

## An Investigation of the Hyperstoichiometric $Zr_{1-x}Ti_xCrFe_y-H_2$ System\*

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The pressure-composition isotherms and relevant crystallographic, thermodynamic, and kinetic parameters are presented and discussed for the  $Zr_{1-x}Ti_xCrFe_y-H_2$  system with  $x = 0.1, 0.3$  and  $y = 1.2-1.4$ . The hyperstoichiometric iron was observed to have a profound effect on the equilibrium dissociation pressure, elevating the plateau pressure several times over that for the corresponding  $Zr_{1-x}Ti_xCrFe$  hydride. The hydrogen capacities of these quaternary intermetallics are quite high, the volumetric capacity being 1.21 to 1.32 with respect to that of liquid hydrogen, the weight capacity 159.9-178.9 cm<sup>3</sup> H<sub>2</sub>/g alloy. The enthalpies and entropies of dissociation are in the range 27.3-31.1 kJ/mole H<sub>2</sub> and 100-107.2 J/K mole H<sub>2</sub>, respectively. The dehydrogenation process was found to follow first-order kinetics with an activation energy 43.4 kJ/mole H<sub>2</sub>. The diffusion of atomic hydrogen was considered to be the rate-determining step. © 1987 Academic Press, Inc.

### Introduction

Much work has been done in this laboratory and others (1-8) on the Zr-containing intermetallic compounds with the C-14 structure. This has been part of the efforts to search out a better hydrogen storage material than the conventional ones, such as LaNi<sub>5</sub> and FeTi, which are good in general but have some disadvantages from the point of view of practical applications. In a previous communication (9) we reported the hydrogen sorption characteristics of the stoichiometric ZrCr<sub>2</sub>-based  $Zr_{1-x}Ti_xCrFe$  quaternary. The present study is to extend that investigation to a nonstoichiometric

area and to examine the effect of hyperstoichiometric iron on the hydrogen storage properties. This paper, which is closely related to the recent study (10) of  $ZrCrFeT_x$  alloys ( $T$  is a 3d transition metal or Cu), presents the experimental results pertaining to the crystallography, thermodynamics and kinetics of the  $Zr_{1-x}Ti_xCrFe_y-H_2$  system.

### Experimental

The specimens used under the present investigation were prepared by induction heating, employing a water-cooled copper boat under a titanium-gettered flowing argon atmosphere. The ingots were melted 6-8 times and held in liquid state for 2 min each time. They were then annealed at 1000-1050°C for 4-6 hr to ensure homogeneity. The Cr loss during melting was taken

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into consideration and compensated by adding an appropriate amount of excess Cr.

All samples were subjected to X-ray diffraction examination and proved to be excellent single-phase material within the limit of this technique. No extra lines were detectable. To obtain  $\beta$  hydride phase of a known composition for X-ray work, we employed the following procedure: (1) admitting  $H_2$  at a pressure corresponding to the desired composition to the entire hydrogenation system and then closing the sample chamber valve; (2) evacuating the system beyond the valve; (3) introducing a mixture of  $H_2$  and  $SO_2$  to the manifold, such that the  $H_2$  partial pressure is equal to the desired  $H_2$  equilibrium pressure ( $p_{SO_2} \approx 55$  psi); (4) keeping  $SO_2$  poisoning for a proper period. If the plateau pressure is well above 1 atm, we usually put the sample chamber into an ice-water bath, i.e., operating the poisoning at  $0^\circ C$ . At reduced temperature the  $SO_2$ -poisoning effect is considerably enhanced and satisfactory results are usually produced. (In some cases the poisoning may be insufficient when the  $H_2$  pressure is higher than 20 atm, which leads to a too-low fraction of  $SO_2$  in the gaseous phase.) A test showed that an  $SO_2$ -poisoned sample in this way retained the  $\beta$  hydride phase, which had a plateau pressure of 3 atm, for more than one month. It should be noted, however, that the hydrogen concentration of the samples prepared in this way is somewhat higher than that expected from the room temperature PCI. This is a consequence of the reduced temperature involved in poisoning. The extra dissolved hydrogen will give an enlarged lattice, and this will result in a larger lattice expansion and therefore affect the calculation of the  $r$  factor slightly. Consequently, the  $r$  factors cited are somewhat underestimated. Some investigators (1, 11) suggested a much lower temperature for poisoning. This technique is useful in the case where the dissociation pressure is extra high. But it should

