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Calorimetric investigation of the hydrogen interaction with $ZrCrFe_{1.2}$

T.V. Ivanova, V.N. Verbetsky*

Chemistry Department, Lomonosov Moscow State University, 119899 Moscow, Russia

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Abstract

The interaction of hydrogen with $ZrCrFe_{1.2}$ intermetallic compound was studied by means of calorimetric and P–C-isotherm methods. The obtained results allow to suppose an existence of two hydride phases in the $ZrCrFe_{1.2}$–H_2 system in the temperature range 315–353 K. At temperatures higher than 393 K the existence of two types of hydrogen solution in metal matrix was found.

Keywords: Intermetallic compounds; Hydride; Calorimetry; $ZrCrFe_{1/2}$ intermetallic compound

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1. Introduction

This work is the continuing study of direct calorimetric determination of reaction enthalpies of hydrogen desorption from AB_2 zirconium Laves phases and temperature dependencies. The results obtained earlier for $Zr_{0.8}Ti_{0.2}CrFe$–H_2 and $ZrCrFe$–H_2 systems [1,2] proved that the temperature alternation considerably influences the reaction enthalpy of hydrogen desorption (absorption). For further studies we chose $ZrCrFe_{1.2}$–H_2 system. The interaction of hydrogen with $ZrCrFe_{1+x}$ intermetallic compounds was studied in detail for compounds with $x=1.4$; 1.5 [3] by PC-isotherm method. $ZrCrFe_{1.2}$–H_2 system is much less studied not only by calorimetric but also by P–C-isotherm methods.

2. Experimental details

The calorimetric method using the calorimeter of Tian-Calvet type was employed in the study. The calorimeter was connected with the apparatus for dose gas feeding. The apparatus scheme was described elsewhere [4]. The intermetallic compound sample was obtained by arc melting in the furnace with nonspending tungsten electrode on a copper water-cooled hearth in the purified argon atmosphere at 2 atm pressure.

X-ray data (DRON-2, CuK_α-radiation) showed that $ZrCrFe_{1.2}$ sample is hexagonal Laves phase $MgZn_2$ type with cell parameters $a=5.020\pm0.002$ Å; $c=8.224\pm0.003$ Å, close enough to those obtained by others [5] ($a=5.019$ Å; $c=8.226$ Å).

The hydrogen concentration in the sample was calculated using the Van-der-Waals equation of state for pressures below 20 atm and using the modified Van-der-Waals equation [6] equation for pressures above 20 atm. The measurement accuracy was taken as a square of average value $\delta^2=\Sigma\Delta^2[n(n-10)]^{-1}$ (Δ, deviation from average value; n, number of measurements).

Absorption (desorption) differential molar enthalpies $|\Delta H_{a(d)}|$ were determined from the heat effect of the reaction

$$ZrCrFe_{1.2}H_x + y/2\,H_2 \Leftrightarrow ZrCrFe_{1.2}H_{x+y}$$

The $|\Delta H_{a(d)}|$ value determined in this way corresponds to the middle of the deviation range of hydrogen concentration in intermetallic compound during absorption (desorption). The amount of absorbed (desorbed)) hydrogen was $(200–900)\times10^{-6}$ mole. Since $ZrCrFe_{1.2}$ reversibly reacts with hydrogen we used the same sample (8826×10^{-6} mole $ZrCrFe_{1.2}$) in all experiments.

3. Results and discussion

The $ZrCrFe_{1.2}$–H_2 system was studied in the temperature range 315–523 K. Fig. 1 shows the P–X-dependencies ($X=H/ZrCeFe_{1.2}$; P, equilibrium pressure). For all temperatures the desorption isotherms are presented and for 315 K also the absorption isotherm.

Contrary to the absorption isotherm at 315 K the desorption isotherm shows two distinct regions (Fig. 2)

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*Corresponding author.

