Hydrogen interaction with intermetallic compounds and alloys at high pressure

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ARTICLE INFO

ABSTRACT

The paper presents a review of the recent work done in MSU on intermetallic hydrides with high dissociation pressure. Hydrogen sorption properties of a large variety of AB_5, AB_2 and BCC intermetallic compounds and alloys were studied at pressures up to 3000 atm. Several new intermetallic hydrides with potential application in high-capacity hydrogen storage devices have been identified for the first time and fully characterised using a gas-volumetric analytical technique in a unique high-pressure apparatus. Basing on the experimental and literature results the relationships between hydrogen absorption capacity, thermodynamic parameters of interaction and composition of alloys were established. Obtained results provide a good perspective for practical application of the studied hydrides especially in metal-hydride compressors.

1. Introduction

First high pressure P–C–T-investigations of hydrogen interaction with intermetallics and alloys date back to late 1970s, when Lakner et al. [1,2] measured the absorption–desorption isotherms for several AB_5 compounds in an attempt to experimentally prove the predicted theoretical hydrogen capacity of the their hydrides. In our laboratory high pressure studies began initially in 1993 [3] and came to full strength after construction of a unique high pressure device allowing to measure PCT-dependences up to 3000 atm [4]. Since then a variety of AB_5-, AB_2- and BCC-type alloys were studied.

Now the increasing interest for high pressure investigations of hydrides is connected with the commercial appearance of high pressure vessels and development of new combined method for efficient hydrogen storage.

2. Experimental part

High pressure device was described earlier [4]. The amounts of absorbed or desorbed hydrogen were calculated using a modified Van der Waals equation [5]:

$$[p + a(p)/V^a][V - b(p)] = RT \tag{1}$$

where a, b – pressure dependent coefficients (for $p > 1$ atm); p – pressure (atm); T – temperature (K); V – system volume (cm^3); R – universal gas constant (82.06 cm^3 atm/mole K).

Thermodynamic parameters of the desorption reaction were determined using the Van't Hoff equation and fugacity values, corresponding to experimental pressure values:

$$RT \ln(f_p) = \Delta H - T\Delta S \tag{2}$$

where f_p – fugacity; ΔH – enthalpy change; ΔS – entropy change.

Finally, the fugacity values were calculated using (Eq. (3)) and real molar volumes obtained from the following equation:

$$RT \ln(f_p) = RT \ln p - \int_0^p (V_{id} - V_{real})dp, \tag{3}$$

where V_{real} – real absorbed/desorbed hydrogen molar volume, V_{id} – ideal absorbed/desorbed hydrogen molar volume.

Pressure values were measured with 5% accuracy, the temperature was determined ±0.5 K, hydrogen concentration in hydrides was determined with accuracy ±0.1 H/IMC (±0.05 mass% H$_2$).

Alloys were prepared from pure metals in an argon atmosphere arc furnace. X-ray characterisation of initial alloys and resulting hydrides was performed in DRON-3 diffractometer (Cu Kα). In order to avoid decomposition of high pressure hydrides the samples were cooled to liquid nitrogen temperature in the sample holder and after 10 min. were exposed to air for 30 min.

3. Results and discussion

3.1. AB_5–H$_2$ systems

Results of PCT-experiments for La-based binary and pseudobinary AB_5-compounds [2] showed that hydrogen absorption at high pressure trends to predicted theoretical maximum AB_5H_9. In our studies we chose CeNi$_5$ and YNi$_5$ since they were reported not to react with hydrogen at comparatively low pressure up to 100 atm. However application of high pressure (1500 atm) allowed Takeshita et al. [6] to synthesise YNi$_5$H$_{3.5}$ hydride phase.

In case of CeNi$_5$ [7] hydrogen absorption began only after several activation cycles because the pressure, required for hydrogen absorption in the first activation cycle, was considerably higher

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Table 1
Hydrogen sorption properties of $ZrFe_{2-x}M_x$ compounds.

