

Interaction of ZrFe_2 Doped with Ti and Al with Hydrogen¹

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Abstract—The influence of doping with Ti and Al on the structure and hydrogen sorption properties of ZrFe_2 was studied by XRD, XRSMA, and measurement of hydrogen absorption and desorption isotherms at pressure up to 300 MPa. The hydrogen capacity and equilibrium desorption pressures of hydrides decrease with increasing Al content at a constant ratio of Ti and Zr. The increase in the Ti content at a constant content of Al in alloys also leads to a decrease in hydrogen capacity; however, the equilibrium desorption pressures of hydrides increase considerably. $\text{Zr}_{1-x}\text{Ti}_x(\text{Fe}_{1-y}\text{Al}_y)_2$ ($x = 0.2\text{--}0.8$; $y = 0.05\text{--}0.4$) alloys were investigated.

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INTRODUCTION

The application of a high hydrogen pressure in studies of hydrogen sorption properties of intermetallic compounds (IMC) is due to several reasons. High pressures allow to one carry out interaction with hydrogen of intermetallics which were considered non-hydride-forming before, as, for example, ZrFe_2 , ZrCo_2 [1, 2], and TiMn_2 [3]. High-pressure hydrides can also be used in metal hydride compressors, where creation of high hydrogen pressure is achieved only by increasing the temperature and varying the alloy composition.

ZrFe_2 possesses fairly high hydrogen capacity—1.7 wt % H_2 at 180 MPa [2]. A nonactivated ZrFe_2 sample starts to interact with hydrogen only at 80 MPa, while equilibrium absorption and desorption pressures of the activated alloy on a plateau are 69 and 32.5 MPa, respectively. An attempt to raise the hydrogen capacity by partial replacement of Zr and Fe by Ti and Al, respectively, was carried out.

The influence of Al on hydrogen sorption properties of $\text{Zr}(\text{Fe}_{1-y}\text{Al}_y)_2$ was investigated in a number of works [4–8]. It was shown by the authors [4–6] that initial intermetallic ZrFe_2 hardly interacts with hydrogen and forms the phase $\text{ZrFe}_2\text{H}_{0.15}$ at 7 MPa and room temperature. However, at rather small content of aluminum, the amount of absorbed hydrogen sharply increases and reaches a maximum at 4 MPa and 80 K for composition $\text{Zr}(\text{Fe}_{0.8}\text{Al}_{0.2})_2\text{H}_3$. The further substitution of Al for Fe ($y > 0.25$) leads to considerable reduction of hydrogen capacity. In addition, the increase in the Al content leads to monotonic reduction of hydrogen equilibrium desorption pressure on the plateau and to an increase in the $\beta \rightarrow \alpha$ phase transition enthalpy. However, in [1, 2], the possibility of obtaining ZrFe_2 hydride at higher pressures was later proved, which partly puts in doubt the results

and laws deduced by the authors [4–6]. The influence of simultaneous doping with Ti and Al on hydrogen sorption properties of ZrFe_2 is not described in the literature. In the present work, the interaction with hydrogen of pseudobinary IMC $\text{Zr}_{1-x}\text{Ti}_x(\text{Fe}_{1-y}\text{Al}_y)_2$ ($x = 0.2\text{--}0.8$; $y = 0.05\text{--}0.4$) is investigated.

EXPERIMENTAL

Samples were prepared by alloying mixtures of pure initial metals on the copper water-cooled bottom of the arc furnace with unspent tungsten electrode in an atmosphere of the pure argon under a pressure of 0.1–0.15 MPa. With the purpose of homogenization, the alloys were remelted three to four times. The alloys were exposed to annealing (240 h, 1173 K) for additional homogenization. After annealing, samples were quenched in cold water. The structure of the alloys was examined by powder X-ray diffraction (XRD). The refinement of diffraction profiles was performed using the Rietveld method.

The composition of alloys and their homogeneity was also examined by means of a LEO Supra 50VP scanning electron microscope (SEM) (cathode with field electron emission). X-ray spectral microanalysis (XRSMA) was carried out using the Oxford INCA Energy+ system (the resolution of the Si (Li) detector is 129 eV on line $\text{Mn } K_\alpha$ 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 the apparatus and the technique of performing the experiment are reported in [9].

