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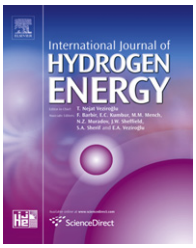

# Calorimetric investigation of the hydrogen interaction with $Ti_{0.9}Zr_{0.1}Mn_{1.2}V_{0.1}$

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ABSTRACT

In the present work we compare such thermodynamic functions as partial molar enthalpies and partial molar entropies of the reaction of the hydrogen desorption from the $Ti_{0.9}Zr_{0.1}Mn_{1.2}V_{0.1}$-H and $Ti_{0.9}Zr_{0.1}Mn_{1.5}V_{0.8}$-H systems, which were calculated on the base of data obtained from the study of these systems by means of P–C measurements and the calorimetric method at pressure up to 50 atm and the temperature range from 75 to 116 °C.



## 1. Introduction

The multicomponent intermetallic compounds (IMC) $AB_2$ with hexagonal structure C14 Laves phase are very significant for the development of ecologically clean power engineering. The investigation of the IMC-H systems where IMCs are the multicomponent compounds with overall formula (Ti,Zr)MnV non-stoichiometric composition with hexagonal structure C14 Laves phase forced us to think about the influence of the deviation from stoichiometric composition $AB_2$ on the process of hydrogen interaction with IMC.

In the present work we studied the hydrogen interaction with two intermetallic compounds $Ti_{0.9}Zr_{0.1}Mn_{1.2}V_{0.1}$ and $Ti_{0.9}Zr_{0.1}Mn_{1.5}V_{0.8}$ by means of calorimetric method and pressure-composition-temperature P-C-T measurements (P – equilibrium hydrogen pressure, and $C = H/AB_2$). As it can be seen the first IMC is the substoichiometric compound with overall composition of $AB_{2-x}$. It is known [1] that in sub-stoichiometric compounds $AB_2$-type with Laves phase structure there is a rearrangement of A and B atoms among the crystallographic positions and the atoms of the A-component partly occupy the positions of the B atoms, so the formula of studied IMC can be rewritten as $Ti_{0.86}Zr_{0.13}Mn_{1.56}V_{0.13}Ti_{0.31}$. It means that about 15% of Ti atoms are arranged among B positions. In this work all calculations were made exactly on this composition.

The IMC $Ti_{0.9}Zr_{0.1}Mn_{1.5}V_{0.8}$ is hyperstoichiometric alloy. In other words its formula is $AB_{2+x}$. From reference data [1–4] it is known that in the IMC with Laves phase C 14 structure excess or hyperstoichiometric B-component substitutes at the A-component sites, that is the composition of the present hypersctoichiometric compound may be rewritten as $(Ti_{0.8}Zr_{0.1}Mn_{0.1})(Mn_{1.28}V_{0.72})$. All calculations in this work were carried out on this formula.

## 2. Experimental

The pseudobinary intermetallic compounds were prepared by arc melting of a stoichiometric mixture of the starting

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elements: Ti (99.99%), Zr (99.99%), Mn (99.9%) and V (99.9%) in an argon atmosphere (1.5 atm). Titanium was used as a getter to purify argon from admixtures. For this purpose it was melted in the arc furnace before alloying of the starting elements. In comparison with the desirable final stoichiometry an excess amount of Mn (4%) was added to compensate a weight loss during the melting. The buttons of a sample were turned over and remelted four times and then annealed in a fused silica tube under the residual argon pressure 0.1 atm at about 950 °C for 240 h to ensure homogeneity.

Powder X-ray diffraction analysis (DRON-2, Cu Kα-radiation) indicated that the prepared samples were single-phase materials with the hexagonal Laves phase structure C14 ($MgZn_2$). The refined unit lattice parameters are: $a = 4.932$ Å, $c = 8.080$ Å, $V = 170.0$ Å$^3$, $c/a = 1.638$ for $Ti_{0.86}Zr_{0.13}Mn_{1.56}V_{0.13}Ti_{0.31}$ and $a = 4.902$ Å, $c = 8.010$ Å, $V = 166.69$ Å$^3$, $c/a = 1.634$ for $(Ti_{0.8}Zr_{0.1}Mn_{0.1})(Mn_{1.28}V_{0.72})$.

