



Calorimetric study of the $\text{ZrMo}_{1.5}\text{V}_{0.5}\text{-H}_2$ system

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Abstract

The study of the $\text{ZrMo}_{1.5}\text{V}_{0.5}\text{-H}_2$ system had been carried out by calorimetric method, plotting P – C isotherms and X-ray diffraction analysis. The $P=f(C)$ and $\Delta H=f(C)$ dependences were obtained for absorption and desorption processes (P —equilibrium hydrogen pressure absorption or desorption, ΔH —partial molar enthalpy of absorption or desorption, $C=H/\text{IMC}$) at 318, 338 and 368 K and the hydrogen pressure up to 50 atm. Moreover, the $\Delta S_{\text{des.}}=f(C)$ dependences were calculated on the base of measured calorimetric data and P – C isotherms ($\Delta S_{\text{des.}}$ —partial molar entropy of desorption) for 318, 338 and 368 K experiment temperatures. Obtained data enable us to make the following conclusion: the $\Delta H=f(C)$ and $\Delta S_{\text{des.}}=f(C)$ dependences change with the hydrogen concentration in the metallic matrix and at the transition from 318 to 368 K. This may be connected with the structural variation in the metallic matrix.

Keywords $\text{ZrMo}_{1.5}\text{V}_{0.5}$ · Hydride · Thermodynamics · Absorption · Desorption · Enthalpy

Introduction

One of the most interesting classes of the intermetallic compounds (IMC) is the cubic C 15 Laves phases AB_2 formed by well absorbing of hydrogen transition metals of 4 and 5 groups (ZrV_2 , HfV_2 and so on). In the series of works [1–12], the structure of the intermetallic hydrides ZrV_2 , HfV_2 , ZrCr_2 , ZrMo_2 was studied by neutron diffraction method in the temperature over the range 4.2 to 400 K. It has been determined that the deuterium atoms occupied two types of tetrahedral interstices: 96 g and 32 e, which formed by $2A+2B$ and $1A+3B$ correspondingly. At that their occupancies in different hydrides vary seriously [2, 6, 8, 9, 12].

It has been established that while cooling of ZrV_2D_4 , HfV_2D_4 , ZrCr_2D_4 and ZrMo_2D_4 , the phase transformations occur, followed by a tetragonal distortion of metallic lattice. Comprehensive study of these transformations permits to determine the influence of hydrogen on these processes.

Didisheim et al. [5] investigated the $\text{ZrV}_2\text{D}_{3.6}$ by means of differential thermal analysis (DTA). It was found out that at 325 K the transition of cubic phase to tetragonal phase

takes place during cooling, and the inverse process takes place during heating.

Maria Rosaria Tine in the article “Recent developments in calorimetry, thermal analysis, and applied thermodynamics” wrote: “Calorimetry and thermal analysis are indeed powerful investigative techniques, especially when their use is combined with other analytical techniques, thus allowing to look at scientific problems from a different point of view and to draw a complete picture of the system under examination in a multi-analytical approach” [13].

In the present work, we studied the $\text{ZrMo}_{1.5}\text{V}_{0.5}\text{-H}_2$ system by means of the calorimetric method and X-ray diffraction analysis. The application of the differential heat conducting calorimeter permits to determine the stages of the hydrogenation process and composition of formation of hydride phases precisely enough. It could be done on the basis of the measuring of the heat reaction of hydrogen with $\text{ZrMo}_{1.5}\text{V}_{0.5}$.

Experimental

The initial $\text{ZrMo}_{1.5}\text{V}_{0.5}$ sample was fused in the arc furnace from pure metals taken in the stoichiometric amount in the purified argon atmosphere. To purify argon from the gas pollutions, we melted titanium sponge before alloying of the original material. The obtained ingot was subjected to

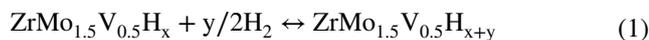
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homogenizer annealing. The purpose of this act was to flatten the distribution of consistent elements at 1500 °C during 50 h in the sealed quartz ampule under vacuum. X-ray analysis of initial alloy and its hydride was performed on Thermo ARL X'TRA diffractometer (Cu $K\alpha_1 + \alpha_2$ radiation). According to obtained data, $ZrMo_{1.5}V_{0.5}$ was the single-phase compound with the cubic Laves phase structure C15 (space group $Fd-3m O_2$, №227, $Z=8$); the refined unit lattice parameters were $a=7.549(4)$ Å, $V=430.198$ Å³.

