JOURNAL OF SOLID STATE CHEMISTRY **65**, 356–362 (1986)

The Effect of Hyperstoichiometric Iron on the Hydrogen Storage Properties of ZrMnFe Ternary*

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Received January 6, 1986; in revised form March 20, 1986

The hyperstoichiometric $ZrMnFe_x$ system with $x = 1.2–1.4$ has been studied as a hydrogen storage material. The stoichiometric excess iron exhibits a profound promoting effect on the decomposition pressure of the hydride. The hydrogen capacity was observed to be very sensitive to the hyperstoichiometric iron content. The host metal underwent a 13% lattice expansion with no structural transformation during hydrogenation. The configurational entropy of hydrogen in the hydride phase is similar to that of deuterium in the $ZrMn_2$ deuteride, suggesting a similar site occupancy situation. The extreme rapidity of hydrogen sorption is attributed to a 3-dimensional network for hydrogen diffusion existing in the hydride lattice. © 1986 Academic Press, Inc.

Introduction

The Laves phase intermetallic compounds containing zirconium have received considerable attention in the past few years as possible hydrogen storage materials (*1*–*4*). A series of Zr-containing Laves phase intermetallics were first studied by Pebler and Gulbransen in the 1960's (*5, 6*). More recently, Shaltiel *et al.* (*1*) extended that study to high pressure and gave more detailed information about their hydrogenation characteristics. It was found that $ZrMn_2$ absorbed substantial amounts of hydrogen (3.6 hydrogen atoms per formula unit at room temperature and 8 atm), but the hydride formed was found to be too stable (0.007 atm at 50°C) to be of practical significance as a hydrogen storage alloy. In order to augment the hydrogen vapor pressure, they also investigated the stoichiometric ZrMnFe ternary and found that the substitution of 50% of the Mn by Fe in the $ZrMn_2$ lattice raised its dissociation pressure nearly 100-fold. The ZrMnFe ternary developed a plateau pressure of 0.65 atm at 50°C.

Recently in this laboratory, Pourarian *et al.* (*7*) have shown that the hyperstoichiometric 3*d* transition metal in $ZrMn_x\mathit{TM}_x$ (*TM* = Mn, Fe, Co, Ni, and Cu) has a significant effect on destabilizing the metal hydride. Sinha *et al.* (*8*) in this group have also studied the hyperstoichiometric ZrMnFe-based $ZrMnFe\mathit{TM}_x$ (*TM* = Cr, Ni, Co) systems. The present work is a continuation of that investigation. Its purpose was to examine the potential of $ZrMnFe_x$ intermetallics for hydrogen storage. As will be shown below, the vapor pressure of

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* This work was supported by a contract with the Koppers Co., Pittsburgh, Pa.

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0022-4596/86 $3.00

ZrMnFe hydride is raised 5–10 times by the introduction of hyperstoichiometric iron and is well above 1 atm at room temperature. The hydrogen capacity of $ZrMnFe_x$ with $x \leq 1.3$ is quite high, comparable with the paradigm hydrogen storage material $LaNi_5$. Unexpectedly, the plateau region is relatively flat and the hydrogen sorption is extremely fast. However, these materials require a severe activation procedure.

Experimental

All the samples studied were prepared in an induction-heated, water-cooled copper boat under a flowing argon atmosphere. The melting loss, due to the high volatility of Mn at elevated temperature, was compensated by adding 10% excess manganese. The melting procedure was as follows: first, the appropriate amounts of Zr and Fe were melted twice; then the manganese were added and the alloy remelted an additional 3–4 times. After each melting the sample was weighed, in order to monitor the Mn content. To get a sample of accurate composition the current and melting time must be controlled carefully. For better mixing, the button was turned over before each melting. In order to ensure homogeneity the samples were annealed at 950–1000°C for 4 hr. All samples were examined by powder X-ray diffraction, using Cu*Kα* radiation. The lines on diffraction patterns were observed to be sharp and intense. No extra lines were detectable.

