Hydrogen interaction with intermetallic compounds and alloys at high pressure

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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 AB5, AB2, 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.

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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 AB5 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 AB5-, AB2- 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]:

\[ p + a/p/V^2 - b/p = RT \]  

(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 (8.206 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:

\[ RT \ln(f_p) = \Delta H - T \Delta S \]  

(2)

where \( f_p \) – fugacity; \( \Delta H \) – enthalpy change; \( \Delta S \) – entropy change.

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

\[ RT \ln(f_p) = RT \ln(p) - \int_0^p \left[V_a - V_{real}\right] dp \]  

(3)

where \( V_{real} \) – real absorbed/desorbed hydrogen molar volume, \( V_a \) – 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 wt%/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 K\( \alpha \)). 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\(_5\)H\(_9\). 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\(_3\)H\(_{13.5}\) 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...
than the equilibrium absorption pressure at the same temperature (700 and 250 atm correspondingly). Also an extremely large value of hysteresis was obtained for CeNi₅–H₂ system.

In case of YNi₅ noticeable reaction with hydrogen started only at pressure more than 500 atm and resulted in formation of YNi₅H₅.₄ hydride at \( \frac{20}{176} \)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 YNi₅ being the lowest among AB₅-type alloys studied by us.

### 3.2. AB₂–H₂ systems

AB₂ alloys initially could be considered as providing better opportunities than AB₅ 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 TiCr₂ hydride undergoes phase transformation from Laves phase to CaF₂ structure type [8]. Verbetsky et al. further found that TiCr₂ exhibits so-called “structure memory” effect [9]. Hydrogen desorption from CaF₂-type high pressure hydride ended in reformation of the starting C14 or C15 modification of TiCr₂.

Later Filipek et al. [10] managed to obtain a hydride of approximate composition ZrFe₁.₈M₀.₂ which was considered not to absorb appreciable amounts of hydrogen [11].

We studied the hydrogen absorption–desorption properties of substituted pseudobinary compounds ZrFe₁.₈M₀.₂ (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.

**Table 1**

<table>
<thead>
<tr>
<th>Compound</th>
<th>( P_0 ) (atm)</th>
<th>( P_1 ) abs/des (atm)</th>
<th>( P_e ) abs/des (atm)</th>
<th>( H/\text{IMC mass}% \text{H}_2 )</th>
<th>( \Delta H ) (kJ/mole H₂)</th>
<th>( \Delta S ) (J/K mole H₂)</th>
<th>V IMC (Å³)</th>
<th>AV/V (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrFe₁.₈V₀.₂</td>
<td>&lt;10</td>
<td>–/–</td>
<td>–/12</td>
<td>3.6₁₀₀/1.₇₉</td>
<td>23.6/3</td>
<td>102/3</td>
<td>175/6</td>
<td>24.1</td>
</tr>
<tr>
<td>ZrFe₁.₈Cr₀.₂</td>
<td>~100</td>
<td>90/50</td>
<td>80/55</td>
<td>3.6₁₀₀/1.₇₉</td>
<td>22.3/4</td>
<td>109/6</td>
<td>353/7</td>
<td>23.8</td>
</tr>
<tr>
<td>ZrFe₁.₈Mn₀.₂</td>
<td>~300</td>
<td>380/120</td>
<td>290/140</td>
<td>3.5₁₀₀/1.₇₈</td>
<td>21.8/6</td>
<td>116/5</td>
<td>353/6</td>
<td>28.0</td>
</tr>
<tr>
<td>ZrFe₁.₈Co₀.₂</td>
<td>800</td>
<td>1120</td>
<td>690/325</td>
<td>3.5₁₀₀/1.₇₂</td>
<td>21.3/4</td>
<td>121/5</td>
<td>351/8</td>
<td>24.3</td>
</tr>
<tr>
<td>ZrFe₁.₈Mo₀.₂</td>
<td>~1000</td>
<td>940/325</td>
<td>725/360</td>
<td>3.5₁₀₀/1.₆₉</td>
<td>16.₈/3</td>
<td>108/4</td>
<td>351/8</td>
<td>22.8</td>
</tr>
<tr>
<td>ZrFe₁.₈Cu₀.₂</td>
<td>~700</td>
<td>620/210</td>
<td>455/250</td>
<td>3.5₂₁₀/1.₇₂</td>
<td>21.₅/6</td>
<td>120/6</td>
<td>351/5</td>
<td>23.7</td>
</tr>
<tr>
<td>ZrFe₁.₈M₀.₂</td>
<td>~300</td>
<td>325/180</td>
<td>–/215</td>
<td>3.₄₉₀/1.₆₅</td>
<td>19.₆/5</td>
<td>112/3</td>
<td>352/5</td>
<td>25.0</td>
</tr>
<tr>
<td>ZrFe₁.₈M₀.₂</td>
<td>~100</td>
<td>145/15</td>
<td>65/20</td>
<td>3.₅₁₀₀/1.₆₂</td>
<td>25.₉/5</td>
<td>112/5</td>
<td>178/8</td>
<td>23.6</td>
</tr>
</tbody>
</table>