The investigation of hydrogen interaction with $Ti_{0.86}Zr_{0.13}Mn_{1.56}V_{0.13}Ti_{0.31}$ and $(Ti_{0.8}Zr_{0.1}Mn_{0.1})(Mn_{1.28}V_{0.72})$ was carried out by the calorimetric method and plotting P–C isotherms using the differential heat-conducting calorimeter of Tean-Calvet type connected to the apparatus for dosed gas feeding. The apparatus scheme, experimental procedure and analysis of observations were described elsewhere [5].

## 3. Results and discussion

### 3.1. P-C-T relationships

The experimentally determined pressure–composition isotherms are plotted for the $Ti_{0.86}Zr_{0.13}Mn_{1.56}V_{0.13}Ti_{0.31}$ – H and $(Ti_{0.8}Zr_{0.1}Mn_{0.1})(Mn_{1.28}V_{0.72})$ – H systems in Figs. 1 and 2, respectively. As it could be seen from the plots of the P–C isotherms presented in Fig. 1 $Ti_{0.86}Zr_{0.13}Mn_{1.56}V_{0.13}Ti_{0.31}$ has a large hydrogen capacity, $H/AB_2 \approx 3.1$ at 75 °C, however, its reversible hydrogen capacity is much less (~2.5 $H/AB_2$) since in the $Ti_{0.86}Zr_{0.13}Mn_{1.56}V_{0.13}Ti_{0.31}$ – H system at $C < 0.5$ the equilibrium hydrogen pressures are negligibly small. This phenomenon may be explained by the high content of the Ti atoms in the IMC (~15% of B sites are occupied by the Ti atoms) and since Ti has a strong affinity to hydrogen this can result in the transformation of part of interstitial sites $[A_2B_2]$ into $[A_3B]$ and $[AB_3]$ into $[A_2B_2]$. Similar phenomena were marked for another IMCs containing Ti [6,7]. In addition it is

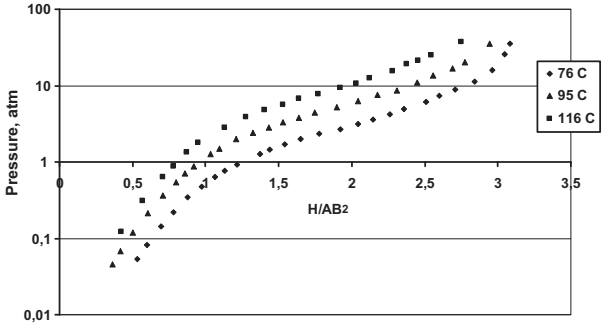


**Fig. 1 – Desorption isotherms for the $Ti_{0.9}Zr_{0.1}Mn_{1.2}V_{0.1}$ – H system ($AB_2$ – $Ti_{0.86}Zr_{0.13}Mn_{1.56}V_{0.13}Ti_{0.31}$).**

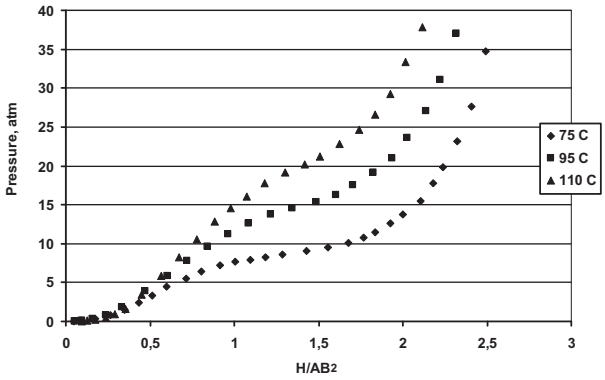


**Fig. 2 – Desorption isotherms for the $Ti_{0.9}Zr_{0.1}Mn_{1.5}V_{0.8}$ – H system ($AB_2$ – $(Ti_{0.8}Zr_{0.1}Mn_{0.1})(Mn_{1.28}V_{0.72})$).**

significant that the present system has a large plateau slope. We calculated this magnitude according to the following formula, recommended in [8]:

$$\text{Plateau slope} = d(\ln p)/d(H/M) \quad (1)$$

For the $Ti_{0.86}Zr_{0.13}Mn_{1.56}V_{0.13}Ti_{0.31}$ – H system this magnitude equals to ~ 1.35. It should be marked that plateau slope does not practically change in the studied temperature range.

