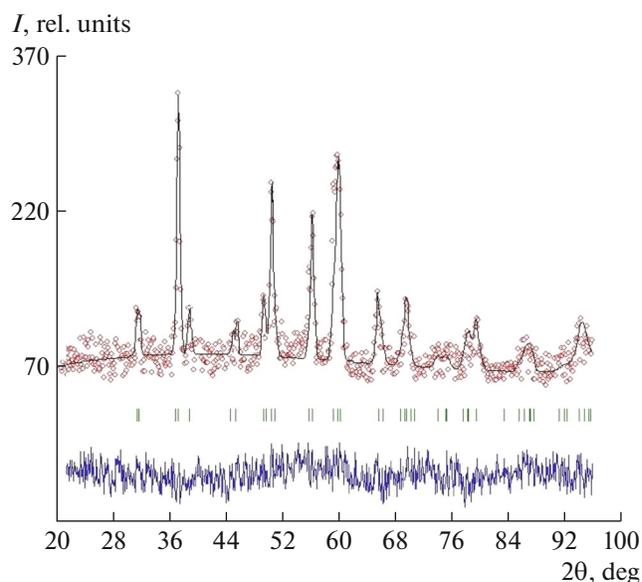


Fig. 2. Neutron diffraction pattern of the $\text{ZrMoVD}_{3.6}$ deuteride sample.

The diffraction patterns of the ZrMoV -based hydride and deuteride samples showed that they had tetragonal lattices and different structures. The structure of $\text{ZrMoVH}_{3.3}$ hydride is described within the sp. gr. $I4_1/a$ (no. 88), $Z = 4$. Based on the analysis of the superstructures [1, 2], it was found that $\text{ZrMoVD}_{3.6}$ deuteride has a tetragonal lattice and a partially ordered superstructure (sp. gr. $I4_1/amd$ (no. 141), $Z = 4$). The neutron diffraction data on $\text{ZrMoVD}_{3.6}$ deuteride showed that deuterium atoms in this superstructure occupy the site $32i$ (Fig. 2, Table 2). The periods of the $\text{ZrMoVD}_{3.6}$ lattice were found to be $a = 5.572(3) \text{ \AA}$ and $c = 8.018(8) \text{ \AA}$. $\text{ZrV}_2\text{D}_{3.0}$ deuteride, which was investigated in [7], has the same superstructure and a similar deuterium distribution. At the same time, ordering of hydrogen atoms in ZrV_2 -based hydride (sp. gr. $Fd\bar{3}m$ (no. 227), $Z = 8$) with a hydrogen content of 2.7–3.7 H/IC, which was investigated in [3], leads to expansion of its lattice without structural changes. Apparently, the difference between the superstructures of ZrMoV -based hydride and deuteride is related to the isotopic effect [8], to which vanadium is sensi-

Table 2. Structural parameters of the $\text{ZrMoVD}_{3.6}$ sample

Atom	Site	Atomic coordinates			Occupancy
		x/a	y/b	z/c	p
Zr	$4a$	0	0.75	0.125	1.0
Mo(V)	$8d$	0.0	0.0	0.5	1.0
D	$32i$	0.810(3)	0.935(2)	0.311(2)	0.45(2)
$R_w = 8.4\%$					

Table 3. Interatomic distances in $\text{ZrMo}_{1.5}\text{V}_{0.5}\text{D}_{3.5}$ and $\text{ZrMoVD}_{3.6}$ deuterides

Compound	Chemical bond	Length, Å
$\text{ZrMo}_{1.5}\text{V}_{0.5}\text{D}_{3.5}$	Zr–Zr	2.778
	Zr–(MoV)	3.262
	Zr–D	2.050
	(MoV)–D	1.703
	D–D	2.501
$\text{ZrMoVD}_{3.6}$	Zr–Zr	2.786
	Zr–(MoV)	3.272
	Zr–D	2.073
	(MoV)–D	1.802
	D–D	2.220

tive. It was noted in [1] that, depending on the lattice parameter, deuterium can occupy both sites 96g and 32e in zirconium-containing C15 Laves phases. In the case under consideration, the ZrMoV and $\text{ZrMo}_{1.5}\text{V}_{0.5}$ lattice periods provide a possibility of filling with deuterium only the site 96g, which corresponds to the sites 16f and 32i in the tetragonal lattice. A comparison of the interatomic distances based on the structural data showed that they are close for both deuterides (Table 3). The interatomic distances in binary zirconium (2.07 \AA [9]) and vanadium (1.65 \AA [10]) deuterides are also close to those in the compounds under investigation ($\text{Zr–D} = 2.07 \text{ \AA}$, $\text{Mo(V)–D} = 1.80\text{--}1.70 \text{ \AA}$). The interatomic distances in molybdenum hydride are longer (2.07 \AA [11]), which is likely related to the character of hydrogen distribution in the hydride metallic sublattice.

CONCLUSIONS

Hydride phases with a hydrogen content of 3.3–3.6 H/IC were synthesized in the ZrMoV–H_2 and $\text{ZrMo}_{1.5}\text{V}_{0.5}\text{–H}_2$ systems. An increase in the vanadium

content in an intermetallic compound decreased the pressure in the hydride-formation reaction. XRD and neutron diffraction analyses revealed that $\text{ZrMoVD}_{3.6}$ and $\text{ZrMo}_{1.5}\text{V}_{0.5}\text{D}_{3.5}$ deuterides have different superstructures (sp. gr. $I4_1/amd$ (no. 141), $Z = 4$ and sp. gr. $I4_1/a$ (no. 88), $Z = 4$, respectively). The neutron diffraction data showed that deuterium atoms occupied the sites 16f and 32i in the deuteride tetrahedral lattice.

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