

CALORIMETRIC INVESTIGATION OF THE HYDROGEN INTERACTION WITH $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5}$

E.Yu. ANIKINA, V.N. VERBETSKY

Chemistry Department, Lomonosov Moscow State University,

119899 Moscow, Russia; E-mail: verbetsky@hydride.chem.msu.ru

Abstract

The interaction of hydrogen with nonstoichiometric $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5}$ Laves phase compound at pressure up to 60 atm and temperature range from 336 to 413 K has been studied by means of calorimetric and P-X isotherm methods. The obtained results allow to propose the existence of two hydride phases in the $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5}$ - H_2 system under this conditions.

Keywords: Intermetallic Compounds (IMC); Hydrides; Calorimetry;

$\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5}$ - H_2 system

1. Introduction

A lot of works are devoted to investigations of multicomponent alloys on the base Zr-Ti-Mn with Laves phase structure AB_2 . These alloys are perspective materials for using them in different stationary and mobile hydrogen accumulators, as they possess fast kinetics, a large hydrogen storage capacities and resistance to degradation during cycling. However, in the most works devoted to the hydrogen interaction with these alloys, the measurements were carried out by means of plotting of pressure – composition isotherms and thermodynamic characteristics for studied system were calculated using Van't Hoff equation. The works, in which thermodynamic properties of intermetallic compound (IMC) – hydrogen system was investigated by calorimetric method, are significantly less.

In the present work as subject under study the alloy with nonstoichiometric composition $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5}$ was chosen. As it is known, in the alloy with nonstoichiometric composition AB_{2-x} the atoms of A-component occupy in structure of alloy crystallochemical position of B-component. In this alloy A position are occupied by atoms of Zr and Ti, and Mn, V and over-stoichiometric Ti atoms are distributed in the B positions. As a matter of fact, the compound $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5}$ is correctly described as a AB_2 , which can be written $(\text{Ti}_{0.89}\text{Zr}_{0.11})(\text{Mn}_{1.39}\text{V}_{0.54}\text{Ti}_{0.07})$. Earlier the hydrogen interaction with this alloy has been investigated by means of P (pressure) – X (concentration) measurements in a conventional Sievert's type apparatus [1]. It has been found that in the region two phases coexistence P_{plat} is not constant, but increases with % conversation of hydride phase, that is characteristic of multicomponent alloys. For this reason it is especial interest to measure the thermodynamic properties of this system in the plateau region by calorimetric method.

2. Experimental

The $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5}$ sample was obtained by arc melting of the pure components in the furnace with tungsten nonconsumable electrode on a copper water cooled hearth under purified argon pressure 1.5 atm. The starting materials had purity: titanium – 99.99%, zirconium – 99.99%, manganese – 99.9%, vanadium – 99.99%. Since manganese is more volatile than the other elements the mixture was prepared with 4% excess of Mn compared to the desired final stoichiometry. The sample was turned over and remelted four times and then annealed at 1100 – 1150 K for 240 h in quartz ampoule under residual argon pressure 0.01 atm to ensure homogeneity. Then the sample was studied by X-ray, electron microscopy, electron probe analysis. X-ray analysis of initial alloy was performed on DRON–2 diffractometer (Cu $K\alpha$ radiation, Ni filter). Electron-probe analysis was done in JXA–733 microanalyses complex with LINK–2 microanalytical system. From the X-ray analysis the crystal structure of the sample was characterized as C14–type Laves phase and no secondary phase was found. The cell parameters and data of quantitative analysis of the alloy composition are listed in Table 1.

TABLE 1. Chemical and phase composition of the $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5}$ alloy

Alloy composition				Phase composition	Cell parameters, Å		Composition of IMC, normalized to AB_2
Ti	Zr	V	Mn		a	c	$(\text{Ti}_{0.89}\text{Zr}_{0.11})(\text{Mn}_{1.39}\text{V}_{0.54}\text{Ti}_{0.07})$
32	4	18	46	C 14	4.92	8.07	

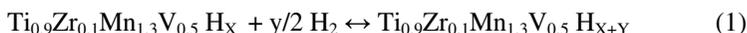
TABLE 2. Temperature dependence of reaction enthalpy for the $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5} - \text{H}_2$ system