The P–C isotherms for the $(Ti_{0.8}Zr_{0.1}Mn_{0.1})(Mn_{1.28}V_{0.72})$ – H system were obtained in the temperature range 75–110 °C (see Fig. 2). In the plots of the P–C dependence there are the points of inflection at $H/AB_2 \approx 1.0$ which gradually shifts towards lower hydrogen concentrations with arising of the experimental temperature. The plateau slope is equal to 1.9 in the region of the hydrogen concentration $0.5 < C < 0.9$ and 0.4 in the region $1.00 < C < 1.80$ at 75 °C.

The plot of the P–C dependence obtained at 95 °C could be divided into some parts: the region with $0 < C < 0.25$ corresponds to the α-region where hydrogen dissolves into metallic matrix with the formation of the solid solution. Further the hydride phase begins to form. The region of the hydrogen concentrations $0.25 < C < 2.00$ corresponds to the existence of two phases namely the α-phase and the forming hydride phase. Since there is the folder on the plot of P–C at $C \approx 1$ we

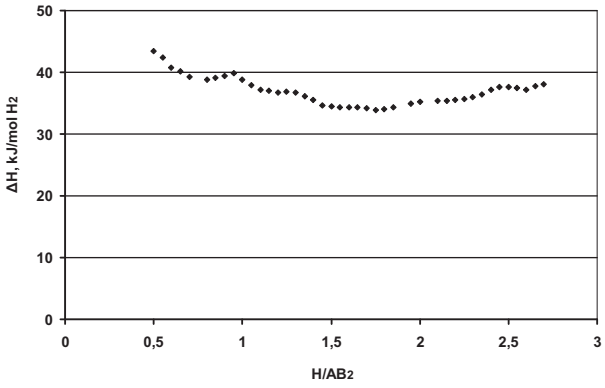


**Fig. 3 – Partial molar desorption enthalpy calculated from Van't Hoff plot for the $Ti_{0.86}Zr_{0.13}Mn_{1.56}V_{0.13}Ti_{0.31}$ – H system (a temperature range 75–116 °C).**

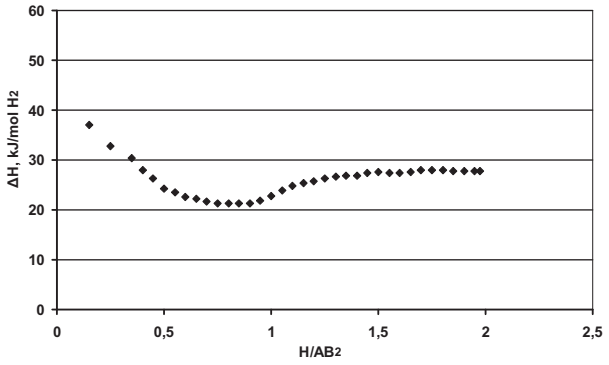


**Fig. 4 – Partial molar desorption enthalpy calculated from Van't Hoff plot for the $(Ti_{0.8}Zr_{0.1}Mn_{0.1})(Mn_{1.28}V_{0.72})$ – H system (a temperature range 75–110 °C).**

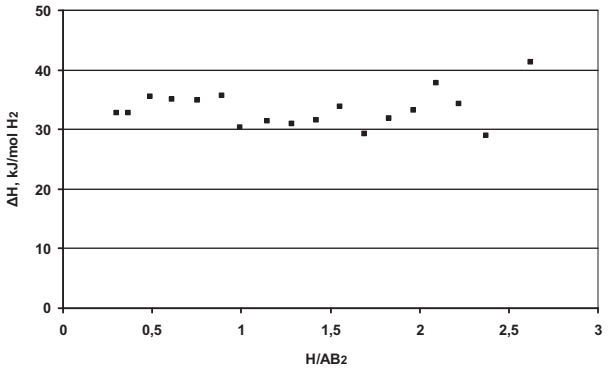


**Fig. 6 – Desorption enthalpy vs. composition at 116 °C for the $Ti_{0.86}Zr_{0.13}Mn_{1.56}V_{0.13}Ti_{0.31}$ – H system.**

could suppose that two hydride phases form $\beta_1$ – and $\beta_2$ – hydrides with following compositions – $(Ti_{0.8}Zr_{0.1}Mn_{0.1})(Mn_{1.28}V_{0.72})H_{\sim 1}$ and $(Ti_{0.8}Zr_{0.1}Mn_{0.1})(Mn_{1.28}V_{0.72})H_{\sim 2}$. The region with the hydrogen concentration C > 2.00 corresponds to $\beta_2$ – hydride phase.

