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Calorimetric Enthalpies of Formation and Decomposition of Hydrides of $ZrMn_2$, $ZrCr_2$, and Related Systems*

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Integral enthalpies of absorption and desorption of hydrogen by hyperstoichiometric $ZrMn_2T_{0.8}$ (T = Mn, Fe, Co, Ni, and Cu) and stoichiometric $ZrMn_2$- and $ZrCr_2$-based alloys have been determined. The measured enthalpies range from ~24 to ~41 kJ/mole H_2. The ΔH values for hydrides formed by the series of metallic hosts $ZrMn_2T_{0.8}$ are smaller than that for $ZrMn_2$, accounting for the enhanced dissociation pressures of the $ZrMn_2T_{0.8}$ hydrides. In the series of $ZrMn_2T_{0.8}$ hydrides there is a pronounced minimum for hydride of $ZrMn_2Co_{0.8}$, accounting for the extraordinarily high decomposition pressure of this system. Site occupancies, provided by published neutron diffraction studies, were used to calculate configurational entropies of $ZrCr_2$ hydrides and related systems. Results obtained were in fair agreement with experiment.

Introduction

ZrT_2-based alloys (T = Mn, Cr and V) readily hydrogenate to form very hydrogen-rich systems. The solubility of hydrogen in these alloys was established by Pebler and Gulbransen (*1*) and by Shaltiel *et al.* (*2*). They have been found to have excellent H_2 capacity but are too stable to be used as materials for hydrogen storage. Partial substitution of Zr by Ti in $ZrMn_2$ and $ZrCr_2$ alloys raises the dissociation pressure of these systems remarkably (*3–5*). Recently, van Essen and Buschow (*6*) and Pourarian *et al.* (*7*) studied the hyperstoichiometric $ZrMn_2$-based system in which the Mn/Zr ratio exceeded 2, vis, $Zr_{1-x}Mn_xMn_2$. It was found that the hyperstoichiometry markedly increased the dissociation pressure of the hydride. The dissociation pressures of the hydrides of the hyperstoichiometric alloys with the formula $ZrMn_2T_x$ (where T = Mn, Fe, Co, Ni, or Cu and $x = 0.8$) were recently reported by Pourarian and Wallace (*8*). Striking effects were noted. Dissociation pressure was increased in all cases, but there was a very sharp maximum in vapor pressure for T = Co. For example, the dissociation pressures of the hydride of $ZrMn_2Co_{0.8}$ exceed that of $ZrMn_2Fe_{0.8}$ by about a factor of 30. These materials exhibited not only good hydrogen capacity but excellent kinetics of H_2 absorption and desorption (*7, 9, 10*). In an earlier article (*11*) we have presented the calorimetric enthalpies of some $Zr_{1-x}Mn_xMn_2$–H_2 systems, where $x = 0.2$ and 0.4, for different hydride

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composition ranges. Results of hydrogenation entropies derived from the calorimetric measurements are found to be in good agreement with the computed configurational entropy values which were deduced from the data obtained by neutron diffraction studies (*12*).

In this article we present the calorimetric measurements of stoichiometric $ZrMn_2$, $ZrCr_2$, and several hyperstoichiometric $ZrMn_2$-based hydride systems. From these, entropies of hydrogenation were obtained and compared with calculated values of the configurational entropy of hydrogen in the $ZrCr_2$ hydrides.

Experimental

Sample Preparation

Metals of 99.9% purity were melted under a Ti-gettered flowing Ar atmosphere. Melting was accomplished by induction heating (to about 1500°C) in a water-cooled copper boat. Compositions were determined by synthesis. In the case of $ZrMn_2$-based alloys, the weight loss, which was ~5–8%, was all ascribed to Mn because of its much higher volatility. The nature of the solid was established by conventional powder X-ray diffraction techniques. All the alloy samples studied were single phase.

Hydride Preparation

The hydrides were activated by exposing them at room temperature (20–30°C) to hydrogen having a pressure in the range of 30 to 50 atm until hydrogen was no longer absorbed. The alloys generally absorbed hydrogen fully within a few minutes. The hydrogenation and dehydrogenation cycles were repeated 9 to 15 times before the calorimetric measurements were made.

