

# Interaction in (Ti,Sc)Fe<sub>2</sub>–H<sub>2</sub> and (Zr,Sc)Fe<sub>2</sub>–H<sub>2</sub> systems

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## Abstract

Results of investigation of hydrogen sorption properties of Ti(Zr)<sub>x</sub>Sc<sub>1-x</sub>Fe<sub>2</sub> ( $x = 1, 0.8$  and  $0.5$ ) alloys are presented. The measurements were performed for pressures up to 3000 atm. In case of titanium alloys hydride formation was established only for  $x = 0.5$ . Estimated equilibrium absorption pressure for  $x = 0.8$  and  $1.0$  was too high for experimental limits of the device. In case of zirconium alloys hydride formation was found for all three concentrations. Absorption–desorption isotherms were measured for the first time for ZrFe<sub>2</sub>–H<sub>2</sub> system. Calculated enthalpy of hydrogen desorption was found to be 21.3 kJ/mole H<sub>2</sub>.

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## 1. Introduction

Intermetallic Laves phase compounds ZrFe<sub>2</sub> and TiFe<sub>2</sub> were known not to form hydrides. At pressures below 150 atm, hydrogen solubility in ZrFe<sub>2</sub> is about 0.16–0.17 H/IMC and for TiFe<sub>2</sub> no visible solubility was detected [1–4]. Recently application of superhigh pressures (up to 10,000 atm) allowed to realize the reaction of ZrFe<sub>2</sub> with hydrogen [5–7]. It was shown that at 100 °C this reaction started at 10,800 atm, the hydride dissociation pressure was about 3400 atm. The unit cell volume change reached 25.9%. Taking into account the average volume increase per 1 H-atom (2.85 Å<sup>3</sup>/H) the composition of obtained hydride was estimated as ZrFe<sub>2</sub>H<sub>4</sub>. According to results of neutron diffraction structure refinement the deuteride composition was ZrFe<sub>2</sub>D<sub>2.5</sub>.

These extremely high formation and dissociation pressures can be significantly reduced by substitution of Zr or Ti for some other metal which is also capable of forming a Laves phase compound with Fe. For example, scandium and iron form ScFe<sub>2</sub> with C14 [8,9] and C36 [11,12] hexagonal Laves phase structures. ScFe<sub>1.8</sub> has cubic C15 structure. Each of modifications reacts with hydrogen forming stable hydrides (dissociation pressure below 1 atm at room temperature). The enthalpy of hydriding is about 30 kJ/mole H<sub>2</sub> [8–12]. This data allows to expect

that alloying Zr(Ti)Fe<sub>2</sub> with scandium will lead to significant decrease of hydride dissociation pressure. The aim of this work was to study the interaction of (Ti,Sc)Fe<sub>2</sub> and (Zr,Sc)Fe<sub>2</sub> with hydrogen.

## 2. Experimental

Alloys were prepared from pure metals in arc furnace in argon atmosphere. Samples were remelted for four times. Hydrogen interaction with alloys was studied by PCT-isotherm method in a high gaseous pressure device, described in Ref. [13]. Amounts of absorbed or desorbed hydrogen were calculated using modified van der Waals equation [14]:

$$\left[ \frac{p + a(p)}{V^\alpha} \right] [V - b(p)] = RT, \quad (1)$$

where  $a$  and  $b$  are the pressure dependent coefficients (for  $P > 1$  atm),  $P$  the pressure (atm),  $T$  the temperature (K),  $V$  the system volume (cm<sup>3</sup>) and  $R$  is the universal gas constant (82.06 cm<sup>3</sup> atm/(mol K)).

Thermodynamic parameters of desorption reaction were calculated with van't Hoff equation using fugacity values, corresponding to experimental pressure values:

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

where  $f_p$  is the fugacity,  $\Delta_r H$  the enthalpy change and  $\Delta_r S$  is the entropy change.

