

Calorimetric investigation of multicomponent Laves phase interaction with hydrogen and deuterium

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Abstract

The interaction of multicomponent TiMn_{1.5}-type Laves phases with hydrogen and deuterium was investigated by means of standard pressure–composition isotherms and a calorimetric method. One of the studied alloys was selected using a mathematical approach based on the Bernauer phenomenological model. The thermodynamic parameters of the reaction of hydrogen desorption for the alloy of composition Ti_{0.98}Zr_{0.02}Mn_{1.5}V_{0.43}Cr_{0.05}Fe_{0.09} were found to be $\Delta H = 22.8 \pm 0.2$ kJ mol H₂⁻¹ and $\Delta S = 96.5 \pm 0.7$ J K⁻¹ mol H₂⁻¹. For the alloy Ti_{0.9}Zr_{0.1}Mn_{1.5}V_{0.25}Cr_{0.1}Fe_{0.05}Ni_{0.05}Co_{0.05} these parameters turned out to be $\Delta H = 22.4 \pm 0.2$ kJ mol H₂⁻¹ and $\Delta S = 94.2 \pm 0.5$ J K⁻¹ mol H₂⁻¹. The latter alloy with a d-electron concentration of 3.93 is characterized by a narrower α region, in good accordance with model predictions. The desorption of deuterium from the alloy Ti_{0.9}Zr_{0.1}Mn_{1.5}V_{0.25}Cr_{0.1}Fe_{0.05}Ni_{0.05}Co_{0.05} is characterized by values of $\Delta H = 28.7 \pm 0.2$ kJ mol H₂⁻¹ and $\Delta S = 93.8 \pm 0.7$ J K⁻¹ mol H₂⁻¹.

1. Introduction

Multicomponent (C14) Laves phases based on the intermetallic compounds (IMCs) TiMn_{1.5} and TiCr₂ show promise for practical use in various hydrogen accumulators. Bernauer and coworkers [1–5] have proposed a phenomenological model for predicting the optimal compositions of such alloys. This model is based on the following assumptions. The quantity of absorbed hydrogen depends on the concentrations of the valency electrons and particularly of the d-electrons (DEC) of transition metals. It is assumed that the most stable configuration of the transition metal atoms corresponds to a half-filled d-band. The absorption of hydrogen by cubic (C15) and hexagonal (C14) Laves phases, according to ref. 1, can be roughly estimated by the equation

$$H/M = 5 - \text{DEC} \quad (1)$$

where H represents the number of hydrogen atoms in the hydride, M represents the number of metal atoms in the alloy and

$$\text{DEC} = \frac{\sum \text{d-electrons in alloy}}{\text{number of metal atoms}} \quad (2)$$

It is also stated [1] that the α solution region is minimal for those IMCs for which the average d-electron concentration is equal to 4 and that deviations from this value lead to broadening of the α phase.

It was noted [1] that the dissociation pressures of C14 hydrides at a temperature of 253 K are about 1 atm if the free cell volume of the starting alloy is around 160–165 Å³ and that the pressure decreases with increasing free cell volume.

Using these criteria and taking into account the price of metals, the alloy Ti_{0.98}Zr_{0.02}Mn_{1.5}V_{0.43}Cr_{0.05}Fe_{0.09} was selected for practical use. This alloy is characterized by calculated values of DEC = 3.78 and H/AB₂ = 3.6. The alloy was investigated by means of the pressure–composition (P–C) isotherm method. Kinetic and operational properties have also been determined [2–5]. The maximum absorption capacity at 253 K was found to be equal to 3.5 H/AB₂, which is in good accordance with the calculated value. The enthalpies of hydriding, determined from P–C isotherms using the van't Hoff equation, increased steadily from 22 kJ molH₂⁻¹ at low concentrations of hydrogen up to 29 kJ molH₂⁻¹ at high concentrations. No calorimetric investigation of the thermodynamic properties of the alloy was performed.

In the present work a calorimetric investigation of hydrogen interaction with Ti_{0.98}Zr_{0.02}Mn_{1.5}V_{0.43}Cr_{0.05}Fe_{0.09} was carried out. Using a mathematical approach based on the Bernauer model, the alloy

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$\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.5}\text{V}_{0.25}\text{Cr}_{0.1}\text{Fe}_{0.05}\text{Ni}_{0.05}\text{Co}_{0.05}$ was also selected and prepared and its interaction with hydrogen and deuterium studied.

