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Hydrogen absorption characteristics of the $Zr_{1-x}Ho_xCo_2$ system in the pressure range 0–40 bar

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Abstract

Hydrogen absorption pressure–composition isotherms were determined for the intermetallic compounds $Zr_{1-x}Ho_xCo_2$ ($x=0.4$, 0.6 and 0.8) belonging to the C-15-type Laves phase structure in the temperature range 50–200 °C at pressures up to 40 bar. The maximum hydrogen concentration (number of hydrogen atoms per formula unit) increases from 0.1 to 3.8 as the holmium concentration (x) is increased from 0 to 1. The ratio of the number density of hydrogen atoms in the alloy to the density of liquid hydrogen lies in the range 0.1–1.24. The absorption of hydrogen is accompanied by a maximum of 19% expansion in the unit cell volume of the host without any change in the C-15-type Laves phase structure. For higher values of x the materials are highly distorted when the hydrogen concentration exceeds about 3.0 and tend towards the amorphous state. The relative partial molar enthalpy ($\Delta\bar{H}_H$) and entropy ($\Delta\bar{S}_H$) of hydrogen absorption in these materials are found to lie in the range 7–43 kJ (mol H)$^{-1}$ and 10–115 J K^{-1} (mol H)$^{-1}$ respectively. The hydrogen absorption kinetics recorded at different temperatures for all the compositions indicate that the kinetics are fast for lower x values.

1. Introduction

Laves phase alloys containing zirconium (Zr) have attracted a great deal of attention as possible hydrogen storage materials [1–3]. The hydriding characteristics of these materials are drastically modified by partial substitution of other elements so as to make them more suitable for practical applications. Recently we have reported the effect of substitution of holmium (Ho) on the hydrogen absorption properties of $Zr_{1-x}Ho_xCo_2$ ($0 \leqslant x \leqslant 1$) alloys over the temperature range from room temperature to 300 °C and the pressure range 0.001–1 bar [4]. The isotherms indicated the occurrence of an α–β phase transition for $x=0.6$ and 0.8 but no such transition for $x=0.2$ and 0.4 in the temperature and pressure ranges studied. In order to obtain a complete picture of the hydrogen absorption properties of the $Zr_{1-x}Ho_xCo_2$ system, the measurements were extended up to a pressure of 40 bar and a more detailed study was carried out. The hydrogen absorption characteristics such as hydrogen storage capacity, change in enthalpy and entropy, kinetics of absorption, effect of hydrogen absorption on the crystal structure, etc. of the intermetallic compounds $Zr_{1-x}Ho_xCo_2$ ($0 \leqslant x \leqslant 1$) in the pressure range 0–40 bar are presented in this paper.

2. Experimental details

2.1. Material preparation

The intermetallic compounds $Zr_{1-x}Ho_xCo_2$ ($x=0$, 0.2, 0.4, 0.6, 0.8 and 1) were prepared by melting the pure elements in stoichiometric proportions in an arc furnace under an argon atmosphere. The purity of Zr and Co was 99.99% and of Ho was 99.9%. The alloy buttons were re-melted several times by turning them upside down to ensure homogeneity. The weight loss of the materials during preparation was less than 0.4% in all cases. The samples were annealed in evacuated (10^{-6} Torr) quartz ampoules at 900 °C for 10 days and slowly cooled to room temperature (RT) in order to obtain a single phase. The materials were characterized by the powder X-ray diffraction technique, which showed the formation of single-phase materials with a C-15-type cubic Laves phase structure. Co Kα radiation was used for the X-ray studies.

2.2. Hydrogenation procedure

Hydrogen absorption pressure–composition isotherms and kinetic data were collected by the conventional gasometric technique. An apparatus based on the pressure reduction method [5] and operating in the pressure range 0–100 bar and temperature range RT–300 °C was fabricated for the purpose. It consisted of constant-volume (calibrated) containers, a reactor, pressure-

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measuring accessories, etc. and the whole unit was made of stainless steel [6]. Precision pressure transducers supplied by Burster Präzisionsmeßtechnik (SEMMEG 9000) were employed in two different ranges to measure the pressure accurately. Their output was fed to a strip chart recorder to continuously monitor the change in pressure due to absorption. The temperature of the sample was controlled to an accuracy of ±1 °C using a proportional controller. The experimental facility was calibrated by plotting the isotherms of palladium and the data agreed well with the values reported in the literature [7].

Initially the whole system was flushed with hydrogen (purity better than 99.999%) several times and evacuated each time to 10^{-6} Torr. Absorption data were collected after activating the samples by hydriding and dehydriding several times at a pressure of about 50 bar and a temperature of 200 °C. The amounts of hydrogen absorbed by the samples at various temperatures were computed by using the gas law with appropriate corrections. Following each measurement, the sample was degassed at elevated temperatures under a vacuum of 10^{-6} Torr.

