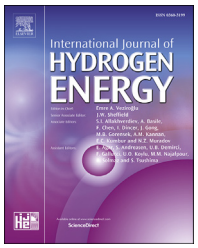
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 42 (2017) 22330–22332

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Interaction of $ZrMo_2$ with hydrogen at high pressure

S.A. Lushnikov [a,*], E.A. Movlaev [a], V.N. Verbetsky [a], V.A. Somenkov [b], S.S. Agafonov [b]

[a] Department of Chemistry, Lomonosov Moscow State University, Leninsky Hills 1/3, 119992 Moscow, Russia
[b] RSC "Kurchatov Institute", Kurchatov Square 1, 123182 Moscow, Russia

ARTICLE INFO

Article history:
Received 5 October 2016
Received in revised form
17 January 2017
Accepted 21 January 2017
Available online 7 April 2017

Keywords:
Hydrogen
Intermetallic compounds
Laves phase C15
Hydrides
Neutron diffraction
High pressure

ABSTRACT

The interaction of hydrogen with $ZrMo_2$ intermetallic compound at pressure up to 2500 bars has been studied. In $ZrMo_2$–H_2 system desorption isotherms were measured and thermodynamic parameters of hydride phase decomposition were calculated. The structure of $ZrMo_2D_{4.0}$ deuteride has been investigated by X-ray and neutron diffraction methods. It was revealed that ordering of deuterium in the cubic lattice of $ZrMo_2$ led to the formation of superstructure with tetragonal lattice. The occupancy of the positions of deuterium and metal atoms was determined.

Introduction

Investigation of hydrogen interaction with numerous cubic and hexagonal intermetallic compounds of Laves phases allows establishing of the several dependences [1]. In case, when compounds contain a hydride formation metals of the IV and V groups the absorption of hydrogen at usual conditions accompanies with formation of the phases with composition correspond to AB_2H_4 and higher. Hydrogen fills out one or several types of sites, depending of the cell parameters of compounds and then ordering after lowering temperature and increasing of hydrogen concentration. As results new superstructures appear and some of these types of superstructures it's possible to calculate theoretically [1,2]. In other cases absorption of hydrogen is small but it may be increased by using of the high hydrogen pressure.

Up to recent times in the row ZrV_2–$ZrCr_2$–$ZrMn_2$–$ZrFe_2$–$ZrCo_2$–$ZrMo_2$ for $ZrFe_2$ and $ZrCo_2$ compounds weren't detected hydrides with the high amount of hydrogen [3–5]. In works [6,7] were synthesized $ZrFe_2H_4$ and $ZrCo_2H_2$ hydrides after implying of the high hydrogen pressure and were investigated their thermodynamic properties and structure.

The interaction of $ZrMo_2$ with hydrogen was first studied in works [3,4]. It was revealed that absorption of hydrogen at 1 bar pressure and 30 °C leads to formation of $ZrMo_2H_{1.4}$ phase and $ZrMo_2H_{2.0}$ phase at 60 bars. In work [8] was established that amount of the absorbed hydrogen corresponds to 1.1 H/f.u. at 15 bars pressure and 30 °C temperature. The interaction of hydrogen with $ZrMo_2$ and measurement of the

* *Corresponding author.*
E-mail address: lushnikov@hydride.chem.msu.ru (S.A. Lushnikov).
http://dx.doi.org/10.1016/j.ijhydene.2017.01.231

pressure–composition isotherms at low temperatures (175–195 K) was studied in Ref. [9]. In this work has been supposed existence of several hydride phases at these conditions with hydrogen amount corresponding to 1.3–2.8 H/f.u. The goal of the present work is to obtain saturated hydrides phases at high pressure and to study their structure.

Experimental

Intermetallic compound was prepared from pure components using by arc-melting in inert atmosphere. After that obtained sample of $ZrMo_2$ was annealed in vacuum at 1500 °C temperature for 50 h. Desorption isotherms were measured at Sieverts apparatus at 2500 bars pressure of hydrogen [10]. Deuterium-containing sample was prepared for neutron study. This sample was passivated after synthesis. To this end, an autoclave with a sample under high 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. Synthesized deuteride contains more deuterium than hydride formed at a high pressure. This difference in the amount of deuterium and hydrogen in the samples appears due to the low temperature of the deuteride synthesis. Neutron diffraction measurements were performed on a DISK installation (λ = 1.668 Å) at the National Research Center "Kurchatov Institute". The structural data were refined with Rietveld method.