Temperature, (K)	Range	$ \Delta H_{\text{des.}} \pm \delta$, (kJ/mol H_2)
336	$0.80 \leq x \leq 1.55$	31.47 ± 0.42
354	$0.60 \leq x \leq 1.10$	30.22 ± 0.36
	$1.20 \leq x \leq 2.00$	36.22 ± 0.43
373	$0.70 \leq x \leq 1.20$	30.13 ± 0.50
	$1.30 \leq x \leq 1.90$	35.21 ± 0.37
393	$0.60 \leq x \leq 1.00$	29.35 ± 0.31
	$1.10 \leq x \leq 1.70$	33.07 ± 0.58
413	$0.30 \leq x \leq 0.90$	28.02 ± 0.33
	$1.00 \leq x \leq 1.70$	33.04 ± 0.42

Twin-cell differential heat-conducting calorimeter of Tian–Calvet type connected to the apparatus for gas dose feeding was applied to measure the dependences of differential molar enthalpy of desorption ($\Delta H_{\text{des.}}$) and equilibrium hydrogen pressure on hydrogen concentration in $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5}$ and reaction temperature. Hydrogen was obtained by desorption from LaNi_5 -hydride. The apparatus scheme was described elsewhere [2]. The hydrogen concentration in the sample was calculated using the Van – der – Waals equation of state for pressure below 20 atm and using the modified Van – der – Waals equation for pressure above 20 atm [3]. The accuracy of the measurements

was taken as square of average value $\delta = \sqrt{\sum \Delta^2 / [n(n-1)]}$ (Δ , deviation from average value; n , number of measurements).

Desorption relative molar enthalpy ΔH_{des} was determined from the heat effect of the reaction:



Since $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5}$ reversibly reacts with hydrogen the same sample ($12639.4 \cdot 10^{-6}$ mole $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5}$) was used in all experiments.

3. Results and discussion

The calorimetric method applied in this work permits to obtain calorimetric data simultaneously with P–X isotherms. The $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5} - \text{H}_2$ system was studied in the temperature range 336 – 413 K and hydrogen pressure from 0 to 60 atm. As the duration of this experiment was about 1 year it was necessary to control of sample characteristics. In this purpose desorption of hydrogen at 336 K was repeated from time to time. Despite the multicomponent nature of the alloy the P–X isotherms and calorimetric data for studied alloy were very reproducible, namely, in the limits of sensitivity of the definition all parameters were fully reproducible.

Fig. 1 shows the P–X dependencies ($X = [\text{H}] / [\text{AB}_2]$; P, equilibrium pressure), obtained in the temperature range 298 – 413 K. For all temperatures the desorption isotherms are presented and for 336 K also the absorption isotherm. As one can see from fig. 1 the $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5} - \text{H}_2$ system has a wide α -region at ambient temperature. The length of α -region significantly decreases with increasing of the experimental temperature and plateau slopping on P–X diagrams increase. At experimental temperature above 336 K there is discontinuity in the plateau region when dP_{H_2}/dx reaches a maximum value at $x \sim 1$. The similar observations have been made on the other alloys in previous works [4,5]. With rising of the temperature the location of this point didn't change significantly. It should be marked one peculiarity of obtained P–X diagrams. As it has been mentioned above for 336 K the absorption and desorption isotherms were measured. From fig. 1 it can be seen that at 336 K the plateau region for the desorption isotherm is $0.5 < x < 2.2$, and for the absorption one is $0.50 < x < 1.90$. There is no practically hysteresis up to value $x=1.6$. But at $x>1.6$ pressure hysteresis appears and P–X reversibility appears only at $x>2.2$, though the sharp change of the slope of the P–X curve is observed at $x=1.7$. One can suggest that in the range $1.7 < x < 2.2$ there also exists a two-phase equilibrium. The similar phenomenon for $\text{AB}_2 - \text{H}_2$ has been described in [5, 6] for $\text{Zr}(\text{Fe}_{0.75}\text{Cr}_{0.25})_2$ and $\text{ZrCrFe} - \text{H}_2$ systems and was accounted for the formation of two hydrides.