3. Results and discussion

The X-ray diffraction studies showed that the compounds $Zr_{1-x}Ho_xCo_2$ ($0 \leqslant x \leqslant 1$) were formed with the C-15-type Laves phase structure. The lattice constant varied linearly with x, obeying Vegard's law [4].

The lattice constants and the r factors of the hydrides of the $Zr_{1-x}Ho_xCo_2$ ($x=0$, 0.2, 0.4, 0.6, 0.8 and 1) compounds are given in Table 1. The r factor (the ratio of the number density of hydrogen in the hydride to the density of liquid hydrogen), which is a measure of the hydrogen storage capacity, increases with increasing x. An expansion in the unit cell volume ($\Delta V/V$) of up to 19% has been observed in these systems owing to the absorption of hydrogen, without any change in the crystal structure. These factors may be even higher for maximum hydrogen concentrations, but this could not be ascertained owing to the difficulty in obtaining X-ray lines of detectable intensity at higher hydrogen concentrations. For instance, the X-ray lines are too weak to be detected at a hydrogen concentration (y) above 3.0 for $Zr_{0.2}Ho_{0.8}Co_2H_y$.

The experimentally determined pressure–composition (P–C) absorption isotherms for the compounds $Zr_{1-x}Ho_xCo_2$ with $x=0.4$, 0.6 and 0.8 in the temperature range 50–200 °C and up to a pressure of 40 bar are given in Figs. 1–3 respectively. For $x=0$ and 0.2 the hydrogen intake is very small and the materials exist only in the α phase in the pressure and temperature ranges studied. For the concentrations $x=0.4$, 0.6 and 0.8 the isotherms show an α–β phase transition. It can be seen from the figures that the maximum hydrogen concentration (y_{max}) increases with increasing x. In the P–C isotherms shown in Figs. 1–3 the regions of the α–β phase transformation at different temperatures are indicated by broken curves. The critical temperature (T_c) and pressure (P_c) are those points on the isotherms where the plateau just ceases to exist. In the $Zr_{1-x}Ho_xCo_2$ system T_c increases from 125 to 200 °C and P_c decreases from 20 to about 1 bar as x is increased from 0.4 to 0.8.

TABLE 1. Lattice constants, r factors, plateau pressures at 100 °C ($P_{\alpha\rightarrow\beta}$) and maximum hydrogen intakes ($y_{max}=n_H/n_{fu}$) at 50 °C and 40 bar for $Zr_{1-x}Ho_xCo_2H_y$ ($0 \leqslant x \leqslant 1$)

System	a (Å)	r[a]	$P_{\alpha\rightarrow\beta}$ (bar)	y_{max}
$ZrCo_2$	6.949	0.1	–	0.17
$ZrCo_2H_{0.17}$	6.951			
$Zr_{0.8}Ho_{0.2}Co_2$	6.986	0.16	–	0.32
$Zr_{0.8}Ho_{0.2}Co_2H_{0.3}$	7.014			
$Zr_{0.6}Ho_{0.4}Co_2$	7.039	0.69	10	2.45
$Zr_{0.6}Ho_{0.4}Co_2H_{1.4}$	7.274			
$Zr_{0.4}Ho_{0.6}Co_2$	7.072	0.78	0.6	2.55
$Zr_{0.4}Ho_{0.6}Co_2H_{1.7}$	7.439			
$Zr_{0.2}Ho_{0.8}Co_2$	7.134	1.1	0.25	3.3
$Zr_{0.2}Ho_{0.8}Co_2H_{2.5}$	7.569			
$HoCo_2$	7.174	1.2	–	3.8
$HoCo_2H_{2.8}$	7.553			

[a] The r factor is the ratio of the number density of hydrogen in the hydride to the density of liquid hydrogen.

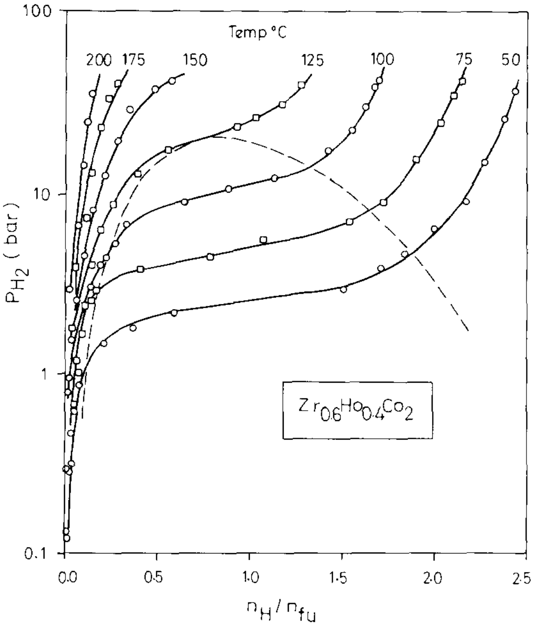

Fig. 1. Hydrogen absorption pressure–composition isotherms for $Zr_{0.6}Ho_{0.4}Co_2$.

