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Journal of Alloys and Compounds 446–447 (2007) 443–446

Journal of ALLOYS AND COMPOUNDS

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Investigation of $ZrMn_{2+x}$-H_2 by means of calorimetric method

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Received 28 September 2006; received in revised form 21 December 2006; accepted 24 December 2006
Available online 18 January 2007

Abstract

The interaction of hydrogen with the $ZrMn_{2+x}$ ($x = 0$, 0.7) Laves phase compounds at pressure up to 50 atm and temperature range from 75 to 305 °C were studied by means of calorimetric and *P–C*-isotherm methods. On the base of obtained results it can be assumed that in the $ZrMn_{2+x}$-H_2 system one or two hydride phases exist according to experimental temperature.

Keywords: Intermetallic compounds; Hydride; Calorimetry; $ZrMn_{2+x}$

1. Introduction

There are a lot of works devoted to a research of thermodynamic parameters of the $ZrMn_{2+x}$-H_2 system. But in these works thermodynamic properties were studied in terms of van't Hoff plots, which suggest temperature independence of partial molar enthalpy (ΔH) of hydrogen reaction with $ZrMn_{2+x}$. The studies of the $ZrMn_{2+x}$-H_2 system, carried out by means of calorimetric method, are significantly less and the data for the changes of the partial molar enthalpy of the reaction $ZrMn_{2+x}$ with hydrogen concentration and experimental temperature are practically absent.

2. Experimental details

The starting alloys were prepared by arc melting a mixture of the metals (purity better than 99.99%) in argon atmosphere. The alloys buttons were turned over and remelted four times to ensure homogeneity. The alloy samples were annealed at 950 °C for 10 days in the sealed quartz ampoules in vacuo. The formation of the $ZrMn_2$, $ZrMn_{2.7}$ intermetallic compounds (IMC) and hydride of $ZrMn_2$ crystallising with the hexagonal $MgZn_2$ Laves phase structure were confirmed by powder X-ray diffraction with Thermo Ariel diffractometer using Cu Kα radiation. Small amounts of ZrO_2 were found as minor phases. The refined unit lattice parameters are: $a = 5.031$ Å, $c = 8.261$ Å for $ZrMn_2$; $a = 4.999$ Å, $c = 8.205$ Å for $ZrMn_{2.7}$ and they are in a good agreement with the reference data [1–3]. The chemical compositions of the starting alloys and their homogeneity also were examined by electron microscopy and electron probe analysis. These results indicate that the starting alloys were well-crystallized, homogeneous; single-phase samples with stoichiometry $ZrMn_2$ and $ZrMn_{2.7}$ or normalazed to AB_2 $Zr_{0.82}Mn_{0.18}Mn_2$. The twin-cell differential heat-conducting calorimeter Tian Calver-type, connecting with a conventional Sieverts-type apparatus for gas dosed feeding, was employed for calorimetric studies and determination of *P–C–T* data. The apparatus scheme was described elsewhere [4].

3. Results and discussion

3.1. P–C–T relationships

Figs. 1 and 2 present isotherms *P–C* (*P* = equilibrium pressure, $C = H/AB_2$) at different temperatures for $ZrMn_2$-H_2 and $ZrMn_{2.7}$-H_2 systems, respectively. As it could be seen from Figs. 1 and 2 the slopping plateaux in the two-phase region are the typical features of the $ZrMn_{2+x}$-H_2 systems, moreover the slope of these plateaux increase with rising of the experimental temperature and the region of two-phase equilibrium is shortened. Further compared the *P–C–T* plots, obtained for the $ZrMn_2$-H_2 system, with ones for the $ZrMn_{2.7}$-H_2 system it should be marked that increasing in x for $ZrMn_{2+x}$ leads to reduction of hydrogen capacity of IMC and increase in plateau slopping. It is known from reference data [1,3,5] that hydrogen atoms in the $ZrMn_{2+x}$ compounds with hexagonal Laves phase structure mainly occupy tetrahedral interstitial sites *24*(*l*), *12*$(k)_1$, *6*$(h)_1$ and *6*$(h)_2$ with $[Zr_2Mn_2]$. Increase in manganese content x for $ZrMn_{2+x}$ leads to decrease of amount of tetrahedral interstitial sites with $[Zr_2Mn_2]$, occupied hydrogen, and reduction of hydrogen capacity of these IMCs. As mentioned above for the $ZrMn_2$-H_2 system at 245 °C the *P–C* isotherms of absorption and desorption were obtained. It can be seen that

