

CALORIMETRIC INVESTIGATION OF HYDROGEN INTERACTION WITH $ZrMn_2$

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Abstract. The interaction of hydrogen with $ZrMn_2$ Laves phase compound at pressure up to 60 atm and temperature range from 100 to 305 °C has been investigated using reaction calorimetry. The obtained results allow us to propose the existence of two hydride phase in the $ZrMn_2$ - H_2 system.

Keywords: Intermetallic Compounds (IMC); Hydrides; Calorimetry; $ZrMn_2$ - H_2 system.

1. Introduction

Intermetallic compound (IMC) $ZrMn_2$ with the hexagonal C 14 structure, belonging to Laves phase, is the forefather of the large family of AB_2 -type IMC, which is applied as materials for hydrogen storage and transportation. There are a lot of works devoted to study of $ZrMn_2$ structure, hydrogen storage capacity and thermodynamic parameters of $ZrMn_2 - H_2$ system. But in these works thermodynamic properties were studied in terms of van'Hoff plots, which suggest temperature independence of partial molar enthalpy (ΔH) of hydrogen reaction with $ZrMn_2$. The studies of $ZrMn_2 - H_2$ system, carried out by means of calorimetric method, are significantly less and the data for changes of partial molar enthalpy of reaction $ZrMn_2$ with hydrogen are practically absent.

2. Experimental

The $ZrMn_2$ was prepared by arc melting from the pure components in the arc-furnace with tungsten nonconsumable electrode on a copper water cooled heart under purified argon pressure 1-1,5 atm. All starting materials had purity better 99.99%. For the additional purification of argon from oxygen and nitrogen the zircon getter was melted before starting smelting procedure. An excess amount of Mn was added (4 wt.%) to compensate of weight loss during melting. The buttons of the melted alloy were turned over and remelted four times to ensure homogeneity. The sample was annealed at 950°C for 10 days in the sealed quartz in vacuo. To prevent an interaction of the sample material with quartz it was put into tantalum container.

The crystal structures of the starting alloy and its hydride were characterized by $Cu K\alpha$ X-ray diffraction using Thermo Ariel diffractometer. The Rietveld refinement of diffraction profiles was performed in RIETAN '97 program. An accuracy of determination of the cell parameters was $\pm 0.001 - 0.005 \text{ \AA}$.

To prevent the hydride of $ZrMn_2$ from burning since it was a very fine powder, a vessel with tested hydride was cooled in liquid nitrogen, slowly opened to air and

then filled with hexsan. This treatment led to a poisoning of the centers of hydrogen recombination that reduced kinetics of dehydriding reaction.

XRD results for $ZrMn_2$ and its hydride confirmed the presence of C 14 structure as a major phase and ZrO_2 as minor phase. X-ray diffraction pattern of starting alloy is shown in Fig. 1. The lattice parameters of the hexagonal C 14-type structure were refined to $a=5.031 \text{ \AA}$ and $c=8.261 \text{ \AA}$ and they are in good agreement with the reference data [1-5]. The hydrogenation of $ZrMn_2$ did not change its crystal structure type but led to an expansion of its unit sell volume about 20%. The chemical composition of alloy and its homogeneity were examined by electron microscopy and electron probe analysis.