2. Experimental details

An analysis of published data on the hydriding characteristics of multicomponent solid solutions of IMCs shows that these properties change monotonously with the concentrations of component metals. This gives the possibility of establishing a mathematical model for determining the dependence of the absorption property on the composition using experimental data. In the simplest case these functions can be expressed by the equation

$$F(x) = y_0 + \sum a_i x_i + \sum b_{ij} x_i x_j, \quad i \geq j \quad (3)$$

where x_i is the atomic concentration of metal i and y_0 , a and b are coefficients.

The programme for determining such dependences was written in TurboPascal for an IBM PC. In the present work we determined the dependence of the absorption capacity on the alloy composition. The coefficients in eqn. (3) were found to be $y_0 = 3.72$, $a_1 = 12.57$, $a_2 = 2.32$, $a_3 = -19.67$, $a_4 = 4.91$, $a_5 = -7.67$, $a_6 = -13.47$, $a_7 = -19.96$, $b_{11} = -15.68$, $b_{12} = -5.14$, $b_{13} = 4.82$, $b_{14} = 0.34$, $b_{15} = 3.30$, $b_{16} = 6.31$, $b_{17} = 6.60$, $b_{22} = -12.07$, $b_{23} = 15.03$, $b_{24} = -19.27$, $b_{25} = -19.33$, $b_{26} = 18.84$, $b_{27} = 12.38$, $b_{33} = 20.28$, $b_{34} = -2.67$, $b_{35} = 17.79$, $b_{36} = -27.46$, $b_{37} = -22.54$, $b_{44} = 22.64$, $b_{45} = 3.74$, $b_{46} = 0.63$, $b_{47} = 1.98$, $b_{55} = -2.39$, $b_{56} = 0.03$, $b_{57} = 0.10$, $b_{66} = 10.79$, $b_{67} = 0.00$ and $b_{77} = 8.55$. These indices from 1 to 7 correspond to the starting metals zirconium, manganese, chromium, vanadium, iron, cobalt and nickel respectively. The determination of the AB_2 alloy composition with optimal absorption properties can be carried out by means of simple computer selection within preset limits of the parameters of DEC value and absorption capacity ($3.85 < \text{DEC} < 4.00$, $2.8 < \text{H}/\text{AB}_2 < 3.0$).

The starting metals used for the preparation of the alloys were of 99.9% purity. The samples were prepared by arc melting in an atmosphere of purified argon. Because of the higher volatility of manganese, this metal was taken as having 1.5 mass% redundancy. For the alloy $\text{Ti}_{0.98}\text{Zr}_{0.02}\text{Mn}_{1.5}\text{V}_{0.43}\text{Cr}_{0.05}\text{Fe}_{0.09}$ two types of manganese were used: electrolytic manganese (sample 1) and manganese remelted from electrolytic manganese (sample 2). This was connected with the fact that electrolytic manganese usually contains rather large quantities of occluded oxygen, which has a negative influence on the sorption properties even at concentrations of 100 ppm [1]. For the preparation of $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.5}\text{V}_{0.25}\text{Cr}_{0.1}\text{Fe}_{0.05}\text{Ni}_{0.05}\text{Co}_{0.05}$ (sample 3) only remelted manganese was used.

TABLE 1. Properties of starting samples $\text{Ti}_{0.98}\text{Zr}_{0.02}\text{Mn}_{1.5}\text{V}_{0.43}\text{Fe}_{0.09}\text{Cr}_{0.05}$ (sample 2) and $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.5}\text{V}_{0.25}\text{Cr}_{0.1}\text{Fe}_{0.05}\text{Co}_{0.05}\text{Ni}_{0.05}$ (sample 3)

Element	Lattice parameters (Å)	Composition			
		Charge		Atomic absorption ^a	
		Formula index	Mass%	Formula index	Mass%
<i>Sample 2</i>					
Ti	$a = 4.869(1)$	0.98	29.49	0.95	29.0
Zr	$c = 7.973(2)$	0.02	1.14	0.02	1.1
Mn		1.5	51.77	1.5	52.0
V		0.43	12.8	0.4	12.9
Fe		0.09	3.16	0.09	3.2
Cr		0.05	1.63	0.05	1.7
<i>Sample 3</i>					
Ti	$a = 4.864(1)$	0.9	26.73	0.89	26.2
Zr	$c = 7.970(2)$	0.1	5.66	0.1	5.7
Mn		1.5	51.1	1.5	51.0
V		0.25	7.99	0.27	8.5
Fe		0.05	1.73	0.05	1.7
Cr		0.1	3.22	0.09	3.0
Co		0.05	1.83	0.05	1.8
Ni		0.05	1.82	0.05	1.8

^aAccuracy of analysis is 5%.