The calorimetric study of hydrogen interaction with $ZrMo_{1.5}V_{0.5}$ was carried out on the twin-cell conducting calorimeter Tian–Calvet type connected to a conventional Sieverts'-type volumetric apparatus. Such apparatus permits us to measure simultaneously by a volumetric method the filling in or picking out of fixed hydrogen portions at the hydrogen absorption or desorption process. It also lets to determine the heat effect of these reactions. The apparatus scheme, the measuring technique and computational procedure analysis of the collected data were described elsewhere [14]. We utilized $LaNi_5H_x$ as a source of pure hydrogen for hydrogenation of the intermetallic compound (IMC). In this study, a purity of utilized hydrogen was 99.9999%.

Absorption (desorption) relative molar enthalpy $\Delta H_{abs.(des.)}$ was determined from the heat effect of the reaction:



In ref. [15], it was shown that the measured heats corresponded to enthalpies of reaction expressed per mole H_2 or $1/2 H_2$.

The experimental error in this work was calculated in accordance with recommendation of the IUPAC chemical thermodynamics committee [16] as a standard deviation of the mean value.

$$\delta = \sqrt{\Sigma \Delta^2 [n(n-1)]^{-1}}, \quad (2)$$

where Δ is the deviation from the mean value and n is the number of data points.

Since $ZrMo_{1.5}V_{0.5}$ reversibly reacts with hydrogen, the same sample (mass 2.6410 g) was used in all experiments. Before each run, the residual hydrogen was desorbed at 683 K under high vacuum outside the calorimeter.

Results and discussion

The data collected from P – C measurements are presented in Fig. 1. The P – C isotherms were obtained for both the hydrogen absorption and desorption processes. As one can see from this plot, the hydrogen capacity of $ZrMo_{1.5}V_{0.5}$ compound is $C=2.3$ at 318 K and 50 atm.

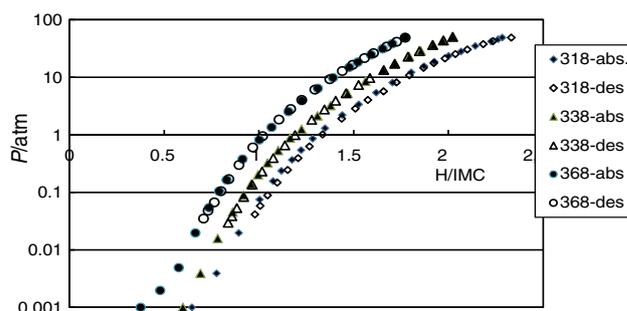


Fig. 1 Absorption and desorption isotherms for the $ZrMo_{1.5}V_{0.5}-H_2$ system

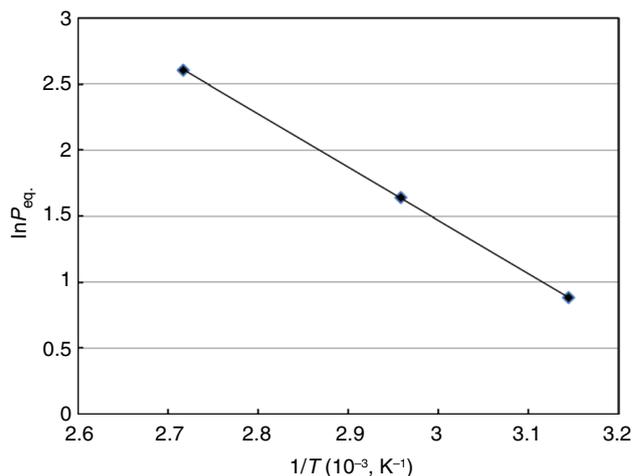


Fig. 2 Equilibrium hydrogen pressure P_{eq} versus T^{-1} of the $ZrMo_{1.5}V_{0.5}-H_2$ system at $C=1.45$

The reversible hydrogen capacity is much less. This is connected with very low equilibrium hydrogen pressure in the $ZrMo_{1.5}V_{0.5}-H_2$ system at these experimental temperatures ($P_{eq} \approx 0.001$ atm. at $C \approx 0.65$ and $T=318$ K). It takes much time for return of the $ZrMo_{1.5}V_{0.5}-H_2$ system to thermodynamic equilibrium state after extraction of recurrent hydrogen portion.

