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Thermodynamic Aspects of the Reversible Absorption of Hydrogen by $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}$ Alloy

E. Yu. Anikina^{a,*} and V. N. Verbetsky^a

^a Department of Chemistry, Moscow State University, Moscow, 119991 Russia

*e-mail: helena-anikina@yandex.ru

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Abstract—A calorimetric study is performed of the thermodynamics of hydrogenation and dehydrogenation of intermetallic compound (IMC) $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}$ with Laves phase structure C14. Experiments are conducted in the temperature range from 323 to 373 K and hydrogen pressures up to 50 atm. Functional relations $P = f(C)$, $\Delta H_{\text{abs}} (\Delta H_{\text{des}}) = f(C)$ (where P is the equilibrium hydrogen pressure, $\Delta H_{\text{abs}} (\Delta H_{\text{des}})$ is the partial molar enthalpy of absorption (desorption), and $C = \text{H/IMC}$) are obtained using a Tian–Calvet-type calorimeter connected to Sieverts volumetric apparatus. It is established that the enthalpies of absorption and desorption are not constant and change according to the experimental temperature. It is also determined that $C_{\text{max}} = 2.9$ at 298 K and a hydrogen pressure of 50 atm.

Keywords: $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}$, hydride, calorimetry, absorption, desorption, enthalpy, entropy

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INTRODUCTION

Intermetallic compounds that react reversibly with hydrogen and form hydrides at ambient temperature and low hydrogen pressure therefore acquire special significance when solving various technological problems. Multicomponent alloys based on Zr–Ti–Mn with hexagonal Laves phase structure C14 belong to the group of IMCs [1–10]. The low cost of these alloys relative to IMCs containing rare earth metals, their high hydrogen capacity, the high rate of the hydrogenation reaction, and their resistance to degradation during cycling are advantages when using them in different technological tasks. Alloys with the Laves phase structure based on Zr–Ti–Mn–V have a wide range of homogeneity. The equilibrium hydrogen pressure and temperature at which the reaction of hydrogen with IMC proceeds can be altered by changing the concentration of different metals in the composition of alloy and its stoichiometrics slightly. The equilibrium hydrogen pressure and the temperature at which the reaction between hydrogen and IMC occurs can be altered by changing the concentration of metal (or metals) in the alloy [11–22], as it is often necessary in order to use them in practice.

In the production of, e.g., hydrogen compressors and stationary and mobile hydrogen accumulators, we must make technological calculations based on the available thermodynamic characteristics of IMC.

The heat of the reaction of hydrogen interacting with IMC is usually calculated using the Van't Hoff

equation [1–3, 11, 12, 16, 17, 19–21]. However, this often does not provide an accurate enthalpy of hydrogen's reaction with IMC, since the enthalpy can change with the temperature of the process and the concentration of hydrogen in the IMC. In this work, we present results from studying the reaction between hydrogen and the non-stoichiometric $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}$ compound in two different ways: via calorimetry and by measuring pressure, composition, and temperature (P – C – T , where P is the equilibrium hydrogen pressure, C is concentration of hydrogen in the IMC, $C = \text{H/IMC}$, and T is the experimental temperature). In [23–25], it was determined through neutron diffraction analysis that in sub-stoichiometric compounds of the AB_2 -type with Laves phase structure C14, atoms of the A-component partly occupied the crystallographic positions of the B-component. Compound $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}$ is therefore correctly described as AB_2 , which can be written as $(\text{Ti}_{0.89}\text{Zr}_{0.11})(\text{Mn}_{1.43}\text{V}_{0.52}\text{Ti}_{0.05})$.

EXPERIMENTAL

IMC $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}$ was synthesized via the arc melting of a stoichiometric mixture of pure metals Ti (99.99%), Zr (99.99%), Mn (99.9%), and V (99.9%) in an argon gas atmosphere at a pressure of 2 atm. The initial amount of Mn metal was corrected for 4 wt %, due to the possible evaporation losses of metal during the melting. In this work, the composition of the resulting alloy was controlled by weighing the charge and final sample before and after melting, respectively,

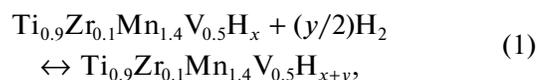
and by X-ray fluorescent analysis on a Rigaku Primus II spectrometer. In order to achieve an even bulk distribution of the components, the ingot was turned over and remelted four times. The final sample was then annealed in a sealed quartz ampoule for 240 h at 1073 K and a residual argon pressure 0.01 atm.