Result and discussion

The XRD data shows that obtained sample of the $ZrMo_2$ intermetallic compound is a single-phase. The lattice parameter of the sample is a = 7.591(2) Å, that is close to the prototype in Ref. [11]. The pressure–composition desorption isotherms obtained for $ZrMo_2$ and it corresponding hydrides are shown in Fig. 1. In this figure is possible to mark a two region. First region corresponds to the formation under a low pressure of stable hydride phase with $ZrMo_2H_{1.8}$ composition, mentioned in Refs. [3,4,8] works. Second region with the plateau corresponds to the formation of high pressure hydride phase. At temperature (−40 °C) the plateau to be found in the interval of the composition from 2.5 to 3.3 H/f.u., at 0 °C from 2.4 to 3.2 H/f.u., at 20 °C from 2.3 to 2.9 H/f.u., and at 44 °C from 2.3 to 2.9 H/f.u. The maximum amount of the hydrogen in hydride phase corresponds to 3.0 H/f.u. at 1000 bars pressure and at room temperature. At low temperature (−40 °C) amount of the hydrogen in hydride increases and reach 3.6 H/f.u. at 1500 bars pressure. When the pressure was reduced to several bars no hydrogen desorption was observed, and in this case amount of the hydrogen in hydride corresponds to interval from 1.5 to 2.5 H/f.u. The values of ΔH (26.38 kJ/mol H_2) and ΔS (127.22 J/(mol H_2 K)) of the decomposition reaction were calculated on bases of the measured isotherms. The calculated values are close to the data of ΔH (22.0 kJ/mol H_2) and ΔS (102.0 J/(mol H_2·K)), obtained in work [4].

The neutron diffraction data and structure of deuteride are presented in Figs. 2 and 3 and in Table 1. The experimental data shows that at the high pressure a cubic lattice of deuteride transformed into tetragonal with cell parameters a = 5.496(2) Å and c = 7.986(1) Å. In works [1,2] was shown, that

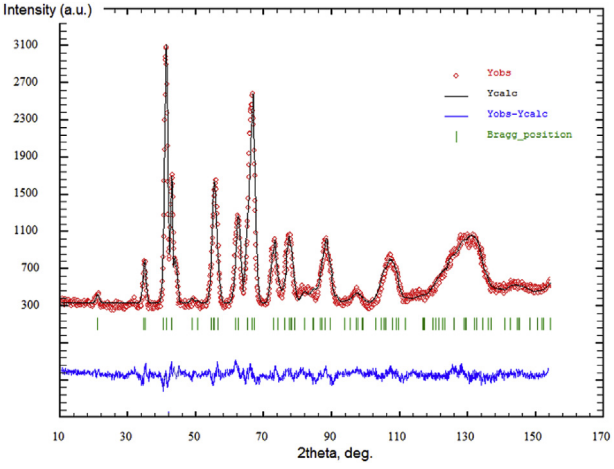


Fig. 2 – Neutron diffraction pattern of $ZrMo_2D_{4.0}$ at 77 K temperature.

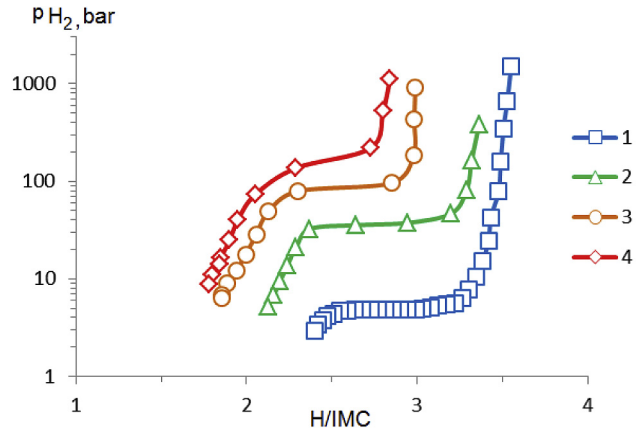


Fig. 1 – Desorption isotherms in $ZrMo_2$–H_2 system at: 1-(−44 °C), 2-0 °C, 3-20 °C and 4–40 °C.