One property of the $ZrMo_{1.5}V_{0.5}-H_2$ system should be noted still. It is characterized by the absence of the P – C hysteresis on whole region of hydrogen concentration ($0 < C < 2.3$). Additionally, it is not possible to define any linear section where the values of $P_{eq} = f(C)$ dependences would be constant. In other words, there is no any horizontal plateau region.

We calculated the enthalpy ($\Delta H_{des.}$) and entropy values ($\Delta S_{des.}$) for the hydrogen desorption at $C=1.45$ from the Van't Hoff plot (see Fig. 2) based on the measured P – C – T relations. A solid line in Fig. 2 represents a plot of pressure versus reciprocal temperature. The obtained

straight line corresponds to $\Delta H_{\text{des.}} = 33.6 \text{ kJ mol}^{-1}\text{H}_2$ and $\Delta S_{\text{des.}} = 112 \text{ J K}^{-1} \text{ mol}^{-1}\text{H}_2$.

The results of our calorimetric study are presented in Table 1 and the plots of the $\Delta H=f(C)$ dependences for absorption and desorption processes for the $\text{ZrMo}_{1.5}\text{V}_{0.5}\text{-H}_2$ system at 318, 338 and 368 K. They are also shown in Figs. 3–5.

In Table 1, one can see the regions with the constant enthalpy values for absorption and desorption processes. As follows from the data presented in Table 1, there is no the enthalpy hysteresis. Thus, the absorption and desorption values coincide within the limits of experimental error.

In the presented plots of the $\Delta H_{\text{abs.}}=f(C)$ dependences for absorption process, we can define the initial region $0 < C < 0.5$ where the enthalpy values are constant while the increase in the experimental temperature is accompanied by slight arising of enthalpy values at absolute magnitude (see Table 1). We decided to find out which phase is formed in the $\text{ZrMo}_{1.5}\text{V}_{0.5}\text{-H}_2$ system at this region of the hydrogen concentrations. We hydrogenated the sample $\text{ZrMo}_{1.5}\text{V}_{0.5}$ up to composition $\text{ZrMo}_{1.5}\text{V}_{0.5}\text{H}_{0.5}$ and carried out X-ray powder diffraction analysis of $\text{ZrMo}_{1.5}\text{V}_{0.5}\text{H}_{0.5}$. The collected data showed that $\text{ZrMo}_{1.5}\text{V}_{0.5}\text{H}_{0.5}$ was single-phase compound with cubic crystal lattice C15. Its unit cell parameters slightly increase ($a = 7.661(9) \text{ \AA}$, $V = 449.6 \text{ \AA}^3$, $\Delta V = 4.1\%$) in comparison with the initial compound. So in the region of hydrogen concentration $0 < C < 0.5$ we deal with the formation of ordered hydrogen solid solution in $\text{ZrMo}_{1.5}\text{V}_{0.5}$. The increase in the hydrogen concentration in the ordered solid solution leads to abrupt decrease in the enthalpy values in absolute magnitude. This can be connected with the appearance of repulsive forces among hydrogen atoms H–H. It should be noted that this tendency is observed for each temperature.

At the experimental temperature 318 K, one can define two regions where the enthalpy values are constant: $1.3 < C < 1.9$ ($-32.3 \pm 0.8 \text{ kJ mol}^{-1}\text{H}_2$) and $1.9 < C < 2.2$ ($-34.4 \pm 1.3 \text{ kJ mol}^{-1}\text{H}_2$). As one can see from presented data, the difference in the obtained values amounts is about $2 \text{ kJ mol}^{-1}\text{H}_2$. And besides the enthalpy values of the second plateau ($1.9 < C < 2.2$) are more than values of the first one ($1.3 < C < 1.9$). And as shown in Table 1 and Fig. 3, these results agree within the experimental errors. Also it should be noted that the absolute enthalpy values obtained