Calorimetry

The experiments were carried out in a calorimeter constructed from a 500-ml Dewar flask. The flask was provided with a motor-driven stirrer, a thermistor, and a heater. The latter, of Evanohm wire (obtained from the Wilber B. Driver Co., Newark, N.J.) had a resistance of about 100 ohms, which was essentially constant in the range 273–320°K. The sample (usually about 2.5 g) was held in a cylindrical brass container provided with an O-ring closure and supported in the water in the Dewar vessel by a thin-walled stainless steel tube about 1.5 mm in diameter. The tube was connected to a pressure gauge and valving system so that the container could either be evacuated or filled with hydrogen from a cylinder.

The thermistor constituted one arm of a Wheatstone bridge which was powered by a 1.5-V cell and employed a strip-chart recorder (1 mV full scale) to indicate the condition of balance. A change in the resistance of the thermistor caused a proportional change in the deflection of the recorder pen, and full-scale deflection corresponded to approximately 0.1°.

At the beginning of a determination the temperature of the calorimeter (containing the sample in its initial state) was increasing at a constant rate (typically about 0.005°/min) because of the heat of stirring. After the initial rate was established, hydrogen was admitted and the temperature rose sharply. After 2 or 3 min the rate resumed its initial constant value. The deflection of the recorder pen corresponding to the heat of the reaction was found by extrapolating the initial rate to the region where the final rate had again become constant. The temperature rise was generally 0.1 to 0.2°. After each run a calibration was carried out by recording the deflection produced by an accurately measured amount of Joule heat. The heat effect accompanying the compression of hydrogen gas in the sample chamber was determined by blank experiments. Experiments to measure the heat of desorption were similar to adsorption experiments except that the reaction was initiated by lowering pressure over the hydride.

It is an interesting feature of metal hydride systems that the heat effects can be determined for both the forward and reverse reactions. While this possibility is not unique, it is relatively rare.

Experimental error was mainly due to the extrapolation procedure described above. This is estimated to contribute less than 1.5% error to the measured heat effect. Error resulting from the difference between the temperatures of hydrogen gas and of the sample was measured to be less than 1.0%. Absolute error associated with determination of the amount of hydrogen gas absorbed by the sample in each experiment is established to be about ±0.0015 mmole. In this work it was assumed that ΔH is equal to the measured heat effect while the calorimetric process does not occur at constant pressure and hence the measured heat effect is not strictly equal to ΔH. Estimates of the error resulting from the assumption that the ΔH and heat effect are identical indicate that it is very small, ranging from 0.1 to 0.25%. The total experimental error in ΔH is therefore estimated to be less than 4%.

Results and Discussion

The measured enthalpies of absorption (ΔH_a) and desorption (ΔH_d) are given in Table I. It is to be noted that ΔH_a and ΔH_d values do not differ greatly for most of the hydrides studied. Results for $ZrMn_2T_{0.8}$ (T = Mn, Fe, Co, Ni, and Cu) exhibit remarkable behavior in the sense that both ΔH_a and ΔH_d show a minimum for the hydride $ZrMn_2Co_{0.8}$ (Fig. 1). The result is consistent with the fact that the hydride of this alloy exhibits the highest vapor pressure (*8*). The phenomenon suggests that Co has a particular effect on the band structure in $ZrMn_2$ when it enters the lattice by partial replacement of Mn and/or Zr. Results for hydrides of $ZrMn_2$, $ZrCr_2$, $Zr_{0.75}Ti_{0.25}Mn_{1.1}Fe_{0.9}$, and $ZrCr_{0.6}Fe_{1.4}$, which correspond to Laves phase stoichiometry, are given in Table I. Data for $LaNi_5$–H_2 were also determined for comparative purposes. The ΔH value for this hydride is in good agreement with that obtained by Bowerman *et al.* (*13*) using a similar calorimeter. Shaltiel *et al.* (*2*) report a value of −53 kJ/mole H_2 for the absorption of hydrogen by $ZrMn_2$. These investigators have also evaluated the heat of hydrogenation of $ZrCr_2$

