

HYDROGEN ABSORPTION PROPERTIES ZrFe₂ AND ZrCo₂ BASED ALLOYS

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Abstract. In this work Zr_{1-x}Ti_x(Fe_{1-y}Al_y)₂ system and the alloys Zr_{0.8}Ti_{0.2}Co_{1.6}Al_{0.4} and Zr_{0.9}Gd_{0.1}Co₂ were studied with the purpose to investigate the influence of zirconium substitution by titanium or a rare earth metals on hydrogen sorption properties of IMC ZrFe₂ and ZrCo₂. The hydrogen absorption properties were studied by measuring PCT absorption and desorption isotherms using a high hydrogen pressure apparatus at a hydrogen pressure below 3,000 atm. Hydrogen desorption pressures and hydrogen storage capacity decrease with increasing aluminium content in Zr_{1-x}Ti_x(Fe_{1-y}Al_y)₂ alloys. The catalytic effect of gadolinium addition on acceleration of reaction of ZrCo₂ with hydrogen was established. The thermodynamic parameters of hydrogen desorption reactions were calculated for number alloys.

Keywords: hydrogen, intermetallic compounds, IMC hydrides, high pressure

1. Introduction

Recently high pressure hydrides were only of scientific interest. Now hydrogen storage and transportation at high pressure attracts attention of auto and energy companies. This makes the high pressure hydrides perspective materials for practical applications.

High pressure hydrides can also be used in metal hydride compressors, where hydrogen pressure raising is realized only by the temperature and alloy composition.

ZrFe₂ and ZrCo₂ with Laves phases structure were considered as hydride non-forming IMC. The reaction with hydrogen was realized for this compounds [1, 2] with the application of super high pressure of 10,000 atm. It was estimated that reaction with hydrogen at 100⁰C starts at 1.1 GPa (10,856 atm). Equilibrium dissociation pressure is 0.35 GPa (3,454 atm) at 100⁰C for ZrFe₂ hydride. Lattice expansion is 25.93% for ZrFe₂ hydride and 14.59% for ZrCo₂ hydride. Hydrogen content was calculated on base of lattice expansion rule to be 2.85 E³/H. Hydride compositions are ZrFe₂H₄ and ZrCo₂H₂.

However, our investigation showed that IMC ZrFe₂ starts to react with hydrogen at room temperature and pressure near 800 atm. Hydride composition at hydrogen pressure of 1,900 atm is ZrFe₂H_{3.5}. Equilibrium absorption pressure is 690 atm and desorption pressure is 325 atm at room temperature [3].

The influence of aluminum substitution for cobalt in Zr(Co_{1-x}Al_x)₂ (0.1 ≤ x ≤ 0.5) alloys [4] and for iron in Zr(Fe_{1-x}Al_x)₂ alloys [5] shows that aluminium substitution

results in reduction of equilibrium dissociation pressure, increase of desorption enthalpy and significant reduction of hydrogen content.

Influence of zirconium substitution by titanium or a rare earth metals on hydrogen sorption properties of IMC $ZrFe_2$ and $ZrCo_2$ was not described in literature. In this work $Zr_{1-x}Ti_x(Fe_{1-y}Al_y)_2$ system and the alloys $Zr_{0.8}Ti_{0.2}Co_{1.6}Al_{0.4}$ and $Zr_{0.9}Gd_{0.1}Co_2$ were studied with this purpose.

2. Experimental

Alloys were prepared by arc-melting the mixtures of pure initial metals under argon atmosphere. With the purpose of homogenization the alloys were remelted four times. The structure and composition of alloys was examined by a scanning electron microscope (SEM) with energy dispersive X-ray analyzer and powder X-ray diffraction. The refinement of diffraction profiles was performed using the Rietveld method.

The hydrogen absorption properties were studied by measuring PCT absorption and desorption isotherms using a high hydrogen pressure apparatus at a hydrogen pressure below 3,000 atm.