Fugacities were calculated with the following equation using real molar volumes obtained from Eq. (1):

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

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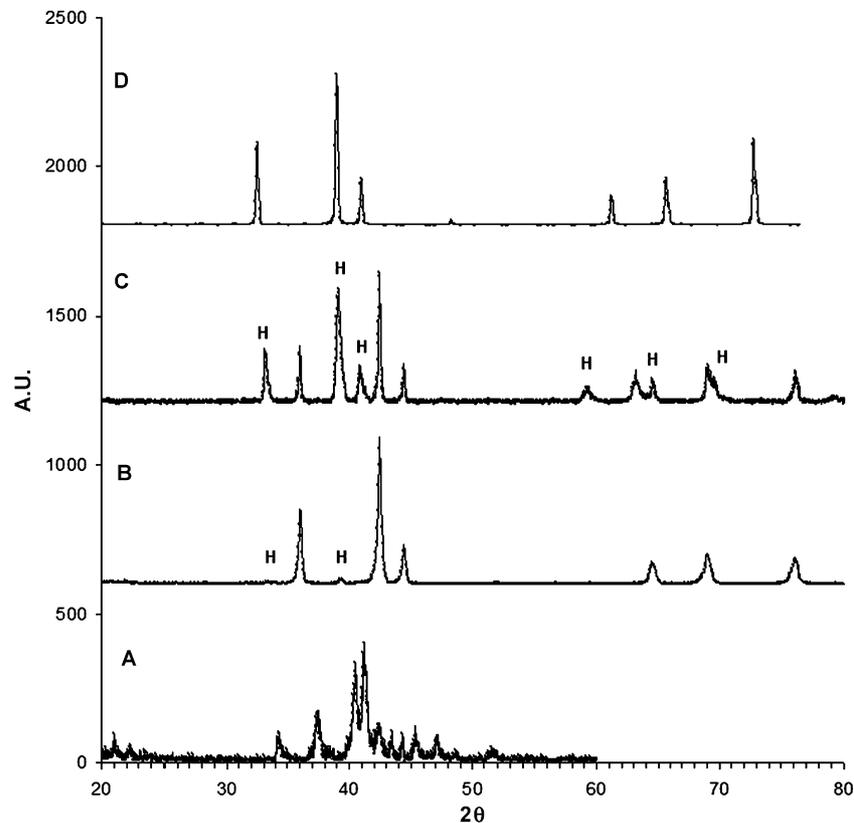


Fig. 1. X-ray pattern of hydrides: (A)  $\text{Ti}_{0.5}\text{Sc}_{0.5}\text{Fe}_2\text{H}_{3.1}$ ; (B)  $\text{ZrFe}_2\text{H}_4$ ; (C)  $\text{Zr}_{0.8}\text{Sc}_{0.2}\text{Fe}_2\text{H}_{3.7}$ ; (D)  $\text{Zr}_{0.5}\text{Sc}_{0.5}\text{Fe}_2\text{H}_{3.6}$ ; (H) reflexions of hydride phase for two-phase samples.

where  $V_{\text{real}}$  is the real hydrogen molar volume and  $V_{\text{id}}$  is the ideal hydrogen molar volume.

Phase compositions and cell parameters of initial samples and their hydrides were determined by X-ray analysis on DRON-3 diffractometer ( $\text{Cu K}\alpha$ ). In case of hydride phases a special procedure was employed in an attempt to prevent decomposition. The high pressure sample holder with hydride was first cooled to liquid nitrogen temperature and then the sample holder was opened to air for 5–10 min (Fig. 1). Cell parameters were calculated using Rietan2000 software. The results of X-ray study were used later for the correction of PCT-calculations to take into account the changes of sample density during hydriding–dehydriding.

