JOURNAL OF SOLID STATE CHEMISTRY 74, 132–137 (1988)

Hydrogenation Characteristics of the Isoelectronic Alloys $ZrMn_2$, ZrCrFe, and ZrVCo*

L. Y. ZHANG† AND W. E. WALLACE

The Advanced Materials Corporation, c/o Mellon Institute, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213-2683

Received August 17, 1987; in revised form November 30, 1987

The hydride forming behavior of the isoelectronic alloys $ZrMn_2$, ZrCrFe, and ZrVCo was studied. All of the host alloys and hydrides crystallize in the C14-type crystal structures. Pressure–composition isotherms (PCIs) were determined for temperatures of 22, 50, 150, and 200°C. The standard thermodynamic quantities were derived from measured PCIs and from calorimetric measurements. ZrVCo, ZrCrFe, and $ZrMn_2$ have approximately the same hydrogen capacities at room temperature. However, the stabilities are quite different. The standard free energy changes, ΔG_d, are 5.75, 13.60, and 19.30 kJ/mole · H_2 for decomposition of the hydrides of ZrCrFe, $ZrMn_2$, and ZrVCo, respectively. The hydrogen capacities and the stabilities for these isoelectronic materials increase with the order of ZrCrFe, $ZrMn_2$, and ZrVCo. This is in accordance with the order of the unit cell volumes of the alloys.

Introduction

It was established a few years ago that the hexagonal Laves phase compounds $ZrMn_2$ and ZrCrFe can incorporate extra 3*d*-transition elements (T) in the lattice (*1–5*). Hydrogenation and magnetic characteristics of these two nonstoichiometric systems $ZrMn_2T_x$ and $ZrCrFeT_x$ were observed to be very similar (*5–9*). Since these are isoelectric materials, it appeared that the hydrogenation characteristics might be essentially identical for chemically similar and isoelectronic Laves phases systems. To test this hypothesis, the hydrogenation characteristics of the isoelectronic triplet $ZrMn_2$, ZrCrFe, and ZrVCo were examined. Results obtained are presented in this paper. Pressure–composition isotherm (PCI) curves are presented along with derived thermodynamic quantities ΔH, ΔS, and ΔG. In addition, calorimetrically determined ΔH values for absorption and desorption are presented for some of the systems.

Experimental Details

1. Sample Preparation

Zirconium and the transition elements (purity, 99.9%) were induction melted in a water-cooled copper boat under a Ti-gettered Ar atmosphere using an r.f. generator. Compositions were determined by synthesis. In the case of the $ZrMn_2$ alloy, because of the volatility of Mn, 5 wt% extra

---

* A portion of the work was performed at the University of Pittsburgh.

† Current address, Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.

0022-4596/88 $3.00

Mn was added. These samples were held molten for a time interval to secure the proper stoichiometry as judged by the weight of the sample after melting. The time interval needed was established in preliminary experiments. The samples were then heat treated for 3 hr at 1000–1100°C.

The structure and homogeneity of the prepared compounds were determined by powder X-ray diffraction. Excellent patterns (narrow lines with high intensity) were obtained for all the systems studied. This and the analysis of the patterns indicated that all the alloy samples were single phase.

2. *Hydride Preparation*

Before hydrogenation, the system containing the sample was flushed with hydrogen up to five times and was evacuated each time to 10^{-6} atm. The alloys were activated by exposing them first at room temperature to hydrogen having a pressure in the range 50–60 atm until hydrogen no longer absorbed, followed by several hydrogenation and dehydrogenation cycles to insure a well-defined active surface. The activated alloys generally absorbed hydrogen fully within a few minutes. To obtain the crystallographic data, the hydrides were poisoned by SO_2, using the technique of Gualtieri *et al.* (*10*). The SO_2-poisoned hydrides were not pyrophoric in air, although before poisoning, they had been converted into a fine powder because of hydride forming.

3. *Measurement of PCI*

PCIs of hydrogen desorption were established by conventional gasometric techniques. The PCIs were determined for temperatures between 22 and 200°C, and the initial pressures were 34.1 atm (500 psi) for all measurements. For all of these samples the PCIs were measured at pressures above and below atmospheric pressure. The amount of time needed for the equilibrium pressure to be reached ranged from 4 to 24 hr, depending on the temperature at which the PCI was measured. The quantity of hydrogen removed and amount of gaseous hydrogen remaining were calculated, utilizing the Beattie–Bridgeman equation of state. A Hoskins tube furnace was used for high temperature PCI measurements. The temperature of the sample chamber was regulated to approximately ±0.5°C using a VFI temperature programmer.

4. *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 thermister, and a heater. The detailed structure and operation of this device are described elsewhere (*11*). The total experimental error in ΔH is estimated to be less than 4%.