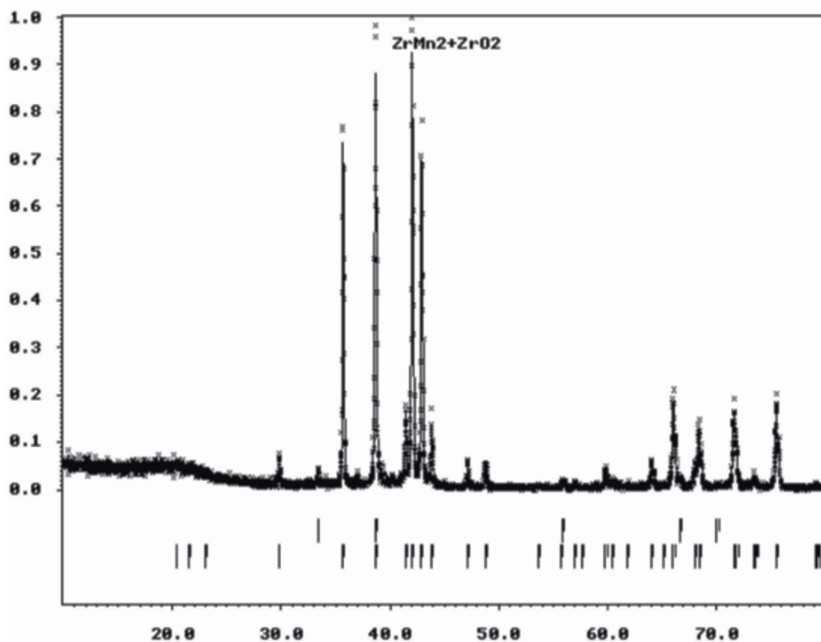


Figure 1. Cu $K\alpha$ diffraction pattern for $ZrMn_2$.

For the measurements of the dependences of differential partial molar enthalpy of absorption and desorption (ΔH_{abs} and ΔH_{des}) and equilibrium hydrogen pressure (P) on hydrogen concentration in $ZrMn_2$ and on temperature of reactions of hydriding and dehydriding, twin-cell differential heat-conducting calorimeter of Tian-Calvet type connected to apparatus for gas dosed feeding was used. The apparatus scheme was described elsewhere [6]. The mass of testing $ZrMn_2$ alloy was 1.8996g.

3. Results and Discussion

The $ZrMn_2$ - H_2 system was studied in the wide temperature range from 100 to 305°C and hydrogen pressure up to 60 atm. The advantage of the calorimetric method, applied in the present work, is the possibility to obtain calorimetric data simultaneously with P-C isotherms (P-equilibrium pressure, $C = [H]/[ZrMn_2]$).

The hydrogen desorption P-C isotherms measured at selected temperatures (100, 170, 245 and 305°C) and the absorption isotherm at 245°C for the ZrMn_2 are plotted in Fig. 2.

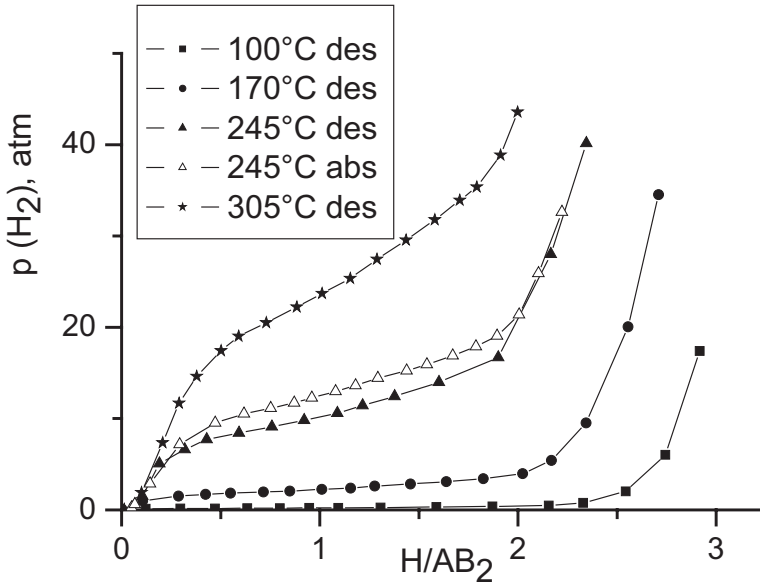


Figure 2. Absorption and desorption isotherms for the ZrMn_2 - H_2 system.