The accordance of the compositions of prepared samples with the composition of starting charges was checked by weighing and by atomic absorption analysis (Table 1). The phase composition of the alloys was determined by powder X-ray diffraction with a DRON-2 diffractometer (CuK α radiation). For calorimetric investigations a Tian-Calvet differential heat-conducting calorimeter connected to an installation for dose gas feeding was employed. Differential molar enthalpies of hydrogen desorption from the hydride phase were determined from the heat effect of hydrogen desorption on the calibrated volume with a hydrogen pressure lower than the equilibrium one. The sample masses were: sample 1, 1.53818 g; sample 2, 1.17323 g; sample 3, 1.20492 g. The weighing error was ± 0.00005 g.

3. Results and discussion

3.1. $\text{Ti}_{0.98}\text{Zr}_{0.02}\text{Mn}_{1.5}\text{V}_{0.43}\text{Cr}_{0.05}\text{Fe}_{0.09}\text{-H}_2$ system

The first step in the investigation was to study the interaction of hydrogen with two samples of the alloy that have been proposed in ref. 1 for practical use. As mentioned above, these samples differed in the purity of the starting manganese. Figure 1 shows the depen-

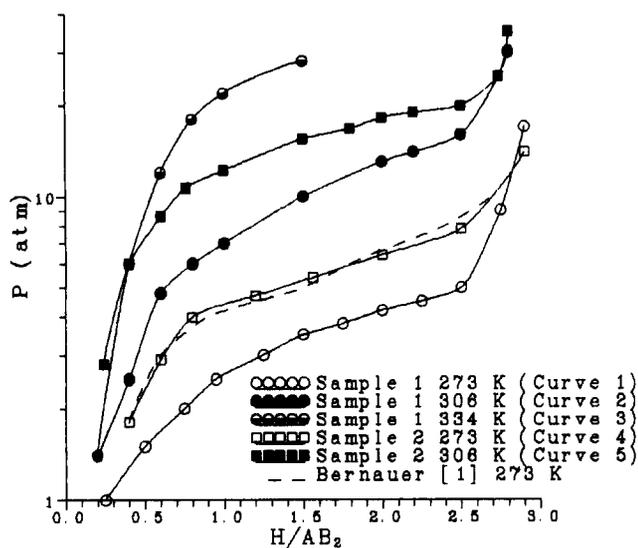


Fig. 1. Equilibrium desorption pressure as a function of hydrogen concentration in Samples 1 and 2.

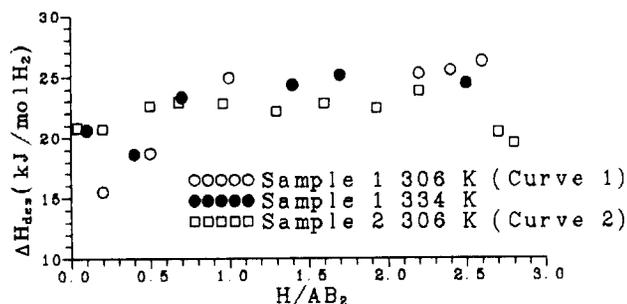


Fig. 2. Hydrogen desorption enthalpy as a function of hydrogen concentration in Samples 1 and 2.

dences of the desorption equilibrium pressure on the hydrogen concentration in alloy 1 at temperatures of 273, 306 and 334 K. The pressure plateau has some slope. As stated in ref. 6, all quaternary IMCs have a sloping plateau region: the more complex the compound, the larger is the slope of the isotherm. Such behaviour is connected with the crystal lattice energetics. The equilibrium pressures determined for the composition of $H/AB_2 \approx 1.3$ are equal to 3, 8 and 26 atm respectively. The maximum absorption capacity ($T=306$ K) is $H/AB_2=2.7$ at 25 atm.

For the composition of $H/AB_2 \approx 1.3$ dependence of $\ln P$ on the reciprocal temperature was determined and the values of enthalpy and entropy of desorption were calculated to be $\Delta H=26.5 \pm 0.3$ kJ molH₂⁻¹ and $\Delta S=106.0 \pm 1$ J K⁻¹ molH₂⁻¹ respectively.