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doi:10.1016/j.jallcom.2006.12.146

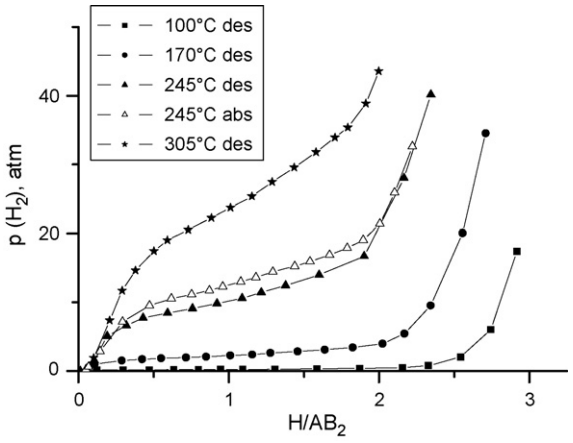

Fig. 1. Absorption and desorption isotherms for the $ZrMn_2$-H_2 system.

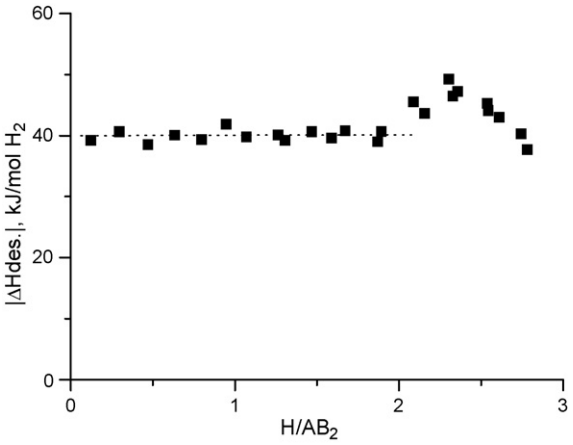

Fig. 3. Desorption enthalpy vs. composition for $ZrMn_2$ at 100 °C.

there is some pressure hysteresis. The value of this hysteresis at 245 °C is equal to approximately 2.5 atm, the dissipation of the free energy at hysteresis $RT\ln(Pf/Pd) = 0.88$ kJ/mol H_2, where Pf and Pd are the plateau pressure for absorption and desorption processes, respectively. It should be marked that the region of α-solid solution hydrogen in the $ZrMn_{2+x}$-H_2 system larger for $ZrMn_2$-H_2 than for the $ZrMn_{2.7}$-H_2 system.

3.2. Calorimetric results

The $|\Delta H_{des.}|$–C isotherms for $ZrMn_2$ are shown in Figs. 3–6. One can see that the $|\Delta H_{des.}|$–C dependences change with temperature. Fig. 3 presents the $|\Delta H_{des.}|$–C plot for the $ZrMn_2$-H_2 system at 100 °C. Since at 100 °C in the $ZrMn_2$-H_2 system there is initial region ($C < 0.125$), where the hydrogen pressures are negligibly small for the pressure gauge used here and so we could not obtain the P–C and $|\Delta H_{des.}|$–C isotherms for the dilute phase. As one can see from Figs. 4–6 with rising temperature the length of α-phase increase a little (from $0 < C < 0.2$ at 170 °C to $0 < C < 0.5$ at 305 °C). The enthalpy values in this region pass through the minimum and then increase up to the values of $|\Delta H_{des.}|_{plat.}$. The values of $|\Delta H_{des.}|_{min}$ and $\Delta H_{des.}|_{plat.}$ difference averages 20 kJ/mol H_2 that is in good agreement with

