Structure and Thermodynamic of Zr(Cr$_{1-x}$Fe$_x$)$_2$
Alloys Under Hydrogen Pressure

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Abstract: Our objective in this study is to try the one hand to increase the equilibrium pressure of ZrCr$_2$ hydride (0.012 bar at 50°C) without much changing its large storage capacity for approximately (4H/formula) and improve on the other hand the low storage capacity of ZrFe$_2$ (0,12H/formula). Such modifications can be made by a set of substitution between Cr and Fe in the Zr(Cr$_{1-x}$Fe$_x$)$_2$ compounds. Hexagonal (C14) Laves phases Zr(Cr$_{1-x}$Fe$_x$)$_2$ alloys with x = 0.4 ; 0.6 and x = 0.75 have been prepared by arc melting and the corresponding hydrides were formed by hydrogen uptake under pressure. X-ray diffraction have been measured and analyzed with the Rietveld method. $^{57}$Fe spectra measured at room temperature cooled by fitted with two doublets 3 :1 area ratio corresponding to the two Fe in the (C14) structure. The hydrides showed volume expansion without any crystal change. The isotherms P-C-T of these intermetallic compound were studied by microthermogravimetry at different temperatures under high hydrogen pressure.

Keywords: Laves phases, hydride, isotherm, hysteresis, absorption, desorption, hydridation.

1. Introduction

The family of MgZn$_2$ hexagonal Laves phases pseudo-binary Zr(A$_{1-x}$B$_x$)$_2$ compounds with A = Fe, Ni, Co, V and B = Cr, Mn have been particular studied [1-10] this is a consequence of the possibility they offer of countinuously vary the hydride thermodynamic properties especially the H$_2$ equilibrium pressure by changing the x value in the above alloys. There is a linear decrease in cell volume with increasing x and as a consequence a linear relationship between the logarithm of H$_2$ equilibrium pressure and the cell volume [11-14]. The normalized pressure dependence method for the evaluation of kinetic rates of metal hydride formation/decomposition were also investigated [15]. New compounds such Zr$_{1-y}$T$_y$ (A$_{1-x}$B$_x$)$_2$ were also developed to form reversible hydrides in the aim to substitute the cadmium in rechargeable nickel-cadmium batteries. These systems have been the subject of several theoretical and experimental studies [16-18].

2. Experimental Details

The compounds are prepared by direct arc melting under argon atmosphere of the pure components in stoichiometric proportions. The samples are made homogeneous by several remelting and are annealed. The compounds are checked by microprobe analysis. Micrographs show that they are single phase. The hydrogen used is the (U) quality of Air Liquide and is made free of residual water and oxygen traces by passing it through cartridge of molecular sieves. All the thermodynamic experiments are carried out by microthermogravimetry in a high pressure microbalance with a limiting sensitivity of 2µg. The mass of the samples is equal to 50mg and the pressure range is from vacuum 2.10$^{-4}$ Pa to pressures up 10 MPa. Temperatures vary from ambiant up to 600°C. Thermogravimetry allows step by step P-C-T diagram determination by equilibrium points i.e.: the system is maintained under stable pressure and temperature conditions until there is no longer a mass change. The isotherms are explored both in formation and decomposition to determine the hysteresis.

3. Results and Discussion

3.1 Structure Data

The Zr (Cr$_{1-x}$Fe$_x$)$_2$ alloys are defined as AB$_2$ type compounds adopting a compact hexagonal structure of the MgZn$_2$ type. Structures of this type are called Laves phases (C14) the atoms A and B formig the AB$_2$ unit cell have coordinates values represented in table.1

<table>
<thead>
<tr>
<th>Atomes</th>
<th>Positions</th>
<th>Sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>(1/3, 2/3, x) (2/3,3/1, 1-Z)</td>
<td>4f</td>
</tr>
<tr>
<td></td>
<td>(2/3,1/3, 1/2+Z), (1/3,2/3, 1/2-Z)</td>
<td></td>
</tr>
<tr>
<td>B(1)</td>
<td>(0,0,0), (0,0,1/2)</td>
<td>2a</td>
</tr>
</tbody>
</table>

X=0.16 ; Z=0.061

3.2 Samples Activation

The first hydridation of Zr(Cr$_{1-x}$Fe$_x$)$_2$ alloys is obtained at 25°C under an H$_2$ Pressure of 2.5MP. Fig.1 shows the curve’s kinetic of the first hydrogen absorption by the Zr(Cr$_{0.5}$Fe$_{0.5}$)$_2$ compound. The transformation begins after an induction period of approximately 15min and requires ten hours of reaction leading to the final composition 2.7H/mol. The other compounds Zr(Cr$_{0.2}$Fe$_{0.8}$)$_2$ and Zr(Cr$_{0.25}$Fe$_{0.75}$)$_2$ absorb respectively 2.85 and 2.5 H/mol. The other hydridations are achieved in time unless than one hour and  
without induction period Fig.2. From the second absorption-desorption cycle the reaction rate becomes constant. The alloys can be considered to be activated.

**Figure 1:** Kinetic of the first hydridation of Zr(Cr_{0.4}Fe_{0.6})_2 compound.

**Figure 2:** Kinetics activation of the sample

### 3.3 thermodynamic results

Zr(Cr_{1-x}Fe_x)_2 compounds readily react with hydrogen at room temperature even under low pressure. Figures 3.a, 3.b and 3.c represent the P-C-T isotherms of the alloys studied.