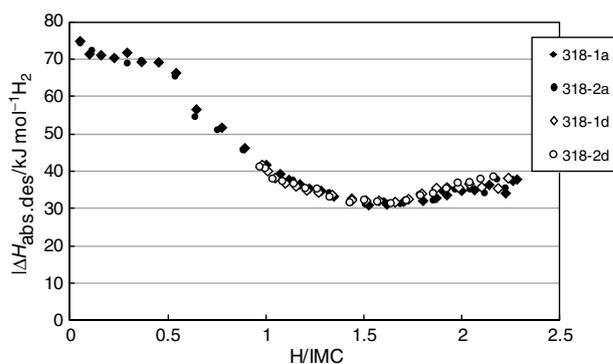


Fig. 3 Absorption and desorption enthalpy versus composition at 318 K. Filled symbols refer to absorption of H_2 ; open symbols refer to desorption. Different symbols refer to different series of determinations

at the greater hydrogen concentration are rather more than the enthalpy values obtained at the smaller hydrogen concentration. We assume that such phenomenon may be connected with the beginning of the lattice transformation from cubic crystal lattice to tetragonal one. In the work [5], Didisheim and colleagues from cooperating groups studied the order–disorder phase transition in $\text{ZrV}_2\text{D}_{3.6}$ by differential thermal analysis (DTA) and neutron diffraction studies. These researchers determined the existence of phase transition between cubic and tetragonal crystal lattices which occurred at $325 \pm 2 \text{ K}$. They marked the heat effect with maximum about 315 K which occurred upon both heating and cooling indicating that reversible phase transformation had taken place ($\Delta H = 3.8 \pm 0.5 \text{ kJ mol}^{-1}$).

If we examine the $\Delta H=f(C)$ dependence obtained for 338 K (see Fig. 4, Table 1), we can see only one region with constant enthalpy values $1.4 < C < 1.9$ where they agree within the experimental error in absolute value ($-31.5 \pm 0.5 \text{ kJ mol}^{-1}\text{H}_2$ and $30.9 \pm 0.3 \text{ kJ mol}^{-1}\text{H}_2$). Moreover, in Fig. 4 we can see that the curve of the $|\Delta H|=f(C)$ dependence for the absorption and desorption reaction shows the tendency to increase in enthalpy values with increasing hydrogen concentration at $C > 1.9$. Unfortunately, we could not continue our experiment at hydrogen concentration $C > 2.0$ as it required the generation of significant

Table 1 Temperature dependence of reaction enthalpy for the $\text{ZrMo}_{1.5}\text{V}_{0.5}\text{-H}_2$ system

Temperature/K	Range/H/IMC (absorption)	$\Delta H_{\text{abs.}}/\text{kJ mol}^{-1} \text{H}_2$	Range/H/IMC (desorption)	$\Delta H_{\text{des.}}/\text{kJ mol}^{-1} \text{H}_2$
318	0–0.5	-69.8 ± 1.6		
	1.3–1.9	-32.3 ± 0.8	1.3–1.8	32.6 ± 0.7
	1.9–2.2	-34.4 ± 1.3	1.8–2.2	35.7 ± 0.7
338	0–0.5	-71.3 ± 2.1		
	1.4–1.9	-31.5 ± 0.5	1.4–1.9	30.9 ± 0.3
368	0–0.5	-75.3 ± 0.8		

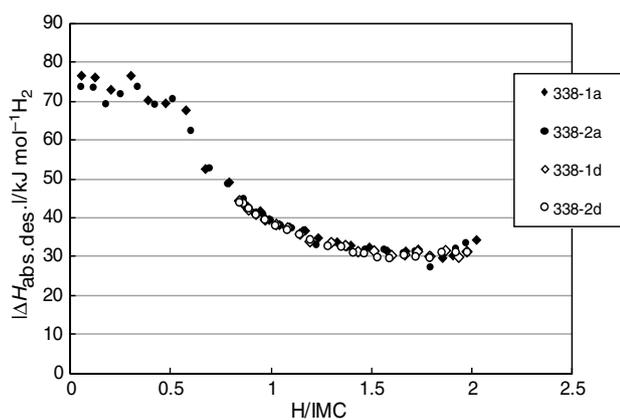


Fig. 4 Absorption and desorption enthalpy versus composition at 338 K. Filled symbols refer to absorption of H_2 ; open symbols refer to desorption. Different symbols refer to different series of determinations