Fig. 2 represents the plot of the enthalpy of desorption as a function of X at 336 K. There is the initial range $0.20 < x < 0.60$ where the function $|\Delta H_{des}| = f(x)$ has linear dependence which can be described by the first order equation

$$y = -13.72x + 42.97 \quad (2)$$

Further, at $x > 0.60$ the character of the $|\Delta H_{des}| = f(x)$ dependence changes sharply, namely, in the range $0.60 < x < 0.75$ the values of $|\Delta H_{des}|$ decrease from ~ 35 kJ/mol H_2 to ~ 25 kJ/mole H_2 and then in the hydrogen concentration range $0.75 < x < 0.80$ this one increases up to the plateau values, corresponding $\alpha \leftrightarrow \beta$ transition. In the range

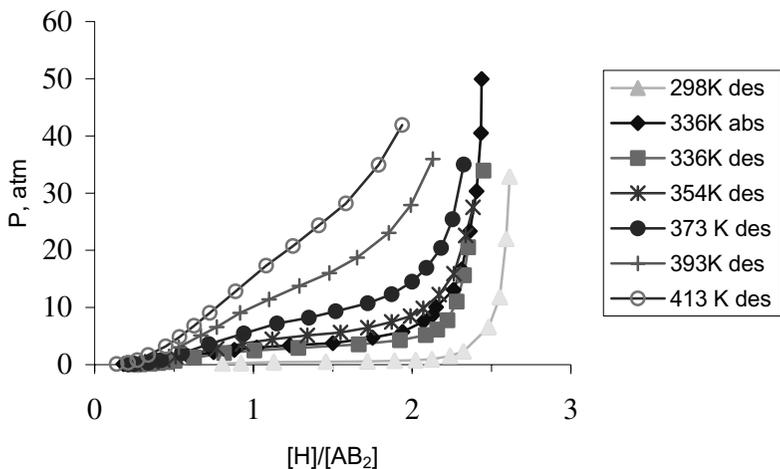


Figure 1. Absorption and desorption isotherms for the $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5} - \text{H}_2$ system

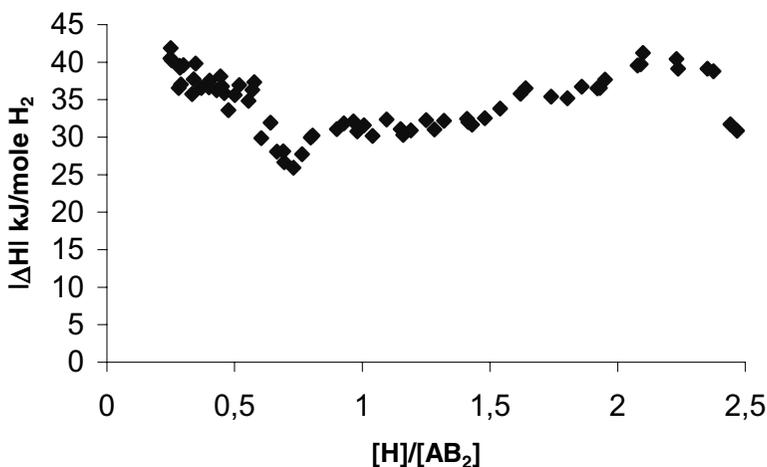


Figure 2. Desorption enthalpy vs. composition at 336 K

$0.80 < x < 1.55$. values of ΔH_{des} . remain constant and after that ($x > 1.6$) the function of $|\Delta H_{\text{des}}| = f(x)$ changes in accordance with the linear law

$$y = 10.89x + 16.53 \quad (3)$$

On the P-X isotherm (see fig. 2) this phenomenon is corresponded with the pressure hysteresis in the range $1.70 < x < 2.2$. I.e. compared the data, obtained from P-X and $|\Delta H_{\text{des}}| = f(x)$ dependences at 336 K, one can suggest that in this hydrogen

concentration region $\beta \leftrightarrow \gamma$ transition occurs which is accompanied by additional thermodynamic processes. This phenomenon, characteristic for multicomponent alloys, was described in the work [7].