As could be seen from Fig. 2 the slopping plateaus in the two-phase region are a typical features of the ZrMn_2 - H_2 system, moreover the slope of these plateaus increase with rising of the experimental temperature and the region of two-phase equilibrium is shortened. Further it should be marked the presence of pressure hysteresis within plateau region. The value of this hysteresis at 245°C is equal ≈ 2.5 atm, the dissipation of the free energy at hysteresis $RT \ln(P_{\text{abs.}}/P_{\text{des.}}) = 0.88 \text{ kJ/moleH}_2$ where $P_{\text{abs.}}$ and $P_{\text{des.}}$ are the plateau pressure for absorption and desorption processes, respectively. Earlier [7] it has been found that the ZrMn_2 - H_2 system has large isothermal pressure hysteresis equal to 7.18 kJ/moleH_2 at 50°C. This value is in a good agreement with present data since it is well known that the magnitude of hysteresis decreases with rising of temperature.

Now let turn to an examination of the obtained calorimetric data presented in Figs. 3-6 and in sequence to analyze the changes of differential partial molar enthalpy depending on hydrogen concentration in the IMC and experimental temperature.

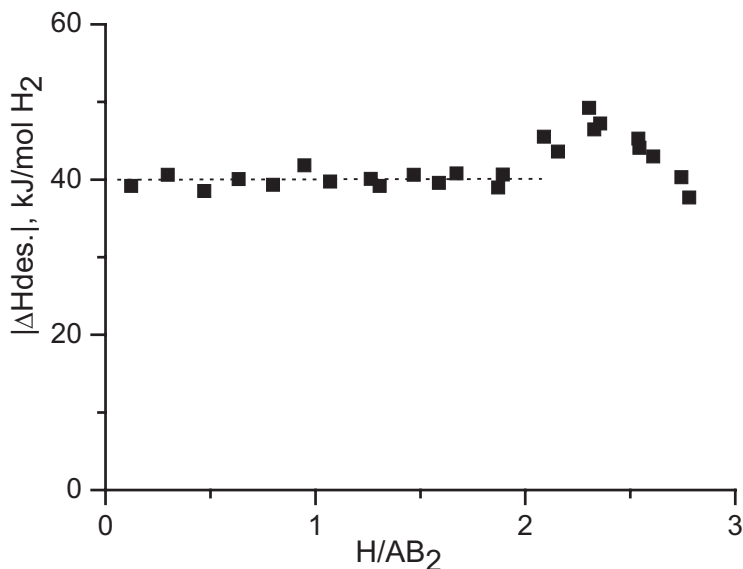


Figure 3. Desorption enthalpy vs. composition at 100°C.

Figure 3 presents the plot of the desorption enthalpy as a function of hydrogen concentration at 100°C. Since at 100 °C in the $\text{ZrMn}_2\text{-H}_2$ system there is an initial region ($C < 0.125$) where hydrogen pressures are negligibly small for the pressure gauge used here we could not obtain the P-C isotherm and the calorimetric data for the region of α -solid solution hydrogen in IMC. The values of $|\Delta H_{\text{des}}|$ in the region of the $\alpha \leftrightarrow \beta$ - transition ($C < 2.0$) are constant and equal to 39.9 ± 0.9 kJ/mole H_2 . It corresponds with the reference data good enough, namely, Flanagan and co-worker [8] obtained $|\Delta H_{\text{des}}| = 37.4$ kJ/mole H_2 at 50°C and $[\text{H}]/[\text{ZrMn}_2] = 1.5$ (that corresponds to the middle of the two-phase region), and Magomedbekov [9] gave the average values of $|\Delta H_{\text{des}}| = 42.5$ kJ/mole H_2 at the middle of the plateau. A special attention should be paid to the range $2.0 < C < 3.0$ on the plot of the $|\Delta H_{\text{des}}|$ -C dependence which is accepted to be considered as the region of the hydrogen dissolution into β -phase. As it could be seen in Fig. 3 when hydrogen is removed from the single-phase hydride region the $|\Delta H_{\text{des}}|$ values increase and pass through a maximum (to $|\Delta H_{\text{des}}| \approx 50$ kJ/mole H_2) and then continuously decrease down to the values of $|\Delta H_{\text{des}}|_{\text{plat}}$. Previously the same dependence has been marked in the works of Magomedbekov [9] and Flanagan [8]. The significant increase in the values of desorption enthalpy on the boundary $\beta/\alpha + \beta$ (≈ 10 kJ/mole H_2) the authors of both works attributed to the fact that crystal lattice of hydride phase has continued to preserve the parameters β -phase for same time when a decomposition of hydride started. It is interesting to note, that Flanagan and co-workers [8] studied $\text{ZrMn}_{2+x}\text{H}_y$ ($x = -0.2, 0, 0.5$ and 1.0) and the same $|\Delta H_{\text{des}}|$ -C dependences were observed for all researched IMC, but the most length this phenomenon had in case of ZrMn_2 (~ 1 $[\text{H}]/[\text{ZrMn}_2]$).