Calculation of amount of absorbed or desorbed hydrogen were done using a modified van-der-Waals equation (1),

$$[p + a(p)/V^\alpha][V - b(p)] = RT, \quad (1)$$

where $a(p)$, $b(p)$ and $\alpha(T)$ parameters were determined by analysis of large massive experimental data of hydrogen compressibility [6].

The thermodynamic characteristics (ΔH and ΔS) IMC hydrides were calculated from vant-Hoff equation for dependence of $\ln f$ on $1/T$:

$$RT \ln(f_p) = \Delta_r H - T \Delta_r S. \quad (2)$$

The values of fugacities were determined with equation (3), using the real molar hydrogen volumes, obtained from equation (1):

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

The hydriding reaction products were investigated by X-ray. At first the autoclave with hydrogen saturated sample was cooled to liquid nitrogen temperature. Then hydrogen pressure in autoclave was reduced to 1–2 atm. After that the sample holder was opened to air. In order to inhibit hydrogen recombination centers on hydride surface, cooled hydride was exposed to air for 5–10 min. IMC hydride was replaced from sample holder to metallic container cooled to liquid nitrogen temperature. All studied samples were inflammable at these conditions. For the additional passivation the container with sample was keep in liquid nitrogen for time more then 1 h. The sample was put out from liquid nitrogen directly before X-rays analysis. The analysis time was extremely shot, but sufficient for identification of lattice periods of hydride phases. The changes of sample volume during hydrogen absorption and desorption were taken into account in calculations of PCT isotherms.

3. Results and discussion

3.1. (Zr-Ti)(Fe-Al)₂ SYSTEM

Three alloys Zr_{0.5}Ti_{0.5}Fe_{2-x}Al_x (x = 0.1, 0.4 and 0.8) and two alloys Zr_{0.2}Ti_{0.8}Fe_{2-x}Al_x (x = 0.2 and 0.3) were prepared for investigate this system. The main phase in all alloys is C14 Laves phase, excepts alloy Zr_{0.5}Ti_{0.5}Fe_{1.9}Al_{0.1} with C15 phase (Table 1).

TABLE 1. The structure of (Zr-Ti)(Fe-Al)₂ alloys

IMC	Phase	a, c (Å)	V (Å ³)
Zr _{0.5} Ti _{0.5} Fe _{1.9} Al _{0.1}	C15	7.052(6)	350.7(9)
Zr _{0.5} Ti _{0.5} Fe _{1.6} Al _{0.4}	C14	4.967(7), 8.085(8)	172.8(1)
Zr _{0.5} Ti _{0.5} Fe _{1.2} Al _{0.8}	C14	5.037(8), 8.193(6)	180.0(9)
Zr _{0.2} Ti _{0.8} Fe _{1.8} Al _{0.2}	C14	4.85(8), 7.91(5)	161.7(5)
Zr _{0.2} Ti _{0.8} Fe _{1.7} Al _{0.3}	C14	4.878(3), 7.93(8)	163.5(9)

The small (>2%) addition of ZrO phase (sp. gr. 225) was present in all alloys. The iron substitution of aluminium leads to evident increase of Laves phase cell parameters.

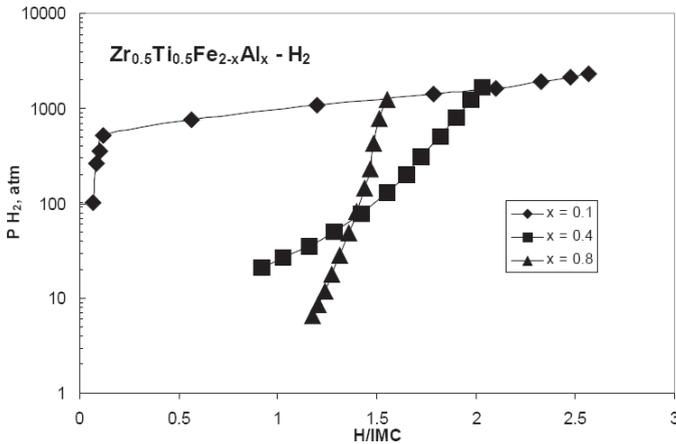


Figure 1. PCT desorption isotherms in the Zr_{0.5}Ti_{0.5}Fe_{2-x}Al_x-H₂ systems at room temperature