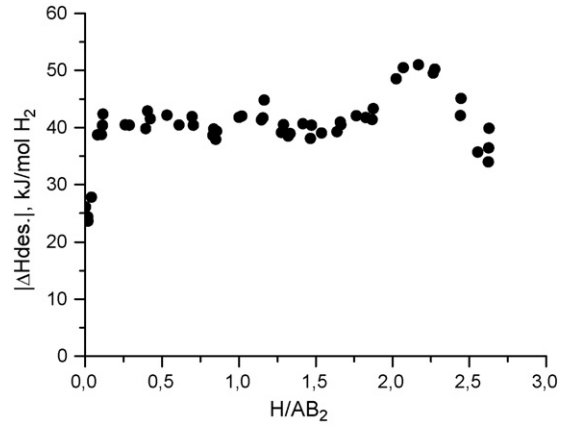

Fig. 4. Desorption enthalpy vs. composition for $ZrMn_2$ at 170 °C.

references data [6]. The presence of minimum in the dilute phase in the $|\Delta H_{des.}|$–C plots is typical for the $ZrMn_2$-H_2 system. Luo et al. [6] explained this phenomenon the presence of trapping sites in $ZrMn_2$, example, interstices surrounded by 3Zr and 1Mn rather than the usual occupied interstices with 2Zr and 2Mn atoms. A special attention should be devoted to the range of the α-solid solution ↔ hydride phase transition. In the $|\Delta H_{des.}|$–C

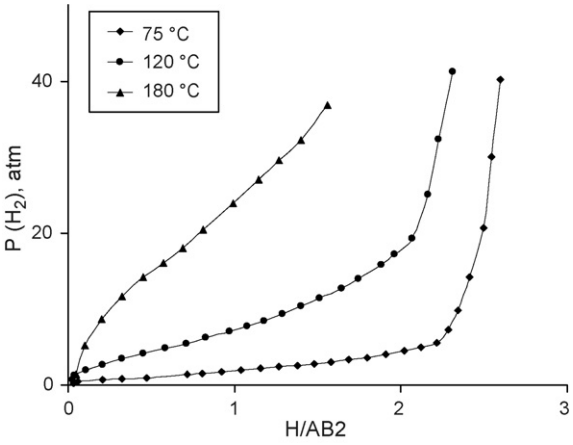

Fig. 2. Desorption isotherms for the $ZrMn_{2.7}$-H_2 system (AB_2-$Zr_{0.8}Mn_{0.18}Mn_2$).

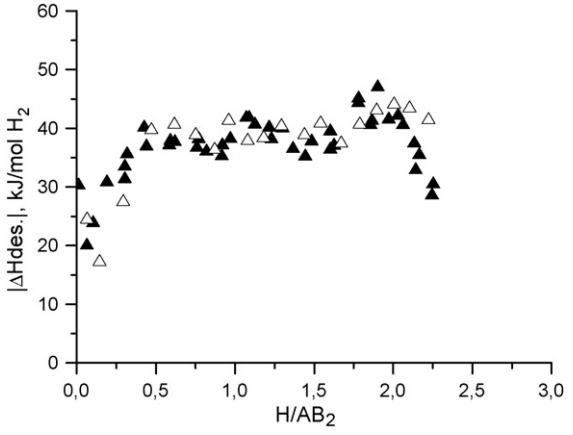

Fig. 5. Absorption and desorption enthalpies vs. composition for $ZrMn_2$ at 245 °C: (△) absorption, (▲) desorption.

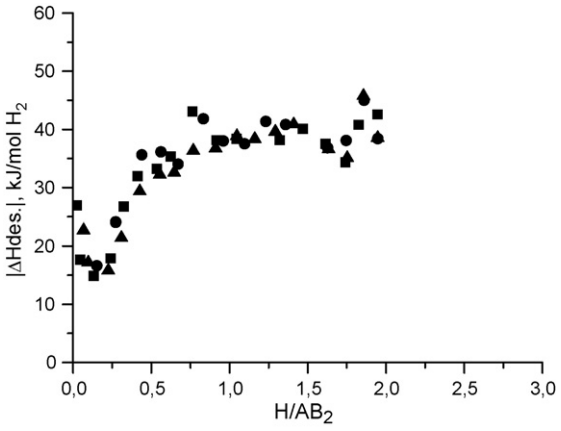

Fig. 6. Desorption enthalpy vs. composition for $ZrMn_2$ at 305 °C.