\( P_0 \) – Starting hydriding pressure, \( P_1 \) – absorption–desorption pressure in the middle of the plateau in the first run, \( P_e \) – equilibrium absorption–desorption pressure in the third run.

In case of YNi₅ noticeable reaction with hydrogen started only at pressure more than 500 atm and resulted in formation of YNi₅H₅.₄ hydride at \( \frac{20}{176} \)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 YNi₅ being the lowest among AB₅-type alloys studied by us.

**Fig. 1.** Desorption isotherms for ZrFe₁.₈M₀.₂–H₂ 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 Zr₁₋ₓTiₓ(Fe₁₋ₓMₓ)₂–H₂ systems at 25 °C: open marks – absorption, filled marks – desorption.

3.2. AB₂–H₂ systems

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We studied the hydrogen absorption–desorption properties of substituted pseudobinary compounds ZrFe₁.₈M₀.₂ (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.
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 Zr₁₋ₓTiₓFe₁₋ₓMₓ₂ (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 H₂ was observed for the Zr₀.₃Ti₀.₇Fe₀.₄Ni₀.₃V₀.₂–H₂ 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 desorption from corresponding hydrides 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] V₁₋ₓCrₓ alloys with X > 0.2 began to absorb hydrogen only at pressure higher than 120 atm (Table 3, Fig. 4).

### Table 2

Hydrogen sorption properties of Zr₁₋ₓTiₓFe₁₋ₓMₓ₂.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phase composition, V (Å³)</th>
<th>ΔV/V (%)</th>
<th>Mass% H₂/H/M</th>
<th>Pₘₐₓ/dₑₙ 20 °C atm</th>
<th>ln(Pₘₐₓ/Pₐₑₙ)</th>
<th>Calculated Pₐₑₙ 90 °C atm</th>
<th>ΔH (kJ/mole H₂)/ΔS (J/K mole H₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr₀.₃Ti₀.₇Fe₀.₄V₀.₂</td>
<td>C₁₄ 170.35(1)</td>
<td>18.0</td>
<td>2.1/1.18</td>
<td>51/4.2</td>
<td>0.20</td>
<td>40</td>
<td>31.1(6)/116(5)</td>
</tr>
<tr>
<td>Zr₀.₃Ti₀.₇Fe₀.₄V₀.₄</td>
<td>C₁₄ 165.088(1)</td>
<td>20.6</td>
<td>1.8/0.99</td>
<td>172/165</td>
<td>0.04</td>
<td>603</td>
<td>19.7(4)/109.9(8)</td>
</tr>
<tr>
<td>Zr₀.₃Ti₀.₇Fe₀.₄V₀.₃</td>
<td>C₁₄ 161.47(2)</td>
<td>22.2</td>
<td>1.8/0.98</td>
<td>1398/1297</td>
<td>0.08</td>
<td>2495</td>
<td>13.5(5)/112.9(5)</td>
</tr>
<tr>
<td>Zr₀.₃Ti₀.₇Fe₀.₄Ni₀.₃</td>
<td>C₁₅ 331.44(3)</td>
<td>24.6</td>
<td>1.64/1.02</td>
<td>1611/1479</td>
<td>0.09</td>
<td>2908</td>
<td>16.5(5)/124(6)</td>
</tr>
<tr>
<td>Zr₀.₃Ti₀.₇Fe₀.₄Ni₀.₃V₀.₂</td>
<td>C₁₅ 343.69(1)</td>
<td>25.0</td>
<td>1.9/1.23</td>
<td>28/27</td>
<td>0.04</td>
<td>198</td>
<td>26.8(4)/118(4)</td>
</tr>
<tr>
<td>Zr₀.₃Ti₀.₇Fe₀.₄Ni₀.₃V₀.₂</td>
<td>C₁₄ 160.042(9)</td>
<td>20.4</td>
<td>1.8/0.99</td>
<td>–/2564</td>
<td>0.08</td>
<td>4088</td>
<td>12.1(3)/119(7)</td>
</tr>
</tbody>
</table>