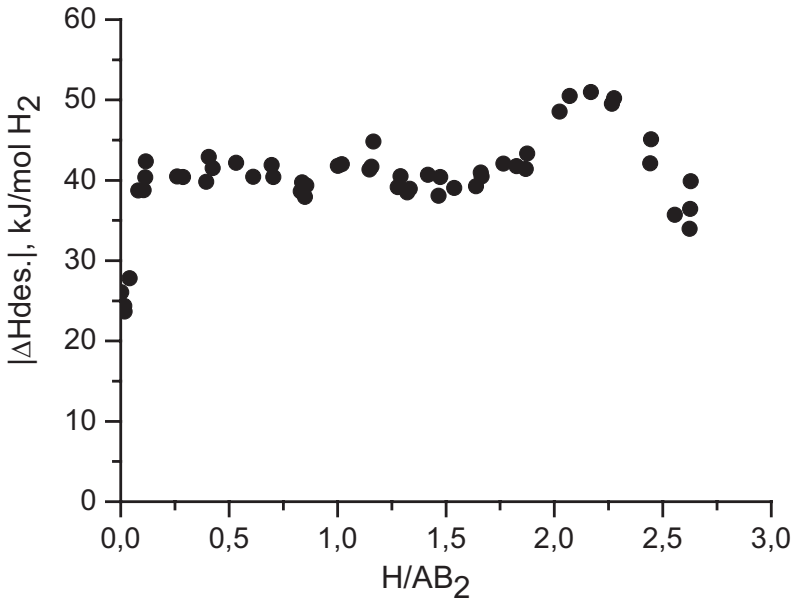


Figure 4. Desorption enthalpy vs. composition at 170°.

With rising of the experimental temperature from 100°C to 170°C the plot of the $|\Delta H_{des.}|$ -C dependence changes its shape (see Fig. 4). In the α -solid solution region of hydrogen in IMC the values of desorption enthalpy $|\Delta H_{des.}|$ increase from 24.2 kJ/moleH₂ to 43.3 kJ/moleH₂ (~20 kJ/molH₂). In comparison with the plot for 100°C the $|\Delta H_{des.}|$ values in the two-phase region (0.2 < C < 1.8) do not remain constant over the plateau range, but the function $|\Delta H_{des.}| = f(C)$ acquires more complex character. The plateau range can be divided into two parts: 0.2 < C < 1.1 and 1.1 < C < 1.8. Earlier it has been established [10-12] that hydrogen atoms in the ZrMn₂ compound with hexagonal Laves phase structure mainly occupy tetrahedral interstitial sites 24(l), 12(k)₁, 6(h)₁ and 6(h)₂. It could be supposed, that when rising temperature hydrogen atoms relocate between occupied sites and the difference in the energy of hydrogen interaction with different metal atoms forming these interstitial sites becomes more noticeable so that calorimetric measurements carried out in the wide temperature range permitted us to notice it. Previously it has been found for TiMn_{1.5}D₃ [13] that relocation of hydrogen atoms takes place at -193°C (~0.25D) and in the work [14] for (Ti_{0.9}Zr_{0.1})(Mn_{0.75}V_{0.15}Ti_{0.1})₂D_{2.8} the authors recognized that at low temperature (-256°C) approximately 0.11 deuterium atoms relocate from the 24(l) to the 12(k)₁ position. Since both compounds are classified as AB₂-type IMC with hexagonal Laves phase structure and they are compositionally similar to ZrMn₂ then our assumption expressed above may be correct.