be regarded with caution for the reasons described above. In addition, the thermodynamic behavior is unknown in very low temperature, and some authors (1, 11) assumed even structural phase transition might occur at lower temperature. So, it seems more desirable for accurate measurements to choose  $0^\circ C$  as poisoning temperature, as long as feasible.

The procedure for PCI and kinetic measurement has been described in detail elsewhere (9). Several charging-discharging cycles were performed before the first PCI measurement to ensure the activity of the host intermetallics. High-purity (99.999%)  $H_2$  was used in all experiments.

## Results and Discussion

### 1. Crystal Structure

All the samples exhibited the hexagonal  $MgZn_2$  structure, the same as that of  $ZrCr_2$  and  $Zr_{1-x}Ti_xCrFe$ . While hydriding, the parent intermetallics underwent a 16.5% lattice expansion with no structural variation. The crystal parameters for the host compounds and corresponding hydrides are computed and listed in Table I.

It should be noted that the lattice constants of hyperstoichiometric  $Zr_{1-x}Ti_xCrFe_y$  are smaller than those of the corresponding stoichiometric  $Zr_{1-x}Ti_xCrFe$ . For instance,  $a$  and  $c$  for  $Zr_{0.7}Ti_{0.3}CrFe$  are 4.983 and 8.179 Å, respectively, whereas the corresponding parameters are 4.975 and 8.143 Å for  $Zr_{0.7}Ti_{0.3}CrFe_{1.2}$ . This fact excludes the possibility of the occupation of interstitials by hyperstoichiometric iron atoms, which would give rise to an increase in lattice constants. A previous study (12) in this laboratory revealed that  $ZrCr_2$  could not be made hyperstoichiometric with Cr, implying that the Cr atom is not able to substitute for the Zr atom at the Zr site in  $ZrCr_2$ -based intermetallics. Since the size of the Fe atom is almost the same as that of the Cr atom, it is

TABLE I

	$a$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )	$\Delta V/V$ (%)	Hydrogen capacity at 40 atm and room temperature	
					cm <sup>3</sup> H <sub>2</sub> /g alloy	$r$
Zr <sub>0.7</sub> Ti <sub>0.3</sub> CrFe <sub>1.2</sub>	4.975	8.143	174.5			
Zr <sub>0.7</sub> Ti <sub>0.3</sub> CrFe <sub>1.2</sub> H <sub>3.2</sub>	5.288	8.631	209	16.5	178.9	1.32
Zr <sub>0.7</sub> Ti <sub>0.3</sub> CrFe <sub>1.3</sub>	4.979	8.135	174.7			
Zr <sub>0.7</sub> Ti <sub>0.3</sub> CrFe <sub>1.3</sub> H <sub>2.7</sub>	5.292	8.629	209.3	16.5	149.1	1.10
Zr <sub>0.9</sub> Ti <sub>0.1</sub> CrFe <sub>1.4</sub>	4.997	8.167	176.6			
Zr <sub>0.9</sub> Ti <sub>0.1</sub> CrFe <sub>1.4</sub> H <sub>3.1</sub>	5.038	8.634	210.7	16.2	159.9	1.21