The structure of hydrides was also examined by XRD. The container with the sample was cooled in liquid nitrogen and kept in air for no less than 1 h for hydride passivation. The sample was removed from the nitrogen immedi-

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Table 1. XRD data of Zr_{1-x}Ti_x(Fe_{1-y}Al_y)₂

Sample	Phase composition	<i>a</i> , Å	<i>c</i> , Å
Zr _{0.8} Ti _{0.2} (Fe _{11/12} Al _{1/12}) ₂	C15 (85%) C14 (15%)	7.049(2) 4.952(2)	— 8.076(5)
Zr _{0.5} Ti _{0.5} (Fe _{0.95} Al _{0.05}) ₂	C14	4.906(0)	8.010(1)
Zr _{0.5} Ti _{0.5} (Fe _{0.8} Al _{0.2}) ₂	C14	4.967(1)	8.085(9)
Zr _{0.5} Ti _{0.5} (Fe _{0.6} Al _{0.4}) ₂	C14	5.037(6)	8.193(6)
Zr _{0.2} Ti _{0.8} (Fe _{0.9} Al _{0.1}) ₂	C14	4.862(6)	7.914(5)
Zr _{0.2} Ti _{0.8} (Fe _{0.85} Al _{0.15}) ₂	C14	4.878(3)	7.938(5)

ately before XRD; thus, the analysis time was as short as possible but sufficient for definition of the lattice periods of hydride phases. The XRD data of hydrides was used in plotting of PC isotherms to account for the change in volume of the sample upon hydrogenation.

EXPERIMENTAL RESULTS

The hydrogen sorption properties of six IMC were studied in this work: Zr_{0.8}Ti_{0.2}(Fe_{11/12}Al_{1/12})₂, Zr_{0.5}Ti_{0.5}(Fe_{1-y}Al_y)₂ (*y* = 0.05, 0.2, 0.4), and Zr_{0.2}Ti_{0.8}(Fe_{1-y}Al_y)₂ (*y* = 0.1, 0.15). According to XRSMA, the composition of all samples corresponded to what was planned. XRD showed single-phase for all samples (hexagonal Laves phase C14) except for Zr_{0.8}Ti_{0.2}(Fe_{11/12}Al_{1/12})₂, the basic phase in which is cubic Laves phase C15 (85 wt %). XRD data of the investigated

samples are presented in Table 1. It is seen that the increase in the Al content naturally leads to an increase in the lattice periods of the Laves phase.

Almost all the investigated alloys react with hydrogen (Table 2). The hydrogen capacity of Zr_{0.8}Ti_{0.2}(Fe_{11/12}Al_{1/12})₂ is 2.6 H/IMC (1.4 wt % H₂) in the first hydrogenation cycle and increases to 2.8 H/IMC (1.5 wt % H₂) in the second cycle (Fig. 1). The values of equilibrium hydrogen absorption and desorption pressures on the plateau differ insignificantly.

The Zr_{0.5}Ti_{0.5}(Fe_{1-y}Al_y)₂ alloys begin to react with hydrogen in the first hydrogenation cycle at room temperature and at 194 MPa for *y* = 0.05 and 10.5–11 MPa for *y* = 0.2 and 0.4. Hydrogen desorption isotherms of Zr_{0.5}Ti_{0.5}(Fe_{1-y}Al_y)₂–H₂ systems are presented in Figs. 2–4.

The values of hydrogen equilibrium absorption and desorption pressures on the plateau at room temperature in the first cycle in the Zr_{0.5}Ti_{0.5}(Fe_{0.95}Al_{0.05})₂–H₂ system are 150 and 90 MPa, respectively. In the third cycle, the values of equilibrium pressures on the plateau are 110 MPa for absorption and 96 MPa for desorption; thus, there is a decrease in the hysteresis value between the absorption and desorption isotherms.