The transition between two states of hydride phase takes place at the composition ZrMn₂H_{~1}. On the P-C diagram at 170°C (see Fig. 2) a small fold in

the range of concentration $[H]/[ZrMn_2] \sim 1.1$ could be seen. The position of this fold agrees with the boundary between two parts on which we have divided the plot of the $|\Delta H_{des.}|$ -C dependence. On the base of these results we assumed that there are two hydride phases in the $ZrMn_2$ - H_2 system at $170^\circ C$, namely, $ZrMn_2H - \beta_1$ -hydride and $ZrMn_2H_{2+\gamma} - \beta_2$ -hydride. At $[H]/[ZrMn_2] > 2$ we also observed rising of the enthalpy values up to maximum magnitude (~ 50 kJ/mol H_2) corresponding to boundary $\beta_1 \leftrightarrow \beta_2/\beta_2$ and then $|\Delta H_{des.}|$ decreased in the range of the existence of β_2 -hydride.

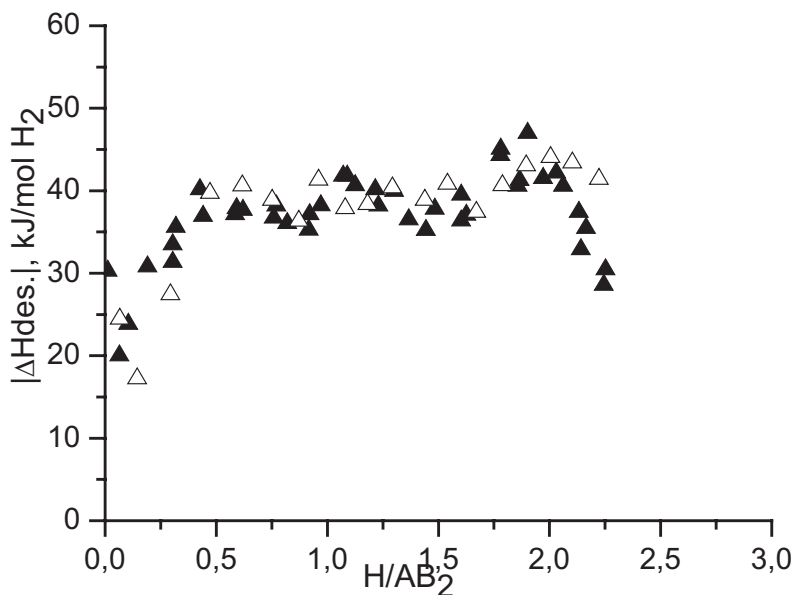


Figure 5. Absorption and desorption enthalpies vs. composition at 245° : Δ – absorption, \blacktriangle – desorption.

The change of $|\Delta H_{abs.}|$ and $|\Delta H_{des.}|$ as a function of H content at $245^\circ C$ are shown in Fig. 5. The shape of desorption isotherm $|\Delta H_{des.}|$ -C at $245^\circ C$ as one can see from Fig. 5 is similar to the isotherm $|\Delta H_{des.}|$ -C obtained for $170^\circ C$ but there are some peculiarities. The length of the α -region increased ($0 < C < 0.4$). The relative partial molar enthalpy changes in this region pass through a minimum and then rise to the values of $|\Delta H_{des.}|_{plat}$. The difference in the $|\Delta H_{des.}|_{min.}$ and $|\Delta H_{des.}|_{plat}$ values is approximately equal to 20 kJ/mole H_2 . The boundaries between two states of hydride phase at $245^\circ C$ are clearer. The boundaries of the $\alpha \leftrightarrow \beta_1$ transition may be defined as $0.4 < C < 1.0$, and $\beta_1 \leftrightarrow \beta_2$ transition as $1.0 < C < 1.8$. It should be noted that at $245^\circ C$ the values of the relative partial molar enthalpy does not remain constant, namely, at $C \approx 0.4$ $|\Delta H_{des.}| \approx 40$ kJ/mole H_2 and at $C \approx 1.0$ $|\Delta H_{des.}| \approx 35$ kJ/mole H_2 . The same dependence is observed for the range $1.0 < C < 1.8$: the lower value of H concentration corresponds to the higher value of $|\Delta H_{des.}|$ and the upper value of H concentration corresponds to the lower of $|\Delta H_{des.}|$ (see $C \approx 1.0$