X-ray powder diffraction studies of the initial sample of $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}$ and its hydride $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}\text{H}_{2.9}$ were performed with a Huber G 670 Image Plate Guinier camera ($\text{CuK}\alpha$ radiation) in the transmission geometry at room temperature. The XRD data showed that the initial sample was single-phase IMC with the hexagonal Laves phase C14 (space group $P6_3/mmc$) crystal structure. Structural data were processed with Rietveld refinement [26]. The cell parameters of the initial IMC and its hydride were $a = 4.917(3)$ Å, $c = 8.049(3)$ Å, $V = 168.5$ Å³, and $c/a = 1.637$ for $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}$ and $a = 5.267(6)$ Å, $c = 8.596(3)$ Å, $V = 206.9$ Å³, $c/a = 1.632$, and $\Delta V = (V_{\text{hyd}} - V_{\text{IMC}})/V_{\text{IMC}} = 22.5\%$ for $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}\text{H}_{2.9}$. As we can see from the X-ray data, hydrogenating the initial IMC did not alter its crystal structure. The obtained hydride was a single-phase compound with the hexagonal Laves phase structure C14, but its lattice parameters grew by 22.5%.

The isothermal pressure–composition relationship and heats of absorption (desorption) in the $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}\text{H}_2$ system were studied in the temperature range of 323–373 K and at hydrogen pressures of up to 50 atm. In this work, we used a Tian–Calvet-type DAK-12 differential heat-conducting calorimeter connected to a conventional Sieverts-type volumetric apparatus for measuring the amount of absorbed or evolved hydrogen. The apparatus, experimental procedure, and analysis of the collected data were described in [27, 28]. The dosing and reaction volumes were determined using measurements of the expansion of gas from calibrated flasks to the volume (using the ideal gas equation of state $0 < P < 1$ atm). The accuracy of the measured value is 0.05%. The design of the calorimeter allowed us to omit corrections to the heat effect of the gas injected into the system and ignore changes in the environment throughout each long experiment.

Since $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}$ reacts reversibly with hydrogen, the same sample (2.4456 g) was used in all experiments. Before starting each run, the residual hydrogen was desorbed at 650–680 K under high vacuum outside the calorimeter. The experimental error in this work was expressed according to the recommendations of IUPAC [29] as the standard deviation of mean value $\delta = \sqrt{\Sigma \Delta^2 [n(n-1)]^{-1}}$, where Δ is the deviation from the mean value and n is the number of data points. The purity of our hydrogen was 99.9999%.

Relative molar enthalpy ΔH_{abs} (ΔH_{des}) of absorption (desorption) was determined from the heat effect of the reaction,



using equation $Q = SA/\Delta n$, where S is the area under the curve of heat release (heat absorption), mm²; A is the sensitivity of the device, determined from the electric calibration for each experiment (mJ/mm²); and Δn is the number of moles of released (absorbed) hydrogen. It was shown in [30] that the measured heats correspond to enthalpies of reaction when expressed per mole of H_2 or $1/2\text{H}_2$.

RESULTS AND DISCUSSION

P–C–T Measurements

Interaction between hydrogen and $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}$ was studied at 323, 333, 353, and 373 K and the hydrogen pressures of up to 50 atm. *P–C* isotherms of absorption and desorption processes were obtained. Diagrams of the $P = f(C)$ dependences are shown in Figs. 1 and 2.

As we can see from the data presented in Fig. 1, $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}\text{H}_2$ has good hydrogen capacity (2.8 H/IMC at 323 K and hydrogen pressure $P = 50$ atm). We can distinguish three regions in the diagrams of the *P–C* dependences (see Figs. 1 and 2): $0 < C < 1.0$, $1.0 < C < 2.3$, and $C > 2.3$. The first region corresponds to the formation of α -solid solution of hydrogen in the IMC. The $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}\text{H}_2$ system has a wide α -region in the temperature range from 323 to 373 K. This wide extension of the α -region is a characteristic property of intermetallic compounds with Laves phase structure C14 containing vanadium [4, 14, 15, 20]. The second is the two-phase $\alpha + \beta$ region. The third region ($C > 2.3$) is that of the hydrogen solid solution in the β -hydride phase. It should be noted that there are points of inflection at $C \sim 1$ in the absorption and desorption plots obtained for each temperature. Raising the temperature of the experiment did not alter this position; it only increased the slope of the plateau and shortened its length.