The absorption and desorption isotherms in first and subsequent cycles for alloys with *y* = 0.2 and 0.4 are practically identical. The hydrogen equilibrium desorption pressures on the plateau at room temperature for Zr_{0.5}Ti_{0.5}(Fe_{0.8}Al_{0.2})₂ is 3.4 MPa and for Zr_{0.5}Ti_{0.5}(Fe_{0.6}Al_{0.4})₂ is near 0.1 MPa.

The increase in Al content in the Zr_{0.5}Ti_{0.5}(Fe_{1-y}Al_y)₂–H₂ system leads to a decrease in the hysteresis value between the absorption and desorption isotherms and a considerable decrease in hydrogen equilibrium desorption pres-

Table 2. Hydrogen sorption properties of Zr_{1-x}Ti_x(Fe_{1-y}Al_y)₂

Sample	<i>p</i> ₀ , MPa	<i>p</i> ₁ ^{abs} , MPa	<i>p</i> ₁ ^{des} , MPa	<i>p</i> _e ^{abs} , MPa	<i>p</i> _e ^{des} , MPa	H/IMC	wt % H ₂	Δ <i>H</i> , kJ/mol H ₂	Δ <i>S</i> , J/(K mol H ₂)	Δ <i>V/V</i> , %
Zr _{0.8} Ti _{0.2} (Fe _{11/12} Al _{1/12}) ₂	10	19	17.5	18.5	18	2.8 ₁₀₅	1.5	18.3 ± 1.0	106 ± 5	23.0
Zr _{0.5} Ti _{0.5} (Fe _{0.95} Al _{0.05}) ₂	194	150	90	110	96	2.8 ₂₆₀	1.6	16.0 ± 1.7	117 ± 6	22.6
Zr _{0.5} Ti _{0.5} (Fe _{0.8} Al _{0.2}) ₂	11	—	—	3.5	3.4	2.1 ₁₈₀	1.2	24.6 ± 1.5	112 ± 5	—
Zr _{0.5} Ti _{0.5} (Fe _{0.6} Al _{0.4}) ₂	10.5	—	—	—	0.1	1.6 ₁₂₂	1.0	32.5 ± 1.3	110 ± 3	—
Zr _{0.2} Ti _{0.8} (Fe _{0.9} Al _{0.1}) ₂	>260	—	—	—	—	—	—	—	—	—
Zr _{0.2} Ti _{0.8} (Fe _{0.85} Al _{0.15}) ₂	120	96	84	95	91	2.0 ₁₉₀	1.3	14.6 ± 1.2	111 ± 4	12.3

Note: *p*₀—starting pressure of reaction with hydrogen in first hydrogenation cycle at room temperature; *p*₁ abs/des—equilibrium absorption and desorption pressures on plateau in first cycle; *p*_e abs/des—equilibrium absorption and desorption pressures on plateau of activated sample.

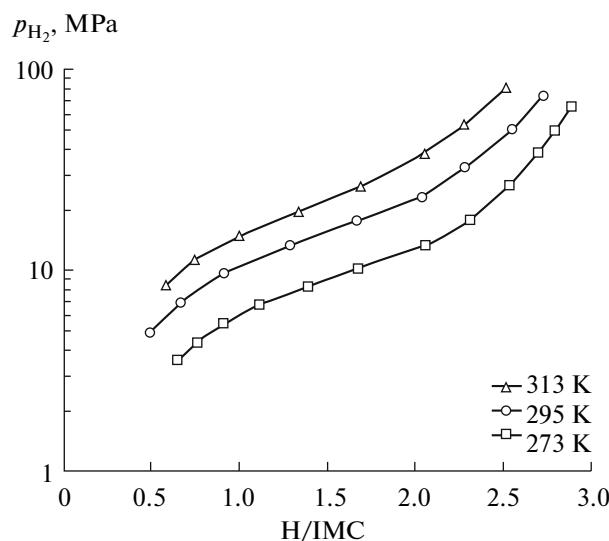


Fig. 1. Hydrogen desorption isotherms of $Zr_{0.8}Ti_{0.2}(Fe_{11/12}Al_{1/12})_2$ -H₂ system.