$|\Delta H_{des.}| \approx 40 \text{ kJ/moleH}_2$, $C \approx 1.8$ ($|\Delta H_{des.}| \approx 35 \text{ kJ/moleH}_2$). One could see on the $|\Delta H_{des.}|$ - C isotherm at 245°C in the range of high H concentration that there is a wide maximum ($1.8 < C < 2.5$) where the magnitudes of $|\Delta H_{des.}|$ reach $\sim 50 \text{ kJ/moleH}_2$ and then slowly decrease. The similar maxima were observed for $|\Delta H_{des.}|$ - C dependences measured at 100 and 170°C .

As mentioned above for 245°C the hydrogen absorption isotherm was obtained (see Fig. 2 and Fig. 5). Comparing the absorption and desorption isotherms one could see that hysteresis of the enthalpy values is absent in practice even for the range of H concentrations $1.8 < C < 2.5$ for which in reference data [8, 9] $|\Delta H_{des.}| > |\Delta H_{abs.}|$.

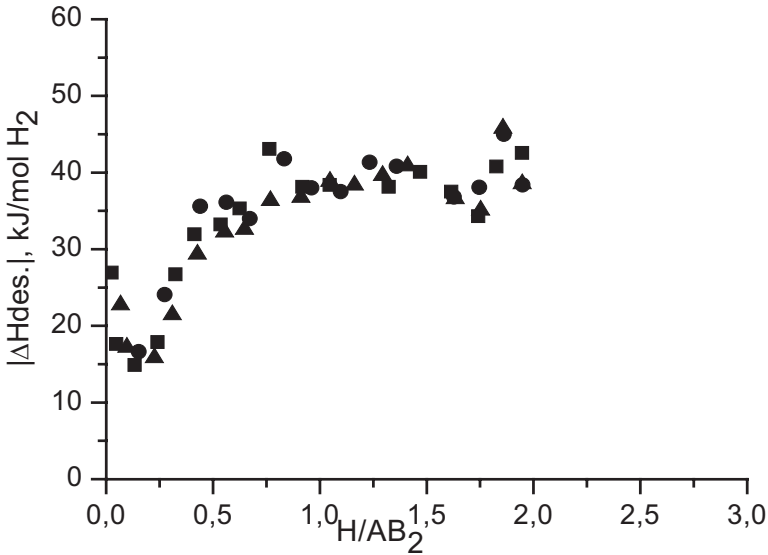


Figure 6. Desorption enthalpy vs. composition at 305°C .

As seen from Fig. 6 at 305°C the values of partial molar enthalpy for different runs of hydrogen desorption have a large deviation probably because of a proximity to critical temperature, thus it is difficult to determine the phase boundaries. The critical temperature for the existence of ZrMn_2 hydride phase estimated by different authors is 277 - 327°C [8] and 318°C [15]. The plot of the $|\Delta H_{des.}|$ - C could be divided into three parts: the hydrogen α -solid solution region ($0 < C < 0.6$), $\alpha \leftrightarrow \beta_1$ transition ($0.6 < C < 1.0$) and $\beta_1 \leftrightarrow \beta_2$ transition ($1.0 < C < 1.8$).

The presence of minimum in the $|\Delta H_{des.}|$ - C dependences in the α -solid solution region is typical for the ZrMn_2 - H_2 system. The magnitude of this minimum is about 20 kJ/moleH_2 , and it coincides with references data [8]. Flanagan and co-workers [8] explained this phenomenon by the presence of trapping sites in ZrMn_2 , e.g. interstices surrounded by 3 Zr and 1 Mn rather than the usual occupied interstices with 2 Zr and 2 Mn atoms.