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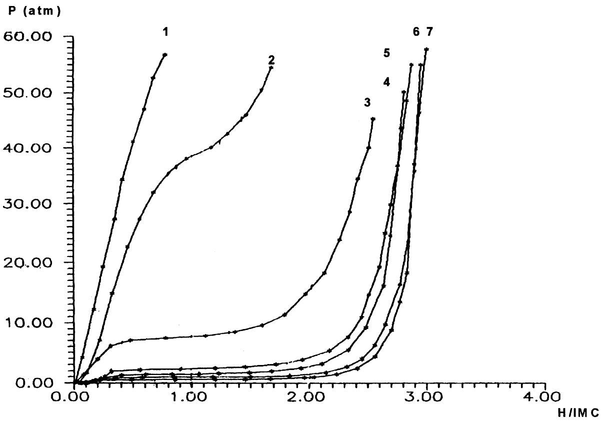

Fig. 1. Desorption isotherm for the system $ZrCrFe_{1.2}$–H_2: 1, 250°C; 2, 200°C; 3, 120°C; 4, 80°C; 5, 60°C; 7, 40°C; 6, 40°C (absorption).

where the desorption enthalpy has a constant value: first $\Delta H_d = 33.6 \pm 0.4$ kJ/mole H_2 in the range $0.4 \leq X \leq 1.8$; second $\Delta H_d = 36.5 \pm 0.5$ kJ/mole H_2 in the range $1.9 \leq X \leq 2.3$. Two regions of constant enthalpy values are possibly due to the existence of two hydride phases $ZrCrFe_{1.2}H_{2-\delta}$ and $ZrCrFe_{1.2}H_{3-\delta}$ corresponding to β- and γ-hydrides. This assumption agrees with the results obtained in reference [7], where interaction of hydrogen with $Zr(Cr_{0.25}F_{0.75})_2$ and $Zr(Cr_{0.45}Fe_{0.55})_2$ was studied by the direct calorimetry method at 273 K with simultaneous P–C-isotherms measurement. The same researchers [7] supposed the existence of two hydride phases in both studied systems. The same phenomenon was found also for the system ZrCrFe–H_2 at 380–497 K [2]. In this case the hydride phase compositions were $ZrCrFeH_{2-\delta}$ and $ZrCrFeH_{3-\delta}$. Obviously the formation of two hydride phases in mentioned systems is their peculiarity. It should be noted that all four studied systems are characterised by a considerably higher dissociation enthalpy value for the γ-hydride than for β-hydride. This can be explained by the structural changes of alloy matrix [2]. In case of the $ZrCrFe_{1.2}$–H_2 system this difference is negligible and is about 3 kJ/mole H_2 (see Table 1).

Table 1
Temperature dependence of reaction enthalpy for the $ZrCrFe_{1.2}$–H_2 system[a]

Temperature (K)	Range	$\lvert\Delta H_{a(d)}\rvert \pm \delta$ (kJ/mole H_2)	
		Absorption	Desorption
315	$0.4 \leq X \leq 1.8$	36.3 ± 0.3	33.6 ± 0.4
	$1.9 \leq X \leq 2.3$	36.3 ± 0.3	36.5 ± 0.5
328	$0.5 \leq X \leq 1.9$		34.8 ± 0.4
	$2.0 \leq X \leq 2.3$		41.2 ± 0.3
353	$0.3 \leq X \leq 1.8$		36.3 ± 0.4
	$1.9 \leq X \leq 2.1$		40.6 ± 0.3
393	$0.4 \leq X \leq 1.3$		32.2 ± 0.4
473	$0.1 \leq X \leq 0.4$		21.5 ± 0.3
	$0.4 \leq X \leq 0.7$		26.5 ± 0.3
	$0.8 \leq X \leq 1.4$		33.0 ± 0.3
523	$0 < X \leq 0.2$		20.0 ± 0.4
	$0.3 < X < 0.7$		17.4 ± 0.5

[a] Accuracy of the determination of boundary compositions $\pm 0.1X$.

Experimental results obtained at 315 K confirm a certain pressure hysteresis as well as an enthalpy hysteresis ($\lvert\Delta H_a\rvert > \Delta H_d$) in the plateau region equal to ~3 kJ/mole H_2.

In the region of hydrogen α-solution in intermetallic compound the behaviour of the $ZrCrFe_{1.2}$–H_2 system is analogous to all AB_2–H_2 systems studied in [8] and mentioned above. In a comparatively narrow range when $0 \leq X \leq 0.4$ the decrease of $\lvert\Delta H_{a(d)}\rvert$ values is observed and further the increase up to the plateau values, meanwhile the quantitative data coincide in full as for absorption and desorption. In the region of hydrogen solution in hydride (Fig. 2) the $\lvert\Delta H_{a(d)}\rvert$ values have a maximum at $X = 2.5$, and then comes a drastic decrease with increasing X value. In the region of $2.2 < X < 2.5 \lvert\Delta H_a\rvert < \Delta H_d$ which agrees with the data obtained for ZrCrMn–H_2, $ZrMn_2$–H_2 and $Zr_{0.7}Mn_{0.3}Mn_2$–H_2 systems [8].