It was necessary to subject these specimens to an activation procedure prior to determination of the pressure composition isotherms (PCI's). They were first heated to 350–400°C under ~60 atm H_2 and held at this temperature for 4–6 hr. Subsequently they were quenched in an ice-water bath or liquid nitrogen. This procedure was repeated several times for $ZrMnFe_{1.4}$. The amount of hydrogen absorbed was observed to increase with cycling number; after it reached a maximum value the PCI measurements were initiated. The equipment and experimental procedure have been described elsewhere (*9*). The pressure was recorded after it remained constant for 0.5–1 hr. At low pressures (below 1 atm), time for the system to reestablish equilibrium was observed to be as long as 10 hr.

Results and Discussion

1. Crystal Structure

As expected, all the $ZrMnFe_x$ intermetallic compounds studied occurred in the hexagonal C-14 ($MgZn_2$) type structure, similar to that of $ZrMn_2$ and ZrMnFe (*1*). The crystallographic parameters and unit cell volume are given in Table 1. It is evident that the crystal parameters of $ZrMnFe_x$ decrease compared with ZrMnFe, which was reported to have $a = 5.011$ and $c = 8.202$ Å (*10*). A recent neutron diffraction study (*11*) has revealed that in the $ZrMn_2Fe_x$ lattice the nonstoichiometry is achieved through the substitution for Zr at the Zr sites, primarily by Mn. It is likely that a similar situation obtains for the present hyperstoichiometric system. Hence, an alloy such as, for example, $ZrMnFe_{1.2}$, is better expressed as $Zr_{0.94}(Mn,Fe)_{0.06}(Mn,Fe)_2$ and, as noted earlier, the amount of Fe at the Zr sites is quite small. Since both Mn and Fe atoms are smaller than the Zr atom, the replacement of Mn and Fe for Zr diminishes the unit cell dimensions. Therefore, the X-ray data in Table I are consistent with the substitutional model, all of the nonstoichiometric alloys possessing smaller unit cells than ZrMnFe. The observed slight increase in the unit cell volume of $ZrMnFe_{1.4}$ is attributed to experimental error, not interstitial occupancy. This error is due to the fact that $ZrMnFe_{1.4}$ departs considerably from stoichiometry and yields broader diffraction peaks than the other materials studies. Also included in Table I are the

TABLE I

CRYSTAL STRUCTURE DATA FOR $ZrMnFe_x$ AND $ZrMnFe_x$ HYDRIDES

Composition	a (Å)	c (Å)	V^a (Å^3)	$\Delta V/V$ (%)	Hydrogen capacity at 20 atm and 23°C: cm^3 H_2/g alloy[b]	Hydrogen capacity at 20 atm and 23°C: r^c
$ZrMnFe^d$	5.011	8.202	178.4			
$ZrMnFe_{3.5}{}^d$	5.422	8.839	225.0	20.7	194.0	1.48
$ZrMnFe_{1.2}$	4.996	8.173	176.7			
$ZrMnFe_{1.2}H_{3.2}$	5.205	8.685	203.8	13.3	186.4	1.40
$ZrMnFe_{1.3}$	4.988	8.163	175.9			
$ZrMnFe_{1.3}H_{2.6}$	5.184	8.618	200.6	12.3	149.2	1.13
$ZrMnFe_{1.4}$	4.990	8.178	176.4			
$ZrMnFe_{1.4}H_{0.35}$	—	—	—	—	17.5	0.16[e]

[a] Unit cell volume.

[b] Measured at 1 atm and 25°C.

[c] r = the amount of H_2 per unit volume of alloy relative to that of the same volume of liquid hydrogen.

[d] Obtained from Ref. (*10*).

[e] Assuming the same unit cell volume for $ZrMnFe_{1.4}H_{0.35}$ as that of host metal.

crystallographic data for $ZrMnFe_x$ hydrides. X-Ray diffraction analysis showed that the hydrogenation of $ZrMnFe_x$ did not transform the crystal structure of the host metal, but did cause a 12–13% lattice expansion. This expansion is relatively small in comparison with those of $LaNi_5$ and other $ZrMn_2$-based (*7*) hydrogen storage materials, which dilate by 25 and 20%, respectively.