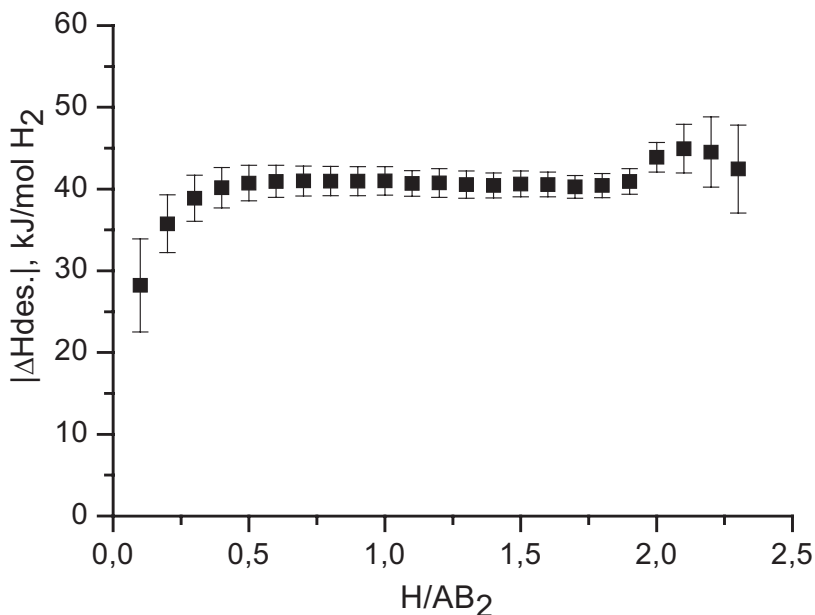


Figure 7. Partial molar desorption enthalpy calculated from van't Hoff plot.

The relative partial molar enthalpy changes for hydrogen desorption were calculated from the van't Hoff plots based on the measured P-C-T relations. The obtained $|\Delta H_{des.}|$ -C dependence was plotted in Fig. 7. The shape of this plot is similar to one obtained for 100°C in this work and those presented in [8, 9] for 50°C. In this plot one can select the α -solid solution region of hydrogen in the ZrMn₂-H₂ system ($0 < C < 0.5$), the plateau region ($0.5 < C < 1.8$) and the region of the single hydride phase ($C > 1.8$). In the plateau region the plot has some slopping. The values of the desorption enthalpy in the plateau range equal to $40 \div 41$ kJ/moleH₂ and they slowly decrease with increasing H concentration, that is in good agreement with calorimetric results, obtained in present work, and reference data [8, 9]. Comparing $|\Delta H_{des.}|$ -C dependences obtained via calorimetric method and plotting of pressure-composition isotherms it should be noted that calorimetric method permits better to understand the processes taking place in the studied system.

4. Conclusions

1. Hydrogen interaction with ZrMn₂ has been studied via calorimetric and P-C isotherm methods at 100, 170, 245 and 305°C.
2. It has been established that in the ZrMn₂-H₂ system the partial molar enthalpy of hydrogen reaction with ZrMn₂ changed with the temperature of experiment and hydrogen concentration in this system. The obtained data allow us to

suppose that these changes are connected with the order of filling of tetrahedral interstitial sites by hydrogen in the metal matrix, that have different facing, and to make an assumption that two hydride phases are formed.

3. We did not observed hysteresis in the values of the absorption and desorption enthalpies at 245°C. At this temperature $|\Delta H_{\text{abs}}|$ is equal to $|\Delta H_{\text{des}}|$ over the range of hydrogen concentrations. It should be recognized that for a further investigation of a region with high hydrogen concentration in the $\text{ZrMn}_2\text{-H}_2$ system is needed.

Acknowledgments

The work has been partially supported by the RFBR Grant № 03-03-33023.

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