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 mesured and analyzed with the Rietveld method.^{57}Fe spectra mesured at room temperature coled 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 cristal change. The isotherms P-C-T of these intermetallic compound were studied by microthermogavimetry 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 particulary studied [1-10] this is a consequence of the possibility they offer of countinuously varing 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 inceasing 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 developped to form reversible hydrides in the aim to substitue 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 athmosphere 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. Micrographies show that they are sigle phased. 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

Shaltiel [11] showed that the $Zr(Cr_{1-x}Fe_x)_2$ compounds are compact hexagonal type $MgZn_2$ for values of x between 0.2 and 0.8 and a face-centered cubic type $MgCu_2$ for other values of x

Table 1: Positions of atoms A and B in the unit cell AB_2 (C14)

Atomes	Positions	Sites
A	(1/3, 2/3, z) (2/3,1/3, 1-Z) (2/3,1/3, 1/2+Z), (1/3,2/3, 1/2-Z)	4f
B(1)	(0,0,0), (0,0,1/2)	2a
B(2)	(1-X,1-2X, 1/4), (1-2X, 1-X, 3/4) (X,2X, 3/4) (2X,X,1/4), (1-X,X,1/4), (X,1-X,3/4)	6h

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 $Zr(Cr_{0.4}Fe_{0.6})_2$ 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 $Zr(Cr_{0.6}Fe_{0.4})_2$ 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 is becomes constant. The alloys can be considered to be activated.

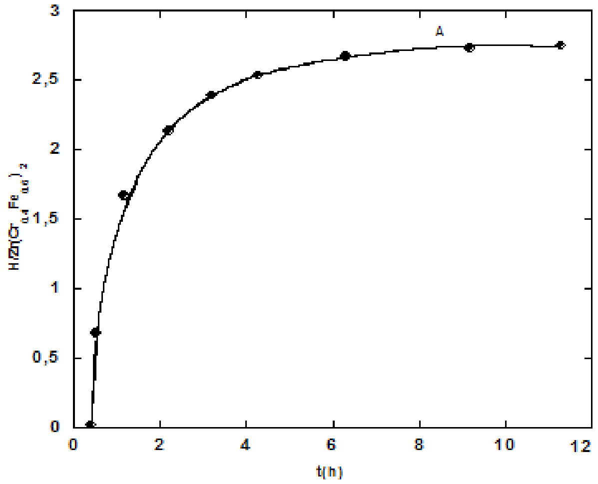

Figure 1: Kinetic of the first hydridation of $Zr(Cr_{0.4}Fe_{0.6})_2$ compound.

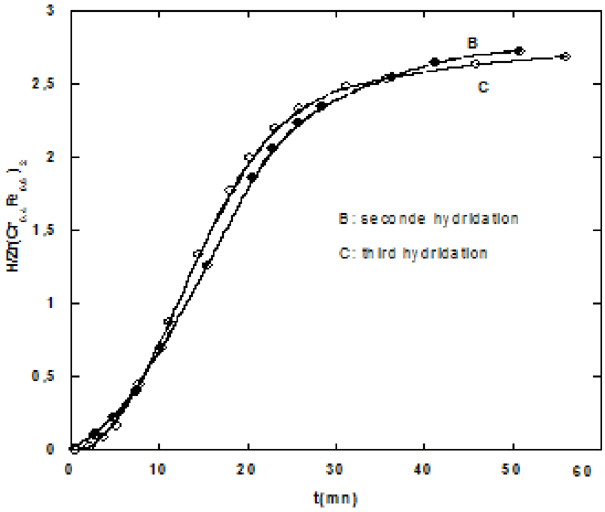

Figure 2 : Kinetics activation of the sample

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.