### Table 3

Structure and hydrogen sorption properties of V–Cr alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>BCC cell parameter (Å)</th>
<th>Cell parameters of stable hydride (Å)</th>
<th>Cell parameters of high pressure hydride (Å)</th>
<th>Hydrogen content (mass%)/pressure (atm)</th>
<th>Reversible hydrogen (mass%)/Pₘₐₓ/dₑₙ 20 °C atm</th>
<th>ΔH (kJ/mole H₂)/ΔS (J/K mole H₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V [22,23]</td>
<td>3.030</td>
<td>VH₀.₉</td>
<td>VH₂.₁</td>
<td>3.9₁₀₀</td>
<td>2.2</td>
<td>41(1)/142(7)</td>
</tr>
<tr>
<td>V₀.₉Cr₀.₁</td>
<td>3.0211(1)</td>
<td>V₀.₉Cr₀.₁H₀.₇</td>
<td>V₀.₉Cr₀.₁H₁.₀</td>
<td>3.6₅₀₀</td>
<td>2.3</td>
<td>29(15.5)</td>
</tr>
<tr>
<td>V₀.₈Cr₀.₂</td>
<td>3.0055(2)</td>
<td>V₀.₈Cr₀.₂H₀.₅</td>
<td>V₀.₈Cr₀.₂H₁.₀</td>
<td>3.6₅₀₀</td>
<td>2.3</td>
<td>33.6(4)/137(5)</td>
</tr>
<tr>
<td>V₀.₇Cr₀.₃</td>
<td>2.9928(2)</td>
<td>V₀.₇Cr₀.₃H₀.₅</td>
<td>V₀.₇Cr₀.₃H₁.₀</td>
<td>3.6₅₀₀</td>
<td>2.3</td>
<td>33.6(4)/137(5)</td>
</tr>
<tr>
<td>V₀.₆Cr₀.₄</td>
<td>2.9677(1)</td>
<td>V₀.₆Cr₀.₄H₀.₃</td>
<td>V₀.₆Cr₀.₄H₁.₀</td>
<td>3.6₅₀₀</td>
<td>2.3</td>
<td>33.6(4)/137(5)</td>
</tr>
<tr>
<td>V₀.₅Cr₀.₅</td>
<td>2.9504(2)</td>
<td>V₀.₅Cr₀.₅H₀.₅</td>
<td>V₀.₅Cr₀.₅H₁.₀</td>
<td>3.6₅₀₀</td>
<td>2.3</td>
<td>33.6(4)/137(5)</td>
</tr>
</tbody>
</table>

Fig. 4. Isotherms for V₁₋ₓCrₓ–H₂ systems at 20 °C.
wards hydrogen component gives rise to the increase in equilib-

\[ X = 0.4. \]

Normally the increase in concentration of less active to-

\[ \text{Fig. 5.} \]

\[ V_{1-x}Cr_x - H_2 \]

Hydride generation for alloys with \( x \leq 0 \) had an FCC structure similar to \( \text{VH}_2 \) whereas for \( 0.4 \leq x \leq 0.5 \) 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 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 \( V_{0.5}Cr_{0.5} \) hydride is an intermediate one between \( V_{0.6}Cr_{0.4}H \) and \( V_{0.6}Cr_{0.6}H \) 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.

Acknowledgements

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References