### 3. Results and discussion

#### 3.1. (Ti,Sc)Fe<sub>2</sub>–H<sub>2</sub> system

Two hexagonal C14 alloys were prepared with compositions  $\text{Ti}_{0.5}\text{Sc}_{0.5}\text{Fe}_2$  and  $\text{Ti}_{0.8}\text{Sc}_{0.2}\text{Fe}_2$  (Table 1). Cell parameters of ini-

Table 1  
X-ray data for (Ti,Sc)Fe<sub>2</sub> alloys and their hydrides

Composition	Cell parameters (C14)			$\Delta V/V_0$ (%)
	$a$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )	
ScFe <sub>2</sub> [9]	4.94	8.13	171.8	
ScFe <sub>2</sub> H <sub>3.2</sub> [9]	5.35	8.61	213.4	24.6
$\text{Ti}_{0.5}\text{Sc}_{0.5}\text{Fe}_2$	4.884(1)	7.966(1)	168.60(2)	
$\text{Ti}_{0.5}\text{Sc}_{0.5}\text{Fe}_2\text{H}_{3.1}$	5.221(1)	8.507(2)	200.87(7)	22.3
$\text{Ti}_{0.8}\text{Sc}_{0.2}\text{Fe}_2$	4.863(2)	7.847(1)	160.71(5)	

tial alloys decreased with decreasing Sc-content. No hydrogen absorption was noted for  $\text{Ti}_{0.8}\text{Sc}_{0.2}\text{Fe}_2$  at pressure up to 2500 atm at  $-50^\circ\text{C}$ . In case of  $\text{Ti}_{0.5}\text{Sc}_{0.5}\text{Fe}_2$  reaction with hydrogen started at 100 atm without any preliminary activation (Fig. 2). At room temperature hydrogen content in hydride corresponds to  $\text{Ti}_{0.5}\text{Sc}_{0.5}\text{Fe}_2\text{H}_{3.1}$  (2.0 mass%, Table 2). Room temperature equilibrium absorption and desorption pressures are 195 and 175 atm correspondingly. Cooling the hydride to low temper-

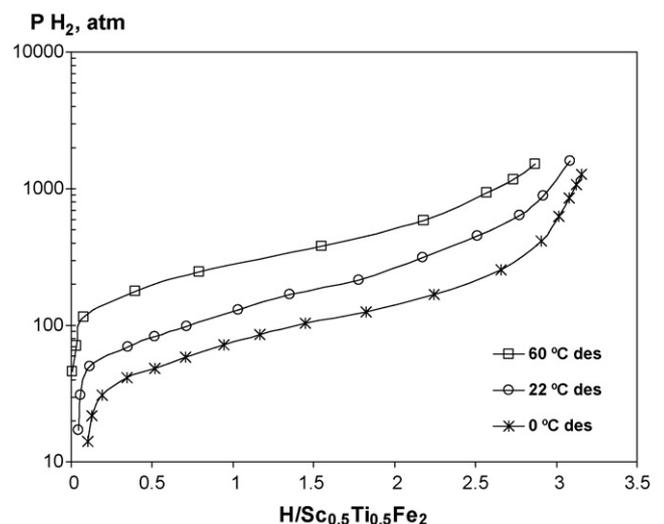


Fig. 2. PC-isotherms for  $\text{Ti}_{0.5}\text{Sc}_{0.5}\text{Fe}_2\text{–H}_2$  system.

Table 2  
Hydriding and thermodynamic properties of (Ti,Sc)Fe<sub>2</sub>-H<sub>2</sub> system

Composition	H/IMC <sub>atm, °C</sub>	P <sub>des</sub> (atm)	t (°C)	f <sub>des</sub> (atm)	ΔH (kJ/mole H <sub>2</sub> )/ΔS (J/(K mole H <sub>2</sub> ))
ScFe <sub>2</sub> [9]	2.9 <sub>15, 22</sub>	6.0	108		35.2/106.7
Ti <sub>0.5</sub> Sc <sub>0.5</sub> Fe <sub>2</sub>	1.45 <sup>a</sup>	102.7	0.5	109	17.7(2)/103.8(7)
	3.1 <sub>1600, 23</sub>	175	22	194	
	3.4 <sub>2700, -56</sub>	356	60	434	

<sup>a</sup> Composition at which thermodynamic parameters were calculated.