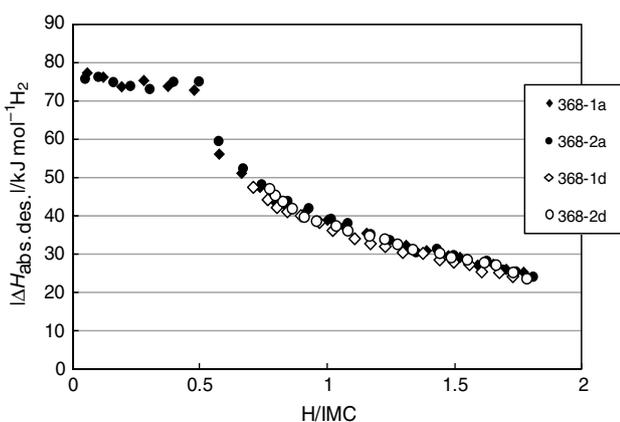


Fig. 5 Absorption and desorption enthalpy versus composition at 368 K. Filled symbols refer to absorption of H_2 ; open symbols refer to desorption. Different symbols refer to different series of determinations

higher pressures (our calorimetric installation is calculated on pressure up to 50 atm).

At 368 K, as shown in Fig. 5 the enthalpy values sharply decrease in absolute magnitude from $-75.3 \pm 0.8 \text{ kJ mol}^{-1} H_2$ ($C=0.5$) to $-24 \text{ kJ mol}^{-1} H_2$ ($C=1.8$). The absorption and desorption enthalpies coincide in absolute values. It should be noted that $|\Delta H_{\text{abs.des.}}| = 24 \text{ kJ mol}^{-1} H_2$ at $C=1.8$ is significant lower

than the enthalpy values obtained at $C=1.8$ for 318 and 338 K ($|\Delta H_{\text{abs.des.}}| \approx 31 \text{ kJ mol}^{-1} H_2$). And if we can see in Figs. 3 and 4 the $|\Delta H|=f(C)$, dependences reveal a tendency to increasing the $|\Delta H|$ at $C > 1.9$ at 318 and 338 K; then, at 368 K such tendency is not observed.

The authors in the works [1–7, 10] investigated hydrogen interaction with the intermetallic compounds with Laves phase structure C15 (ZrV_2 , HfV_2 , $ZrCr_2$ etc.) by X-ray powder diffraction analysis and neutron diffraction method. It was determined that H atoms may occupy two types of tetrahedral interstitial sites with $2Zr-2V$ and $1Zr-3V$ faceting. For $C \leq 2.5$, the hydrogen atoms occupy only the $2Zr-2V$ sites. In the present work, we deal with more complex compound $ZrMo_{1.5}V_{0.5}$. As it was established in the work [17] in this compound, there are tetrahedral interstitial sites with $2Zr-2V$, $2Zr-(V,Mo)$ and $2Zr-2Mo$, since V and Mo occupy B site. As it was noticed previously, there are two plateau regions $1.3 < C < 1.9$ and $1.9 < C < 2.2$ with the constant enthalpy values in the plot of $|\Delta H|=f(C)$ dependences at 318 K. Moreover, the partial molar enthalpy values of the hydrogen reaction with IMC increase in absolute values with the increase in hydrogen concentrations in the metallic matrix. To understand what phenomenon we observed, we prepared the $ZrMo_{1.5}V_{0.5}H_{2.5}$ sample and carried out X-ray powder diffraction analysis at the room temperature. The data of the X-ray analysis showed that $ZrMo_{1.5}V_{0.5}H_{2.5}$ had tetragonal structure. In other words, this means that the increasing of hydrogen concentration in the metallic matrix carries out lowering of symmetry of host structure. The unit cell parameters are: $a = 5.612(3) \text{ \AA}$, $c = 7.856(2) \text{ \AA}$, $V = 247.4 \text{ \AA}^3$, $\Delta V = 15\%$.

On the basis of X-ray analysis data, we may assume that at 318 K in the $ZrMo_{1.5}V_{0.5}-H_2$ system at $C \geq 2$ further hydrogen absorption is accompanied by the transition from the cubic phase into tetragonal one. We may observe this transition in the plot of $|\Delta H|=f(C)$ dependences. At $C \geq 2$ $|\Delta H|$ values slightly increase.

Refined unit lattice parameters for $ZrMo_{1.5}V_{0.5}$, $ZrMo_{1.5}V_{0.5}H_{0.5}$ and $ZrMo_{1.5}V_{0.5}H_{2.5}$ are presented in Table 2. In Fig. 6a–c, we can see X-ray diffraction patterns of $ZrMo_{1.5}V_{0.5}$, $ZrMo_{1.5}V_{0.5}H_{0.5}$ and $ZrMo_{1.5}V_{0.5}H_{2.5}$.