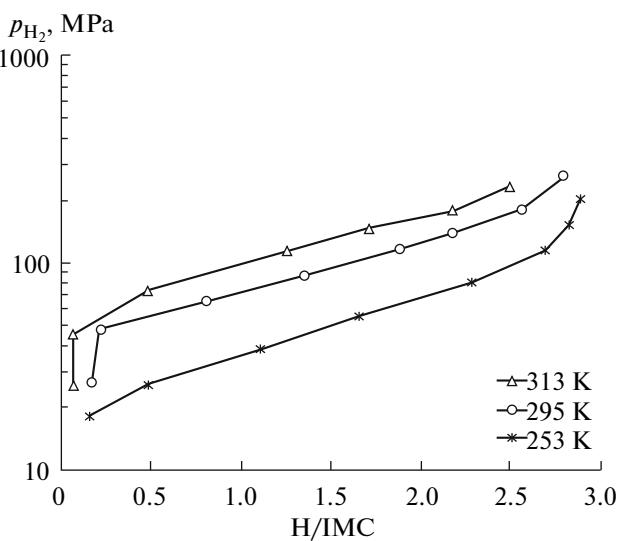


Fig. 2. Hydrogen desorption isotherms of $Zr_{0.5}Ti_{0.5}(Fe_{0.95}Al_{0.05})_2$ -H₂ system.

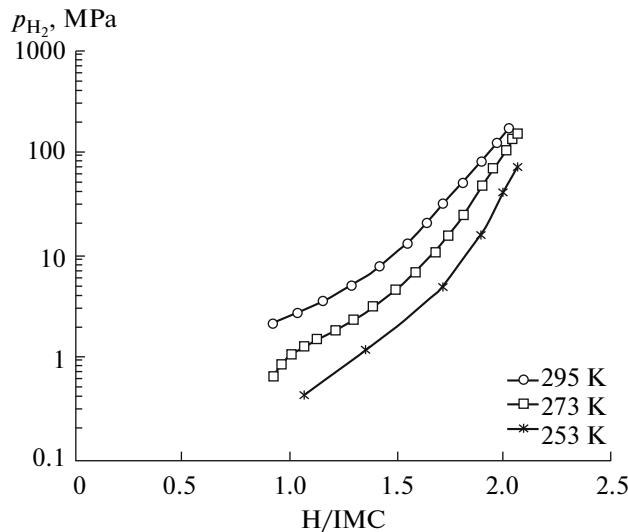


Fig. 3. Hydrogen desorption isotherms of $Zr_{0.5}Ti_{0.5}(Fe_{0.8}Al_{0.2})_2$ -H₂ system.

sures on the plateau. However, there is also a considerable decrease in sample capacity.

$Zr_{0.2}Ti_{0.8}(Fe_{0.4}Al_{0.1})_2$ does not react with hydrogen at pressures up to 260 MPa, while $Zr_{0.2}Ti_{0.8}(Fe_{0.85}Al_{0.15})_2$ begins to react at 120 MPa in the first hydrogenating cycle. The hydrogen capacity of alloy reaches its maximum only after the second hydrogenating cycle and is 2.0 H/IMC (1.3 wt % H₂) at 190 MPa. However, as we can see from Fig. 5, the plateau region does not finish in the presented isotherms. Consequently, it is possible to expect higher values of capacity upon an increase in pressure.

XRD data of hydrides of $Zr_{1-x}Ti_x(Fe_{1-y}Al_y)_2$ alloys show that the structure type of alloys does not change upon hydrogen absorption. The increase in Al content

