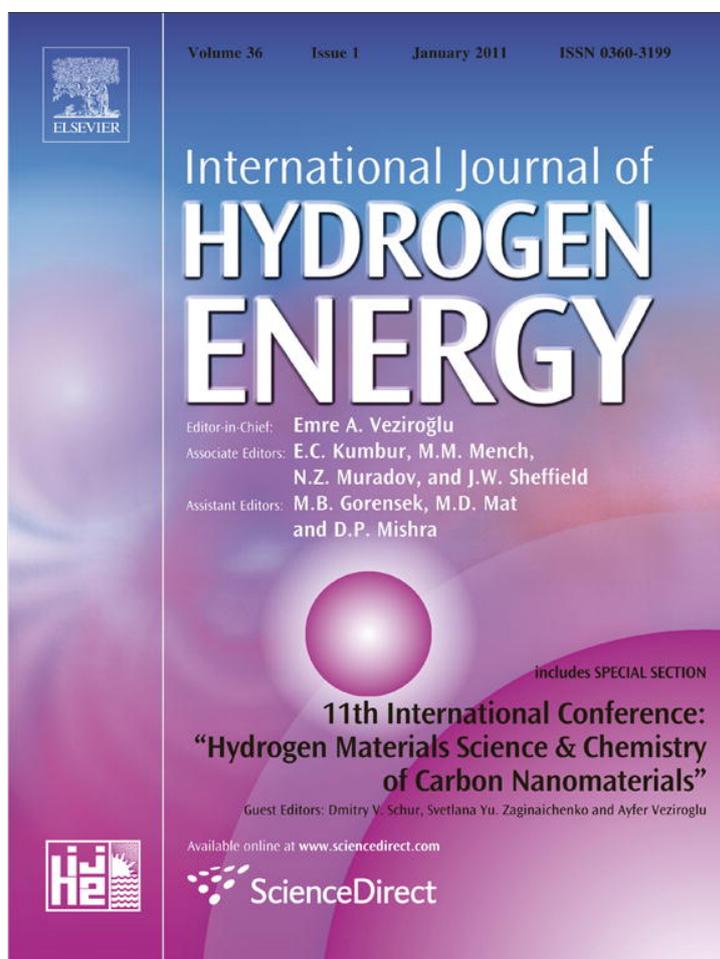


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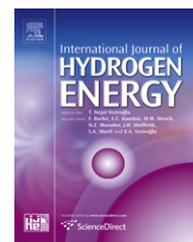


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## Hydrogen sorption properties of $ZrFe_x$ ( $1.9 \leq x \leq 2.5$ ) alloys

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### ABSTRACT

The hydrogen sorption properties of  $ZrFe_x$  ( $1.9 \leq x \leq 2.5$ ) alloys were studied by measuring Pressure-Composition (PC) absorption and desorption isotherms at pressure up to 300 MPa. The increase in the Fe content in alloys leads to increase in hydrogen absorption and desorption pressures of hydrides and reduction of the  $\beta \rightarrow \alpha$  phase transition enthalpy while both the atomic hydrogen content in hydrides (H/M) and the hydrogen capacity expressed in wt %  $H_2$  decrease.

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## 1. Introduction

Recently high pressure hydrides of intermetallic compounds (IMC) were only of scientific interest. However hydrogen storage and transportation at high pressure attract attention of auto and energy companies now. 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.

$ZrFe_2$  with Laves phase structure C15 was considered as hydride non-forming IMC. The reaction with hydrogen was realized for this compound [1,2] with the application of super high pressure. It was estimated that reaction with hydrogen at 373 K starts at 1.1 GPa. Equilibrium desorption pressure is 0.35 GPa at 373 K for  $ZrFe_2$  hydride; lattice volume expansion is 25.93%. Hydrogen content was calculated on base of lattice volume expansion rule of  $2.85 \text{ \AA}^3/\text{H}$ . Hydride composition is  $ZrFe_2H_4$ .

Our earlier investigation showed that  $ZrFe_2$  starts to react with hydrogen at room temperature and pressure near 80 MPa. Hydride composition at 180 MPa is  $ZrFe_2H_{3.5}$ ,

hydrogen capacity is 1.7 wt %  $H_2$ . Hydrogen equilibrium absorption and desorption plateau pressures at room temperature are 69 and 32.5 MPa accordingly [3].