reasonable to expect that the lattice contraction is occasioned mainly by the substitution of the Zr and/or Ti atom by the smaller Fe atom. Assuming there is no vacancy in the lattice and only Fe substitutes at Zr sites, the structural formula, which reflects the distribution of various atoms at two different sites and is needed for the calculation of the  $r$  factor, can be derived from the chemical formula and the ratio of the number of Zr sites to Cr sites, as both must be satisfied simultaneously. Accordingly, from the structural viewpoint, it is better to express Zr<sub>0.7</sub>Ti<sub>0.3</sub>CrFe<sub>1.2</sub> as Zr<sub>0.66</sub>Ti<sub>0.28</sub>Fe<sub>0.06</sub>Cr<sub>0.94</sub>Fe<sub>1.06</sub>, Zr<sub>0.7</sub>Ti<sub>0.3</sub>CrFe<sub>1.3</sub> as Zr<sub>0.64</sub>Ti<sub>0.27</sub>Fe<sub>0.09</sub>Cr<sub>0.91</sub>Fe<sub>1.09</sub> and Zr<sub>0.9</sub>Ti<sub>0.1</sub>CrFe<sub>1.4</sub> as Zr<sub>0.79</sub>Ti<sub>0.09</sub>Fe<sub>0.12</sub>Cr<sub>0.88</sub>Fe<sub>1.12</sub>. These derived formulas are supported, indirectly, by density measurements; e.g., the calculated density for Zr<sub>0.7</sub>Ti<sub>0.3</sub>CrFe<sub>1.3</sub>, 7.10 g/cm<sup>3</sup>, is in good agreement with the measured value, 7.14 g/cm<sup>3</sup>.

The hydrogen capacities, both volumetric capacity and weight capacity, have been calculated from the thermodynamic and crystallographic data and are also listed in Table I. The  $r$  factor is the hydrogen density in metal hydride relative to that in liquid hydrogen. The hydrogen volume in weight capacity is measured at 1 atm and 25°. On comparison with the corresponding Zr<sub>1-x</sub>Ti<sub>x</sub>CrFe intermetallics, the hydrogen capacity is not significantly impaired by

the introduction of hyperstoichiometric iron, and these data qualify this material for consideration for use in hydrogen storage.

## 2. Pressure-Composition Isotherms and Thermodynamic Functions

The experimentally determined desorption PCIs for the Zr<sub>1-x</sub>Ti<sub>x</sub>CrFe<sub>y</sub>-H<sub>2</sub> system are plotted in Figs. 1-3. As with the Zr<sub>1-x</sub>

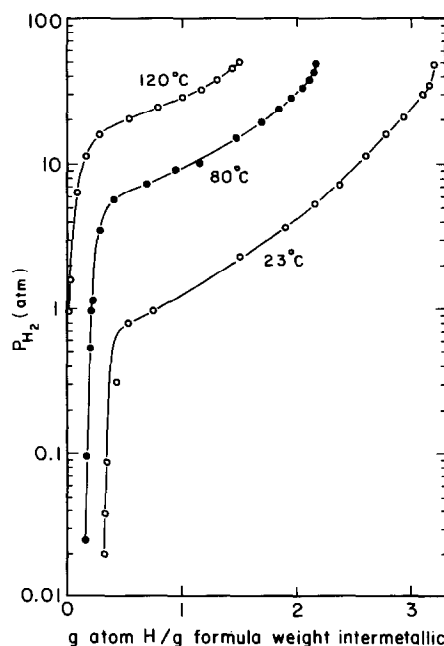


FIG. 1. Pressure-composition isotherm for the Zr<sub>0.7</sub>Ti<sub>0.3</sub>CrFe<sub>1.2</sub>-H<sub>2</sub> system.