In the work [17], the authors studied hydride and deuteride of $ZrMo_{1.5}V_{0.5}$ by means of X-ray diffraction analysis and the neutron diffraction analysis. These data showed that $ZrMo_{1.5}V_{0.5}H_{3.5}$ had tetragonal structure (space group $I4_1/aO2$, $\mathbb{N}88$, $Z=4$). The neutron diffraction data allowed to

Table 2 Structural parameters of $ZrMo_{1.5}V_{0.5}$, $ZrMo_{1.5}V_{0.5}H_{0.5}$ and $ZrMo_{1.5}V_{0.5}H_{2.5}$ obtained at room temperature

Compound	Space group	$a/\text{\AA}$	$c/\text{\AA}$	$V/\text{\AA}^3$	$\Delta V/\%$
$ZrMo_{1.5}V_{0.5}$	$Fd-3m O2$, $\mathbb{N}227$, $Z=8$	7.549(4)	–	430.198	–
$ZrMo_{1.5}V_{0.5}H_{0.5}$	$Fd-3m O2$, $\mathbb{N}227$, $Z=8$	7.661(9)	–	449.6	4.1
$ZrMo_{1.5}V_{0.5}H_{2.5}$	$I4_1/a O2$, $\mathbb{N}88$, $Z=4$	5.612(3)	7.856(2)	247.4	15

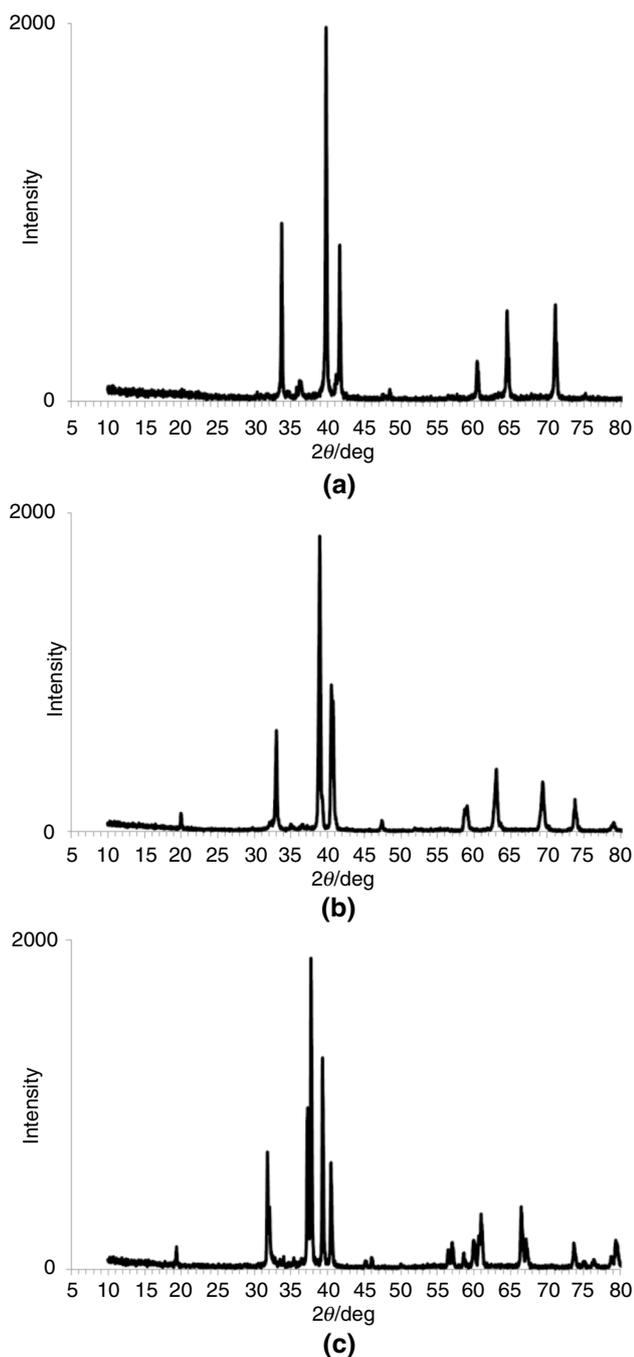


Fig. 6 a–c X-ray diffraction patterns of **a** $\text{ZrMo}_{1.5}\text{V}_{0.5}$, **b** $\text{ZrMo}_{1.5}\text{V}_{0.5}\text{H}_{0.5}$ and **c** $\text{ZrMo}_{1.5}\text{V}_{0.5}\text{H}_{2.5}$