Compound	P_0 (atm)	P_1 abs/des (atm)	P_e abs/des (atm)	H/IMC_{atm}/mass% H_2	ΔH (kJ/mole H_2)	ΔS (J/K mole H_2)	V IMC (Å^3)	$\Delta V/V$ (%)
$ZrFe_{1.8}V_{0.2}$	<10	–/–	–/12	3.6_{800}/1.79	23.6(3)	102(3)	C15 356.3(1)	24.1
							C14 179.5(1)	24.2
$ZrFe_{1.8}Cr_{0.2}$	∼100	90/50	80/55	3.6_{1660}/1.79	22.3(4)	109(6)	353.7(1)	23.8
$ZrFe_{1.8}Mn_{0.2}$	∼300	380/120	290/140	3.6_{1700}/1.78	21.8(6)	116(5)	353.6(1)	28.0
$ZrFe_2$	800	1120/–	690/325	3.5_{1800}/1.72	21.3(4)	121(5)		24.3
$ZrFe_{1.8}Co_{0.2}$	∼1000	940/325	725/360	3.5_{1730}/1.69	16.8(3)	108(4)	351.8(1)	22.8
$ZrFe_{1.8}Ni_{0.2}$	∼700	620/210	455/250	3.5_{2100}/1.72	21.5(6)	120(6)	351.5(1)	23.7
$ZrFe_{1.8}Cu_{0.2}$	∼300	325/180	–/215	3.4_{900}/1.65	19.6(5)	112(3)	352.5(1)	25.0
$ZrFe_{1.8}Mo_{0.2}$	∼100	145/15	65/20	3.5_{1080}/1.62	25.9(5)	112(5)	178.8(1)	23.6

P_0 – Starting hydriding pressure, P_1 – absorption–desorption pressure in the middle of the plateau in the first run, P_2 – equilibrium absorption–desorption pressure in the third run.
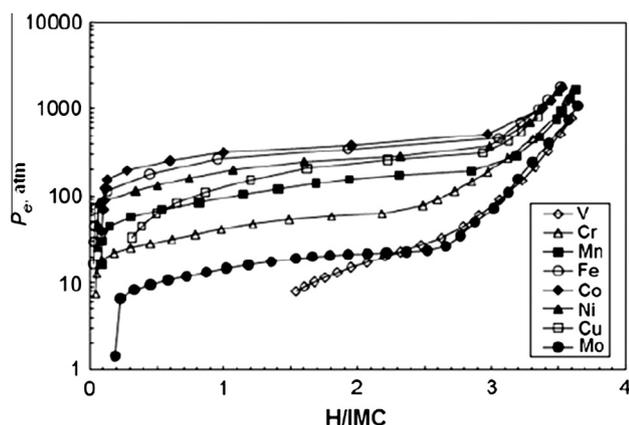

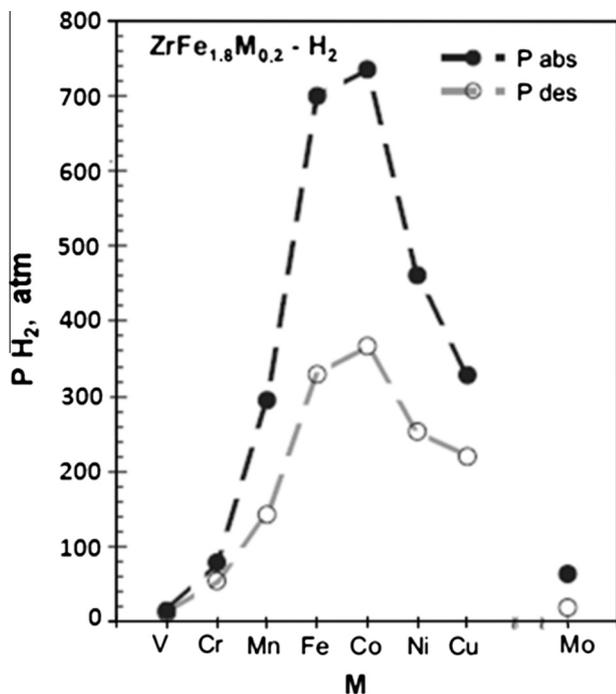**Fig. 1.** Desorption isotherms for $ZrFe_{1.8}M_{0.2}$–H_2 systems at 25 °C.

Fig. 2. The dependence of the equilibrium absorption/desorption pressures on the atomic number of the substituting metal.

Fig. 3. Isotherms for $Zr_{1-x}Ti_x(Fe_{1-y}M)_2$–$H_2$ systems at 25 °C: open marks – absorption, filled marks – desorption.

In case of YNi_5 noticeable reaction with hydrogen started only at pressure more than 500 atm and resulted in formation of $YNi_5H_{5.4}$ hydride at −20 °C. It is worth noting that the reaction rate was extremely low and the equilibrium in each absorption–desorption step was established only in 2–4 h. Possible explanation of these peculiar behaviour could be found in compressibility and cell volume of YNi_5 being the lowest among AB_5-type alloys studied by us.