$ZrFe_2$  possesses wide homogeneity range 27.7–34.3 at % Zr ( $ZrFe_{1.9}$ – $ZrFe_{2.7}$ ). A change of hydrogen sorption characteristics of IMC towards improvement or deterioration of their properties can be achieved by the change of structure stoichiometry. However the hydrogen sorption properties of alloys in the homogeneity range of  $ZrFe_2$  was not described in literature until now. In present work the  $ZrFe_x$ – $H_2$  systems ( $1.9 \leq x \leq 2.5$ ) were studied with this purpose.

## 2. Experimental

Samples were prepared by alloying of the mixtures of pure initial metals on copper water-cooled bottom of the arc furnace with nonconsumable tungsten electrode in atmosphere of pure argon under the pressure of 0.1–0.15 MPa. With purpose of homogenization alloys were remelted 3–4 times. Then alloys were exposed to annealing (240 h, 1173 K) for additional homogenization. After annealing samples were

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Nomenclature		wt % H <sub>2</sub>	weight percent of hydrogen content in hydride
IMC	intermetallic compound	at %	atomic percent of content
PC	pressure-composition	C14	hexagonal Laves phase
XRD	X-ray diffraction	C15	cubic Laves phase
XRSMA	X-ray spectral microanalysis	k	hysteresis factor
SEM	scanning electronic microscope	P <sub>0</sub>	starting pressure of reaction with hydrogen in first hydrogenation cycle at room temperature
ΔH	enthalpy change	P <sub>1</sub>	equilibrium absorption/desorption plateau pressures in first cycle
ΔS	entropy change	P <sub>e</sub>	equilibrium absorption/desorption plateau pressures of activated sample
β→α	hydride-intermetallic phase transition		
H/M	atomic hydrogen content in hydride		

quenched to cold water. The structure of alloys was examined by powder X-ray diffraction (XRD). The refinement of diffraction profiles was performed using the Rietveld method.

Alloys composition and their homogeneity were also examined by means of scanning electronic microscope (SEM) LEO Supra 50 VP (the cathode with field electron emission). X-ray spectral microanalysis (XRSMA) was carried out using system Oxford INCA Energy + (the resolution of the Si (Li) detector is 129 eV on line Mn K<sub>α</sub> 5.894 eV).

The hydrogen sorption properties of samples were studied by measuring PC absorption and desorption isotherms using a high hydrogen pressure apparatus at hydrogen pressure up to 300 MPa. The description of apparatus and technique of experiment are stated in work [4].

investigated samples is resulted in Table 1. It is visible that the increase in the Fe content naturally leads to decrease in the lattice periods of Laves phase.

All investigated alloys react with hydrogen (Table 2). Hydrogen capacity of ZrFe<sub>1.9</sub> is 1.2 H/M (1.8 wt % H<sub>2</sub>) at 170 MPa (Fig. 1). The values of equilibrium hydrogen absorption and desorption plateau pressures significantly differ (Table 2).

ZrFe<sub>2</sub> possesses a relatively high hydrogen capacity- 1.2 H/M (1.74 wt % H<sub>2</sub>) at 225 MPa (Fig. 2). It starts to react with hydrogen at room temperature and pressure near 90 MPa. In the first cycle hydrogen equilibrium absorption and desorption plateau pressures are 117 and 27.5 MPa accordingly while

### 3. Results

Hydrogen sorption properties of 3 IMC: ZrFe<sub>1.9</sub> (ZrFe<sub>1.97</sub>Zr<sub>0.03</sub>), ZrFe<sub>2</sub> and ZrFe<sub>2.5</sub> (Zr<sub>0.86</sub>Fe<sub>0.14</sub>Fe<sub>2</sub>) are studied in present work. According to XRSMA, the composition of all samples corresponded to the planned. XRD has shown the single-phase for all samples (cubic Laves phase C15). XRD data of the

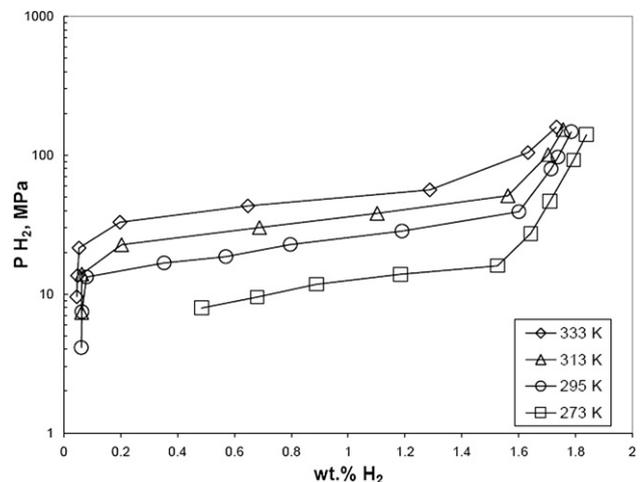


Fig. 1 – Hydrogen desorption isotherms of ZrFe<sub>1.9</sub>-H<sub>2</sub> system.