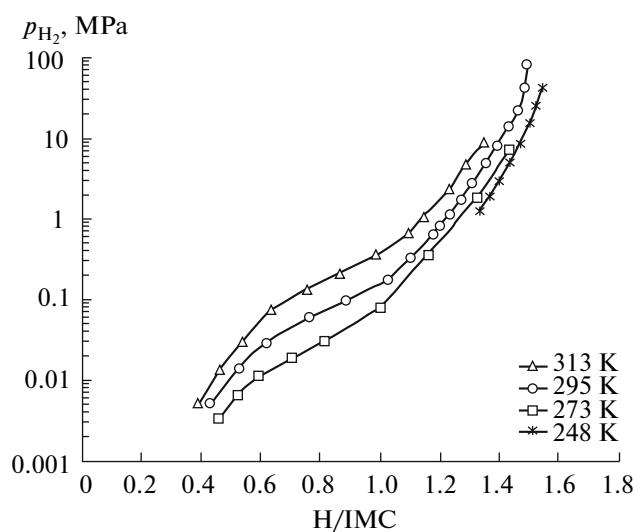


Fig. 4. Hydrogen desorption isotherms of $Zr_{0.5}Ti_{0.5}(Fe_{0.6}Al_{0.4})_2$ -H₂ system.

leads to a decrease in relative hydrogenating lattice expansion ($\Delta V/V$), which can be explained by a decrease in hydrogen content in hydrides.

DISCUSSION

Analysis of the hydrogen sorption data of $Zr_{1-x}Ti_x(Fe_{1-y}Al_y)_2$ alloys revealed that, with an increase in the Ti content in the system, an increase in hydrogen equilibrium absorption and desorption pressures on the plateau and reduction of the $\beta \rightarrow \alpha$ phase transition enthalpy take place. Both the atomic content of hydrogen (H/IMC) in hydrides and the hydrogen capacity expressed in wt % H₂ decrease.

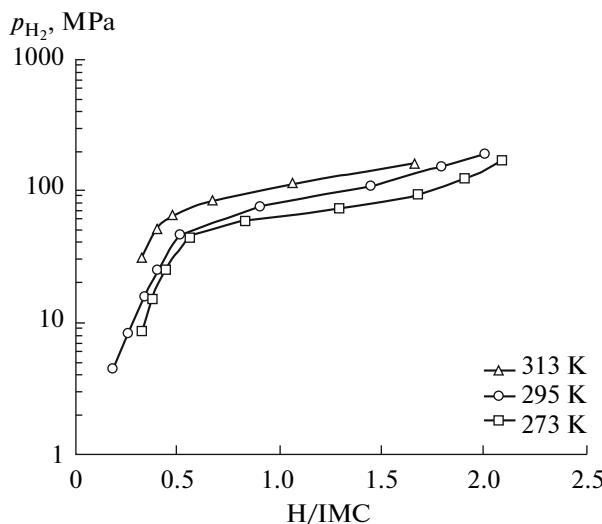


Fig. 5. Hydrogen desorption isotherms of $Zr_{0.2}Ti_{0.8}(Fe_{0.85}Al_{0.15})_2-H_2$ system.

The partial replacement of Fe by Al in $Zr_{1-x}Ti_x(Fe_{1-y}Al_y)_2$ leads to considerable reduction of the hydrogen capacity (in all cases), to an increase in the $\beta \rightarrow \alpha$ phase transition enthalpy, to hysteresis reduction between hydrogen absorption and desorption isotherms, and to reduction of the pressure necessary to start hydrogenation of nonactivated samples (at a constant ratio of Zr and Ti). It is also necessary to note that, in the systems with high Al content ($Zr_{0.5}Ti_{0.5}(Fe_{1-y}Al_y)_2-H_2$, $y = 0.2, 0.4$), the plateau corresponding to the $\beta \rightarrow \alpha$ phase transition has a sharp slope. This trend of isotherms was also noted in [4–6], which is connected with a decrease in the critical temperature of the $\beta \rightarrow \alpha$ phase transition upon an increase in the Al content.

The dependence of hydrogen content in hydride on composition of $Zr(Fe_{1-y}Al_y)_2-H_2$ based on the data [4, 5] is depicted in Fig. 6. It should be noted that all experimental results obtained by the researchers [4–6]