3.2. AB_2–H_2 systems

AB_2 alloys initially could be considered as providing better opportunities than AB_5 alloys to obtain new phases at high pressure and finding new phase transitions. Even at mild pressure conditions and at low temperature Reilly et al. found that $TiCr_2$ hydride undergoes phase transformation from Laves phase to CaF_2 structure type [8]. Verbetsky et al. further found that $TiCr_2$ exhibits so-called "structure memory" effect [9]. Hydrogen desorption from CaF_2-type high pressure hydride ended in reformation of the starting C14 or C15 modification of $TiCr_2$.

Later Filipek et al. [10] managed to obtain a hydride of approximate composition $ZrFe_2H_4$, which was considered not to absorb appreciable amounts of hydrogen [11].

We studied the hydrogen absorption–desorption properties of substituted pseudobinary compounds $ZrFe_{1.8}M_{0.2}$ (M = V, Cr, Mn, Fe, Co, Ni, Cu, Mo) [12–15]. Their hydrogen absorption–desorption properties are listed in Table 1. All alloys had C15 type structures except for the alloys with V (a mixture of C15 + C14) and Mo

than the equilibrium absorption pressure at the same temperature (700 and 250 atm correspondingly). Also an extremely large value of hysteresis was obtained for $CeNi_5$–H_2 system.
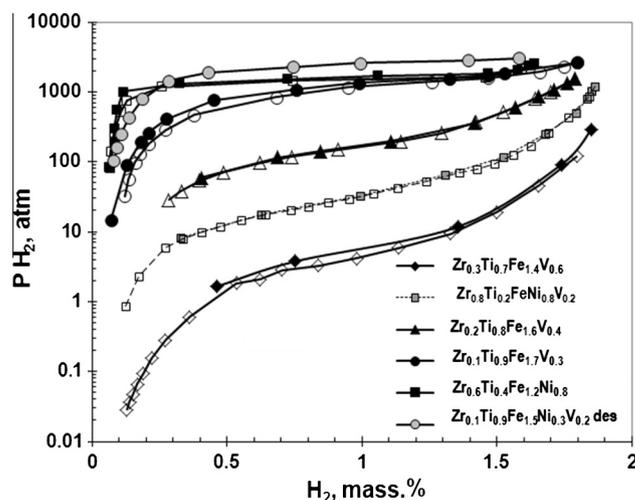
Table 2
Hydrogen sorption properties of $Zr_{1-x}Ti_x(Fe_{1-y}M)_2$.

Compound	Phase composition, V (Å³)	$\Delta V/V$ (%)	Mass% H_2/H/M	$P_{abs}/_{des}$ 20 °C atm	$\ln(P_{abs}/P_{des})$	Calculated P_{des} 90 °C (atm)	ΔH (kJ/mole H_2)/ΔS (J/K mole H_2)
$Zr_{0.3}Ti_{0.7}Fe_{1.4}V_{0.6}$	C14 170.35(1)	18.0	2.1/1.18	5.1/4.2	0.20	40	31.1(6)/116(5)
$Zr_{0.2}Ti_{0.8}Fe_1V_{0.4}$	C14 165.088(1)	20.6	1.8/0.99	172/165	0.04	603	19.7(4)/109.9(8)
$Zr_{0.1}Ti_{0.9}Fe_{1.7}V_{0.3}$	C14 161.47(2)	22.2	1.8/0.98	1398/1297	0.08	2495	13.5(5)/112.9(5)
$Zr_{0.6}Ti_{0.4}Fe_{1.2}Ni_{0.8}$	C15 331.44(3)	24.6	1.64/1.02	1611/1479	0.09	2908	16.5(5)/124(6)
$Zr_{0.8}Ti_{0.2}FeNi_{0.8}V_{0.2}$	C15 343.69(1)	25.0	1.9/1.23	28/27	0.04	198	26.8(4)/118(4)
$Zr_{0.1}Ti_{0.9}Fe_{1.5}Ni_{0.3}V_{0.2}$	C14 160.042(9)	20.4	1.8/0.99	–/2564	$0.08_{-20°C}$	4088	12.1(3)/119(7)

Table 3
Structure and hydrogen sorption properties of V–Cr alloys.