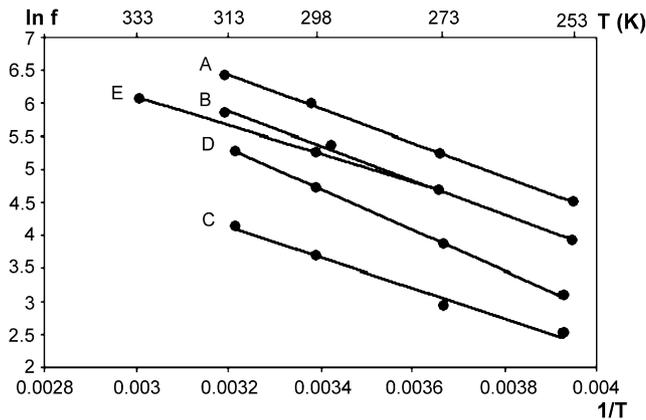


Fig. 3. Van't Hoff plots of  $\ln f$  vs.  $1/T$ : (A) ZrFe<sub>2</sub>-H; (B) Zr<sub>0.8</sub>Sc<sub>0.2</sub>Fe<sub>2</sub>-H; (C) Zr<sub>0.5</sub>Sc<sub>0.5</sub>Fe<sub>2</sub>-H ( $\beta_1$ -hydride); (D) Zr<sub>0.5</sub>Sc<sub>0.5</sub>Fe<sub>2</sub>-H ( $\beta_2$ -hydride); (E) Ti<sub>0.5</sub>Sc<sub>0.5</sub>Fe<sub>2</sub>-H.

ature (-50 °C) showed that no new hydride phase transition occurs. Hydrogen content at -56 °C at 2700 atm is 3.4 H/IMC (2.16 mass%).

Thermodynamic parameters of hydrogen desorption reaction were calculated for hydrogen content H/IMC = 1.45 (Fig. 3). Comparing data in Table 2 for ScFe<sub>2</sub> and Ti<sub>0.5</sub>Sc<sub>0.5</sub>Fe<sub>2</sub> it is possible to draw a dependence of enthalpy or entropy on concentration of A-component—scandium and titanium. Assuming linear dependence of enthalpy and entropy for scandium concentration between 0 and 33.3 at% it is possible to estimate the enthalpies and entropies for Ti<sub>0.8</sub>Sc<sub>0.2</sub>Fe<sub>2</sub> and TiFe<sub>2</sub>. Results of calculations show that the enthalpy of hydrogen desorption is 7.0 and 0.2 kJ/mole H<sub>2</sub> correspondingly. Calculated hydrogen desorption pressure for Ti<sub>0.8</sub>Sc<sub>0.2</sub>Fe<sub>2</sub> at room temperature is approximately 2500 atm. However, the actual pressure to initiate the hydriding reaction should be even higher because it was not possible to synthesise the hydride phase by application of pressure 3000 atm.

For TiFe<sub>2</sub> calculated desorption pressure at room temperature is about 5600 atm. This makes it impossible to obtain relevant hydride in our device because of 3000 atm pressure limit.

### 3.2. (Zr,Sc)Fe<sub>2</sub>-H<sub>2</sub> system

Zr<sub>0.5</sub>Sc<sub>0.5</sub>Fe<sub>2</sub> and Zr<sub>0.8</sub>Sc<sub>0.2</sub>Fe<sub>2</sub> both crystallise in cubic Laves phase C15 structure type (Table 3). Desorption isotherms for both systems are shown in Figs. 4 and 5.