With increasing experimental temperature the position of minimum values of $|\Delta H_{des.}|$, which took place in the α -region at 336 K, shifts towards the range of the lower hydrogen concentrations (to compare $x=0.75$ at 336 K and $x=0.50$ at 393 K), and the length of α – phase decreases (see fig. 2–4). On the plot of $|\Delta H_{des.}|$ -X dependence at 353 K one can assign two region with constant values of $|\Delta H_{des.}|$: $0.60 < x < 1.10$ $|\Delta H_{des.}|=30.22 \pm 0.71$ kJ/ mol H₂ and $1.20 < x < 2.00$ $|\Delta H_{des.}|=36.15 \pm 1.00$ kJ/ mol H₂.

Rising the experimental temperature from 353 to 393 K does not influence the shape of $|\Delta H_{des.}|$ -X though the region boundaries $\alpha \leftrightarrow \beta$ and $\beta \leftrightarrow \gamma$ shift to the lower hydrogen concentrations and the values of $|\Delta H_{des.}|$ decrease slightly.

At 413 K the plot of $|\Delta H_{des.}|$ -X drastic changes its shape (see fig. 5). There is no minimum value of $|\Delta H_{des.}|$, which could be seen on the plots of $|\Delta H_{des.}|$ -X isotherms at lower temperatures. Three regions can be selected on the obtained $|\Delta H_{des.}|$ -X diagram with constant values of $\Delta H_{des.}$. Initial range $0 < x < 0.3$ corresponds to the formation of α -solution hydrogen in IMC ($|\Delta H_{des.}|=41.79 \pm 0.92$ kJ/ mol H₂). At $x=0.30$ the values $|\Delta H_{des.}|$ sharply decrease and in the range $0.30 < x < 0.90$ $|\Delta H_{des.}|=28.02 \pm 0.68$ kJ/ mol H₂). And at last there is the third region of constant values of $|\Delta H_{des.}|$ in the range $1.00 < x < 1.70$ $|\Delta H_{des.}|=33.04 \pm 0.97$ kJ/ mol H₂.

The existence of β - and γ -hydride phases of $Ti_{0.9}Zr_{0.1}Mn_{1.3}V_{0.5}$ -H₂ system revealed in the work may be caused by two factors. Firstly, it could be supposed that the formation of β -hydride under rising temperature is accompanied by the transformation of metal sublattice. However, the existence of two hydride phases could be connected with peculiarity of the structure of this IMC. As mentioned above investigated IMC has nonstoichiometric composition. It is known, that in the hexagonal AB₂ Laves phase hydrogen atoms mainly occupy two kinds of interstitial sites: [A₂B₂] and [AB₃]. Using the data of deuteride $(Ti_{0.89}Zr_{0.11})(Mn_{1.47}V_{0.31}Ti_{0.22})D_{2.8}$ –structure research based on compositionally familiar IMC studied in this work it has been found [8], that in $(Ti_{0.89}Zr_{0.11})(Mn_{1.47}V_{0.31}Ti_{0.22})D_{2.8}$ deuterium atoms occupy three sites 24(l), 12(k)₁ and 6(h)₁ with [A₂B₂]. But since V and Ti, which have strong affinity to hydrogen, as well as Mn occupy some B sites there is a possibility to regard an interstitial site [A₂B₂] as formed by active (Ti, Zr, V), which conditionally signed as A*, and inactive (Mn) to hydrogen components. On the base carried out calculations the authors [8] drew the conclusion that 24(l) transforms to [A*₄] and [A*₃B] in higher extent than 12(k)₁ and 6(h)₁ and therefore 24(l) positions are occupied by hydrogen at hydride formation in the first order. The authors have concluded that $(Ti_{0.89}Zr_{0.11})(Mn_{1.47}V_{0.31}Ti_{0.22})D_{2.8}$ with consideration of distribution deuterium atoms among interstitial sites may be written as $(Ti_{0.89}Zr_{0.11})(Mn_{1.47}V_{0.31}Ti_{0.22})D_{1.86}^1 D_{0.69}^2 D_{0.25}^3$, D¹, D², D³ – deuterium atoms, arranged in 24(l), 12(k)₁ and 6(h)₁ respectively.