We should also note another characteristic property of the $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}\text{H}_2$ system: the hysteresis of hydrogen pressure absorption and desorption is very small, as we can see in Figs. 1 and 2. In addition, the magnitude of this hysteresis differs in diverse parts of the concentrations of hydrogen in $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}$, as is shown in Table 1. We calculated the magnitude of the pressure hysteresis as $\ln(P_{\text{abs}}/P_{\text{des}})$ and the losses of heat to the environment during a cycle (per $1/2\text{H}_2$) [31]:

$$w = 1/2RT \ln(P_{\text{f}}/P_{\text{d}}) = -q. \quad (2)$$

Calorimetric Results

The plots of the dependences of partial molar enthalpies of absorption and desorption on concentra-

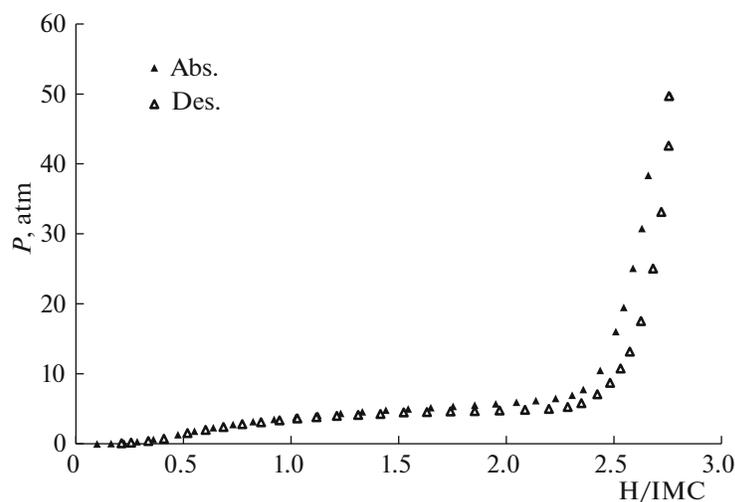


Fig. 1. Isotherms of absorption and desorption at 323 K for the $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}\text{-H}_2$ system.

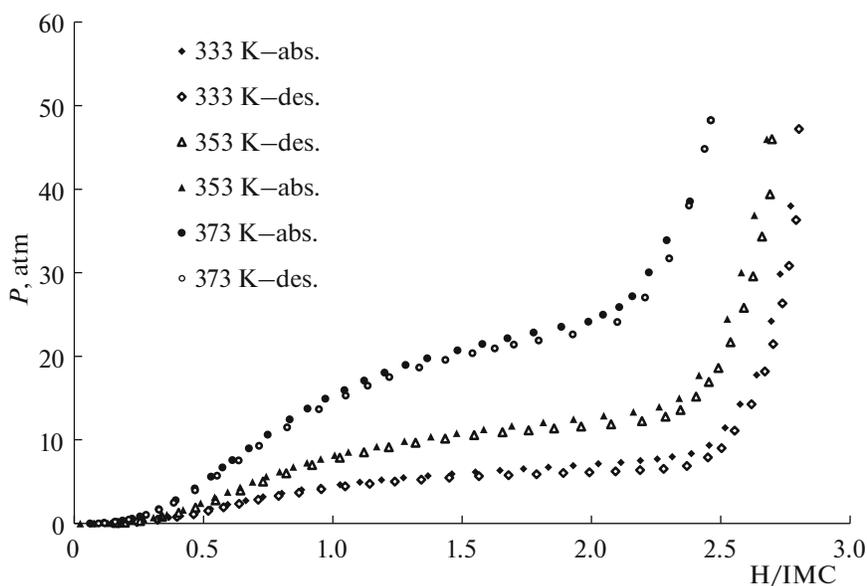


Fig. 2. Isotherms of absorption and desorption at 333, 353, and 373 K for the $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}\text{-H}_2$ system.

tion C of hydrogen in the studied compound, obtained at 323, 333, 353, and 373 K, are presented in Figs. 3–5.