Figure 2 shows the dependence of ΔH_{des} on the hydrogen concentration at temperatures of 306 and 334 K (curve 1). The differential molar enthalpies in the plateau region were equal to 24.9 ± 0.2 and 24.8 ± 0.4 kJ molH₂⁻¹ respectively. This means that in the in-

vestigated range of temperatures the enthalpies are temperature independent.

Using the equation

$$\Delta S_{des} = \frac{\delta H_{des}}{T} + R \ln P_{H_2des} \quad (4)$$

the values of ΔS_{des} in the plateau region were calculated as 99.4 ± 0.6 and 98.1 ± 1 J K⁻¹ molH₂⁻¹ at 306 and 334 K respectively (Table 2). Comparing the results obtained from the calorimetric experiment with those calculated using the van't Hoff equation, one may note the larger values of ΔH_{des} and ΔS_{des} in the second case. According to ref. 7, this is connected with the hysteresis phenomenon characteristic of such systems. However, hysteresis does not alter the thermodynamic parameters obtained in the calorimetric experiment.

Similar investigations were carried out on sample 2 at 273 and 306 K (Fig. 1, curves 4 and 5; Fig. 2, curve 2; Table 2). The desorption pressure for the sample 2–H₂ system is higher than that for sample 1 at the same temperature and is equal to 13 atm at $H/AB_2=1.3$; the maximum absorption capacity is $H/AB_2=2.8$ at 25 atm. Comparing these values of absorption capacity and equilibrium pressure with literature data [1], one can draw the following conclusions. The absorption capacity remains practically the same for all samples. The equilibrium pressure for sample 2 coincides with the literature value but for sample 1 is considerably lower. This implies that sample 2 is identical to the sample described by Bernauer *et al.* [1]. The deviations in the properties of sample 1 are evidently connected with the purity of the starting manganese.

The average values of enthalpy and entropy in the plateau region obtained in the calorimetric experiment (ΔH_{des}) and by combination of calorimetric and equilibrium data (ΔS_{des}) are equal to 22.8 ± 0.2 kJ molH₂⁻¹ and 96.5 ± 0.7 J K⁻¹ molH₂⁻¹ respectively. The larger endothermicity of hydrogen desorption in the case of sample 1 compared with sample 2 is in good agreement with the lower equilibrium pressure of its hydride (Fig. 1, curves 2 and 5).

3.2. $Ti_{0.9}Zr_{0.1}Mn_{1.5}V_{0.25}Cr_{0.1}Fe_{0.05}Co_{0.05}Ni_{0.05}-H_2$ system

Using the Bernauer model and the computer programme described earlier, the alloy $Ti_{0.9}Zr_{0.1}Mn_{1.5}V_{0.25}Cr_{0.1}Fe_{0.05}Co_{0.05}Ni_{0.05}$ (sample 3) was selected (DEC=3.9, calculated absorption capacity $H/AB_2=2.9$).

Figure 3 shows the desorption isotherms at 273 and 306 K for the sample 3–H₂ system. The pressure plateau is less sloping than in the case of samples 1 and 2 (Fig. 1). The equilibrium pressure values for samples 2 and 3 at the same temperature are very close to one another and higher than for sample 1. The absorption capacities of samples 2 and 3 are also very close and

TABLE 2. Thermodynamic properties of studied systems $\text{Ti}_{0.98}\text{Zr}_{0.02}\text{Mn}_{1.5}\text{V}_{0.43}\text{Cr}_{0.05}\text{Fe}_{0.09}\text{-H}_2$ and $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.5}\text{V}_{0.25}\text{Fe}_{0.05}\text{Cr}_{0.1}\text{Co}_{0.05}\text{-Ni}_{0.05}\text{-H}_2(\text{D}_2)$

Sample	$(\text{H}/\text{AB}_2)_{\text{max}}$ ($P=25$ atm)	ΔH (kJ mol $\text{H}_2(\text{D}_2)^{-1}$)		ΔS (J K $^{-1}$ mol $\text{H}_2(\text{D}_2)^{-1}$)	
		Calorimetric	P - C - T	Calorimetric	P - C - T
1	2.7	24.9 ± 0.2	27.8	99.4 ± 0.6	108.7
2	2.9	22.8 ± 0.2		96.5 ± 0.7	
3	$\left\{ \begin{array}{l} \text{H}_2 \\ \text{D}_2 \end{array} \right.$	2.8	22.4 ± 0.2	94.2 ± 0.5	
		2.8	28.7 ± 0.2	93.8 ± 0.7	