To make analogy it could be supposed that in our case the formation of β -hydride corresponds the occupation by hydrogen atoms positions 24(l), and the formation of γ – hydride is connected with the occupation by hydrogen atoms the positions 12(k)₁ and 6(h)₁. As well as it is possible that namely the transformation the part of [A₂B₂] into [A*₄] and [A*₃B] could be the reason so prolonged α -region. In the work [9] this phenomenon in explained the same reasons.

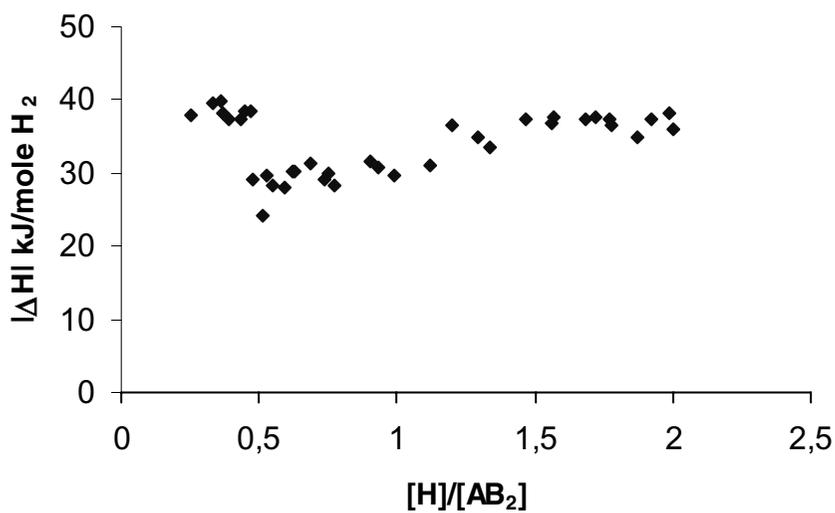


Figure 3. Desorption enthalpy vs. composition at 353 K

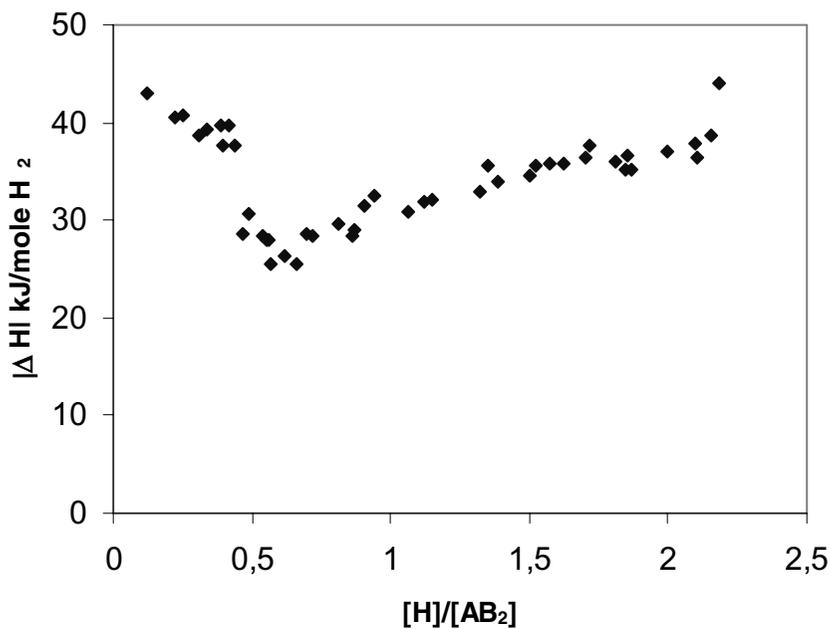


Figure 4. Desorption enthalpy vs. composition at 373 K

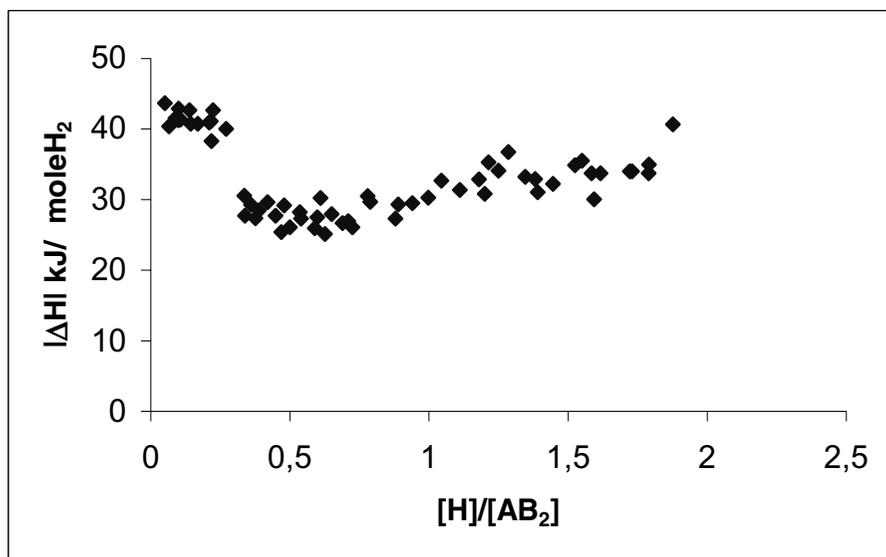


Figure 5. Desorption enthalpy vs. composition at 413 K

4. Conclusions

On the base of obtained data it can be concluded that during hydrogen interaction with $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5}$ at the temperature range 336-413 K two hydride phases forms: β - and γ -hydrides. It has been found that the boundaries of these phases and the values of ΔH_{des} depend on temperature.

5. Acknowledgements

The work has been partially supported by the RFBR Grant № 03-03-33023 and 02-02-17545.

6. References

1. Mitrokhin, S.V., Bezuglaya, T.N. and Verbetsky, V.N. (2002) Structure and hydrogen sorption properties of (Ti,Zr)-Mn-v alloys, *J. of Alloys and Compounds* **330-332**, 146-151.
2. Anikina, E.Yu. and Verbetsky, V.N. (2002) Calorimetric investigation of the hydrogen interaction with $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.1}\text{V}_{0.1}$, *J. Alloys and Compounds* **330-332**, 45-47.