It can be seen that when $0 < C < 0.1$ the enthalpies of absorption are very high in absolute value (-68 kJ/mol H_2). We assume that in this region of the concentration of hydrogen in $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}$, we are dealing with the chemisorption of hydrogen on the surface of the IMC. The enthalpy then falls in absolute value. The curve of the $|\Delta H_{\text{abs}}|$ vs. C dependence moves away from the minimum when $0.4 < C < 0.7$ ($|\Delta H_{\text{abs}}| \sim 25\text{--}26 \text{ kJ/mol H}_2$), and the enthalpy starts to rise. The high values of $|\Delta H_{\text{abs}}|$ in the initial region are explained by the presence of hydrogen trappings in the IMC formed by the elements (Ti and V) with high

affinities for hydrogen. It is known from the literature [23–25] that hydrogen collects in tetrahedral interstitial sites $[\text{A}_2\text{B}_2]$ and $[\text{AB}_3]$ in the IMC with the hexagonal Laves structure C14. If we consider ZrMn_2 , where interstitial sites are formed by two zirconium atoms and two manganese atoms, the trapping sites are imperfections in the intermetallic compound where hydrogen solution is especially energetic.

In our case, B sites were occupied by vanadium atoms and some titanium atoms (28 at %). This resulted in the formation of interstitial sites with strong affinities for hydrogen that acted as traps. We may assume that some interstitial sites $[\text{A}_2\text{B}_2]$ transformed into $[\text{A}_4]$ and $[\text{A}_3\text{B}]$, which react with hydrogen and

Table 1. Hystereses at different temperatures and diverse parts of the hydrogen concentration in the $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}-\text{H}_2$ system

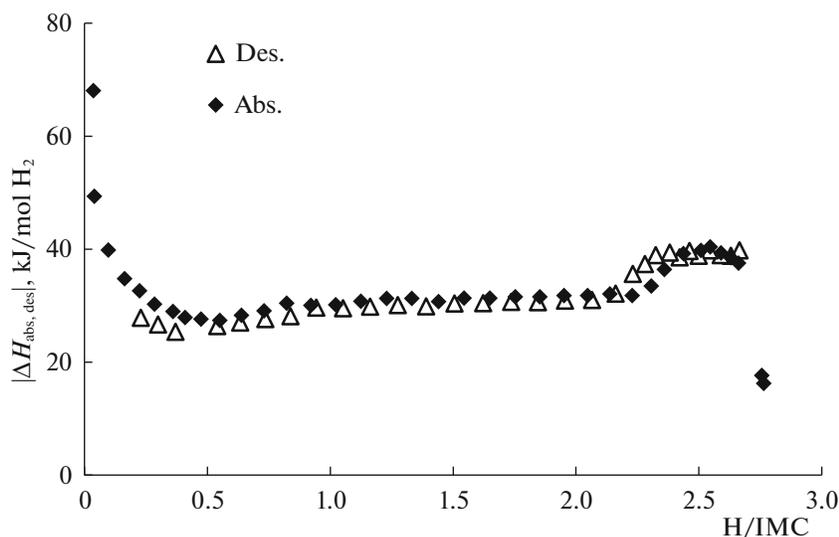
Compound	T , K	H/IMC	$\ln(P_{\text{abs}}/P_{\text{des}})$	$\frac{1}{2}RT\ln(P_{\text{abs}}/P_{\text{des}})$, J/(mol $\frac{1}{2}\text{H}_2$)
$\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}$	323	1.5	0.166	223.9
		2.5	0.321	432.3
	333	1.5	0.079	110.0
		2.5	0.236	326.9
	353	1.5	0.061	90.1
		2.4	0.156	229.2
$\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.7}$ [32]	345	2.5	0.29	415.9
$\text{Ti}_{0.8}\text{Zr}_{0.2}\text{Fe}_{0.1}\text{V}_{0.4}\text{Mn}_{1.5}$ [31]	298	1.5	—	≈ 300

release a large amount of energy. We may therefore conclude that the traps that hydrogen filled in the initial stage of hydrogenation were in this case not imperfect tetrahedrons, as was claimed in [33]. Instead, they were formed by elements that have high affinities for hydrogen.

Raising the concentration of hydrogen in the IMC resulted in repulsive forces among H–H atoms in the $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}-\text{H}_2$ system. A subsequent increase concentration of hydrogen in the IMC raised the $|\Delta H_{\text{abs}}|$ values, and the β -phase began to precipitate at $C \sim 0.9$ (323 K). The P – C isotherms contain inflection points in this region of concentrations. The absolute magnitude of enthalpy grow slightly along the plateau ($0.9 < C < 2.1$) from -30.3 to -32.0 kJ/mol H_2 at 323 K (~ 1.5 kJ/mol H_2). The average value is ΔH_{abs} (-31.0 ± 0.2 kJ/mol H_2) at 323 K in the region of the plateau ($0.9 < C < 2.0$). There is a maximum in $|\Delta H_{\text{plat}}|$ ($2.3 < C < 2.7$) $|\Delta H_{\text{abs}}| = 38.9 \pm 1.5$ kJ/mol H_2 at