Alloy	BCC cell parameter (Å)	Cell parameters of stable hydride (Å)	Cell parameters of high pressure hydride (Å)	Hydrogen content (mass%)/pressure (atm)	Reversible hydrogen (mass%)	$P_{abs}/_{des}$ 20 °C (atm)	ΔH(kJ/moleH_2)/ΔS (J/K mole H_2)
V [22,23]	3.030	$VH_{0.9}$ BCT: $a = 6.04$ $c = 6.72$	$VH_{2.1}$ FCC: $a = 4.24$	3.9_{100}	2.2		41(1)/142(7)
$V_{0.9}Cr_{0.1}$	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_{560}	2.3	29/15.5	33.6(4)/137(5)
$V_{0.8}Cr_{0.2}$	3.0055(2)	$V_{0.2}Cr_{0.2}H_{0.6}$ 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_{900}	0.7	120/35	26.3(4)/120(4)
$V_{0.7}Cr_{0.3}$	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_{700}	0.9	170/21.3	33.3(5)/134(6)
$V_{0.6}Cr_{0.4}$	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_{700}	1.2	130/32.6	29.5(4)/129(5)
$V_{0.5}Cr_{0.5}$	2.9504(2)		$V_{0.5}Cr_{0.5}H_{0.9}$ HCP: $a = 2.731(1)$ $c = 4.630(3)$	1.8_{2000}	1.7	340/66	25.4(4)/122(5)

(C14). The unit cell volume of the C15 phase decreased in the series V to Ni and increased for the Cu-substituted alloy.

As could be expected the hydrogen content was about 1.8 mass% for V, Cr and Mn and about 1.7 mass% for Fe, Co, Ni and Cu. Mo-substituted compound showed the lowest hydrogen content 1.6 mass% among all studied systems (Fig. 1). The dependence of the equilibrium absorption/desorption pressures on the atomic number of the substituting metal is shown in Fig. 2. The equilibrium pressures are maximal in the case of the Co substituted alloy. The drop of equilibrium pressures occurs in case of Ni and Cu. In case of Ni this may be accounted for by the nature of Ni–H bonding, in view of the fact that the enthalpy of binary hydride formation increases in the row of 3d-metal from V to Co and slightly decreases for Ni.

In case of more complicated compositions $Zr_{1-x}Ti_x(Fe_{1-y}M_y)_2$ (M = V, Ni) hydrogen absorption and desorption pressures of relevant hydrides vary on a broad scale (Fig. 3, Table 2). The highest desorption pressure of 2560 atm at 20 °C and the lowest desorption enthalpy of 12 kJ/mole H_2 was observed for the $Zr_{0.1}Ti_{0.9}Fe_{1.5}Ni_{0.3}V_{0.2}$–$H_2$ system. The complete saturation of the corresponding hydride is possible only at a temperature below −20 °C and a pressure of 3000 atm.

3.3. Hydrides of V-based BCC-alloys

First studies of hydrogen interaction with BCC-alloys were done in our laboratory in late 1980s. Investigations of Ti–V–Al, Ti–V–Fe, Ti–V–Co and Ti–V–Ni systems [16–19] showed that hydrogen
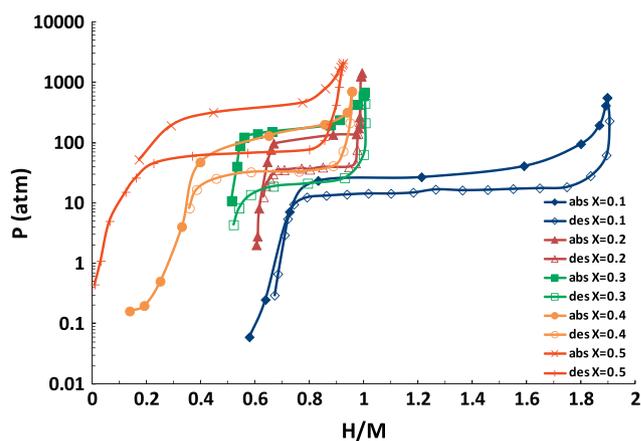

Fig. 4. Isotherms for $V_{1-x}Cr_x$–H_2 systems at 20 °C.

desorption from corresponding hydride phases was rather complicated process, determined by the component metal ratio and, in case of multiphase alloys, an integral one with respect to formative hydride phases.

Hydrogen interaction with alloys of V–Cr system was studied at low pressure [20]. Starting from 20 at.% of chromium content alloys did not react with hydrogen up to 70 atm.