TABLE I

CALORIMETRIC ENTHALPIES OF ABSORPTION AND DESORPTION AT 23°C

Alloy	$-\Delta H_a$ (kJ/mole H_2)	ΔH_d (kJ/mole H_2)	No. of measurements
$ZrMn_2Mn_{0.8}$	32.9	29.9	8
$ZrMn_2Fe_{0.8}$	25.9	25.0	7
$ZrMn_2Co_{0.8}$	23.8	20.9	7
$ZrMn_2Ni_{0.8}$	26.4	25.0	6
$ZrMn_2Cu_{0.8}$	35.9	31.6	6
$ZrMn_2Mn_{1.8}$	29.8	—	10
$Zr_{0.75}Ti_{0.25}Mn_{1.1}Fe_{0.9}$	30.2	29.4	7
$ZrCr_{0.6}Fe_{1.4}$	29.1	28.5	7
$ZrMn_2$	40.4	38.0	7
$ZrCr_2$	39.2	36.4	7
$LaNi_5$[a]	32.2	30.0	11

[a] Results determined for comparative purposes.

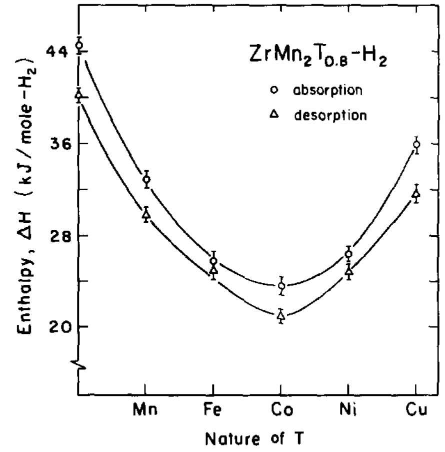

FIG. 1. Absolute values of the enthalpies of absorption and desorption of hydrogen by the $ZrMn_2T_{0.8}$ systems, T = Mn, Fe, Co, Ni, and Cu. The leftmost points pertain to the stoichiometric material $ZrMn_2$.

from the measurements of Pebler and Gulbransen (*1*); they obtained for this system −46 kJ/mole H_2. These data are obtained by the use of the Van't Hoff expression for pressure-composition isotherms measured at various temperatures. The ΔH values obtained in this way differ significantly from the calorimetric results given in Table I. There are at least two factors which may contribute to the observed differences: (1) The thermodynamic processes are different in the two cases in that initial and final states in the calorimetric process are not precisely the same as that involved in the Van't Hoff expression: (2) The use of the Van't Hoff expression entails the assumption that the system is behaving reversibly, whereas the systems invariably exhibit hysteresis effects in the pressure-composition isotherms and hence they are not behaving reversibly. Perhaps both factors are involved.

The integral entropy of desorption is readily computed from the expression $\ln P_{H_2} = -\Delta H°_d/RT + \Delta S°_d/R$ and the known dissociation pressure of the hydride. Assuming that the measured values of ΔH_d are a reasonable approximation of $\Delta H°_d$, the $\Delta S°_d$ values given in Tables II and III were calculated. In making this calculation it is necessary to regard the measured desorption pressure as the equilibrium pressure. However, because of the hysteresis effect alluded to in the previous paragraph, this is not strictly correct. (The $ZrCr_2$–H_2 system is an exception in this respect in that no hysteresis was observed by Pebler and Gulbransen (*1*).) Even so, because P_{H_2} is in all cases of the order of unity, the error introduced from this source is very slight, but the procedure employed does represent a slight overestimate of $\Delta S°_d$.

Using $\Delta S°_d$ to estimate the effective entropy of hydrogen in the metal, $S°_{H_2(g)} - \Delta S°_d$, one obtains for the hyperstoichiometric systems values ranging from ~18 to 26 J $(°K)^{-1}$ $(\text{mole H})^{-1}$. This is considerably larger than the corresponding value for the hydride of $LaNi_5$. Since this entropy is largely configurational in nature, it suggested that the hyperstoichiometric systems are more highly disordered than $LaNi_5H_6$, whose configurational entropy was recently quantitatively accounted for by Wallace *et al.* (*14*).

