CALORIMETRIC INVESTIGATION OF THE HYDROGEN INTERACTION WITH $ZrMn_2$

Anikina E.Yu.*, Gerasimova E.V., Verbetsky V.N.
Chemistry Department, Lomonosov Moscow State University, 119899 Moscow, Russia
**E-mail: anikina@hydride.chem.msu.ru*

Introduction

Intermetallic compound (IMC) $ZrMn_2$ with the hexagonal C 14 structure, belonging to Laves phase, is the forefather of the large family of IMC AB_2-type, which are applied as materials for hydrogen storage and transportation. There are a lot of works devoted to study of $ZrMn_2$ structure, hydrogen storage capacity and thermodynamic parameters of $ZrMn_2$ – H_2 system. But in these works thermodynamic properties were studied in terms of van'Hoff plots, which suggest temperature independence of partial molar enthalpy (ΔH) of hydrogen reaction with $ZrMn_2$. The studies of $ZrMn_2$ – H_2 system, carried out by means of calorimetric method, are significantly less [1-8] and the data for changes of partial molar enthalpy of reaction $ZrMn_2$ with hydrogen are practically absent.

Result and discussion

The goal of our study was a research of $ZrMn_2$–H_2 system by means of calorimetric method in the wide range of temperatures (from 100 to 305° C) and hydrogen pressure up to 60 atm. We applied twin-cell differential heat-conducting calorimeter Tian-Calvet type, connected with the apparatus for gas dose feeding,, to measure the dependences of partial molar enthalpy for hydride formation and decomposition and equilibrium hydrogen pressure on hydrogen concentration in $ZrMn_2$ and on reaction temperatures.

It has been found that P–x isotherms (x = [H]/[IMC]) had sloping plateau (fig. 1), and the magnitude of sloping increased with a rise of temperature. It is interesting to note that P-x isotherms had a kind of fold in the region of concentrations x ≈ 1. For the |ΔH| – x isotherm at 100°C there is a region (0.3<x<1.9) of the constant magnitudes of $|\Delta H_d|$ = 39.7± 0.9 kJ/mol H_2. However, the character of this dependence changes with increasing temperature of experiment (fig. 2). On the isotherms |ΔH| - x at T> 100°C it is difficult to mark out a segment with constant values of |ΔH|.

We suggested that it may be connected with the order of filling to different interstitial sites of metallic matrix by hydrogen.

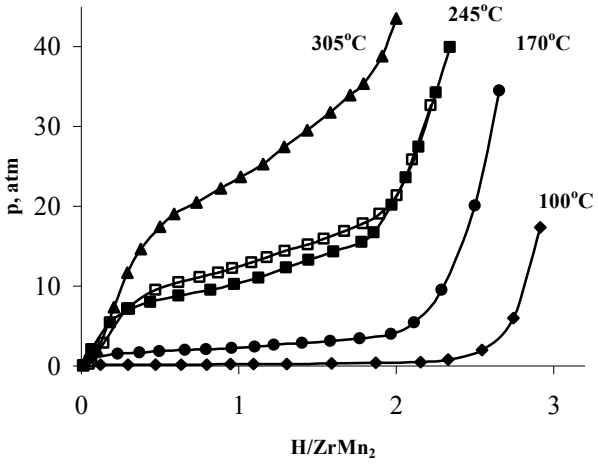

Fig.1. Isotherms of absorption (open symbols) and desorption (filling symbols) in the $ZrMn_2$-H_2 system.

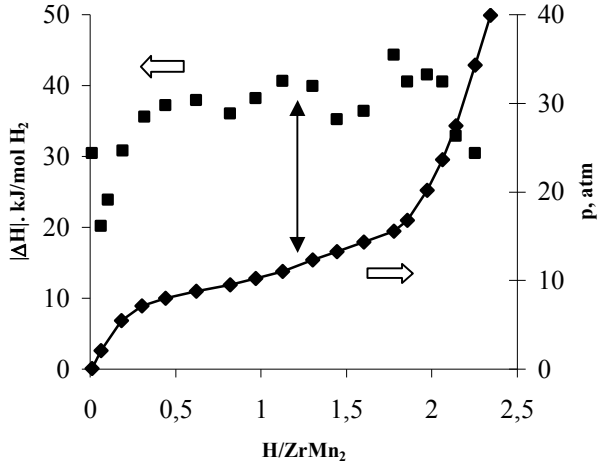

Fig.2. Calorimetric data and equilibrium pressures for the desorbtion of hydrogen for $ZrMn_2$ at 245°C.

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

References

1. Luo W., Majorowski S., Clewley J.D. and Flanagan T.B. (1989) The thermodynamics of the $ZrMn_{2+x}$ – hydrogen system, Z. Phys. Chem. 163, 81-86

2. Luo W., Clewley J.D., Flanagan T.B., Oates W.A., Thermodynamic characterization of the Zr-Mn-H system Part 1. Reaction of H_2 with single-

phase $ZrMn_{2+x}$ C-14 Laves phase alloys, Journal of Alloys and Compounds, 185 (1992) 321-338

3. Pourarian F., Sinha V.K., Wallace W.E., Pedziwiatr, A.T., Craig, R.S., Hydrogenation entropies of $ZrMn_{2+y}$ system., Proc.NATO Int.Symp.Elec.struct.prop.hydrogen met., 1983, p. 385-390

4. Pedziwiatr A.T., Craig R.S., Wallace W.E., Pourarian F. Calorimetric enthalpies of formation and decomposition of hydrides of $ZrMn_2$, $ZrCr_2$ and related systems, Journal of solid state chemistry, 46 (1983) 336-341.

5. Pourarian F., Sinha V.K.,. Wallace W.E., and Smith H.K. Kinetics and thermodynamics of $ZrMn_2$-based hydrides, Journal of the Less Common Metals, 1982, Vol 88, Issue 2, p. 451-458.

6. Krupenchenko A.V. and Magomedbekov E.P. Study of stability of intrmetallic compounds ZrB_2–type (B= V, Cr, Mn) at hydrogen interaction by equilibrium-calorimetric method, Russ. Zh. Neorganicheskoy khimii 1992 37 (1), p.174-181.

7. Krupenchenko A.V., Magomedbekov E.P., Andreev B.M. and Dyatlova O.V. (1991) Calorimetry of hysteresis transition in the $ZrMn_2$ – hydrogen system, Russ. Zh. Neorganicheskoi khimii 1994 39, (1), p.156-162.

8. Krupenchenko, A.V. and Magomedbekov, E.P. (1994) Hysteresis in the IMC system AB_2- type. Influence of IMC composition, hydrogen concentration in the solid phase and annealing, Russ. Zh. Neorganocheskoy khimii, 1994,39(1) 151-155.