Experimental Results

Crystal Structures

All three host metals crystallize in the C_{14} ($MgZn_2$) structure with unit cell size increasing in the order ZrCrFe to $ZrMn_2$ to ZrVCo. Lattice parameters for the host metals and their hydrides are shown in Table I. By X-ray diffraction the hydrides appear to form in the C_{14} structure. Hydrogenation is accompanied by about a 20% increase in unit cell size. The first two materials show a larger expansion in the basal plane than along the unique axis. For ZrVCo the expansion is nearly isotropic. The anisotropic expansion of ZrCrFe and $ZrMn_2$ indicates preferential interstitial site occupancy by hydrogen in these materials (*12*). ZrVCo has the largest unit cell volume of three alloys studied. As might be expected at the fixed hydrogenation pressure (500 psi), it has the highest hydrogen capacity.

TABLE I

HYDROGEN CAPACITY AND CRYSTAL STRUCTURE PARAMETERS

Host alloy[a]	Mole weight	Structure	a_0 (Å)	c_0 (Å)	V_0 (Å^3)	c/a	Hydride	Structure	a (Å)	c (Å)	V (Å^3)	$\Delta V/V_0$ (%)	c/a
ZrCrFe	199.06	C14	5.029	8.258	180.87	1.64	$ZrCrFeH_{3.3}$	C14	5.314	9.707	215.34	19.1	1.629
$ZrMn_2$	201.096	C14	5.030	8.370	181.21	1.644	$ZrMn_2H_{3.6}$	C14	5.442	8.848	226.93	25.2	1.627
ZrVCo	201.094	C14	5.073	8.282	184.59	1.633	$ZrVCoH_{3.8}$	C14	5.404	8.861	224.18	22.1	1.638

[a] The initial pressure applied to these isoelectronic materials to form hydrides are the same: 34.1 atm (500 psi).

Pressure–Composition Isotherms and Thermodynamic Properties

These data are shown in Figs. 1–3. Recognizable plateau regions are observed for ZrCrFe and $ZrMn_2$, but not for ZrVCo. Hydrides of ZrCrFe and $ZrMn_2$ generate a two-phase system. This does not happen for ZrVCo, at least in the pressure–temperature region studied. Perhaps a two-phase region develops at lower temperatures and/or pressures. All three systems form stable hydrides at room temperature, in that the decomposition pressure is less than 1 atm.

Thermodynamic properties (ΔH, ΔS, and ΔG) were derived from the van't Hoff relationship,

$$\ln P = -\frac{\Delta H_d}{RT} + \Delta S_d/R,$$

where P = hydrogen decomposition pressure and ΔH_d and ΔS_d are the enthalpies and entropies of decomposition, respectively. Results obtained, computed at 298 K, are shown in Tables II–IV. Mean values are shown in Table V.

Calorimetry and Thermodynamic Properties

The measured enthalpies of absorption (ΔH_a) and desorption (ΔH_d) are shown in

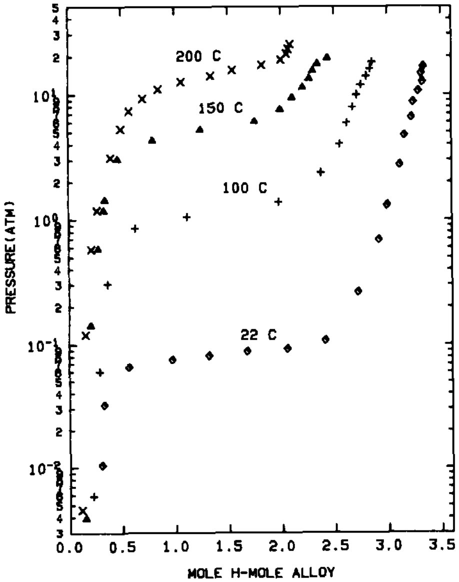

FIG. 1. Pressure–composition isotherms for ZrCrFe.

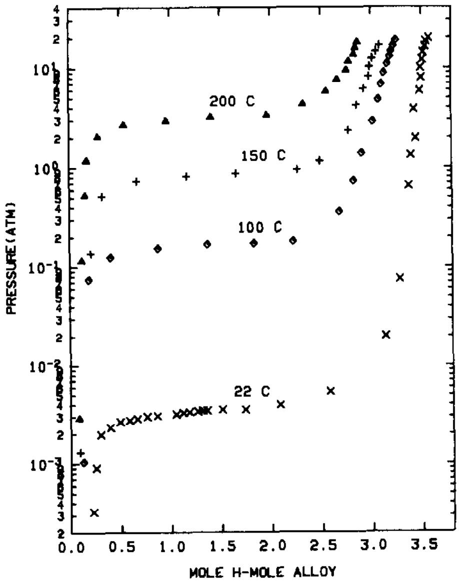

FIG. 2. Pressure–composition isotherms for $ZrMn_2$.