determine that all deuterium atoms were in the 16f position surrounded by $\text{Zr}_2(\text{Mo},\text{V})_2$. A small difference between the enthalpy values ($\sim 2 \text{ kJ mol}^{-1}\text{H}_2$) is apparently related to the existence of the great number of multiplicity similar energy type interstices in the complex lattice of intermetallic compound.

From the thermodynamic data collected during the calorimetric measurements of the heat effects of hydrogen

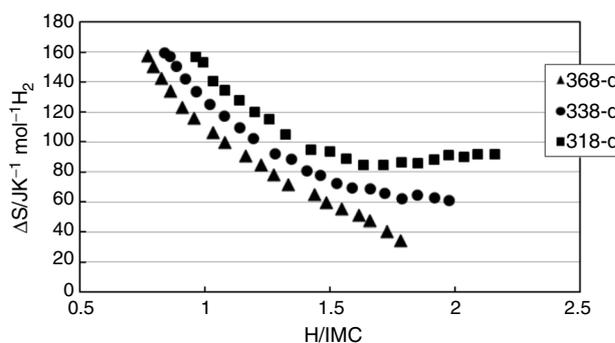


Fig. 7 Desorption entropy versus composition at different temperatures

reaction with IMC and the equilibrium hydrogen pressures, we calculated the partial molar entropy values of hydrogen desorption from $\text{ZrMo}_{1.5}\text{V}_{0.5}\text{H}_x$ hydride and plotted the $\Delta S_{\text{des.}} = f(C)$ dependences for each studied experimental temperature (see Fig. 7).

From the presented plot, one can see that at 318 K the entropy values decrease with the increase in hydrogen concentration to $C \sim 1.6$ and then begin to increase. The entropy values are constant on the region $1.9 < C < 2.3$ ($\Delta S_{\text{des.}} = 89.2 \pm 1.8 \text{ JK}^{-1}\cdot\text{mol}^{-1}\text{H}_2$). We can assume that such phenomenon may be connected with the beginning of the transformation of host cubic structure C 15 to tetragonal one and the formation of new interstitial sites which hydrogen atoms may occupy.

At 338 K in the plot of the $\Delta S_{\text{des.}} = f(C)$ dependence, we observe that the entropy values decrease and at $C \approx 1.8$ there is the region where the entropy values are constant ($\Delta S_{\text{des.}} \approx 61 \text{ JK}^{-1}\cdot\text{mol}^{-1}\text{H}_2$).

At 368 K, the entropy values decrease on the full region of the studied hydrogen concentrations.

Conclusions

The investigation of the hydrogen interaction with $\text{ZrMo}_{1.5}\text{V}_{0.5}$ was carried out by means of the calorimetric method in the temperature region from 318 to 368 K and hydrogen pressure up to 50 atm. The $\Delta S_{\text{des.}} = f(C)$ and $|\Delta H_{\text{abs. des.}}| = f(C)$ dependences were obtained for each temperature. The enthalpy values of hydrogen absorption and desorption were measured in the wide region of the concentrations H/IMC. It was shown that in the $\text{ZrMo}_{1.5}\text{V}_{0.5}\text{-H}_2$ system in this temperature range there is a large region of ordered solid solution of hydrogen in IMC ($0 < C < 0.5$, $\Delta H_{\text{abs.}} \approx -70 \text{ kJmol}^{-1}\text{H}_2$). The further hydrogen absorption takes place differently at different temperatures. At 318 K, there are two regions with the constant enthalpy values.

Moreover, the rise of hydrogen concentration leads to the increase in enthalpy values.

The data of X-ray analysis of $\text{ZrMo}_{1.5}\text{V}_{0.5}\text{H}_{2.5}$ at room temperature showed that the transition from cubic structure to tetragonal one takes place. It is possible to assume that at 318 K and hydrogen concentration $C \geq 2.0$ we see the transition of the host cubic phase to tetragonal one. Obtained dependence $\Delta S_{\text{des.}} = f(C)$ could be the indirect proof of this conclusion.

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