boundary phase $\alpha + \beta/\beta$ in isotherms $|\Delta H_{\text{abs}}| - C$. The authors observed this phenomenon in AB_2-H_2 systems in [11, 33–38]. Flanagan [33] explained this phenomenon by assuming there is some overlap in the enthalpy values when the portion of hydrogen is added to or removed from the hydride IMC near the phase boundary ($\alpha + \beta/\beta$). In other words, the measured enthalpy can contain contributions from both the single- and the two-phase regions when the portion of hydrogen is added to the end of plateau.

Our calorimetric data are presented in Table 2 for 323, 333, 353, and 373 K. It should be noted that the enthalpies of hydrogenation and dehydrogenation in the 2.3–2.7 range of hydrogen concentrations coincide in absolute value within the limits of error. We then analyzed the 1.0–2.0 range of hydrogen concentrations and noticed an enthalpy hysteresis. The enthalpies of hydrogenation and dehydrogenation coincide in absolute value in the 1.5–2.0 range, but

**Fig. 3.** Enthalpies of absorption and desorption vs. composition at 323 K.

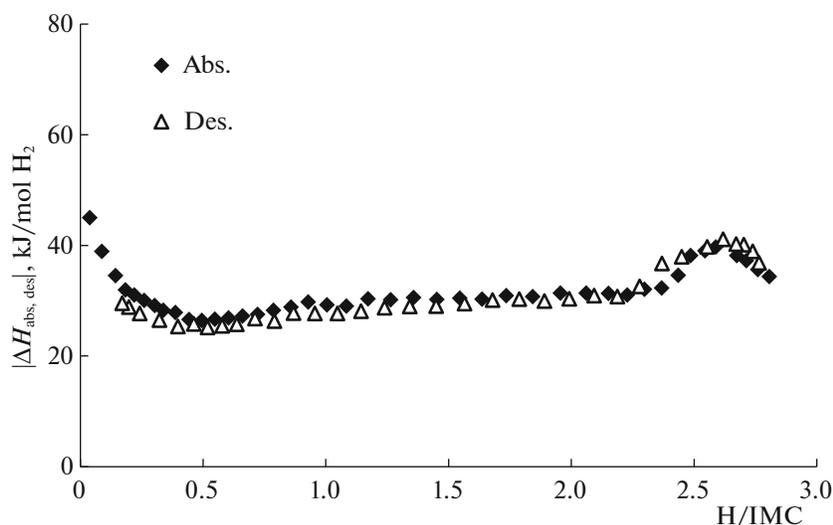


Fig. 4. Enthalpies of absorption and desorption vs. composition at 333 K.

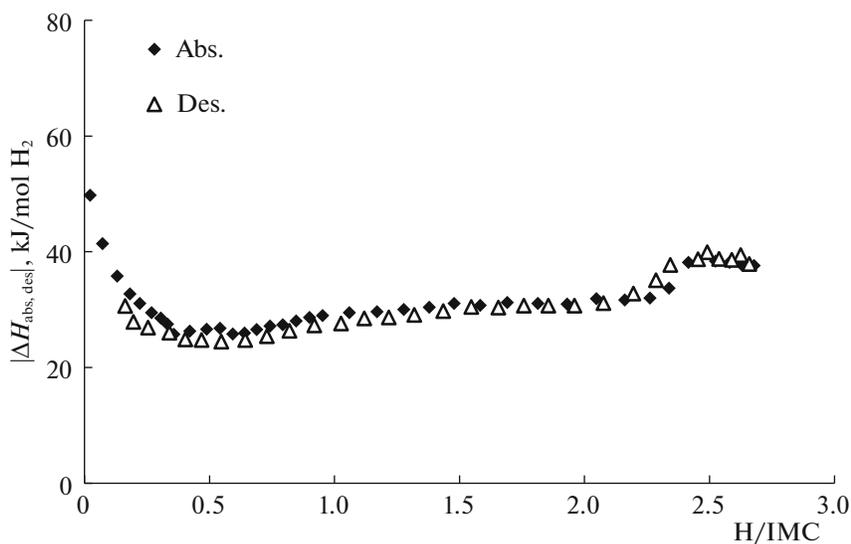


Fig. 5. Enthalpies of absorption and desorption vs. composition at 353 K.

there is a minor enthalpy hysteresis in the region where $0.9 < C < 1.5$.