The peaks on the X-ray pattern of $ZrMnFe_x$ hydride were observed to be relatively narrow and well defined, indicating that the lattice distortion occasioned by the insertion of the hydrogen atoms was not significant. There are many crystallographically different types of interstices in the $ZrMn_2$ lattice, which are all tetrahedral sites. A neutron diffraction study on $ZrMn_2D_3$ (*12*) indicated that only those tetrahedral holes are occupied in which hydrogen atoms are surrounded by 2 Zr and 2 Mn atoms. From the thermodynamic implications of this investigation, as discussed below, it seems likely that the site-occupying situation in $ZrMnFe_x$ hydrides does not change very much in spite of the partial substitution of Mn and Fe for Zr and of Fe for Mn.

2. Thermodynamic Properties

The pressure–composition isotherms were established over the temperature range 0–100°C and pressures up to 50 atm for $ZrMnFe_{1.2}$–H_2 and $ZrMnFe_{1.3}$–H_2. These isotherms manifest a well-defined pressure plateau region (see Figs. 1 and 2), although a distinct slope is evident, as has been observed for other non-stoichiometric systems. The volumetric capacity r, which is the hydrogen density in metal hydrides relative to that of liquid hydrogen, and weight capacity are listed in Table I. It can be seen from this table that the hydrogen capacities are very sensitive to the hyperstoichiometric iron content, decreasing sharply with increasing hyperstoichiometric Fe. The volumetric capacity and r factors of $ZrMnFe_{1.2}$, for example, are 186.4

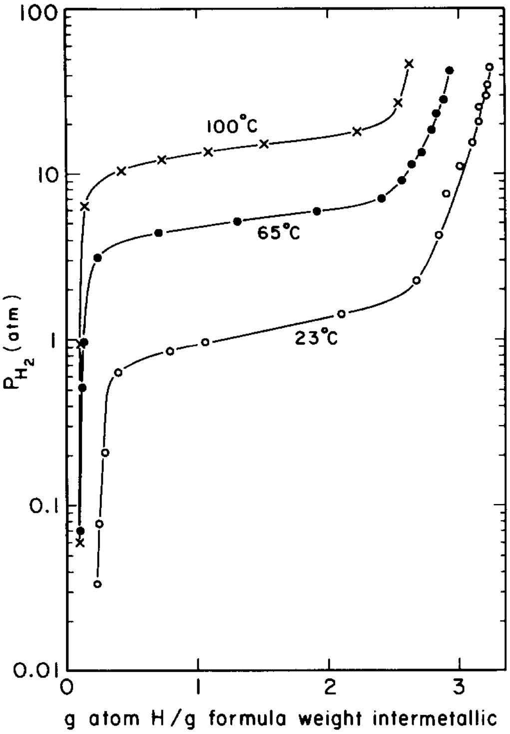

FIG. 1. Pressure–composition isotherms for the $ZrMnFe_{1.2}$–H_2 system.

cm^3 H_2/g alloy and 1.40, respectively, which are comparable with the paradigm hydrogen storage material $LaNi_5$. The corresponding quantities of $ZrMnFe_{1.4}$, however, are only 17.5 cm^3 H_2/g alloy and 0.16. The very small hydrogen capacities of $ZrMnFe_{1.4}$ are in accord with a previous observation (*8*) in this laboratory that $ZrMnCo_{1.4}$ did not absorb any measurable quantity of hydrogen, since Co was found to have a most profound effect in destabilizing the Zr-containing Laves phase metal hydride (*7*).

It is of practical interest to note that the plateau regions in these PCI's are relatively flat, compared to other nonstoichiometric systems, and the plateau pressures, at moderate temperatures, are well above 1 atm. For instance, the $ZrMnFe_{1.3}$ hydride exhibits dissociation pressures of 3 atm at room temperature and 7 atm at 50°C, which are 10-fold over those of ZrMnFe hydride and 700-fold over those of $ZrMn_2$ hydride.