All Zr_{0.5}Ti_{0.5}Fe_{2-x}Al_x alloys react with hydrogen. Active hydrogen absorption in first cycle starts at pressure of 1,940 atm for the sample with x = 1, but alloys with x = 0.4 and 0.8 reacted with hydrogen at pressure of 105–110 atm. The desorption isotherms at room temperature are presented at Fig. 1. Hydrogen desorption pressures and hydrogen storage capacity decrease with increasing aluminium content (Table 2). Although we couldn't detect the equilibrium desorption pressures of the Zr_{0.5}Ti_{0.5}Fe_{1.2}Al_{0.8} hydride to calculate the thermodynamic parameters, we suppose that it's desorption enthalpy are maximal in the Zr_{0.5}Ti_{0.5}Fe_{2-x}Al_x system. Also we can see that the hysteresis effect is disappearing with increasing aluminium concentration (Table 2). The hydrogen sorption activity also increases: the equilibrium absorption and desorption pressures in first cycle approach to pressures values at following cycles.

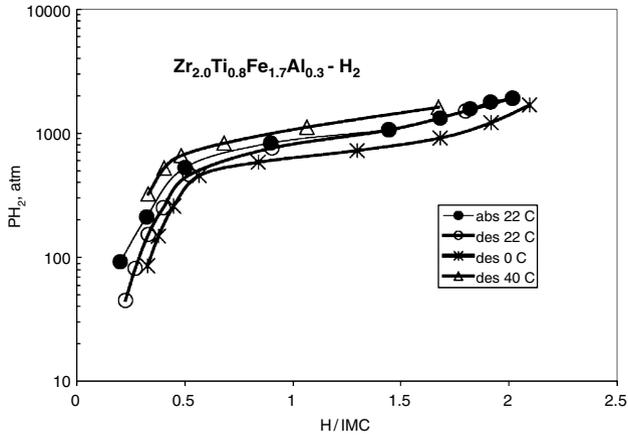


Figure 2. The interactions in $Zr_{0.2}Ti_{0.8}Fe_{1.7}Al_{0.3}-H_2$ system

The $Zr_{0.2}Ti_{0.8}Fe_{1.8}Al_{0.2}$ alloy doesn't react with hydrogen at pressure up to 2,300 atm. Whereas $Zr_{0.2}Ti_{0.8}Fe_{1.7}Al_{0.3}$ alloy begin to absorb hydrogen at pressure of 1,200 atm. This sample reach it's maximum hydrogen capacity only after second absorption–desorption cycle. The alloy $Zr_{0.2}Ti_{0.8}Fe_{1.7}Al_{0.3}$ is characterised by negligible hysteresis and very small hydrogen desorption enthalpy (Fig. 2, Table 2).

TABLE 2. Hydrogen sorption properties of the $Zr_{0.5}Ti_{0.5}Fe_{2-x}Al_x$ alloys

IMC	P H ₂ , atm labs/ldes	P H ₂ , atm 3abs/3des	H/IMC (mass%)	ΔH (kJ/mol H ₂)/ ΔS (J/K mol H ₂)
$Zr_{0.5}Ti_{0.5}Fe_{1.9}Al_{0.1}$	~1,300/890	1,190/970	2.8 ₂₆₀₀ , 1.56	$16.0 \pm 1.7/117 \pm 6$
$Zr_{0.5}Ti_{0.5}Fe_{1.6}Al_{0.4}$	35/34	35/34	2.05 ₁₈₀₀ , 1.2	$24.6 \pm 1.5/112 \pm 5$
$Zr_{0.5}Ti_{0.5}Fe_{1.2}Al_{0.8}$	~1.5/~1	~1.5/~1	1.55 ₁₂₂₀ , 0.98	–
$Zr_{0.2}Ti_{0.8}Fe_{1.8}Al_{0.2}$	–	–	–	–
$Zr_{0.2}Ti_{0.8}Fe_{1.7}Al_{0.3}$	960/841	950/910	2.02 ₁₉₀₀ , 1.26	$14.6 \pm 1.9/111 \pm 5$