In [25], we studied the $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5}-\text{H}_2$ system via X-ray powder diffraction, neutron diffraction, and calorimetry. $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5}$ is an intermetallic compound with the Laves phase structure C14 of substoichiometric composition (recalculated for AB_2 $\text{Ti}_{0.89}\text{Zr}_{0.11}\text{Mn}_{1.39}\text{V}_{0.54}\text{Ti}_{0.07}$). The results from our calorimetric measurements demonstrated the dependence of enthalpy on the experimental temperature and concentration of hydrogen in the IMC. One or two regions with constant enthalpy existed while the values in the region with higher concentration of hydrogen in the IMC were greater than ones obtained in the region

with lower concentrations of hydrogen. The compound studied in this work differed slightly from the $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5}$ compound in chemical composition. This led to a change in the faceting of tetrahedral interstitial sites $24l$, $12k_1$, $6h_1$, and $6h_2$.

We found that enthalpy grew slightly in absolute value along with the concentration of hydrogen in the $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}-\text{H}_2$ system. This increase was approximately 1.5 kJ/mol H_2 .

Comparing our results and the data obtained in [25, 38], we can see that minor changes in the ratio of metallic atoms in the IMC, and thus in the faceting of interstitial sites occupied by hydrogen atoms, result in notable differences in the thermodynamic characteris-

Table 2. Temperature dependence of reaction enthalpy for the $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}-\text{H}_2$ system (I and II are ranges of absorption and desorption, respectively)

T, K	I	$\Delta H_{\text{abs}},$ kJ/(mol H_2)	II	$\Delta H_{\text{des}},$ kJ/(mol H_2)
323	0.9–2.1	-31.0 ± 0.2	1.2–2.1	30.3 ± 0.2
	2.3–2.7	-38.9 ± 1.5	2.3–2.7	39.3 ± 0.3
333	1.1–2.1	-30.7 ± 0.2	1.5–2.1	30.1 ± 0.4
	2.4–2.7	-37.6 ± 1.7	2.3–2.7	38.7 ± 0.7
353	1.5–2.1	-31.2 ± 0.4	1.4–2.1	31.1 ± 0.4
	2.3–2.7	-37.7 ± 1.2	2.3–2.7	38.3 ± 0.8
373	1.1–1.9	-29.0 ± 0.3	1.1–1.9	30.3 ± 0.3

tics of the reaction. The increase in $|\Delta H_{\text{abs}}|$ along the plateau could be due to some distortion of the crystal lattice and the emergence of interstitial sites occupied by hydrogen, accompanied by the release of large amounts of heat.

After completing our calorimetric study of the $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}-\text{H}_2$ system, we hydrogenated a sample of $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}$ up to composition $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}\text{H}_{0.3}$ and performed an X-ray diffraction powder analysis. It showed that the crystal structure of the sample retained the structure of the initial alloy C14 Laves phase with slightly larger lattice parameters ($a = 4.936(3) \text{ \AA}$, $c = 8.109(3) \text{ \AA}$, $V = 171.1 \text{ \AA}^3$, $(V_{\text{hyd}} - V_{\text{IMC}})/V_{\text{IMC}} = 1.5\%$), compared to the parameters of the initial compound. This corresponds to the formation of α -solid solution of hydrogen in the given IMC.

CONCLUSIONS

We studied the reaction between hydrogen and the intermetallic compound $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}$ in the temperature range from 323 to 373 K and at hydrogen pressures up to 50 atm. The $P = f(C)$ and $\Delta H_{\text{abs}}(\Delta H_{\text{des}}) = f(C)$ dependences were obtained. These data showed that the partial molar enthalpy values of the reaction between hydrogen and $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}$ change upon moving from one temperature to another. It should be noted that the absolute values of enthalpy grow slightly along with the concentration of hydrogen in the $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}$. In addition, a characteristic feature of the $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.4}\text{V}_{0.5}\text{H}_2$ system is the existence of pressure and enthalpy hystereses. The values of the pressure hysteresis in the $P-C$ isotherms differ in diverse parts of the hydrogen concentration. Comparing the data obtained in this work to those in [36], we can see that even a minimal change in the composition of the initial intermetallic compound can lead to considerable changes in the thermodynamic properties of the IMC– H_2 system.

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