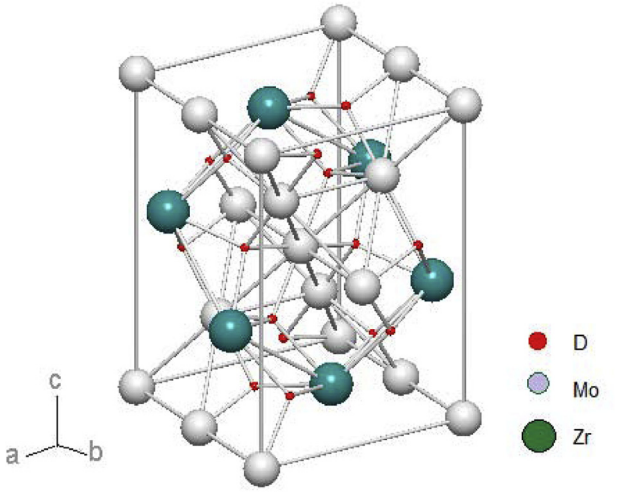


Fig. 3 – Structure of $ZrMo_2D_{4.0}$.

Table 1 – The structure data of $ZrMo_2D_{4.0}$, SG 88, $I4_1/aO_2$.

Atom	Position types	Occupancy	Atomic coordinates		
			x	y	z
Zr	4*a*	1.0	0.000	0.250	0.125
Mo	8*d*	1.0	0.000	0.000	0.500
D	16*f*	1.02(2)	0.1835(2)	−0.0698(3)	0.6360(2)
$R_w = 8.5\%$					

this behavior is typical for Laves phases and occurs as a result of hydrogen ordering in the lattice by reason of rising of hydrogen concentration or lowering temperature. In work [2] were calculated all possible cases of formation of the ordered superstructures at different hydrogen concentration. At the XRD pattern of the $ZrMo_2D_{4.0}$ sample were revealed additional peaks of the tetragonal superstructure (*SG88*, $I4_1/aO_2$), calculated in work [2]. This superstructure was selected as a model for the refining of neutron data and location of the positions of deuterium atoms. In result we calculated that practically all deuterium atoms occupy 16*f* position with Zr_2Mo_2 atoms neighboring. In work [1] was noticed that in zirconium-based C15 Laves phases deuterium can occupy both 96*g* and 32*e* positions depending of the lattice parameter. In our case the lattice parameter of $ZrMo_2$ allows to fill out only 96*g* position, and in further, when deuterium starts ordering, the 96*g* position transferred into 16*f* position. These calculations are in agreement with the obtained neutron data. Calculated on the base of the neutron data interatomic distances corresponds: Zr–D 2.08 Å, Mo–D 1.90 Å and D–D 2.15 Å. In comparison with the literature data for hydrides of $ZrH_{1.68}$ [12] and $MoH_{0.95}$ [13], in our case interatomic distances for Mo (Mo–H 2.07 Å) are less and for Zr (Zr–H 2.07 Å) practically do not change. The D–D interatomic distances in $ZrMo_2$ deuteride are less in comparison with the distances in the zirconium (2.39 Å) and molybdenum (2.92 Å) hydrides. The neutron data of $ZrMo_2D_{4.0}$ at low temperature are similar to the deuteride sample after the exposure in air at room temperature.

The XRD data of $ZrMo_2D_{4.0}$ after the exposure in air at room temperature for one month demonstrated only a slight decrease in the lattice parameters $a = 5.495(3)$ Å, $c = 7.984(3)$ Å and volume expansion $\Delta V/V = 11\%$. The value of $\Delta V/V$ of the lattice is close to the data obtained in work [14] for $HfV_2D_{4.0}$ hydride phase ($\Delta V/V$ corresponds 14%) with a tetragonal superstructure and the same amount of hydrogen. This fact indicates the high stability of deuteride sample after passivation in air. A slight expansion of the volume of $ZrMo_2D_{4.0}$ deuteride occurs by the reason of a small added volume to non-compressed Van der Vaal's volume of the lattice, in analogy for *d*-metals in VI and VII groups [15].