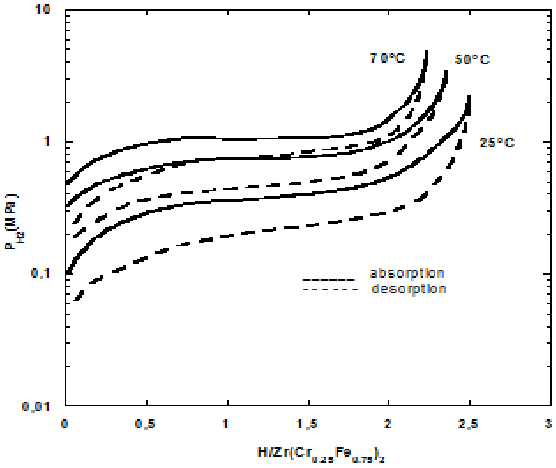

Figure 3 a : : Isotherms P-C-T of the $Zr(Cr_{0.25}Fe_{0.75})_2$ – Hydrogen system

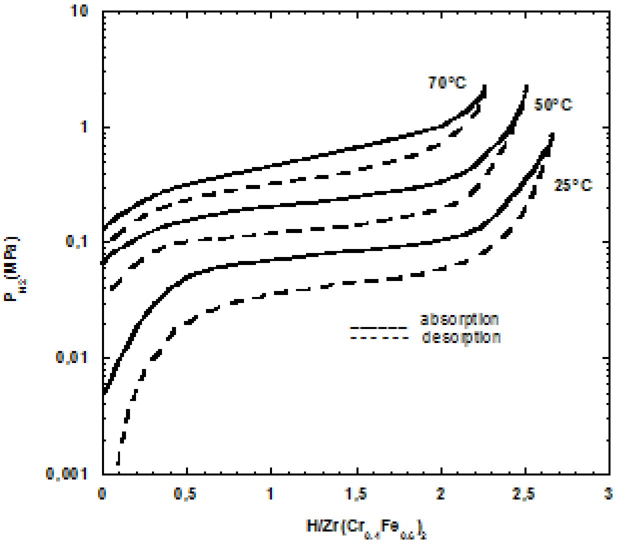

Figure 3b: Isotherms P-C-T of the $Zr(Cr_{0.4}Fe_{0.6})_2$ – Hydrogen system

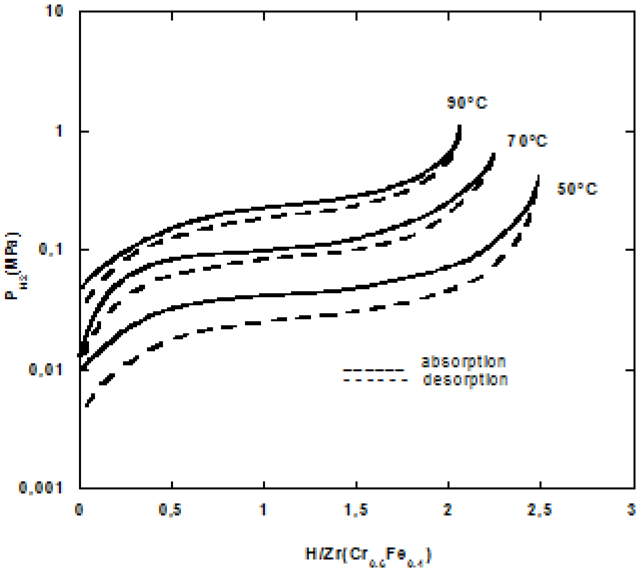

Figure 3c: Isotherms P-C-T of the $Zr(Cr_{0.6}Fe_{0.4})_2$ – Hydrogen system

Comparing the slopes of the lines $\ln P_{eq} = f(1/T)$ 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.