There are three branches in these isotherms. On the left where the curve rises sharply with increasing hydrogen content, is an α-phase field that is the solid solution of hydrogen in the parent intermetallic compound. When the host metal is saturated with hydrogen, a second solid phase, β-hydride phase, occurs. In this two solid phase coexistence region (plateau region), changes involve only the relative amounts of the two phases, while the hydrogen concentration in each phase remains nearly constant during the hydrogenation process. In this stage, more and more α phase with terminal hydrogen solubility is converted into β-hydride phase as the overall hydro-

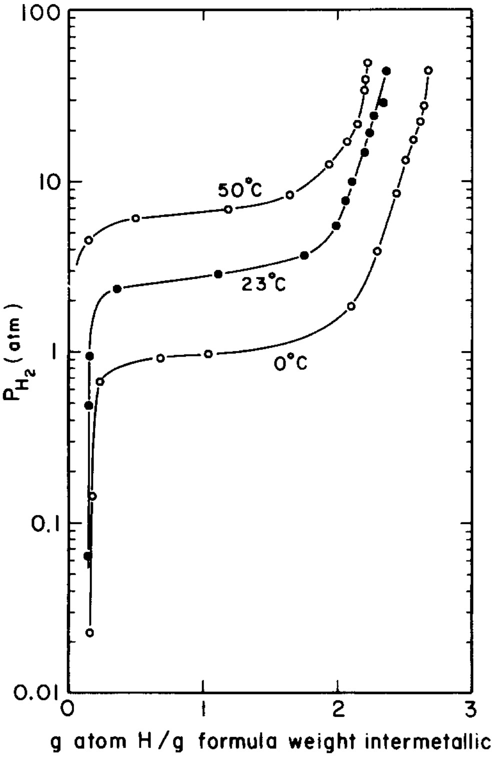

FIG. 2. Pressure–composition isotherm for the $ZrMnFe_{1.3}$–H_2 system.

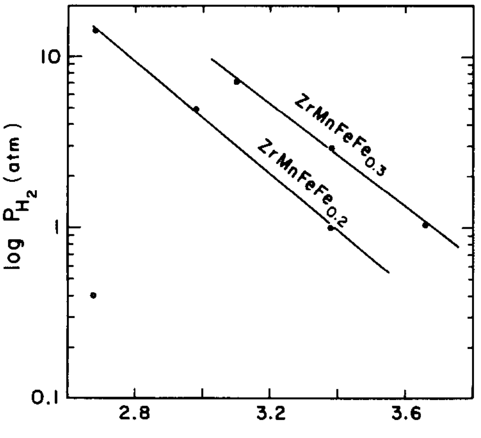

FIG. 3. The van't Hoff plot of log P_{H_2} vs reciprocal temperature for the $ZrMnFeFe_x$–H_2 system at the composition 1.25 g atom H/g formula weight intermetallic.

gen content in solid is successively increased. Finally, when all the α phase is exhausted, the system regains a degree of freedom and a steeply ascending curve, which represents the solid solution of hydrogen in metal hydride, again appears on the right of an isotherm. In the plateau region the hydrogenation of the metal matrix is essentially a chemical reaction, e.g., for $ZrMnFe_{1.2}$–H_2:

$$0.91\ ZrMnFe_{1.2}H_{0.4} + H_2 \rightleftarrows 0.91\ ZrMnFe_{1.2}H_{2.6}.$$

It is well known that the standard enthalpy and entropy changes accompanying this reaction can be derived from the van't Hoff equation. The transformation of gaseous diatomic molecules to hydrogen atoms situated in the interstitial sites of the host metal contributes to these thermodynamic quantity changes to a dominant extent. In the present case there is no structural transition but only a relatively small lattice dilation and distortion during hydrogenation. It may therefore be assumed that the host intermetallic possesses nearly the same $\overline{H}^\circ$ and $\overline{S}^\circ$ in both α and β phases. That is, the enthalpy and entropy changes for the reaction are all attributed to the contribution from hydrogen. Consequently, the relative partial molal enthalpy and entropy of hydrogen in the hydride phase can be evaluated from the van't Hoff plot. An excellent linear fit of log P versus $1/T$ was observed in all cases (the correlation coefficients >0.999). The representative plots are shown in Fig. 3. The values of $2\overline{H}_H - \overline{H}^\circ_{H_2}$ and $2\overline{S}_H - \overline{S}^\circ_{H_2}$ are listed in Tables II and III as a function of the overall hydrogen content in the solid in the two-solid phase field.