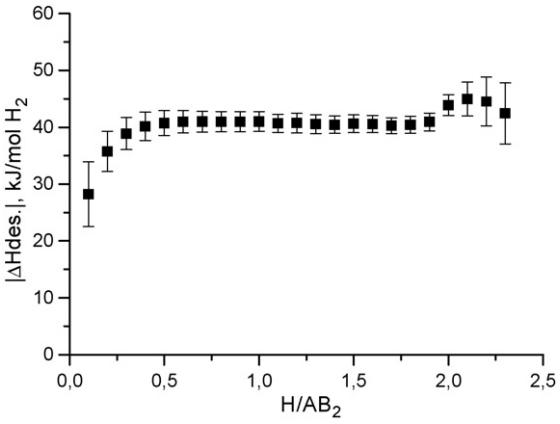

Fig. 7. Partial molar desorption enthalpy calculated from van't Hoff plot for $ZrMn_2$.

plot measured at 100 °C there is one region where the enthalpy values are constant (~40 kJ/mol H_2) that is the α ↔ β-transition ($C < 2.0$) occurs. It corresponds with the reference data good enough [6]. With rising of the experimental temperature from 100 to 170 °C the plot of the $|\Delta H_{des.}|$–C dependence changes its shape (Fig. 4). In comparison with the plot, obtained for 100 °C (Fig. 3), the values of enthalpy in the region $0.2 < C < 1.8$ does not remain constant, and the $|\Delta H_{des.}| = f(C)$ function acquires complex character. This region can be divided into two parts: $0.2 < C < 1.1$ and $1.1 < C < 1.8$. On the base of these results we assumed that there are two hydride phases in the $ZrMn_2$-H_2 system at 170 °C, namely, $ZrMn_2H$ – β_1-hydride and $ZrMn_2H_{2+Y}$ – β_2-hydride. Rising of the experimental temperature to 245 °C results in that the extension of the α-solid solution ↔ hydride phase region reductions and the boundaries between two states of hydride phase at 245 °C become more distinct. The boundaries of the α ↔ β_1 transition may be defined as $0.4 < C < 1.0$, and the β_1 ↔ β_2 transition as $1.0 < C < 1.8$. It should be noted that at 245 °C the values of the partial molar enthalpy do not remain constant within the limits of each two-phase region and once decrease slightly with increasing of C within the each transition (Fig. 5). As mentioned above for 245 °C the hydrogen absorption isotherm was obtained (Figs. 1 and 5). Compared the absorption and desorption isotherms one could see that hysteresis of the enthalpy values is absent in practice even for the range of H concentrations $1.8 < C < 2.5C$ for which in reference data [6] $|\Delta H_{des.}| > |\Delta H_{abs.}|$. As seen from Fig. 6 at 305 °C, the values of partial molar enthalpy for different runs of hydrogen desorption have a large deviation. Probably such behaviour of the $|\Delta H_{des.}|$–C dependence is explained by a proximity to critical temperature of the existence $ZrMn_2$ hydride phase estimated by different authors as 277–327 °C [6] and 318 °C [7], thus it is difficult to determine the phase boundaries. At 305 °C one can select the region of α-solid solution ($C < 0.5$), and then the enthalpy values increase droningly up to $C \sim 1.5$. As one can see from Figs. 3–6 there is maximum of the enthalpy values at high hydrogen concentrations in $ZrMn_2$. During the hydrogen desorption from the saturated hydride phase the $|\Delta H_{des.}|$ values increase, pass through maximum ($|\Delta H_{des.}| \sim 50$ kJ/mol H_2) and then gradually reduce until reach the $|\Delta H_{des.}|_{plat.}$ values. It is interesting to note that Luo et al. [6] studied hydrogen interaction with $ZrMn_{2+x}$ ($x = -0.2$, 0, 0.5 and 1.0) and the same shape of the $|\Delta H_{des.}|$–C dependences were observed for all researched IMC, but the biggest extension of this maximum is observed for $ZrMn_2$ (from $ZrMn_2H_{3.2}$ to $ZrMn_2H_{2.2}$, [6]). This gradual reduction of the $|\Delta H_{des.}|$ values at the time when α-phase has just appeared rather than sharp reduction to the $|\Delta H_{des.}|_{plat.}$ values are explained by the fact that crystal structure of forming α-phase still preserve the strains, induced during the hydride formation. As one can see from the results obtained in present work the extension of this maximum reduces with rising temperature.