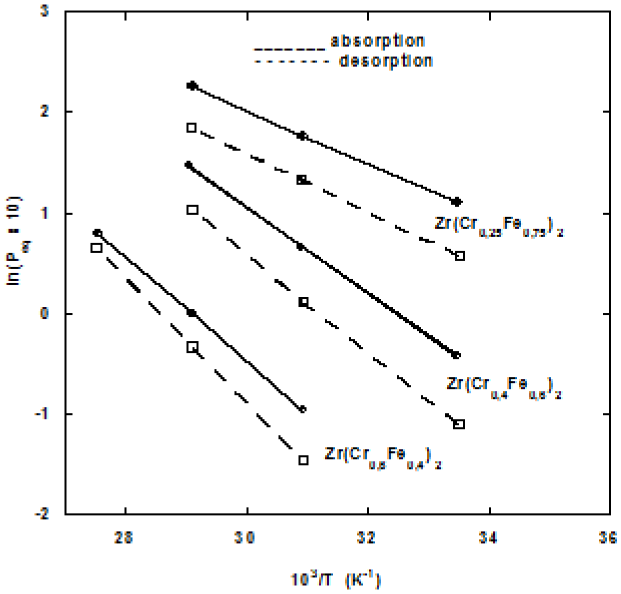

Figure 4: Representation of Ln(P_{eq}) versus 1/T (Van't Hoff law)

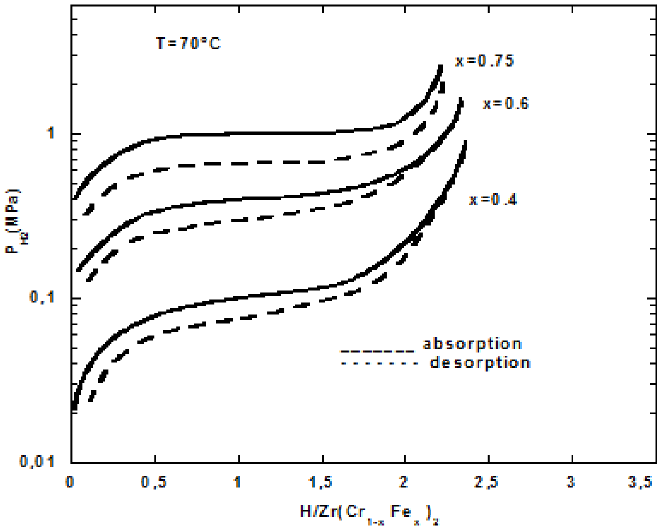

Figure 5: Comparaison of the P-C-T isotherm at 70°C of the $Zr(Cr_{1-x}Fe_x)_2$ – Hydrogen system

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 $\frac{1}{2}RTLn\frac{P_{ef}}{P_{ed}}$ (P_{ef} : equilibrium pressure formation , P_{ed} : equilibrium pressure decomposition) 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:

$V = ax + b$ and $LnP_e = a'x + b'$

a,a'and b, b'are constants for a given temperature. From

these results we deduce

$\ln P_e = AV + B$ in which $A = \frac{a'}{a}$ and $B = b' - \frac{a'b}{a}$

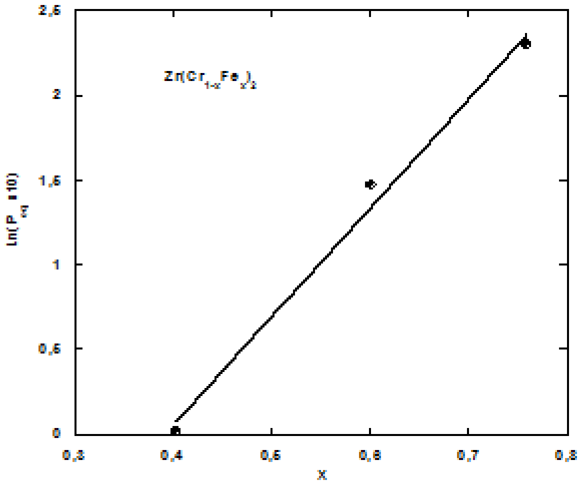

Figure 6: Variation of the equilibrium pressure logarithm versus x in $Zr(Cr_{1-x}Fe_x)_2$ compounds