$ZrCr_2$ hydrides were treated using the

TABLE II

ENTROPIES OF DESORPTION AND EFFECTIVE HYDROGEN ENTROPIES FOR $ZrMn_2T_{0.8}$ HYDRIDES (T = Mn, Fe, Co, Ni, and Cu)

Alloy	Hydride comp. (g · atom H per mole alloy)	Pressure (atm)	Enthalpy ΔH_d (kJ/mole H_2)	Entropy ΔS_d (J/mole H_2 °K)	$\frac{1}{2}(S°\ H_2 - \Delta S_d)$ (J/mol H °K)
$ZrMn_2Mn_{0.8}$	1.0	0.31	29.9	91.3	19.7
	2.0	0.44		94.2	18.2
$ZrMn_2Fe_{0.8}$	1.5	0.47	25.0	78.2	26.2
	2.0	1.35		87.0	21.8
$ZrMn_2Co_{0.8}$	1.0	4.0	20.9	82.1	24.5
	1.5	6.5		86.2	22.2
$ZrMn_2Ni_{0.8}$	1.0	1.6	25.0	88.4	21.1
	1.5	2.5		92.1	19.3
$ZrMn_2Cu_{0.8}$	1.0	0.06	31.6	83.4	23.6
	2.0	0.06		83.4	23.6

TABLE III

ENTROPIES OF DESORPTION AND EFFECTIVE HYDROGEN ENTROPIES OF HYDRIDES OF SEVERAL STOICHIOMETRIC HYDROGEN STORAGE MATERIALS

Alloy	Hydride comp. (g · atom H per mole alloy)	Pressure (atm)	Entropy ΔS_d (J/mole H_2 °K)	Entropy ΔS_d (J/mole H_2 °K)	$\frac{1}{2}(S^\circ H_2 - \Delta S_d)$ (J/mole H °K)
$Zr_{0.75}Ti_{0.25}Mn_{1.1}Fe_{0.9}$	1.0	0.9	29.4	98.45	16.1
	2.0	1.2		100.8	14.9
$ZrCr_{0.6}Fe_{1.4}$	1.0	0.8	28.5	94.45	18.1
	2.0	0.85		94.95	17.8
$LaNi_5$[a]	6	1.7	30.0	101.1	14.8

[a] Included for comparison purposes.

method set forth by Wallace *et al.* (*14*). The needed sites occupancy information was provided by the neutron diffraction study of Fruchart *et al.* (*15*). Wallace *et al.* showed that the configurational entropy S^c can be obtained from the expression

$$S^c = -R \sum_i g_i \{\theta_i \ln \theta_i + (1 - \theta_i) \ln(1 - \theta_i)\},$$

where g_i is the multiplicity of the *i*th site and θ_i is its fractional occupancy. According to the neutron diffraction results, only the 96*g* positions are occupied. Using the site occupancy data θ, for the deuteride of $ZrCr_2$ with compositions $ZrCr_2D_{2.89}$, $ZrCr_2D_{3.08}$, and $ZrCr_2D_{3.8}$ the computed S^c values are 19.0, 18.4, and 16.3 J/mole H K°, respectively. The corresponding experimental values for $ZrCr_2D_{2.89}$ and $ZrCr_2D_{3.08}$, obtained using the ΔH_d values measured in the present work combined with measurements of vapor pressure by Pebler and Gulbransen (*1*), are ~18 and 14 J $(°K)^{-1}$ (mole $H)^{-1}$. (Calculations cannot be made for $ZrCr_2D_{3.8}$ since this exceeded the range covered by Pebler and Gulbransen.)

The experimental entropy of the hydride of $ZrCr_{0.6}Fe_{1.4}$ is in the same range as that of $ZrCr_2$ hydride, suggesting that replacement of Cr by Fe does not significantly alter the group of sites occupied by hydrogen. Under this assumption, $ZrCr_{0.6}Fe_{1.4}H_2$ has a configurational entropy of 22.5 J $(°K)^{-1}$ (mole $H)^{-1}$ which compares reasonably well with the experimental value, 17.8 J $(°K)^{-1}$ (mole $H)^{-1}$ listed in Table III. In the earlier study (*11*), the computed configurational entropy of $ZrMn_2D_{2.75}$ was found to be 18.3 J $(°K^{-1})$ (mole $H)^{-1}$. This is also close to the value determined for $Zr_{0.75}Ti_{0.25}Mn_{1.1}Fe_{0.9}$ hydride and in the general range of the values obtained for the $ZrMn_2T_{0.8}$ hydrides, which suggests that the site occupancy of hydrogen in these $ZrMn_2$-derived systems may be rather similar to that in $ZrMn_2$.

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