The changes of the partial molar enthalpy for hydrogen desorption were calculated from the van't Hoff plots based on the measured P–C–T relations. The obtained $|\Delta H_{des.}|$–C dependence was plotted in Fig. 7. The shape of this plot is similar to one obtained for 100 °C in this work and those presented in [6] for 50 °C. In this plot, one can select the α-solid solution region of hydrogen in the $ZrMn_2$-H_2 system ($0 < C < 0.5$), the plateau region ($0.5 < C < 1.8$) and the region of the single hydride phase ($C > 1.8$). In the plateau region, the plot has some slopping. The values of the desorption enthalpy in the plateau range equal 40–41 kJ/mol H_2 and they slowly decrease with increasing H concentration, that is in good agreement with calorimetric results, obtained in present work, and references data [6]. Compared to the $|\Delta H_{des.}|$–C dependences obtained via calorimetric method and plotting of pressure–composition isotherms it should be noted that calorimetric method permits to understand the processes taking place in the studied system better.

Figs. 8–10 present the $|\Delta H_{des.}|$–C–T plots for the $ZrMn_{2.7}$-H_2 system at 75, 120 and 180 °C. As one can see from Fig. 8, the $|\Delta H_{des.}|$–C isotherm at 75 °C can be divided into four parts, namely, α-solid solution region ($0 < C < 0.1$), on which the values of $|\Delta H_{des.}|$ change from ~20 to ~34 kJ/mol H_2; next part is $0.2 < C < 1.2$ where the values of $|\Delta H_{des.}|$ are constant (~34 kJ/mol H_2), in this region it can be supposed the α ↔ β_1 transition, then there is the second region ($1.2 < C < 2.2$) with the constant values of $|\Delta H_{des.}|$ (~30 kJ/mol H_2), here it can be assumed the β_1 ↔ β_2 transition and at last the hydrogen solution in β_2-hydride. As one can see from Fig. 9 the $|\Delta H_{des.}|$–C plot, obtained at 120 °C, changes its shape in comparison with one,

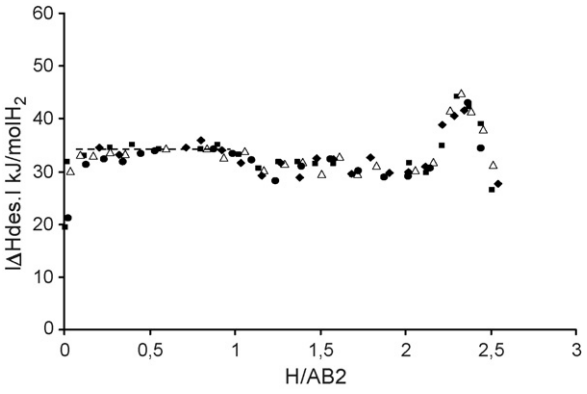

Fig. 8. Desorption enthalpy vs. composition for $ZrMn_{2.7}$ at 75 °C.