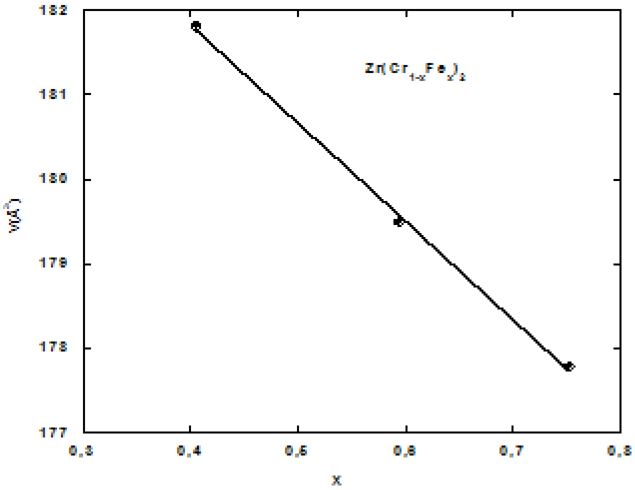

Figure 7: Variation of the $Zr(Cr_{1-x}Fe_x)_2$ compounds cell volume versus substitution rate x.

It follows that the increase in cell volume of the pseudo-binary $Zr(Cr_{1-x}Fe_x)_2$ causes a decrease in the equilibrium pressure of the hydride and therefore improves its stability. Fig.8

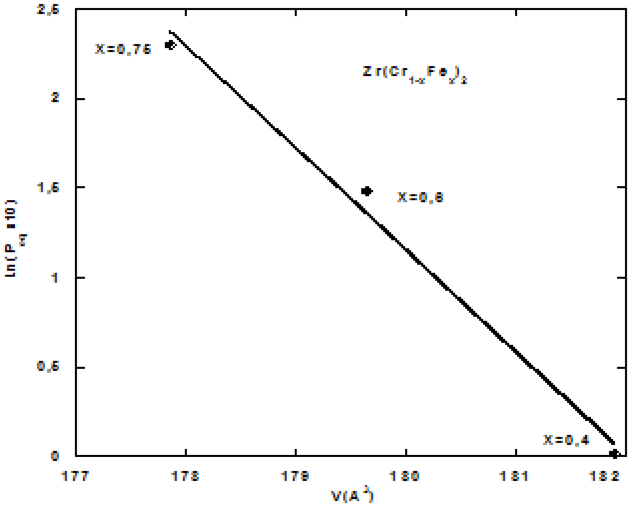

Figure 8: Representation of the equilibrium pressure logarithm versus cell volume of the $Zr(Cr_{1-x}Fe_x)_2$ compounds.

These results suggest that the thermodynamic quantities ΔH , ΔS 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 :

$RT\ln P_e$ = ΔH-TΔS (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 studied compounds $Zr(Cr_{1-x}Fe_x)_2$ compared to those in the literature are summarized in tableau.2

Table 2: Thermodynamic data on the hydride of $Zr(Cr_{1-x}Fe_x)_2$ compounds

$Zr(Cr_{1x}Fe_x)_2$		Pe(MPa) atT=70°C **P_{ef} P_{ed}**	V(Å)^3	H/alloy	ΔH(kj/mol) **abs des**	ΔS(j/mol.K) **abs des**	Hysteresis (j/mol)
X=0.4	[*]	0.1 0.076	181.75	2.85	-46 50.2	-133 127	412
X=0.6	[*]	0.450 0.31	179. 45	2.7	-33.4 36.5	-110 81	534
	ref [14]	0.235 0.18	179.39	2.95	..... …..	....	382
	ref [11]	0.69 0.354	179.26	3.05	-28.9 32.9	-90 99	969
X=0.75	[*]	1 0.65	177.80	2.5	-21 22.3	-81 40	617
	ref[11]	… 0.55at50°C	178.52	2.85	-24.2 …..	-92 …..	…..

[*]: this work ; **abs**: absorption ; **des**: desorption

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 absorption capacity and cell volume is a purely geometrical phenomenon witch can be related to the size of the sites in $Zr(Cr_{1-x}Fe_x)_2$ compounds. In fact the more 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 ΔH, ΔS, Pe, 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 hystersis 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 extention 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.

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