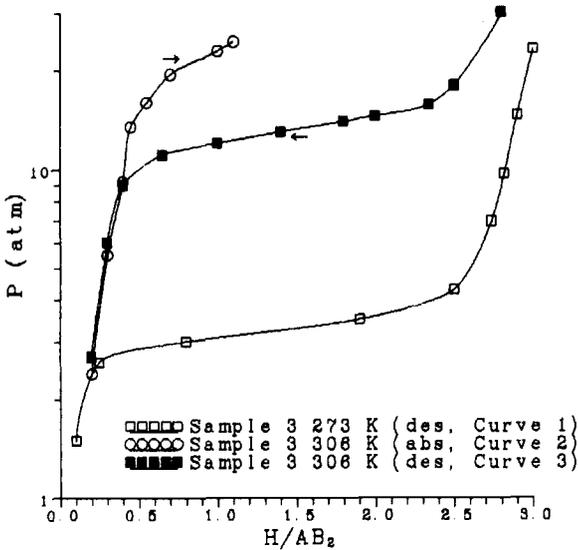


Fig. 3. Equilibrium desorption pressure as a function of hydrogen concentration in Sample 3.

slightly lower than the value calculated for sample 3 ($\text{H}/\text{AB}_2 = 3.3$). The α phase region for the sample 3- H_2 system ($\text{H}/\text{AB}_2 < 0.35$) is narrower than for samples 1 and 2 ($\text{H}/\text{AB}_2 < 0.65$). This result is quite in accordance with the Bernauer model, since the DEC value for sample 3 is equal to 3.9 (DEC=3.78 for samples 1 and 2).

Figure 3 shows part of the absorption isotherm for sample 3 at 306 K (curve 2). The absorption pressure is considerably higher than the desorption pressure. Thus, in practice, the charging of an accumulator should be done at pressures higher than 30 atm at room temperature or at temperatures well below 273 K. (According to ref. 1, the charging of an accumulator with sample 2 requires 50 atm at 297 K.)

The desorption curve for sample 3 was obtained by adding various portions of hydrogen ($\Delta x = 0.05\text{--}0.5$). Changing the portion in our case does not alter the hysteresis value and confirms the equilibrium of the hydrogen absorption process. This result contradicts the results of ref. 8 that different portions of hydrogen alter the hysteresis value. This might be due to the greater proximity of the parameters of our experiment

to the isothermal values (smaller sample mass, 1.5 g, as compared with 5-10 g in a classical P - C - T experiment).

Calorimetric studies of the interaction of sample 3 with hydrogen and deuterium were carried out at 306 K. The enthalpy and entropy of hydrogen desorption, determined in three series of runs, are equal to 22.4 ± 0.2 kJ mol H_2^{-1} and 94.2 ± 0.5 J K $^{-1}$ mol H_2^{-1} respectively (Fig. 4, Table 2). Figure 5 shows the deuterium de-

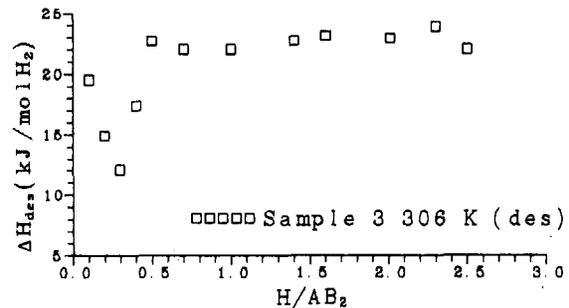


Fig. 4. Hydrogen desorption enthalpy as a function of hydrogen concentration in Sample 3.

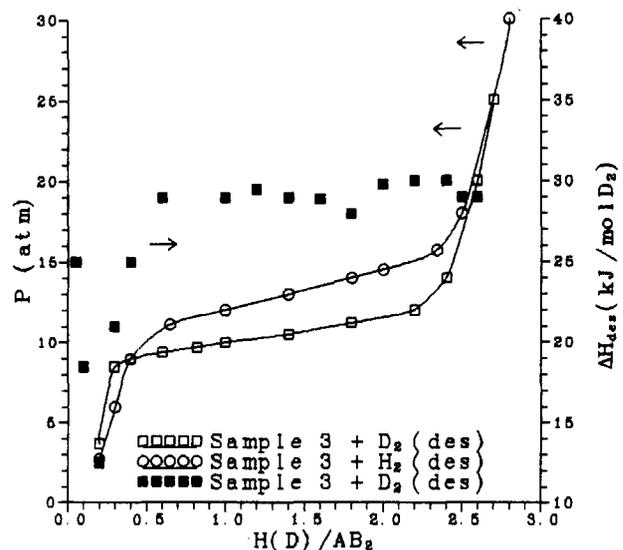


Fig. 5. Equilibrium desorption pressure and desorption enthalpy as a function of deuterium concentration in Sample 3, compared with hydrogen desorption isotherm for Sample 3.