3.2. THE $ZrCo_2$ -BASED ALLOYS

It was shown during preliminary investigations that IMC $ZrCo_2$ doesn't absorb hydrogen at pressures below 2,500 atm. It means that hydrogen absorption and desorption pressures of the $ZrCo_2-H_2$ system are the highest among describing in this paper IMC. Therefore the particle rare earth metal substitution of zirconium was applied for the expanding the lattice and increase hydrogen uptake ability. The gadolinium was taken for this purpose. This substitution is probable because the gadolinium solubility in zirconium is significant among other rare earth metals (~10% at 1,000°C) and besides the gadolinium forms Laves phase with cobalt. Also the $Zr_{0.8}Ti_{0.2}Co_{1.6}Al_{0.4}$ alloy was prepared and studied.

The investigation SEM with EDX and XRD analyses shows that $Zr_{0.9}Gd_{0.1}Co_2$ consists from three phases: the main C15-type Laves phase, addition $Gd_{12}Co_{9.2}$ phase (sp. gr. 176) and small amount of zirconium oxide phase. By means of EDX the gadolinium concentration in Laves phase A-component is near 3–4 at. %.

The alloy $Zr_{0.8}Ti_{0.2}Co_{1.6}Al_{0.4}$ is crystalline in C14 and C15 Laves phase structures with small amount of zirconium oxide phase (Table 3).

TABLE 3. The structure of ZrCo₂-based alloys

IMC	Phases	a, c (Å)	V (Å ³)
Zr _{0.9} Gd _{0.1} Co ₂	C15 97%	6.963(3)	337.6(3)
	Gd ₁₂ Co _{9,2} 3%	11.2(3), 4.06(1)	44(4).0
Zr _{0.8} Ti _{0.2} Co _{1.6} Al _{0.4}	C14 54%	4.993(3), 8.043(5)	173.6(8)
	C15 46%	7.012(2)	344.7(9)

Both alloys interact with hydrogen at pressures below 100 atm. The Zr_{0.9}Gd_{0.1}Co₂-H₂ system has great hysteresis effect (Fig. 3): it's equilibrium absorption pressure at room temperature is 970 atm and desorption pressure is 230 atm, but in the Zr_{0.8}Ti_{0.2}Co_{1.6}Al_{0.4}-H₂ system hysteresis is insignificant.

TABLE 4. Hydrogen sorption properties of ZrCo₂-based alloys

IMC	P H ₂ , atm 1abs/1des	P H ₂ , atm 3abs/3des	H/IMC (mass%)	ΔH (kJ/mol H ₂)/ΔS (J/K mol H ₂)
Zr _{0.9} Gd _{0.1} Co ₂	~1,050/205	970/230	2.22 ₁₉₉₀ , 1.03	23.4 ± 0.7/125 ± 2
Zr _{0.8} Ti _{0.2} Co _{1.6} Al _{0.4}	-	-/7.4	2.14 ₂₀₀₀ , 1.14	-

The appearance of wide alpha-region in PCT curves of the Zr_{0.9}Gd_{0.1}Co₂-H₂ (Fig. 3) can be explained by the presence of stable hydride forming addition phase. Furthermore hydrogen equilibrium absorption and desorption pressures changes small in following cycles at contrast of first cycle in both systems. We assume that it is catalytic effect of the rare earth metal or the aluminium presence.

There are two factors which can account for the catalytic effect of rare earth addition for the Zr_{0.9}Gd_{0.1}Co₂-H₂ system. At first the presence of the gadolinium atoms in A-component of Laves phase increases the hydride stability and decrease absorption and desorption hydride pressures. At second we believe that the hydrogen absorption starts at low pressure due to Gd₁₂Co_{9,2} phase presence. This phase react with hydrogen in the first time with dispersion and enlarging active surface of the main phase at result.