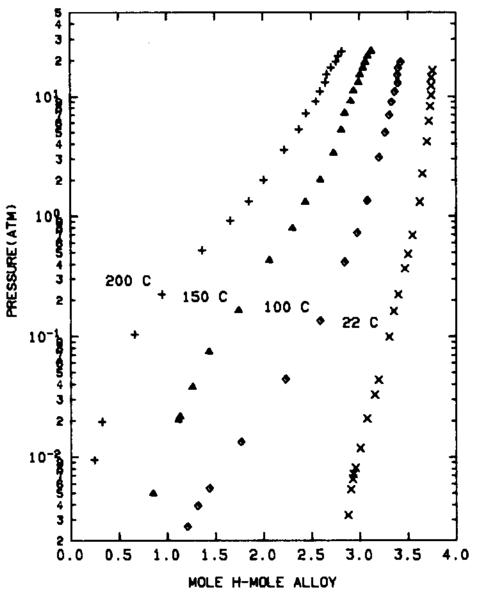

FIG. 3. Pressure–composition isotherms for ZrVCo.

Table VI. It is to be noted that ΔH_a and ΔH_d differ, but this is not unexpected since these systems exhibit hysteresis. By combining the observed decomposition pressure with the calorimetrically measured ΔH_d values, one can calculate calorimetrically derived thermodynamic quantities. These are shown in Table VI.

Discussion of Results

The ΔH_d values obtained from the PCI curves and from calorimetry agree within experimental error for the hydrides of $ZrMn_2$ and ZrCrFe, but not for the hydride of ZrVCo. The disagreement for the ZrVCo hydrides follows because the PCI determinations for this system are inherently more susceptible to experimental error than the determinations for ZrCrFe and $ZrMn_2$ hydrides. This originates with the absence of a plateau region in the ZrVCo–H_2 system. Experimental error is suppressed in a plateau region since a slight mistake in composition does not affect pressure, which is compositionally invariant. This is not the case for the situation which occurs in the ZrVCo–H_2 system. It is likely that the calorimetrically derived quantities are more reliable in this latter system. Another source of disagreement between the results in Tables V and VI is that the hydrogen content is different. This is not important for the $ZrMn_2$ and ZrCrFe hydrides since ΔH_d varies only slightly with composition. It is a

TABLE III

THERMODYNAMIC PROPERTIES OF $ZrMn_2H_x$ AT 298 K

Composition	ΔH_d (kJ/mole H_2)	ΔS_d (J/K · mole H_2)	ΔG_d (kJ/mole H_2)
$ZrMn_2H_{0.5}$	45.2	103.5	14.3
$ZrMn_2H_{1.0}$	44.8	104.1	13.8
$ZrMn_2H_{1.5}$	44.3	103.5	13.5
$ZrMn_2H_{2.0}$	44.1	103.4	13.3
$ZrMn_2H_{2.5}$	44.8	107.8	12.6
Mean value	44.6	104.5	13.5

TABLE II

THERMODYNAMIC PROPERTIES OF $ZrCrFeH_x$ AT 298 K

Composition	ΔH_d (kJ/mole H_2)	ΔS_d (J/K · mole H_2)	ΔG_d (kJ/mole H_2)
$ZrCrFeH_{0.5}$	30.0	78.8	6.5
$ZrCrFeH_{1.5}$	33.3	91.0	6.2
$ZrCrFeH_{1.5}$	34.1	94.6	6.0
$ZrCrFeH_{2.0}$	35.0	98.4	5.7
Mean value	33.1	90.7	6.1

TABLE IV

THERMODYNAMIC PROPERTIES OF $ZrVCoH_x$ AT 298 K

Composition	ΔH_d (kJ/mole H_2)	ΔS_d (J/K · mole H_2)	ΔG_d (kJ/mole H_2)
$ZrVCoH_{1.5}$	67.5	139.3	26.0
$ZrVCoH_{2.0}$	64.9	142.8	22.3
$ZrVCoH_{2.5}$	63.8	152.6	18.3
$ZrVCoH_{3.0}$	56.0	151.8	10.7
Mean value	63.0	146.2	19.4

TABLE V

MEAN VALUES OF THERMODYNAMIC PROPERTIES

Hydride	ΔH_d (kJ/mole H_2)	ΔS_d (J/K · mole H_2)	ΔG_d (kJ/mole H_2)
$ZrCrFeH_{2.0}$	35.0	98.4	5.7
$ZrMn_2H_{2.5}$	44.8	107.8	12.6
$ZrVCoH_{3.0}$	56.0	151.8	10.7

more likely source of discrepancy for the ZrVCo hydrides since in this system ΔH_d depends significantly on composition.