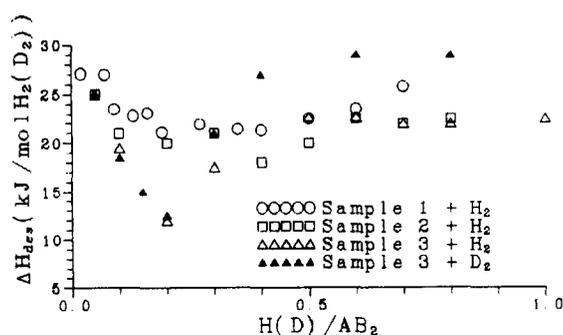


Fig. 6. Hydrogen (deuterium) desorption enthalpy as a function of hydrogen (deuterium) concentration in Samples 1, 2 and 3 in the range of compositions $H(D)/AB_2 < 1.0$ at $T=306$ K.

sorption pressure and enthalpy as functions of the deuterium concentration at 306 K. The shape of the isotherm is similar to that for the sample 3– H_2 system. The equilibrium deuterium pressure is about 2 atm lower than the hydrogen value, although the absorption capacity remains the same ($H/AB_2 \approx 2.8$). We did not notice any visual difference in the rates of hydrogen and deuterium desorption. The average thermodynamic values for desorption on the plateau region, determined in five series of runs, are $\Delta H_{des} = 28.7 \pm 0.2$ kJ mol H_2^{-1} and $\Delta S_{des} = 93.8 \pm 0.7$ J K $^{-1}$ mol H_2^{-1} . The value of the deuterium desorption enthalpy is more endothermic than that for hydrogen ($\Delta H_{des} = 21.4 \pm 0.2$ kJ mol H_2^{-1}), which is in accordance with the lower value of equilibrium pressure of deuterium and reveals the greater strength of deuterium–metal bonding.

The region of low hydrogen concentration ($H/AB_2 < 1.0$) was studied in more detail for samples 1–3 (Fig. 6). One can see three regions on the curve of ΔH_{des} as a function of hydrogen concentration (Fig. 6): the first region is connected with some lowering of the ΔH_{des} value in the range of concentration $H/AB_2 < 0.2$; the second ($0.2 < H/AB_2 < 0.6$) region shows a practically constant $\Delta H_{des} = 21.9 \pm 0.3$ kJ mol H_2^{-1} ; in the third region the value of ΔH_{des} increases to the value of the $\alpha \leftrightarrow \beta$ transition. The first region is connected with the chemisorption of hydrogen on the surface of the alloy, the second region with the formation of an α solution of hydrogen in the metal matrix and the third region with the formation of a hydride phase. The α region for the sample 3– H_2 system is narrower than for the systems with samples 1 and 2. There are, however, no obvious changes in the character of the ΔH_{des} dependence with concentration.

Comparison of the data of sample 3 for hydrogen and deuterium (Fig. 6) also shows no difference between isotopes in the character of the interaction.

4. Conclusions

The results obtained in the present work allow us to draw some conclusions regarding the peculiarities of the interaction of TiMn $_{1.5}$ -type Laves phases with hydrogen and deuterium.

It is worth mentioning once more the strong influence of the quality of the component metals on the absorption properties of the alloys. In our case the use of manganese with a higher concentration of oxygen led to decreases in equilibrium pressure.

According to our results, the values of differential molar enthalpies on the plateau region under exactly isothermal experimental conditions are not altered by changes in the amount of added hydrogen.

We did not find any striking differences in the sample 3 interaction with hydrogen and deuterium except for the lower dissociation pressure of the deuteride phase. This fact is consistent with such a type of IMC interaction with hydrogen isotopes.

Our results confirm the assumption [1] that if the DEC value is approximately equal to 4, then the α region of the isotherm is the narrowest. The application of mathematical approaches based on one or other phenomenological model can be rather useful in predicting the properties of hydrogen-absorbing alloys.

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