Summary

In $ZrMo_2$–H_2 system at high pressure has been synthesized hydride phase with hydrogen amount corresponds to 3.6 H/f.u. Hydrogen absorption–desorption isotherms were measured at divers temperatures. Thermodynamic values of decomposition reaction of hydride phases were calculated on base of the isotherms. The structure of $ZrMo_2D_{4.0}$ has been investigated by XRD and neutron diffraction methods. It was revealed, that ordering of deuterium in the cubic lattice of $ZrMo_2$ led to the formation of superstructure with tetragonal lattice (*SG 88*, $I4_1/aO_2$). In tetragonal lattice deuterium atoms occupy 16*f* site. As a result, in hydrides of $ZrMo_2$ synthesized at the high pressure was observed similar dependences as in other analogical compounds.

Funding

This study was supported by the Russian Science Foundation project no 16-12-10065 and the Russian Foundation for Basic Research; project no 14-22-00158.

REFERENCES

[1] Somenkov VA, Irodova AV. Lattice structure and phase transitions of hydrogen in intermetallic compounds. J Less Common Met 1984;101:481–92.
[2] Irodova AV. Orientation ordering (k = 0) in interstitial solid solutions based on cubic (C 15) Laves phases. Solid State Phys 1980;22(9):2559–68.
[3] Pebler A, Gulbransen EA. Equilibrium studies of the systems $ZrCr_2$-H_2, ZrV_2-H_2 and $ZrMo_2$-H_2 between 0° and 900 °C. Trans Met Soc AIME 1967;239:1593–600.
[4] Pebler A, Gulbransen EA. Thermochemical and structural aspects of the reaction of hydrogen with alloys and intermetallic compounds of zirconium. Electrochem Technol 1966;4(5–6):211–5.
[5] Sivov RB, Zotov TA, Verbetsky VN. Novel $ZrFe_2$-based absorbing hydrogen alloys with high dissociation pressure of hydrides. Altern Energy Ecol 2010;85(5):13–20.
[6] Filipek SM, Paul-Boncour V, Percheron-Guegan A, Jacob I, Marchuk I, Dorogova M, et al. J Phys Condens Matter 2002;14:11261–4.
[7] Filipek SM, Jacob I, Paul-Boncour V, Percheron-Guegan A, Marchuk I, Mogilyanski D, et al. Pol J Chem 2001;75:1921–6.
[8] Semenenko KN, Verbetsky VN, Mitrokhin SV, Burnasheva VV. Investigation IMC zirconium with hydrogen, crystallized in phase Laves structures. Russ J Neorg Khim 1980;7:1731–6.
[9] Semenenko KN, Verbetsky VN, Pilchenko VA. Interaction $ZrMo_2$ with at low temperatures. Vestn MGU, 2, Chem 1986;27(3):332–3.
[10] Mitrokhin SV, Zotov TA, Movlaev EA, Verbetsky VN. Synthesis and properties of AB_5 type hydrides at elevated pressures. J Alloys Compd 2007;446–447:603–5.
[11] Domagala RF, McPherson DJ, Hansen M. Systems zirconium-molybdenum and zirconium-wolfram. Trans Am Inst Min Metall Pet Eng 1953;197:73–9.
[12] Beck RL. Zirconium-hydrogen phase system. ASM Trans 1962;55:542–55.
[13] Irodova AV, Glaskov VP, Somenkov VA, Shilshtein SS, Antonov VE, Ponyatovskii VG. Neutron-diffraction investigation of the structures of the hydrides of molybdenum, rhodium, and nickel. Phys Crystallogr 1988;33:453–5.
[14] Irodova AV, Glaskov VP, Somenkov VA, Shilshtein SS. Hydrogen ordering in the cubic Laves phases HfV_2. J Less Common Met 1981;77:89–98.
[15] Somenkov VA, Shilshtein SS. Volume changing at hydrogen dissolution in *d*-metals and intermetallic compounds. Fiz Mettalov Metalloved 1998;86(3):114–22.