Isido *et al.* (*13*) made PCI measurements on $ZrMn_2$ hydrides and deduced ΔH_d from van't Hoff plots. They obtained ΔH_d of 39 kJ/mole H_2, about 13% lower than those obtained in this study. The present results seem more reliable judging from the observed PCIs. The data in Fig. 2 show well-defined plateaus whereas the PCIs of Isido *et al.* (*13*) showed barely discernible plateaus. Therefore, doubt exists in regard to the quality of their host alloys and/or their measuring technique.

The data in Table V show that the release of hydrogen from the lattice is endothermal for each of the three host alloys. The decomposition free energy (ΔG_d) increases, as noted earlier, in the sequence $ZrCrFe–H_2 < ZrMn_2–H_2 < ZrVCo–H_2$. This is the same as the order of the size for the unit cell for the host alloys. The relationship between stability (as measured by ΔG_d or $-RT\ln P_H$) and unit cell dimensions follows because of the Lundin Correlation (*14*). Lundin related stability to the size of the interstitial hole which is occupied by hydrogen. In a family of related hydrogen host materials, as the size of the interstice increased, the stability of the hydride increased. Since the size of the interstice increases as the unit cell size increases, it follows that the Lundin Correlation is equivalent to the assertion that ΔG_d parallels the size of the unit cell.

Summary

ZrVCo, ZrCrFe, and $ZrMn_2$ all absorb hydrogen to roughly the same extent. The host metals and hydrides appear by X-ray diffraction examination to be isostructural. The hydrides are stable at room temperature in that the dissociation pressure is <1 atm. The hydride of ZrVCo is most stable; that of ZrCrFe is least stable. This reveals that while the three host alloys are isostructural and possess equal numbers of *d*-electrons, their hydride forming behaviors are not identical. The three systems studied exhibit behavior which accords with the Lundin Correlation (*14*).

TABLE VI

ENTHALPIES OF ABSORPTION AND DESORPTION DERIVED FROM CALORIMETRIC MEASUREMENT

Hydride	ΔH_a (kJ/mole H_2)	ΔH_d (kJ/mole H_2)	ΔS_d (J/K · mole H_2)	ΔG_d (kJ/mole H_2)
$ZrCrFeH_{3.3}$	34.1	35.7 (3)[a]	100.6	5.8
$ZrMn_2H_{3.6}$	43.3	45.4 (6)	106.6	13.6
$ZrVCoH_{3.8}$	50.9	52.4 (3)	115.0	18.1

[a] The quantity in parentheses is the number of calorimetric measurements made.

Acknowledgment

The authors acknowledge the benefits of many useful discussions with Dr. F. Pourarian.

References

1. R. M. van Essen and K. H. J. Buschow, *Mater. Res. Bull.* **15,** 1149 (1980).
2. F. Pourarian, H. Fujii, W. E. Wallace, and H. Kevin Smith, *J. Phys. Chem.* **85,** 3105 (1981).
3. W. Bruckener, K. Kleinstuck, and G. E. R. Schulze, *Phys. Status Solidi* **23,** 415 (1967).
4. W. H. Pechin, D. E. Williams, and W. L. Larsen, *Trans. ASM* **57,** 464 (1964).
5. V. K. Sinha, F. Pourarian, and W. E. Wallace, *J. Phys. Chem.* **86,** 4952 (1982).
6. F. Pourarian and W. E. Wallace, *Solid State Commun.* **45,** 223 (1983).
7. F. Pourarian, V. K. Sinha, and W. E. Wallace, *J. Less-Comm. Metals* **96,** 237 (1984).
8. F. Pourarian and W. E. Wallace, *J. Solid State Chem.* **55,** 181 (1984).
9. S. Hirosawa, F. Pourarian, and W. E. Wallace, *J. Magn. Magn. Mat.* **43,** 187 (1984).
10. D. M. Gualtieri *et al., J. Appl. Phys.* **49,** 3432 (1976).
11. A. T. Pedziwiatr, R. S. Craig, W. E. Wallace, and F. Pourarian, *J. Solid State Chem.* **46,** 336 (1983).
12. J. J. Didisheim, K. Yuon, D. Shaltiel, and P. Fischer, *Solid State Commun.* **31,** 47 (1979).
13. Y. Isido, N. Nishimiya, and A. Suzuki, *Energy Dev. Japan* **1,** 207 (1978).
14. C. E. Lundin *et al., J. Less-Comm. Metals* **56,** 19 (1977).