Table 1 – XRD data of ZrFe<sub>x</sub>.

Sample	Phase	Lattice constant, Å	Cell volume, Å <sup>3</sup>
ZrFe <sub>1.9</sub>	C15	7.085(2)	355.6(3)
ZrFe <sub>2</sub>	C15	7.077(3)	354.5(4)
ZrFe <sub>2.5</sub>	C15	7.055(1)	351.2(2)

Table 2 – Hydrogen sorption properties of ZrFe<sub>x</sub>.

Sample	P <sub>0</sub> , <sup>a</sup> MPa	P <sub>1</sub> , <sup>b</sup> MPa	P <sub>e</sub> , <sup>c</sup> MPa	(H/M <sup>d</sup> )/wt % H <sub>2</sub>	ΔH, kJ/mole H <sub>2</sub>	ΔS, J/(K.mole H <sub>2</sub> )
ZrFe <sub>1.9</sub>	60	85/20	63.5/24	1.2 <sub>170</sub> /1.80	21.8 ± 0.6	121 ± 4
ZrFe <sub>2</sub>	90	117/27.5	70/33	1.2 <sub>225</sub> /1.74	21.2 ± 0.7	122 ± 5
ZrFe <sub>2.5</sub>	110	158/68	104/69.5	1.1 <sub>255</sub> /1.63	18.3 ± 0.8	120 ± 5

a Starting pressure of reaction with hydrogen in first hydrogenation cycle at room temperature.

b Equilibrium absorption/desorption pressures on plateau in first cycle.

c Equilibrium absorption/desorption pressures on plateau of activated sample.

d Hydrogen content at room temperature and subscript pressure (MPa).

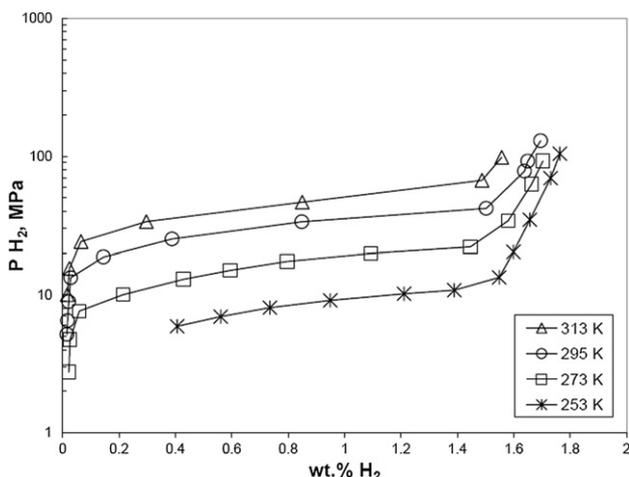


Fig. 2 – Hydrogen desorption isotherms of  $ZrFe_2-H_2$  system.

hydrogen equilibrium absorption and desorption plateau pressures of activated alloy are 70 and 33 MPa accordingly.

Hydrogen equilibrium absorption and desorption pressures on plateau in the first cycle in system  $ZrFe_{2.5}-H_2$  at room temperature are 158 and 68 MPa accordingly (Fig. 3). In the third absorption–desorption cycle equilibrium pressures are 104 MPa for absorption and 69.5 MPa for desorption, i.e. there is a reduction of a hysteresis between isotherms of absorption and desorption. Equilibrium absorption pressure after alloy activation changes more considerably than equilibrium desorption pressure. Hydrogen capacity of this sample is minimal for the investigated alloys—1.1 H/M (1.63 wt %  $H_2$ ).

#### 4. Discussion

Analysis of the obtained hydrogen sorption properties of  $ZrFe_x$  ( $1.9 \leq x \leq 2.5$ ) revealed that with increase in the Fe content in

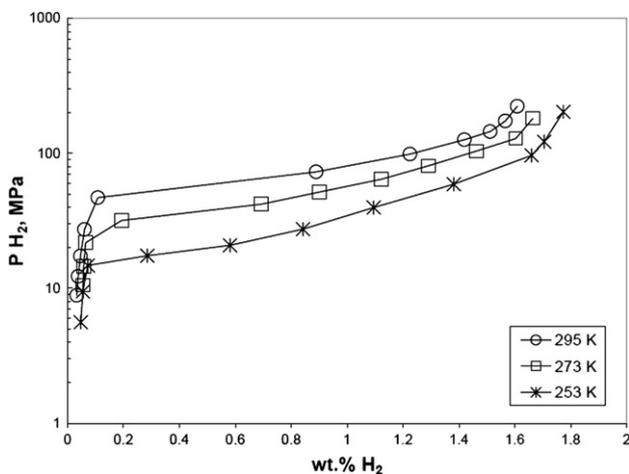


Fig. 3 – Hydrogen desorption isotherms of  $ZrFe_{2.5}-H_2$  system.