Comparing the slopes of the lines lnP_eq = f(1/T) figure 4 suggests that the heat liberated by the reaction between hydrogen and Zr(Cr_{1-x}Fe_x)_2 compounds increases when the degree x of substitution decreases.

**Figure 3a:** Isotherms P-C-T of the Zr(Cr_{0.25}Fe_{0.75})_2 – Hydrogen system

**Figure 3b:** Isotherms P-C-T of the Zr(Cr_{0.4}Fe_{0.6})_2 – Hydrogen system

**Figure 3c:** Isotherms P-C-T of the Zr(Cr_{0.6}Fe_{0.4})_2 – Hydrogen system

**Figure 3:** Isotherms P-C-T of the Zr(Cr_{0.25}Fe_{0.75})_2 – Hydrogen system
Otherwise the superposition in the same graph, Fig.5 P-C-T isotherms of the hydrides studied also shows that the equilibrium pressure and the hysteresis factor \( \frac{1}{2} RT \ln \frac{P_{ef}}{P_{cd}} \) increase rapidly with increasing x. Hydridation of the compounds showed that the logarithm of equilibrium pressure and the cell volume vary linearly with the substitution rate x, Fig.6 and Fig.7. This permits to write the following equations:

\[
V = ax + b \quad \text{and} \quad \ln P_e = a'x + b'
\]

where a, a’ and b, b’ are constants for a given temperature. From these results we deduce

\[
\ln P_e = AV + B \quad \text{in which} \quad A = \frac{a'}{a} \quad \text{and} \quad B = b' - \frac{a'b}{a}
\]

It follows that the increase in cell volume of the pseudo-binary \( \text{Zr(Cr}_{1-x}\text{Fe}_x)\text{)}_2 \) causes a decrease in the equilibrium pressure of the hydride and therefore improves its stability. Fig.8
These results suggest that the thermodynamic quantities $\Delta H$, $\Delta S$ and the degree of hysteresis may also vary linearly with cell volume or the substitution rate $x$. This is because the equilibrium pressure is related to these parameters by the following relation:

$$RTlnP_e = \Delta H - T\Delta S$$

(Van’t Hoff law). We also noticed that the absorption capacity varies linearly with the substitution rate $x$. For Shaltiel [11] this variation is less pronounced since it remains constant for values of $x$ between 0.2 and 0.7.

All the crystallographic and thermodynamic parameters of the studied compounds Zr(Cr$_{1-x}$Fe$_x$)$_2$ compared to those in the literature are summarized in Tableau 2.

### Tableau 2: Thermodynamic data on the hydride of Zr(Cr$_{1-x}$Fe$_x$)$_2$ compounds

<table>
<thead>
<tr>
<th>$x$</th>
<th>$P_e$ (MPa) at $T=70^\circ$C</th>
<th>$V$ (Å$^3$)</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$\Delta S$ (J/mol.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X=0.4</td>
<td>[ ]</td>
<td>0.1 0.076</td>
<td>181.75</td>
<td>2.85</td>
</tr>
<tr>
<td></td>
<td>ref [11]</td>
<td>1.1 0.31</td>
<td>179.45</td>
<td>-46.52</td>
</tr>
<tr>
<td>X=0.6</td>
<td>ref [14]</td>
<td>0.125 0.081</td>
<td>179.39</td>
<td>2.95</td>
</tr>
<tr>
<td></td>
<td>ref [11]</td>
<td>0.19 0.354</td>
<td>179.26</td>
<td>-28.43</td>
</tr>
<tr>
<td>X=0.75</td>
<td>ref [11]</td>
<td>0.235 0.31</td>
<td>178.80</td>
<td>-21.23</td>
</tr>
</tbody>
</table>

These results suggest that the thermodynamic quantities $\Delta H$, $\Delta S$ and the degree of hysteresis may also vary linearly with cell volume or the substitution rate $x$. This is because the equilibrium pressure is related to these parameters by the following relation:

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### 3.4 Attempt At Interpretation

The increase in cell volume is accompanied by an increase in the stability which explains the increased enthalpies of the corresponding hydrides. Variation in the same direction of the stability which explains the increased enthalpies of the compound is larger the more its sites are larger. Therefore their affinity for hydrogen increases which leads to increased disorder resulting in an increase of entropy of the system.

### 4. Conclusion

Study of hydriding-dehydriding properties inside a family of pseudo-binary Zr(Cr$_{1-x}$Fe$_x$)$_2$ alloys have shown a linear relationship between the main thermodynamic parameters $\Delta H$, $\Delta S$, $P_e$, hysteresis factor and the cell volume fixed by the substitution rate $x$. On the other hand increasing $x$ causes a reduction of cell volume, stability of hydride and storage capacity but against an increase in hysteresis factor. However, the variation of $x$ from 0.25 to 0.75 in the Zr(Cr$_{1-x}$Fe$_x$)$_2$ compounds causes no change on the crystal structure. A logical extension of this work is the study kinetic mechanisms of absorption-desorption of hydrogen by the family of these intermetallic compounds. Preliminary results obtained are very encouraging and can give rise to article.

### References


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