The partial molar enthalpy values ($\Delta H_{des}$) for the hydrogen desorption were calculated from the Van't Hoff plots based on the measured P-C-T relations. The plots of the function $\Delta H_{des} = f(C)$ are presented in Figs. 3 and 4, respectively. For the $Ti_{0.86}Zr_{0.13}Mn_{1.56}V_{0.13}Ti_{0.31}$ – H system as one can see from Fig. 3 the values of the partial molar enthalpy gradually decrease with increasing of the hydrogen concentration in the metallic matrix. Fig. 4 presents the dependence of $\Delta H_{des}$ – C for the $(Ti_{0.8}Zr_{0.1}Mn_{0.1})(Mn_{1.28}V_{0.72})$ – H system. As one can see from Fig. 4 the partial molar enthalpy of hydrogen in the α-solid solution region (0.2 < C < 0.5) gradually decreases (to ~22 kJ/mol $H_2$), then there are two plateau regions: 0.5 < C < 1.0, $\Delta H_{des}$ ~ 22 kJ/mol $H_2$ and 1.5 < C < 2.0, $\Delta H_{des}$ ~ 28 kJ/mol $H_2$.

### 3.2. *Calorimetric results*

The $\Delta H_{des.}$-C isotherms for $Ti_{0.86}Zr_{0.13}Mn_{1.56}V_{0.13}Ti_{0.31}$ obtained at 75 and 116 °C are shown in Figs. 5 and 6. It is seen from Fig. 5 that the enthalpy values slightly change with arising of the hydrogen concentration at 75 °C. In the initial region (0.5 < C < 1.0) the values of $\Delta H_{des}$ decrease from 36.8 to 32.3 kJ/mol $H_2$. At C ≈ 1 the enthalpy values rise to 34.5 kJ/mol $H_2$ and remain practically constant up to C ≈ 2.2. The enthalpy values in the region 2.3 < C < 2.5 pass through the maximum and then decrease. Analyzing the obtained data we can assume that in the range of hydrogen concentration 1.0 < C < 2.2 there is two-phase equilibrium $\alpha \leftrightarrow \beta$ and $Ti_{0.86}Zr_{0.13}Mn_{1.56}V_{0.13}Ti_{0.31}H_{\sim 2}$ forms. The hydrogen concentration C ≈ 2.4 corresponds to the phase boundary of (α+β)/β phases. Further hydrogen dissolves in the hydride phase.

With the rising of the experimental temperature from 75 °C to 116 °C the plot of the $\Delta H_{des.}$-C dependence changes its shape (see Fig. 6). In comparison with the plot obtained for 75 °C (see Fig. 5) there are two regions where the values of enthalpy remain constant, namely 0.3 < C < 1.0 ($\Delta H_{des}$ ≈ 35.3 kJ/mol $H_2$) and 1.0 < C < 1.8 ($\Delta H_{des}$ ≈ 31.0 kJ/mol $H_2$). Then the $\Delta H_{des}$ values increase, pass through maximum (C ≈ 2.1, $\Delta H_{des}$ ~ 40 kJ/mol $H_2$) and then gradually reduce. The region of hydrogen concentration 2.0 < C < 2.2 corresponds to the phase boundary $(\beta_1 + \beta_2)/\beta_2$. On the base of these results we assumed that there were two hydride phases, $\beta_1$ and $\beta_2$, in the $Ti_{0.86}Zr_{0.13}Mn_{1.56}V_{0.13}Ti_{0.31}$-H system at 116 °C, namely, $Ti_{0.86}Zr_{0.13}Mn_{1.56}V_{0.13}Ti_{0.31}H_{\sim 1}$-hydride and $Ti_{0.86}Zr_{0.13}Mn_{1.56}V_{0.13}Ti_{0.31}H_{\sim 2}$.