Table 3  
X-ray data for (Zr,Sc)Fe<sub>2</sub> alloys and their hydrides

Composition	Cell parameters (C15)		ΔV/V <sub>0</sub> (%)
	a (Å)	V (Å <sup>3</sup> )	
ScFe <sub>1.8</sub> [10,11]	7.06	351.9	12.3
ScFe <sub>1.8</sub> H <sub>2.4</sub> [10,11]	7.34	395.45	
Zr <sub>0.5</sub> Sc <sub>0.5</sub> Fe <sub>2</sub>	7.051(1)	350.69(2)	24.0
Zr <sub>0.5</sub> Sc <sub>0.5</sub> Fe <sub>2</sub> H <sub>3.6</sub>	7.573(4)	434.31(8)	
Zr <sub>0.8</sub> Sc <sub>0.2</sub> Fe <sub>2</sub>	7.053(1)	350.94(2)	26.0
Zr <sub>0.8</sub> Sc <sub>0.2</sub> Fe <sub>2</sub> H <sub>3.7</sub>	7.618(1)	442.13(5)	
ZrFe <sub>2</sub> [5–7]	7.072	353.7	25.9
ZrFe <sub>2</sub> H <sub>4</sub> [5–7]	7.637	445.4	

Hydrogen absorption in Zr<sub>0.5</sub>Sc<sub>0.5</sub>Fe<sub>2</sub> starts at ~100 atm without any preliminary activation. There is no marked hysteresis in this system and absorption and desorption pressures are rather close. Hydrogen content at 22 °C and 1560 atm is 3.6 H/IMC. The shape of isotherms allows to suggest that there are two hydride phases forming in Zr<sub>0.5</sub>Sc<sub>0.5</sub>Fe<sub>2</sub>-H<sub>2</sub> system. At room temperature the composition of the first one ( $\beta_1$ -phase) is close to dihydride and that of the second one ( $\beta_2$ -phase) is approximately to trihydride. Hydrogen desorption enthalpies and entropies were calculated for both phases (Fig. 3 and Table 4). Such a behavior resembles ScFe<sub>1.8</sub>-H<sub>2</sub> system [11] where a stable monohydride and much less stable ScFe<sub>1.8</sub>H<sub>2.4</sub>

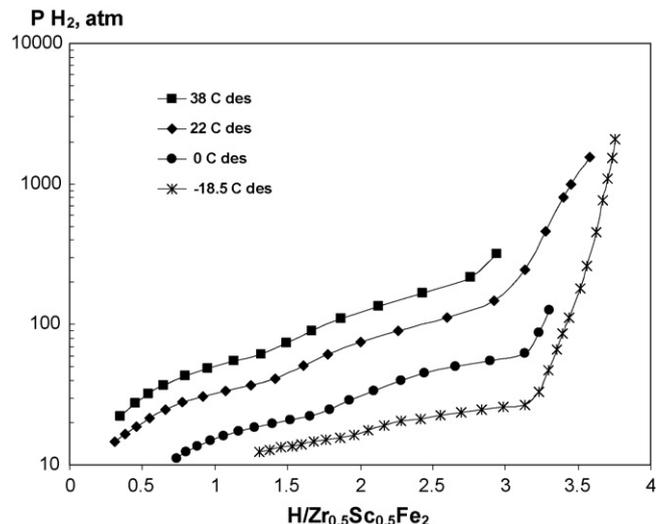
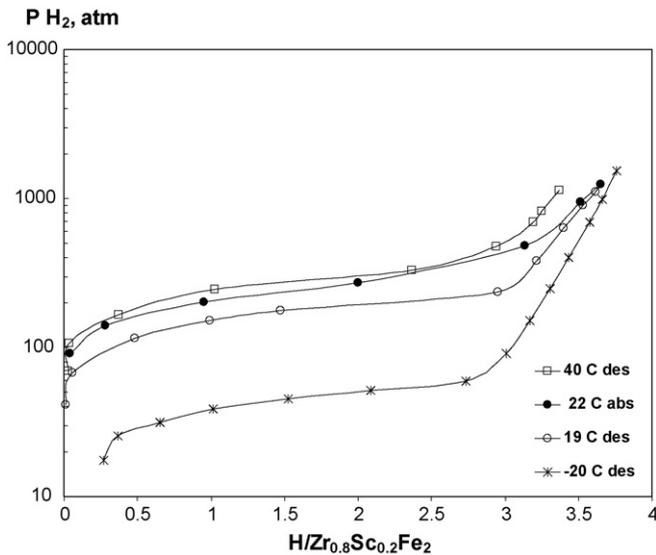


Fig. 4. PC-isotherms for Zr<sub>0.5</sub>Sc<sub>0.5</sub>Fe<sub>2</sub>-H<sub>2</sub> system.