Rising the experimental temperature from 315 to 353 K (Figs. 3, 4) does not influence the shape of $\lvert\Delta H_{a(d)}\rvert$–$X$ dependence. The region boundaries stay practically the same, the β-hydride dissociation enthalpy value increases negligibly. At the same time the γ-hydride dissociation

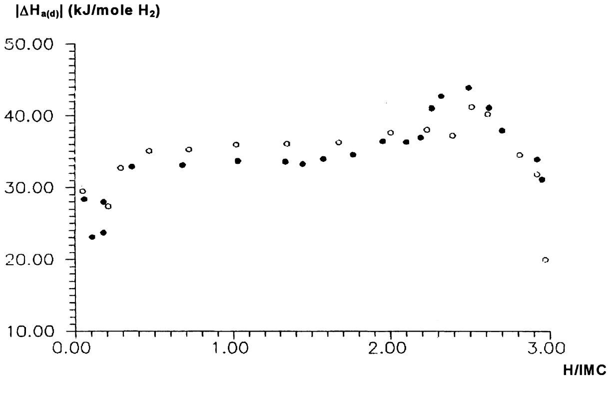

Fig. 2. Absorption (○) and desorption (●) enthalpy vs. composition at 315 K.

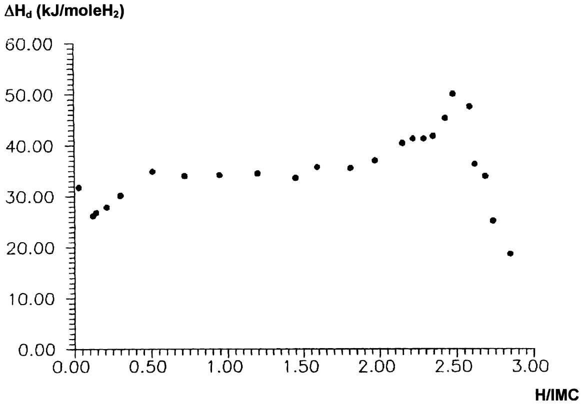

Fig. 3. Desorption enthalpy vs. composition at 338 K.

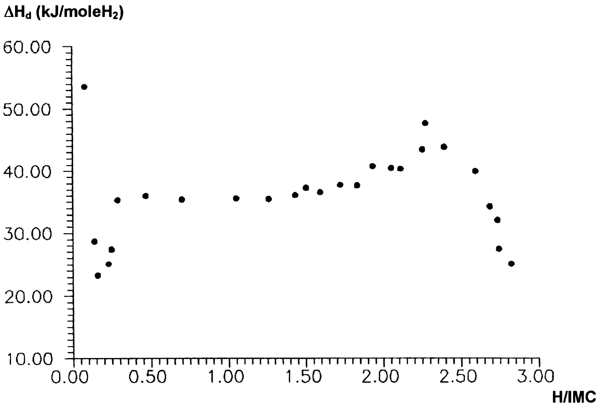

Fig. 4. Desorption enthalpy vs. composition at 353 K.

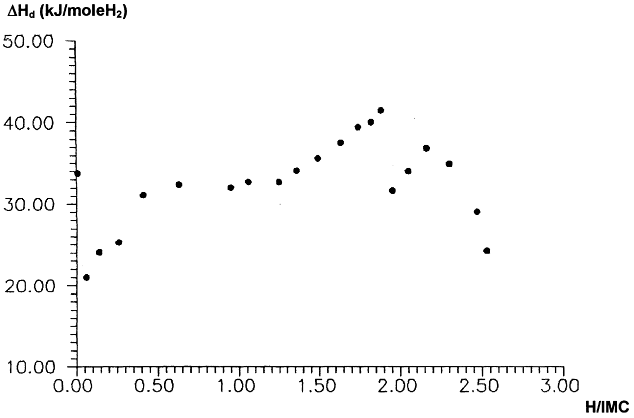

Fig. 5. Desorption enthalpy vs. composition at 393 K.

enthalpy value at 338 K reaches 41.2±0.3 kJ/mole H_2 and practically does not change up to 353 K.