On the base of data obtained at 75 °C the values of the partial molar entropy of the reaction of hydrogen interaction with $Ti_{0.86}Zr_{0.13}Mn_{1.56}V_{0.13}Ti_{0.31}$ were calculated (see Fig. 7).

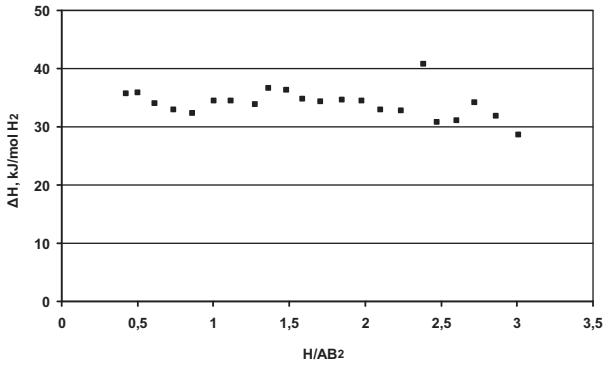


**Fig. 5 – Desorption enthalpy vs. composition at 75 °C for the $Ti_{0.86}Zr_{0.13}Mn_{1.56}V_{0.13}Ti_{0.31}$ – H system.**

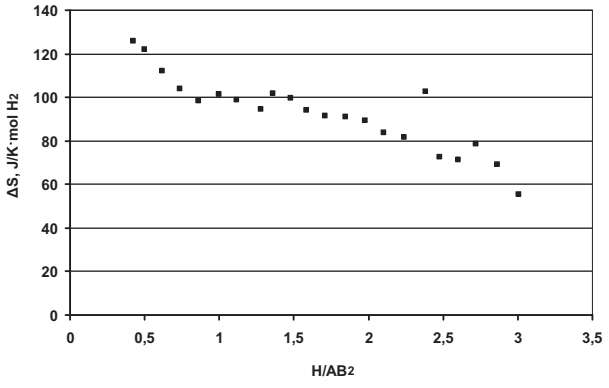


**Fig. 7 – Desorption entropy vs. composition at 75 °C for the $Ti_{0.86}Zr_{0.13}Mn_{1.56}V_{0.13}Ti_{0.31}$ – H system.**

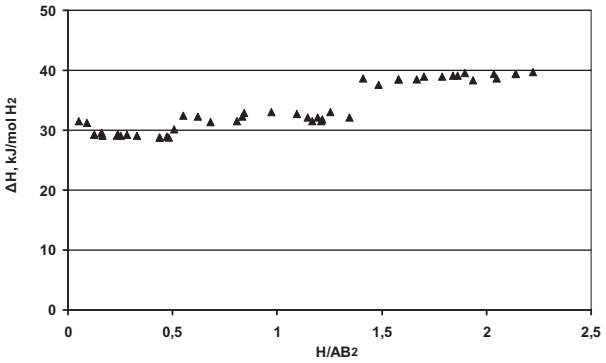


**Fig. 8 – Desorption enthalpy vs. composition at 95 °C for the $(Ti_{0.8}Zr_{0.1}Mn_{0.1})(Mn_{1.28}V_{0.72})$ – H system.**

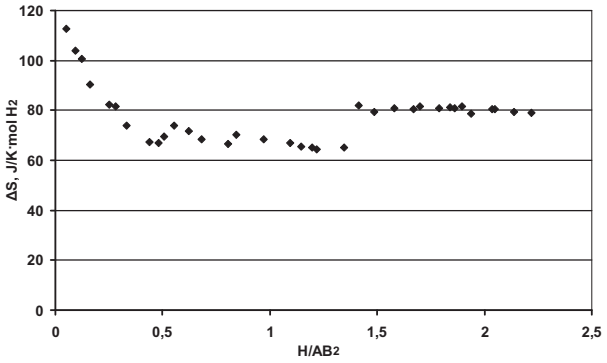


**Fig. 10 – Desorption entropy vs. composition at 95 °C for the $(Ti_{0.8}Zr_{0.1}Mn_{0.1})(Mn_{1.28}V_{0.72})$ – H system.**

One can see that the values of $\Delta S_{des}$ decrease ($0.50 < C < 0.75$) until reach $\Delta S_{des} \approx 100$ J/K·mol $H_2$. Then there is the region where the values of partial molar entropy remain constant ($0.8 < C < 1.5$) and after that the entropy values gradually reduce. These results allow us to assume that such dependence of $\Delta S_{des} - C$ could be explained by the existence of high configurational entropy caused by a very complex structure of the studied IMC. Such phenomenon was observed in the works [9–12].