Fig. 5. PC-isotherms for  $Zr_{0.8}Sc_{0.2}Fe_2-H_2$  system.

are formed [10,11]. In our case substitution of half of scandium for zirconium leads to significant increase of stability of lower hydride, which enthalpy is lower than that of trihydride (Table 4).

For  $Zr_{0.8}Sc_{0.2}Fe_2-H_2$  system hydrogen absorption also starts at 100 atm without activation. Hydrogen content in hydride at room temperature and 1650 atm is  $Zr_{0.8}Sc_{0.2}Fe_2H_{3.7}$ , and  $Zr_{0.8}Sc_{0.2}Fe_2H_{3.8}$ , at  $-54^\circ C$  and 1730 atm (Fig. 3 and Table 4).

Comparing hydrides  $ScFe_{1.8}H_{1.8}$ ,  $Zr_{0.5}Sc_{0.5}Fe_2H_{2.5}$  (second plateau) and  $Zr_{0.8}Sc_{0.2}Fe_2H_{1.8}$  it is possible to draw a conclusion that the increase of zirconium content in alloys leads to decrease in desorption enthalpy value (Table 4). However, entropy change goes through a maximum at  $Zr_{0.5}Sc_{0.5}Fe_2H_{2.5}$  (Table 4).

Table 4  
Hydriding and thermodynamic properties of  $(Sc,Zr)Fe_2-H_2$

Composition	H/IMC <sub>atm, °C</sub>	$P_{des}$ (atm)	$t$ (°C)	$f_{des}$ (atm)	$\Delta H$ (kJ/mole $H_2$ )/ $\Delta S$ (J/(K mole $H_2$ ))
$ScFe_{1.8}$ [10,11]	1.0	3.3	115		Stable up to $500^\circ C$ 29.6/90.0
	1.8 <sup>a</sup>				
	2.4 <sub>30</sub>				
$Zr_{0.5}Sc_{0.5}Fe_2$		12.5	-18.5	12.5	19(2)/95(6)
		18.7	-0.4	18.7	
	1.3 <sup>a</sup>	38.8	22.1	39.7	
		60.5	37.9	62.5	
		22	-18.5	22	
		46.4	-0.4	47.4	
	2.5 <sup>a</sup>	105	22.1	111.5	25.4(4)/125(1)
		177	37.9	195.5	
	3.6 <sub>1560, 22</sub>				
	3.8 <sub>1660, -50</sub>				
$Zr_{0.8}Sc_{0.2}Fe_2$		49	-19.6	50	21(1)/117(5)
	1.8 <sup>a</sup>	190	19.1	212	
		290	40.1	343	
	3.7 <sub>1652, 23</sub>				
	3.8 <sub>1730, -54</sub>				

<sup>a</sup> Composition at which thermodynamic parameters were calculated.

Table 5  
X-ray data for  $ZrFe_2$  and its hydride

Composition	Cell parameters (C15)		$\Delta V/V_0$ (%)
	$a$ (Å)	$V$ (Å <sup>3</sup> )	
$ZrFe_2$	7.064(1)	352.46(3)	24.3
$ZrFe_2H_{3.5}$	7.595(3)	438.1(3)	

Calculations similar to that performed for  $(Ti,Sc)Fe_2-H_2$  system were done for  $(Zr,Sc)Fe_2-H_2$  system basing on data in Table 4. According to these results enthalpy and entropy of hydrogen desorption for  $ZrFe_2$  hydride is about 19–20 kJ/mole  $H_2$  and 112–117 J/(K mole  $H_2$ ). Hence, hydrogen desorption pressure at room temperature can be estimated as 275–332 atm, which makes rather high the possibility of reaction between  $ZrFe_2$  and hydrogen at pressure below 3000 atm.