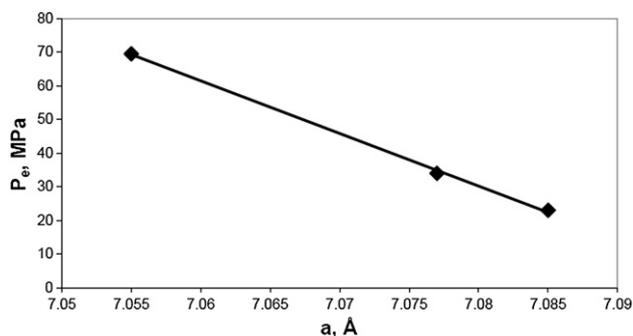


Fig. 4 – Dependence of equilibrium hydrogen desorption plateau pressure at 295 K on lattice constant of  $ZrFe_x$  ( $1.9 \leq x \leq 2.5$ ).

system the increase in hydrogen equilibrium absorption and desorption plateau pressures and reduction of the  $\beta \rightarrow \alpha$  phase transition enthalpy take place. Both the atomic content of hydrogen (H/M) in hydrides and the hydrogen capacity expressed in wt %  $H_2$  decrease.

Geometrical factors easily explain the increase in equilibrium absorption and desorption pressures at increase in Fe content in alloys. At increase in Fe content in stoichiometry region of  $ZrFe_x$  the part of Fe besides the regular B-positions in structure of Laves phase occupies A-positions (for example,  $ZrFe_{2.5}$  actually represents composition  $Zr_{0.86}Fe_{0.14}Fe_2$ ). In this connection there is reduction of elementary lattice volume, reduction of the content of tetrahedral interstices rich in zirconium and, as consequence, increase in hydrogen absorption and desorption pressures. On the other hand, at the shift to substoichiometry Zr occupies B-positions besides regular A-positions that leads to increase in elementary lattice volume, increase of content of tetrahedral interstices rich in zirconium and, as consequence, to reduction of hydrogen absorption and desorption pressures. For the same reason it is possible to explain the reduction of hydrogen capacity at increase in Fe content proceeding from geometrical reasons.

The lattice constant of  $ZrFe_x$  depends practically linearly on Fe content (Table 1). It has also been found that hydrogen equilibrium desorption plateau pressure in system  $ZrFe_x-H_2$  also depends almost linearly on lattice constant (cell volume) of alloys (Fig. 4).

With reduction of Fe content in system  $ZrFe_x-H_2$  there is increase in hysteresis between absorption and desorption isotherms and considerable reduction of hydrogen equilibrium desorption plateau pressure is observed. Hysteresis factors ( $k = P_{e\ abs}/P_{e\ des}$ ) for  $ZrFe_{1.9}$ ,  $ZrFe_2$  and  $ZrFe_{2.5}$  are 2.65, 2.10 and 1.50 accordingly.

#### 5. Conclusions

The increase in Fe content in  $ZrFe_x$  alloys ( $1.9 \leq x \leq 2.5$ ) leads to increase in hydrogen absorption and desorption pressures of hydrides and reduction of the  $\beta \rightarrow \alpha$  phase transition enthalpy. The atomic content of hydrogen in hydrides (H/M) and the hydrogen capacity expressed in wt % decrease.

Thus, sample composition in homogeneity domain boundaries can be considered as the additional factor influencing on hydrogen sorption properties of alloys based on ZrFe<sub>2</sub>.

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### REFERENCES

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- [1] Filipek SM, Jacob I, Paul-Boncour V, Percheron-Guegan A, Marchuk I, Mogilyanski D, et al. *Pol J Chem* 2001;75:1921–6.
- [2] Filipek SM, Paul-Boncour V, Percheron-Guegan A, Jacob I, Marchuk I, Dorogova M, et al. *Cond Mat* 2002;14:11261–4.
- [3] Zotov T, Movlaev E, Mitrokhin S, Verbetsky V. *J Alloys Comp* 2008;459:220–4.
- [4] Mitrokhin S, Zotov T, Movlaev E, Verbetsky V. *J Alloys Comp* 2007;446-447:603–5.