In our study [21] $V_{1-x}Cr_x$ alloys with $X \geqslant 0.2$ began to absorb hydrogen only at pressure higher than 120 atm (Table 3, Fig. 4).
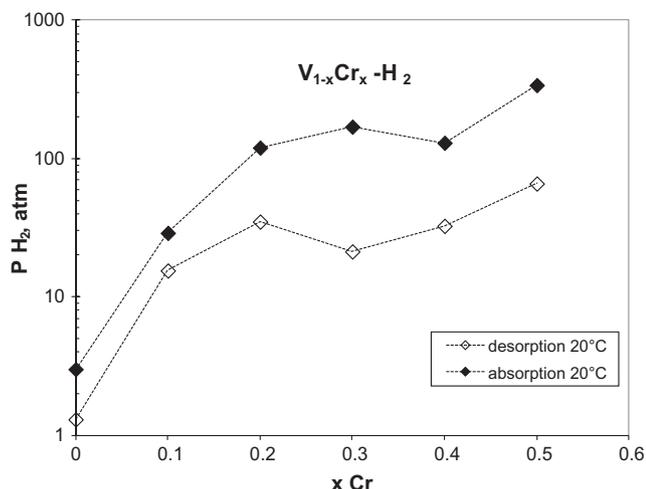
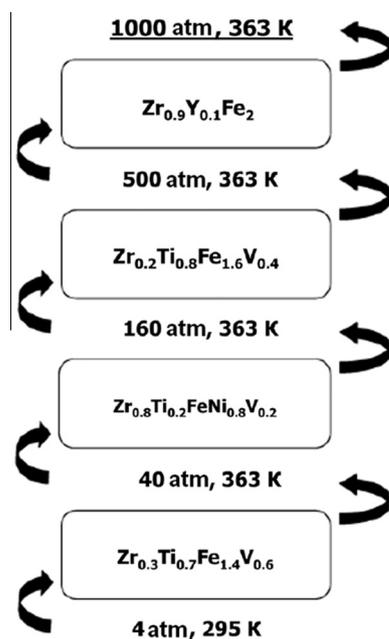**Fig. 5.** The dependence of equilibrium pressure on chromium content for $V_{1-x}Cr_x$–H_2 systems.

Fig. 6. Possible stages of the high pressure metal-hydride compressor.

However, unlike pure vanadium, absorption started even at room temperature. Hydride generation for alloys with $0 \leqslant X \leqslant 0.4$ is characterised by two stages – formation of stable hydride and formation of hydride phase with high dissociation pressure. Hydrogen content in stable phase decreases from $H/M = 0.7$–0.3 with X increasing from 0.1 to 0.4. No stable phase was found for $V_{0.5}Cr_{0.5}$ alloy. Maximum hydrogen content in high pressure hydride phases also gradually decreases with increasing chromium content. However, remarkable is the fact that for $V_{0.9}Cr_{0.1}$ the value of reversible hydrogen (2.3 mass%) is higher than that for $VH \leftrightarrow VH_2$ transition.

The dependence of equilibrium pressure on chromium content (Fig. 5) looks rather unusual because of its sudden drop at $X = 0.4$. Normally the increase in concentration of less active towards hydrogen component gives rise to the increase in equilib-

rium pressure value of corresponding transition. In our case the answer is given by X-ray analysis of hydride phases (Table 3). All initial alloys were of a BCC-structure. Stable hydrides except for $X = 0.5$ crystallised in a BCT structure same as V_2H. High pressure hydrides for $0 \leqslant X \leqslant 0.2$ had an FCC structure similar to VH_2 whereas for $0.4 \leqslant X \leqslant 0.5$ their structure changed to an HCP same as structure of CrH. For $X = 0.3$ hydride appeared to be a two-phase one with FCC:HCP = 0.7:0.3. This can be explained by the fact that CrH_y hydride has an HCP structure for $Y < 0.5$ and for $Y > 0.55$ it is a mixture of an HCP and an FCC structures. Thus $V_{0.7}Cr_{0.3}H$ phase is an intermediate one between $V_{0.8}Cr_{0.2}H$ and $V_{0.6}Cr_{0.4}H$ phases.

The most important consequence of these results is the fact that since the structure of $V_{0.5}Cr_{0.5}H$ hydride is similar to CrH, doping of chromium leads to the stabilisation of its hydride phase.

4. Conclusions

Stated results of investigations clearly show that the application of high pressure method provide a powerful tool for retrieval of new materials, perspective for various metal-hydride applications. Obtained results for Zr–Ti substituted alloys could be of considerable practical importance providing perspective materials for use in metal-hydride compressors. Possible stage scheme of such a compressor is shown in Fig. 6. Starting with 4 atm it is possible to obtain an outlet pressure of 1000 atm in four steps.

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