3. Hemmes, H., Driessen, A. and Griessen, R. (1986) Thermodynamic properties of hydrogen at pressure up to 1 Mba and temperature between 100 and 1000 K, *J. Phys. C: Solid State Phys* **19**, 3571-3585.
4. Flanagan, T.B., Luo, W. and Clewley, J.D. (1993) The characterization of multi-component metal hydrides using reaction calorimetry, *Z. Phys. Chem.*, 35-44.

5. Grant, D.M., Murray, J.J. and Post, M.L. (1990) The thermodynamics of the system for $\text{Zr}(\text{Fe}_{0.75}\text{Cr}_{0.25})_2 - \text{H}_2$ using of heat conduction calorimetry, *J. Solid State Chem.* **87**(2), 415-422.
6. Sirotina, R.A., Umerenko, E.A. and Verbetsky, V.N. (1996) Calorimetric investigation of hydrogen interaction with intermetallic compound $\text{ZrCrFe}-\text{H}_2$, *Russ. Neorganicheskie materialy* **32**(6), 710-714.
7. Post, M.L., Murray, J.J. and Grant, D.M. (1989) The LaNi_5-H_2 system at $T=358$ K: An investigation by Heat-Conduction Calotimetry, *Zeitschrift fur Physikalische Chemie Neue Folge. Bd.* **163**, 135-140.
8. Mitrokhin, S.V., Smirnova, T.N., Somenkov, V.A., Glazkov, V.P. and Verbetsky, V.N. (2003) Structure of (Ti,Zr)–Mn-V nonstoichiometric Laves phases and $(\text{Ti}_{0.9}\text{Zr}_{0.1})(\text{Mn}_{0.75}\text{V}_{0.15}\text{Ti}_{0.11})\text{D}_{2.8}$ deuteride, *J. Alloys and Compounds* **356-357**, 80-83.
9. Bin-Hong Lin, Dong-Myung Kim, Ki-Young Lee and Jai-Young Lee (1996) Hydrogen storage properties of TiMn_2 -based alloys, *J. Alloys and Compounds* **240**, 214-218.