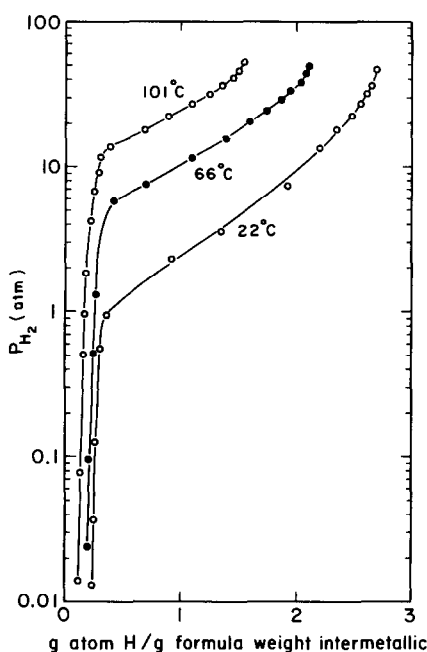


FIG. 2. Pressure-composition isotherm for the  $Zr_{0.7}Ti_{0.3}CrFe_{1.3}-H_2$  system.

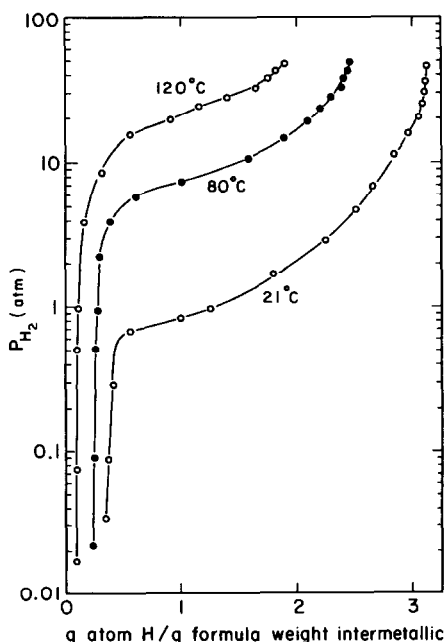


FIG. 3. Pressure-composition isotherm for the  $Zr_{0.9}Ti_{0.1}CrFe_{0.4}-H_2$  system.

$Ti_xCrFe-H_2$  system, there is no well-defined plateau region in these isotherms. This does not exclude the existence of a two-solid-phase field. In contrast, the X-ray pattern clearly showed the occurrence of the  $\beta$  hydride phase. The reason for a sloping "plateau" is at present unclear. Some researchers (13) ascribe it to a so-called "local interfacial equilibrium" or "incomplete equilibrium" thermodynamically.

It is to be noted that the addition of hyperstoichiometric iron raises the equilibrium dissociation pressure appreciably; e.g., the hydrogen vapor pressures of  $Zr_{0.7}Ti_{0.3}CrFe_{1.2}$  hydride and  $Zr_{0.7}Ti_{0.3}CrFe_{1.3}$  hydride are nearly four times and eight times that of  $Zr_{0.7}Ti_{0.3}CrFe$  hydride, respectively. This effect is obviously a consequence of both lattice shrinkage and reduction in chemical affinity for hydrogen caused by the substitution of iron for zirconium.

The enthalpy  $\Delta H_{\beta \rightarrow \alpha}$  and entropy  $\Delta S_{\beta \rightarrow \alpha}$  for the dehydrogenation process were calculated from the slope and intercept of the plot of  $\ln p_{H_2}$  against  $1/T$  at various compositions in the two-solid-phase region using a least-square calculation. The results are summarized in Tables II-IV. It is interesting to note that the correlation coefficients in these least-squares computations are excellent (nearly 1) for all cases in spite of the quite sloping plateaux. This fact implies the applicability to the present system of the van't Hoff equation, which, derived from

TABLE II  
ENTHALPY AND ENTROPY OF DEHYDROGENATION  
FOR  $Zr_{0.7}Ti_{0.3}CrFe_{1.2}$  HYDRIDE

Overall hydrogen content g atom H/g formula weight intermetallic	$\Delta H_{\beta \rightarrow \alpha}$ kJ/mole $H_2$	$\Delta S_{\beta \rightarrow \alpha}$ J/K mole $H_2$	Correlation coefficient in least-squares calculation
0.5	32.0	106	0.9999
0.75	31.7	107	0.9999
1.00	31.1	107	0.9999
1.25	30.1	106	0.9997
1.50	30.7	110	0.9991
Mean	31.1	107.2	