The Figs. 8 and 9 present the plots of the $\Delta H_{des} - C$ dependences obtained at 95 and 110 °C for $(Ti_{0.8}Zr_{0.1}Mn_{0.1})(Mn_{1.28}V_{0.72})$ – H system. Comparing the results of the calorimetric measurements, obtained for the $Ti_{0.86}Zr_{0.13}Mn_{1.56}V_{0.13}Ti_{0.31}$ – H and $(Ti_{0.8}Zr_{0.1}Mn_{0.1})(Mn_{1.28}V_{0.72})$ – H systems one could see that the plots of $\Delta H_{des} - C$ dependences differ significanlty. At 95 °C (see Fig. 8) on the plot of $\Delta H_{des} - C$ there are two regions with the constant enthalpy values ($0.20 < C < 1.20$ $\Delta H_{des} \approx 30$ kJ/mol $H_2$ and $1.25 < C < 2.99$ $\Delta H_{des} \approx 40$ kJ/mol $H_2$). In other words it could be supposed that in these conditions two hydride phases form in the $(Ti_{0.8}Zr_{0.1}Mn_{0.1})(Mn_{1.28}V_{0.72})$ – H system mono- and dihydride and the enthalpy values rise with the increasing of the hydrogen concentration in this system that is one can see as the contrary behaviour of $\Delta H_{des} - C$ dependence which was observed for substoichiometric IMC. The increase of experimental temperature up to 110 °C does not result in notable change in the character of hydrogen interaction with $(Ti_{0.8}Zr_{0.1}Mn_{0.1})(Mn_{1.28}V_{0.72})$ (see Fig. 9).

The $\Delta S_{des}$-C dependence was obtained for the $(Ti_{0.8}Zr_{0.1}Mn_{0.1})(Mn_{1.28}V_{0.72})$-H system (see Fig. 10) at 95 °C. The entropy values decrease in the region of α-solid solution ($C < 0.5$), then there are two regions with constant entropy values. It should be emphasized that the entropy values for $(Ti_{0.8}Zr_{0.1}Mn_{0.1})(Mn_{1.28}V_{0.72})$-H system are lower than for many other the IMC-H systems. We associate this phenomenon with the high configurational entropy.

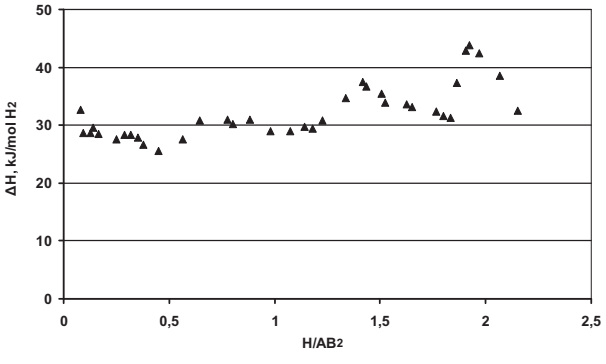


**Fig. 9 – Desorption enthalpy vs. composition at 110 °C for the $(Ti_{0.8}Zr_{0.1}Mn_{0.1})(Mn_{1.28}V_{0.72})$ – H system.**

## 4. Conclusions

The results of investigation of the $Ti_{0.86}Zr_{0.13}Mn_{1.56}V_{0.13}Ti_{0.31}$ – H and $(Ti_{0.8}Zr_{0.1}Mn_{0.1})(Mn_{1.28}V_{0.72})$-H systems in the temperature range from 75 to 116 °C are presented. On the base of obtained data it could be concluded that the composition of IMC and experimental temperature define the character of the interaction between these IMCs and hydrogen. The formation of one or two hydride phases at certain temperatures is possible.

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