Experiments at 393 K (Fig. 5) showed that a drastic collapse of a plateau region takes place from the side of hydrogen solution in hydride region, accompanied by a decrease of desorption enthalpy value to 32.2±0.4 kJ/mole H_2 and by disappearance of the plateau corresponding to γ-hydride in previous experiments. Such a behaviour of the system implies the fact that the critical temperature at which γ-hydride does not form is in the range of 353–393 K.

From data in Figs. 1 and 6 it is clear that at 473 K the tendency of the region boundaries shortening is continued, but mainly from the side of the hydrogen solution in intermetallic compound region. Meanwhile the ΔH_d value stays practically constant in a narrow range $0.8 \leq X \leq 1.4$ and almost coincides with the value at 315 K. Broadening up to $X = 0.8$ the region of hydrogen solution in intermetallic compound consists of two ranges of constant ΔH_d values 26.5±0.3 and 21.5±0.3 kJ/mole H_2 which are considerably lower than the values in plateau region. In view of the data from P–X-isotherms (Fig. 1) the assignment of these two ranges to the region of hydrogen solution in intermetallic compound is quite definite since there the P–X-dependence is linear. We have come across this phenomenon while studying $Zr_{0.8}Ti_{0.2}CrFe–H_2$ and $ZrCrFe–H_2$ systems [1,2]. Obviously, analogous to mentioned above systems, there exist several type of hydrogen solution in $ZrCrFe_{1.2}$ at 393 K.

Unfortunately we failed to obtain the full desorption isotherm at 523 K due to the value of dissociation pressure, corresponding to the plateau region in case of its existence, being higher than 60 atm. Still the obtained results for the

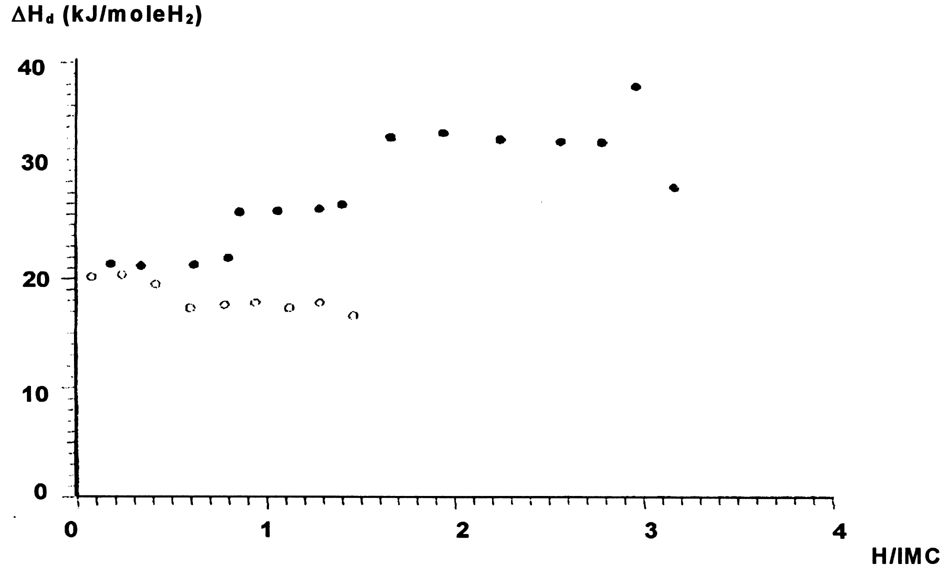

Fig. 6. Desorption enthalpy vs. composition at 473 K (●) and 523 K (○).

α-solution region (see Table 1 and Fig. 6) show that the decrease of the enthalpy value of hydrogen dissolution in intermetallic compound trends to decrease.

4. Conclusions

Calorimetric investigation of hydrogen interaction with $ZrCrFe_{1.2}$ allowed to ascertain the existence of two hydride phases with compositions $ZrCrFe_{1.2}H_{2-\delta}$ and $ZrCrFe_{1.2}H_{3-\delta}$ and to determine their thermodynamic parameters. The dissociation enthalpies of both hydride phases increase in the temperature range 315–353 K and for the $ZrCrFe_{1.2}H_{2-\delta}$ phase its dissociation enthalpy decreases at $T \geq 393$ K. The critical temperature for the $ZrCrFe_{1.2}H_{x>2.4}$ phase is in the range of 353–393 K. At higher temperatures, besides the hydride phase, two types of hydrogen solution in the intermetallic compound form with constant ΔH_d values, which decrease with increasing experimental temperature up to 523 K.

Acknowledgements

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