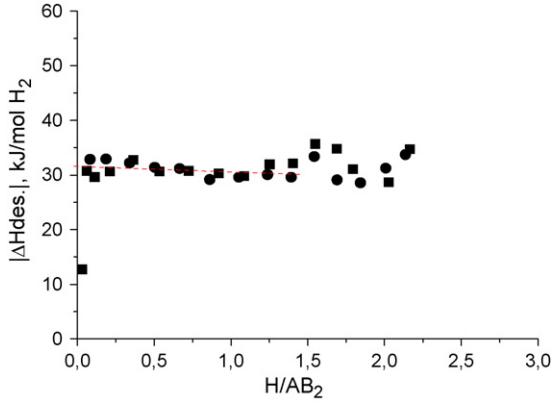

Fig. 9. Desorption enthalpy vs. composition for $ZrMn_{2.7}$ at 120 °C.

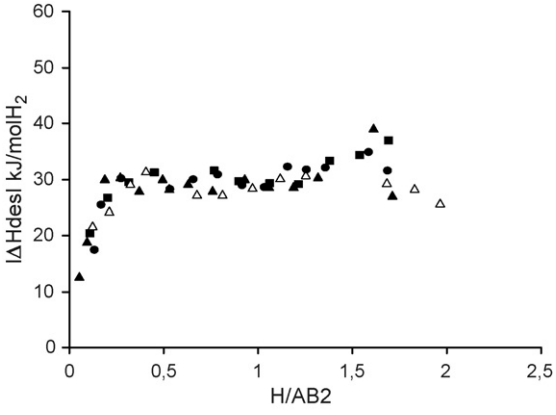

Fig. 10. Desorption enthalpy vs. composition for $ZrMn_{2.7}$ at 180 °C.

obtained at 75 °C, namely, following the minimum in enthalpy values in dilute phase the enthalpies increase to reach the plateau at $C = 0.2$. The $|\Delta H_{des.}|_{plat.}$ values decrease with increasing of C along the plateau ($0.2 < C < 1.5$). The average value of the enthalpy across the plateau is $|\Delta H_{des.}| \sim 30$ kJ/mol H_2. In other words there is one $\alpha \leftrightarrow \beta$ transition and hence one β-hydride forms in the $ZrMn_{2.7}$-H_2 system at 120 °C. On the $|\Delta H_{des.}|$–C isotherm measured at 180 °C it can mark out three ranges: α-solid solution region of hydrogen in IMC ($0 < C < 0.3$), the plateau region ($0.3 < C < 1.3$), where the enthalpies are constant (∼29 kJ/mol H_2), and then there is the range where the enthalpies values pass through the maximum. As one can see from Figs. 8–10 there are maxima in the plots of $|\Delta H_{des.}|$–C for the $ZrMn_{2.7}$-H_2 system after the $\beta + \alpha/\beta$ phase boundary. This phenomenon was marked for the $ZrMn_2$-H_2 system (see Figs. 3–6) but the extension of this maximum shortens with increasing x in the $ZrMn_{2+x}$ alloys (compare: for $ZrMn_2$ at 100 °C $1.8 < C < 2.7$, for $ZrMn_{2.7}$ at 75 °C $2.1 < C < 2.5$).

4. Conclusion

On the base of obtained data, it could be concluded that the composition of IMC and experimental temperature define the character of the interaction between $ZrMn_{2+x}$ and hydrogen. Thus, formation of two hydride phases in certain conditions is very possible, namely, we suppose that for the $ZrMn_2$-H_2 system the formation of two hydride phases is observed at high temperatures: 170 °C ($0.2 < C < 1.1$ $ZrMn_2H$ and $1.1 < C < 1.8$ $ZrMn_2H_{\sim 2}$) and 245 °C ($0.4 < C < 1.0$ $ZrMn_2H$ and $1.0 < C < 1.8$ $ZrMn_2H_{\sim 2}$), and vice versa for the $ZrMn_{2.7}$-H_2 system we observed the formation of two hydride phases at lower temperature (at 75 °C $0.2 < C < 1.2$ $ZrMn_{2.7}$-$H_{\sim 1}$ and $1.2 < C < 2.2$ $ZrMn_{2.7}$-$H_{\sim 2}$).

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