were described taking into account that $ZrFe_2$ does not react with hydrogen. In our opinion, low values of capacity of the samples ($y = 1/12-0.25$) are caused by incompleteness of the hydrogenation reaction, because, for small replacement of Fe by Al, the hydrogen equilibrium desorption pressure on the plateau still continues to remain rather high ($p_e(ZrFe_2, 293 K) = 32.5$ MPa), but the experiments in the works mentioned were conducted at pressures up to 7 MPa. Moreover, in recent research into interaction of $ZrFe_2$ with hydrogen [2], it was determined that its hydrogen capacity is 3.5 H/IMC (the corresponding point is also presented in Fig. 6), which considerably exceeds the value that can be obtained by linear approximation from data [4, 5] for $y = 2/12-0.75$. In this case, the hydrogen content in hydride can be described as a linear dependence on IMC composition without resorting to the phenomenological model proposed by the authors [4, 5]. However, it is not meant at all that the given model based on a short-range nearest neighbor effect is incorrect. Only the results obtained with its application look doubtful. Since in calculations it was necessary to use experimental values of hydrogen capacities for $ZrFe_2$ and $ZrAl_2$ known at that time, this led to misrepresentation of the data. If the experimental values of capacity known today were used, it is quite probable that, by means of this model, more reliable results could be obtained. In addition, the authors [4–6] predicted the possibility of formation of $ZrFe_2$ hydride upon a further increase in pressure, as was carried out later in works [1, 2].

The dependence of the $\beta \rightarrow \alpha$ phase transition enthalpy on composition according to [6] is shown in Fig. 7. As one can see, the extrapolated value of the $\beta \rightarrow \alpha$ phase transition enthalpy of $ZrFe_2$ is equal to 7.5 kJ/mol H_2 . However, in [2], it was later established that $\Delta H = 21.3$ kJ/mol H_2 (marked in Fig. 7). In view of the fact that, as already mentioned, samples were not hydrogenated completely, the values of ΔH obtained by the authors [6] proved slightly understated for compositions with

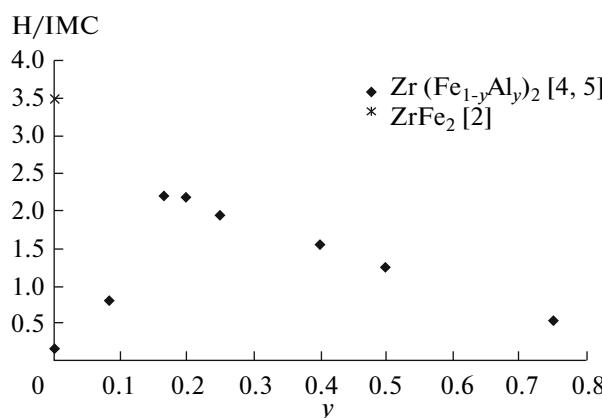


Fig. 6. The dependence of hydrogen content in hydride on composition of $Zr(Fe_{1-y}Al_y)_2$ [2, 4, 5].

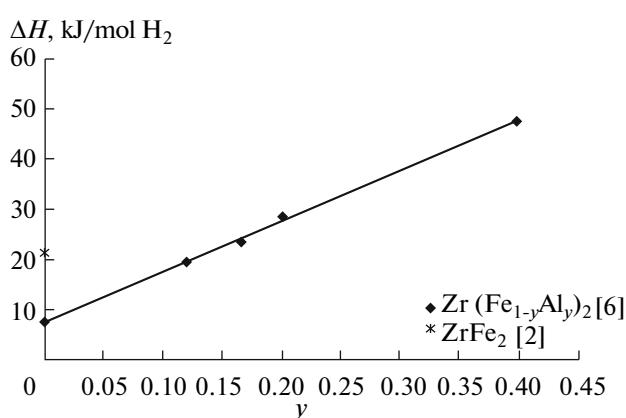


Fig. 7. The dependence of the $\beta \rightarrow \alpha$ phase transition enthalpy on composition of $Zr(Fe_{1-y}Al_y)_2$ [2, 6].