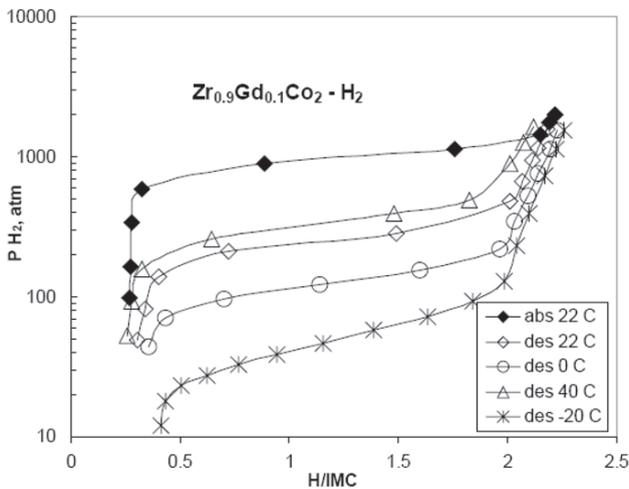


Figure 3. The interactions in Zr_{0.9}Gd_{0.1}Co₂-H₂ system

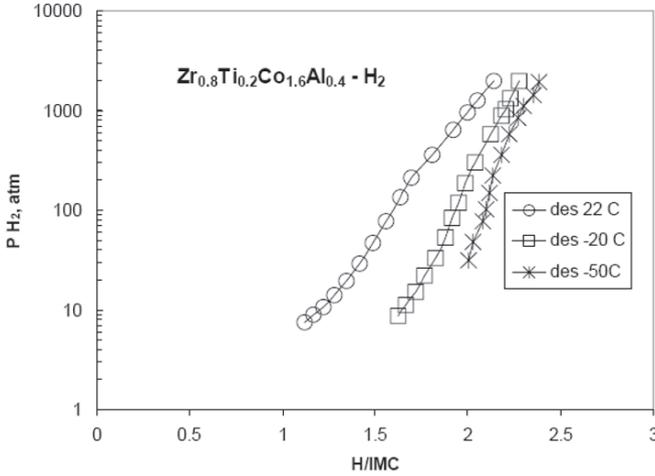


Figure 4. PCT desorption isotherms in $Zr_{0.8}Ti_{0.2}Co_{1.6}Al_{0.4}-H_2$ system

4. Conclusions

The influence titanium and aluminium substitution on structure and hydrogen sorption characteristics of $(Zr-Ti)(Fe-Al)_2$ system were investigated.

The catalytic effect of gadolinium addition on acceleration of reaction of $ZrCo_2$ with hydrogen was established.

The thermodynamic parameters of hydrogen desorption reactions were calculated for number alloys.

References

1. Filipek S.M., Jacob I., Paul-Boncour V., Percheron-Guegan A., Marchuk I., Mogilyanski D., Pielaszek J. *Polish J. Chem.*, 2001, **75**, **12**:1921–1926.
2. Filipek S.M., Paul-Boncour V., Percheron-Guegan A., Jacob I., Marchuk I., Dorogova M., Hirata T., Kaszukur Z. *J. Phys.-Condens. Mat.*, 2002, **14**:11261–11264.
3. Zotov T.A., Movlaev E.A., Mitrokhin S.V., Verbetsky V.N. *J. Alloy. Compd.* 2008, **459**:200–224.
4. Bereznitsky M., Jacob I., Bloch J., Mintz M.H. *J. Alloy. Compd.*, 2002, **346**:217–221.
5. Bereznitsky M., Jacob I., Bloch J., Mintz M.H. *J. Alloy. Compd.*, 2003, **351**:180–183.
6. Hemmes H., Driessen A., Griessen R. *J. Phys. C Solid State*, 1986, **19**:3571–3585.