Using the well-known value $\overline{S}^\circ_{H_2} = 130.6$ J/K mole H_2, the partial molal entropy $2\overline{S}_H$ of hydrogen in β hydride phase was readily calculated. The $\overline{S}_H$ values (J/K g atom H) are given in the last column of Tables II and III. These values are around 13 J/K g atom H. Pourarian *et al.* have calculated the configurational contribution to the entropy, $S_c = 18.3$ J/K g atom D, for deuterium in the $ZrMn_2$ deuteride, the deuterium content of which is close to the hydrogen content of the $ZrMnFe_{1.2}$ hydride, using the expression by Wallace *et al.* (*13, 14*) and the site occupancy data by Didisheim *et al.* (*12*). They also pointed out that this value may be somewhat overestimated due to the inclusion of some energetically unfavored configurations. In light of the fact that the S_c for $ZrMn_2$ may be overestimated, the S_c

TABLE II

RELATIVE PARTIAL MOLAL QUANTITIES OF HYDROGEN IN $ZrMnFe_{1.2}$ HYDRIDE

Overall hydrogen content (g atom H/g formula weight intermetallic)	$-(2\overline{H}_H - \overline{H}^\circ_{H_2})$ (kJ/mole H_2)	$-(2\overline{S}_H - \overline{S}^\circ_{H_2})$ (J/K mole H_2)	$\overline{S}_H$ (J/K g atom H)
0.75	32.3	108	11.3
1.00	31.5	106	12.3
1.25	31.5	106	12.3
1.50	31.1	106	12.3
1.75	30.5	105	12.8
2.00	29.8	103	13.8
Mean:	31.1	105.6	12.5

TABLE III

RELATIVE PARTIAL MOLAL QUANTITIES OF HYDROGEN IN $ZrMnFe_{1.3}$ HYDRIDE

Overall hydrogen content (g atom H/g formula weight intermetallic)	$-(2\bar{H}_H - H^\circ_{H_2})$ (kJ/mole H_2)	$-(2\bar{S}_H - S^\circ_{H_2})$ (J/K mole H_2)	$\bar{S}_H$ (J/K g atom H)
0.50	28.4	103	13.8
0.75	28.3	103	13.8
1.00	28.3	103	13.8
1.25	27.8	103	13.8
1.50	28.5	106	12.3
Mean:	28.3	103.6	13.5

for $ZrMn_2$ deuteride and $ZrMnFe_x$ hydride are in reasonably close agreement. This accordance suggests that the site-occupying picture for the $ZrMnFe_y$ hydride is quite similar to that of the $ZrMn_2$ deuteride.

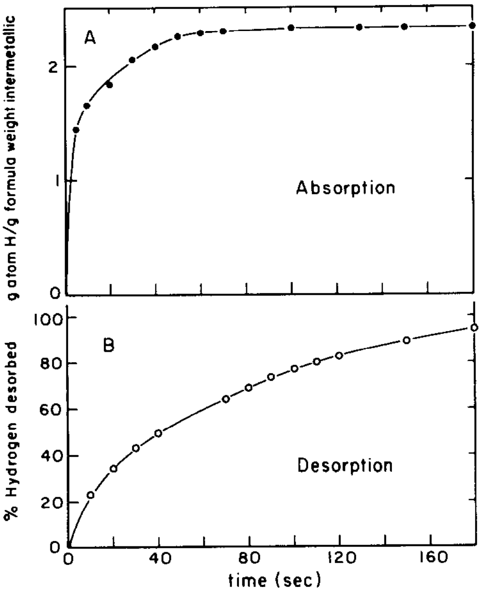

FIG. 4. (A) Hydrogen absorption rate of the $ZrMnFe_{1.3}$ at 23°C and 50 atm. (B) Hydrogen desorption rate of the $ZrMnFe_{1.3}$ hydride at 23°C.