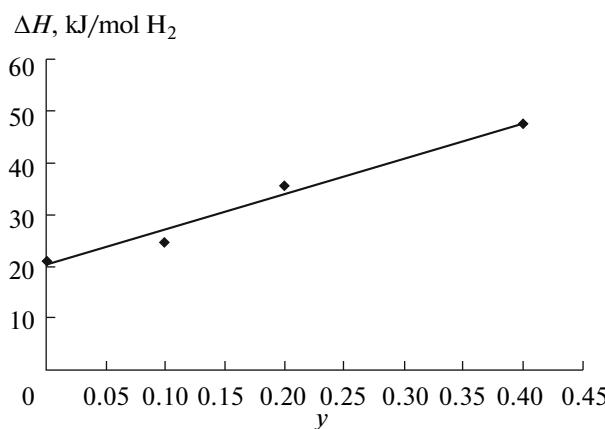


Fig. 8. The dependence of the $\beta \longleftrightarrow \alpha$ phase transition enthalpy on composition of $Zr(Fe_{1-y}Al_y)_2$ [2, 6–8].

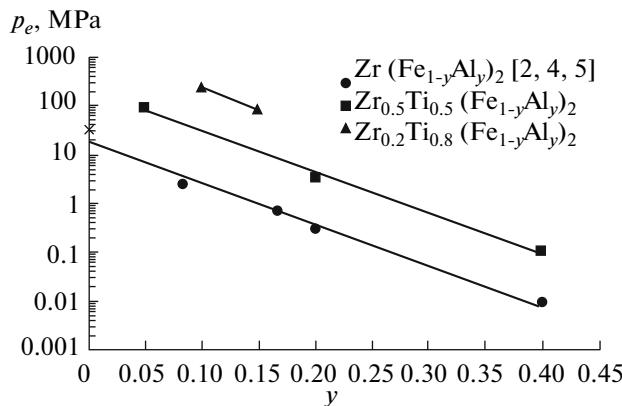


Fig. 9. The dependences of equilibrium hydrogen desorption pressures on plateau at 295 K on composition of $Zr(Fe_{1-y}Al_y)_2$ [2, 4, 5], $Zr_{0.5}Ti_{0.5}(Fe_{1-y}Al_y)_2$, and $Zr_{0.2}Ti_{0.8}(Fe_{1-y}Al_y)_2$.

$y = 0\text{--}0.4$. The values of ΔH obtained in [7] and [8] for $Zr(Fe_{0.8}Al_{0.2})_2$ and $Zr(Fe_{0.9}Al_{0.1})_2$, respectively, look more reliable, since the measurement of isotherms was carried out at pressures up to 10 MPa instead of 6 MPa as in [6]. Having combined the most reliable, in our opinion, data on values of ΔH presented in [2, 6–8], it is possible to obtain a practically linear dependence of the $\beta \rightarrow \alpha$ phase transition enthalpy on IMC composition (Fig. 8).

The dependences of equilibrium hydrogen desorption pressures on the plateau at room temperature on Al content in the $Zr_{1-x}Ti_x(Fe_{1-y}Al_y)_2$ –H₂ system are presented in Fig. 9. The dependence for compositions $Zr(Fe_{1-y}Al_y)_2$ [4, 5] is indicated by circles. The point corresponding to hydrogen equilibrium desorption pressure on the plateau of $ZrFe_2$ [2] is added to this series of results (cross in Fig. 9). As one can see, it hardly deviates from the linear dependence obtained by the authors [4, 5]. The angular coefficient of the given straight line is -19.56 . The dependence of equilibrium hydrogen desorption

pressures on the plateau on composition of $Zr_{0.5}Ti_{0.5}(Fe_{1-y}Al_y)_2$ investigated in the present work is indicated by squares. The straight line obtained with use of our data (its angular coefficient is -19.51) is practically parallel to the straight line obtained from data [2, 4, 5]. The point corresponding to $Zr_{0.2}Ti_{0.8}(Fe_{0.85}Al_{0.15})_2$ and the point obtained by interpolation of a straight line taking into account the parallelism to the first two dependences and corresponding to $Zr_{0.2}Ti_{0.8}(Fe_{0.9}Al_{0.1})_2$ are also marked on the diagram (triangles). As one can see, the estimated equilibrium hydrogen desorption pressure on the plateau of $Zr_{0.2}Ti_{0.8}(Fe_{0.9}Al_{0.1})_2$ is 240 MPa, which, as was also shown in practice, does not allow the hydride to be obtained at pressures up to 300 MPa because of the high value of the pressure necessary to start the hydrogenation reaction.

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