TABLE III  
ENTHALPY AND ENTROPY OF DEHYDROGENATION  
FOR  $Zr_{0.9}Ti_{0.3}CrFe_{1.3}$  HYDRIDE

Overall hydrogen content g atom H/g formula weight intermetallic	$\Delta H_{\beta \rightarrow \alpha}$ kJ/mole H <sub>2</sub>	$\Delta S_{\beta \rightarrow \alpha}$ J/K mole H <sub>2</sub>	Correlation coefficient in least-squares calculation
0.5	29.5	102	0.9989
0.75	27.4	98	0.9990
1.00	26.8	98	0.9996
1.25	26.4	99	0.9999
1.50	26.5	103	0.9999
Mean	27.3	100	

equilibrium criteria  $\Delta G = 0$ , strictly, is applicable only to the case where there is no hysteresis. This condition is unlikely to prevail with this alloy. The mean  $\Delta H_{\beta \rightarrow \alpha}$  values are established at 31.1, 27.3, and 31.0 kJ/mole H<sub>2</sub> for  $Zr_{0.7}Ti_{0.3}CrFe_{1.2}-H_2$ ,  $Zr_{0.7}Ti_{0.3}CrFe_{1.3}-H_2$ , and  $Zr_{0.9}Ti_{0.1}CrFe_{1.4}-H_2$ , respectively. The corresponding  $\Delta S_{\beta \rightarrow \alpha}$  are 107.2, 100, and 104.4 J/K mole H<sub>2</sub>. The  $\Delta H$  values are significantly lower than that calorimetrically measured in this laboratory (14) for  $ZrCr_2$ . This is not unexpected since the replacement of Zr by Ti and/or Fe invariably diminishes the enthalpy of dehydrogenation.

### 3. Kinetic Features

These materials were found to be rapid hydrogen absorbers. Similar to  $Zr_{1-x}Ti_xCrFe_y$ , they require no activation at high temperature, but they do involve a short-time

TABLE IV  
ENTHALPY AND ENTROPY OF DEHYDROGENATION  
FOR  $Zr_{0.9}Ti_{0.1}CrFe_{1.4}$  HYDRIDE

Overall hydrogen content g atom H/g formula weight intermetallic	$\Delta H_{\beta \rightarrow \alpha}$ kJ/mole H <sub>2</sub>	$\Delta S_{\beta \rightarrow \alpha}$ J/K mole H <sub>2</sub>	Correlation coefficient in least-squares calculation
0.5	30.2	99	1.0000
0.75	30.8	103	0.9997
1.00	31.4	105	0.9994
1.25	31.7	108	1.0000
1.50	31.0	107	1.0000
Mean	31.0	104.4	

induction period before the first hydrogenation. The subsequent hydrogen occlusion and evolution were observed to be quite rapid, 80% of the hydrogen being absorbed or desorbed in about 2 min. Representative plots of hydrogen amounts absorbed or released versus time are shown in Fig. 4.

The desorption of hydrogen from a metal hydride sometimes obeys second-order kinetics (15) and other times obeys first-order kinetics (16). To ascertain the kinetic nature of the present  $ZrCr_2$ -based system, an attempt was made to fit the experimental data to the general kinetic equations, which have the following common forms:

$$-\frac{dc}{dt} = kc \quad \ln \frac{c_0}{c} = kt$$

for first order

$$-\frac{dc}{dt} = kc^2 \quad \frac{1}{c} - \frac{1}{c_0} = kt$$

for second order

where  $c_0$  is the hydrogen concentration in

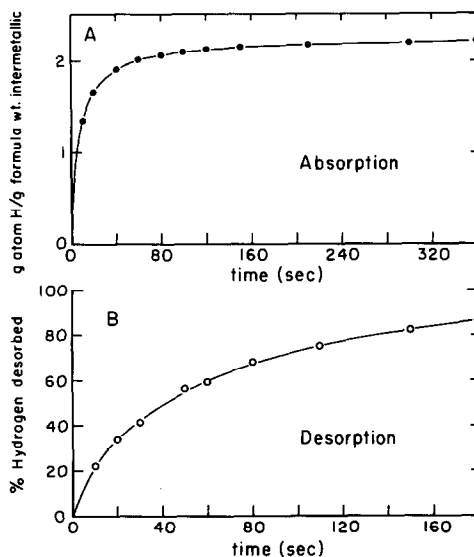


FIG. 4. (A) Hydrogen absorption rate of  $Zr_{0.7}Ti_{0.3}CrFe_{1.3}$  at 23°C. (B) Hydrogen desorption rate of  $Zr_{0.7}Ti_{0.3}CrFe_{1.3}$  hydride at 23°C.

the intermetallic matrix at  $t_0$ , and  $c$  at  $t$ .  $k$  is the rate constant.

An examination by plotting experimental data showed that  $\ln c/c_0$  exhibits a better linearity with time than  $1/c - 1/c_0$ . The excellent linearity of the plot of  $\ln c/c_0$  vs  $t$  (see Fig. 5) indicates that the dehydrogenation of  $Zr_{1-x}Ti_xCrFe_y$  hydride follows first-order kinetics. The kinetic parameters are given in Table V. The activation energy was derived from the Arrhenius equation  $K = Ae^{-E_a/kT}$  using a least-squares technique.

To account for the second-order nature of hydrogen sorption by some rare earth intermetallics, a model has been proposed by Wallace *et al.* (17), based on the experimental results of surface analysis, kinetic measurements, and heterogeneous catalysis. Although this model is specifically for the mechanism of hydrogen sorption by  $LaNi_5$ , it is believed that the general idea is commonly applicable to other metal-hydrogen systems. According to this model, involved in the dehydrogenation process are the following five steps: (1) phase transformation ( $\beta \rightarrow \alpha$ ); (2) diffusion of atomic hydrogen in bulk; (3) interfacial diffusion of atomic hydrogen; (4) recombination of atomic hydrogen on the surface; (5) desorption of molecular hydrogen from the surface. It has been ascertained by extensive evidence (17) that for a second-order kinetics the RDS (Rate-Determining Step) is step (4), the recombination of atomic hydrogen

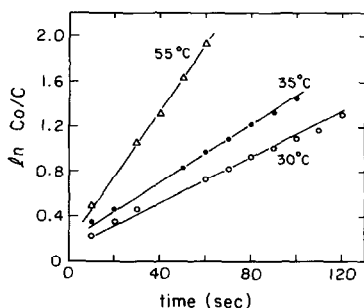


FIG. 5. First-order fit plots for the  $Zr_{0.7}Ti_{0.1}CrFe_{1.2}-H_2$  system.

TABLE V  
KINETIC PARAMETERS FOR DEHYDROGENATION OF  
 $Zr_{0.7}Ti_{0.3}CrFe_{1.2}$  HYDRIDE

Temperature (°C)	Rate constant $k \times 10^2$ (S <sup>-1</sup> )	Activation energy (kJ/mole H <sub>2</sub> )
30	1.03	43.4
35	1.30	
50	2.96	

to form the hydrogen molecule. For the present case, it is not unreasonable to assume that step (2) or (3) is rate-determining. Fick's law reveals that the diffusion rate is linearly proportional to the concentration gradient. Now assuming that neither step (4) nor (5) is rate-controlling, the hydrogen concentration in the surface must be zero or a negligible amount. Hence the diffusion rate is essentially dependent only on the hydrogen concentration in bulk. This may be the essence of the first-order kinetics. The activation energy of 43.4 kJ/mole H<sub>2</sub> favors this assumption, since it falls in the range involved in the diffusion of hydrogen in metals (18).

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