### 3.3. $ZrFe_2-H_2$ system

X-ray analysis showed that initial alloy is cubic Laves phase with C15-structure. Cell parameter is close to that found in [6–8]. In case of hydride no change in cell symmetry was found and the cell volume expansion is 24.3%, that is slightly lower than the 25.9% determined in [6–8] (Tables 3 and 5).

Noticeable hydrogen absorption in the first cycle starts at approximately 800 atm without preliminary activation. In consequent cycles absorption starts at lower pressures. Absorption equilibrium pressure in the first run is 1120 atm while in second and further—at 690 atm (Fig. 6). Hydrogen content in hydride at room temperature and 1800 atm is 3.5 H/IMC. At low temperature ( $-55^\circ C$ ) and 1900 atm hydride compositions is  $ZrFe_2H_{3.7}$ . The isotherms show a marked hysteresis: at room temperature absorption equilibrium pressure is 690 atm, while desorption

Table 6  
Thermodynamic properties of ZrFe<sub>2</sub>–H<sub>2</sub> system

$\Delta H$ (kJ/mole H <sub>2</sub> ) calculated	$\Delta H$ (kJ/mole H <sub>2</sub> ) experiment	$\Delta S$ (J/(K mole H <sub>2</sub> )) calculated	$\Delta S$ (J/(K mole H <sub>2</sub> )) experiment	$P_{\text{dis}}$ (atm)	$t$ (°C)	$f_{\text{dis}}$ (atm)
19–20	21.3(3)	117–122	121(1)	86	–19.9	90.5
				170	0	188
				325.1	22.7	396.7
				468.8	40	619

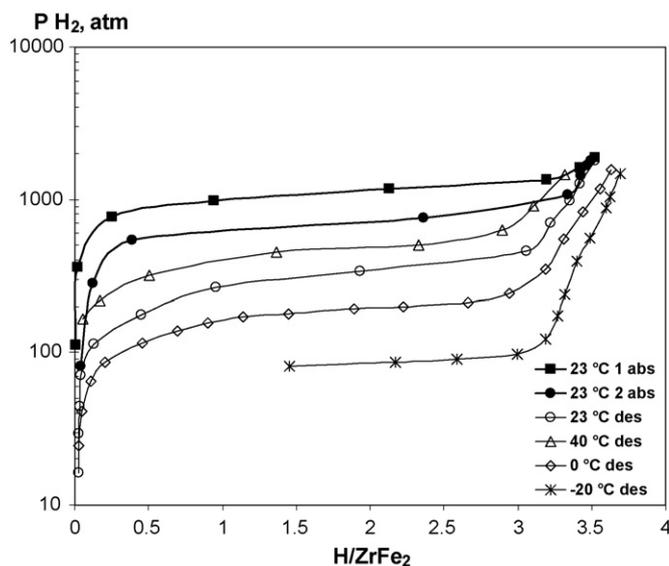


Fig. 6. PC-isotherms for ZrFe<sub>2</sub>–H<sub>2</sub> system.

one is 325 atm. It should be noted that the hydride is highly pyrophoric and readily burns in open air. Experimental thermodynamic parameters of reaction with hydrogen, obtained from van't Hoff equation (Fig. 3 and Table 6), are close to those calculated. Experimental value of equilibrium desorption pressure at room temperature also is in the predicted interval 275–332 atm.

#### 4. Conclusions

Hydrogen absorption and desorption characteristics were determined for alloys of Ti(Zr)<sub>x</sub>Sc<sub>1-x</sub>Fe<sub>2</sub>–H<sub>2</sub> ( $x = 1.0, 0.8$  and  $0.5$ ) systems. In case of increased titanium contents changed the

absorption properties considerably and hydride formation was found only in case of Ti<sub>0.5</sub>Sc<sub>0.5</sub>Fe<sub>2</sub>. In zirconium system hydride formation takes place in all three cases.

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