3. *Kinetic Behavior*

The hydrogen absorption and desorption for activated $ZrMnFe_x$ were observed to be extremely fast. The absorption process, for instance, was almost complete in about 1 minute for $ZrMnFe_{1.3}$ at room temperature and 50 atm. The desorption was 90% complete in about 2.5 min at the same temperature and against 1 atm for the same sample (see Fig. 4).

First-order kinetics behavior was observed in a previous study on a hyperstoichiometric $ZrCr_2$-based system (*15*). Because of the chemical and structural similarities, the present system is assumed to have the same kinetic nature; that is, the desorption of $ZrMnFe_x$ hydrides obey first-order kinetics and the diffusion of atomic hydrogen is the rate-determining step. The neutron diffraction study (*11*) has revealed that all D atom sites in the $ZrMn_2$ deuteride lattice are connected in such a way as to form a 3-dimensional infinite network of diffusion paths. The deuterium atoms, therefore, can migrate freely along the network. A similar network should exist in the $ZrMnFe_x$ hydride lattice, too, since the site occupancy by hydrogen in $ZrMnFe_x$ hydrides is considered essentially the same as that of $ZrMn_2$ deuteride, as described above. It appears that it is this 3-dimensional network which is responsible for the observed extremely fast hydrogen sorption. Another possible reason for the rapidity of hydrogen sorption is related to the surface condition. An earlier Auger spectroscopy study (*2*) in this laboratory indicated that the oxide coating on the surface of the $ZrMn_{2+x}$ is quite thin (~75 Å). A similar situation may also obtain for the present case. This would reduce the resistance of the diffusion of hydrogen through the surface, and hence enhance the hydrogen sorption rate.

References

1. D. SHALTIEL, I. JACOB, AND D. DAVIDOV, *J. Less-Common Met.* **53,** 117 (1977).

2. F. POURARIAN, H. FUJII, W. E. WALLACE, V. K.

SINHA, AND H. KEVIN SMITH, *J. Phys. Chem.* **85**, 3105 (1981).

3. H. OESTERREICHER AND H. BITTNER, *Mater. Res. Bull.* **13**, 83 (1978).
4. A. SUZKI, N. NISHIMIYA, AND S. ONO, *J. Less-Common Met.* **89**, 263 (1983).
5. A. PEBLER AND E. A. GULBRANSEN, *Electrochem. Technol.* **4**, 211 (1966).
6. A. PEBLER AND E. A. GULBRANSEN, *Trans. Metall. Soc. AIME* **239**, 1593 (1967).
7. F. POURARIAN, V. K. SINHA, AND W. E. WALLACE, *J. Less-Common Met.* **96**, 237 (1983).
8. V. K. SINHA, G. Y. YU, AND W. E. WALLACE, *J. Less-Common Met.* **106**, 67 (1985).
9. G. Y. YU, F. POURARIAN, AND W. E. WALLACE, *J. Less-Common Met.* **107**, 79 (1985).
10. H. FUJII, V. K. SINHA, F. POURARIAN, AND W. E. WALLACE, *J. Less-Common Met.* **85**, 43 (1982).
11. W. JAMES AND W. E. WALLACE, unpublished work.
12. J. DIDISHEIM, K. YVON, D. SHALTIEL, AND P. FISCHER, *Solid State Commun.* **31**, 47 (1979).
13. F. POURARIAN, V. K. SINHA, W. E. WALLACE, AND A. T. PEDZIWIATR, Proc. of the Symposium on Hydrogen in Metals, Richmond, Va., March, 1982, p. 385, Plenum, New York.
14. W. E. WALLACE, HOWARD E. FLOTOW, AND D. OHLENDORF, *J. Less-Common Met.* **79**, 157 (1981).
15. G. Y. YU AND W. E. WALLACE, to be published.