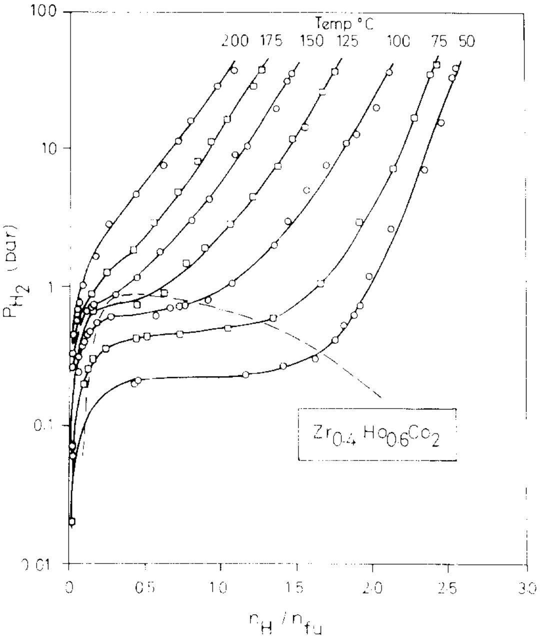

Fig. 2. Hydrogen absorption pressure–composition isotherms for $Zr_{0.4}Ho_{0.6}Co_2$.

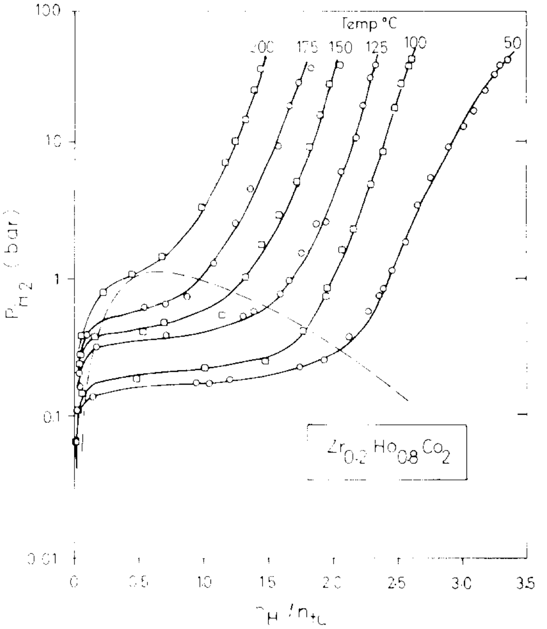

Fig. 3. Hydrogen absorption pressure–composition isotherms for $Zr_{0.2}Ho_{0.8}Co_2$.

The variations in the pressure corresponding to the α–β transformation ($P_{\alpha\rightarrow\beta}$) at 100 °C and the maximum hydrogen intake (y_{max}) at 50 °C are also given in Table 1 for comparison. As seen from the table, the plateau pressure decreases drastically with increasing Ho concentration (x) without a significant change in hydrogen intake. The plateau pressure for $x=0.8$ is about 40 times less than that for $x=0.4$, which shows the effect of holmium substitution in the $ZrCo_2$ lattice. This is in accordance with the fact that the vapour pressure of the hydrides can be modified by proper substitution of some elements so as to make them more suitable for practical applications [1–3, 8, 9]. For instance, in the $ZrMn_2$ system [10] a three- to eightfold increase in vapour pressure was observed on substitution of 20%–30% Ce for Zr.

In the case of $Zr_{0.2}Ho_{0.8}Co_2H_y$ the isotherm (Fig. 3) at 50 °C shows a deviation at a hydrogen concentration above 2.5. The X-ray powder diffractograms recorded at hydrogen concentrations $y=0$ and 3.0 (Fig. 4) show that all the sharp Bragg peaks characteristic of the C-15-type Laves phase are replaced by a few broad and weak lines due to the absorption of hydrogen. This may be an indication of the complete distortion of the crystal lattice due to the formation of very fine particles during hydrogen absorption and the material may be tending towards the amorphous state. This effect is more pronounced in Ho-rich compounds, *i.e.* $Zr_{0.2}Ho_{0.8}Co_2H_y$ and $HoCo_2H_y$. Buschow and Van der Kraan [11] reported that in $HoCo_2H_y$ a partial decomposition of the material can take place during hydrogen absorption, which leads to a broadening of X-ray lines or to their complete disappearance. Results on hydrogen-induced amorphization have been reported in the $GdCo_2H_y$ and $TbCo_2H_y$ systems [12, 13], RFe_2 systems [14] and RNi_2 systems [15].

The changes in enthalpy and entropy of hydrogen absorption were determined from the temperature dependence of the equilibrium pressure derived from the pressure–composition isotherms shown in Figs. 1–3. These parameters were computed using the least-squares technique from the slope and intercept respectively of the van't Hoff plot of ln P_{H_2} *vs.* $1/T$ for different hydrogen concentrations (y). Tables 2–4 sum-

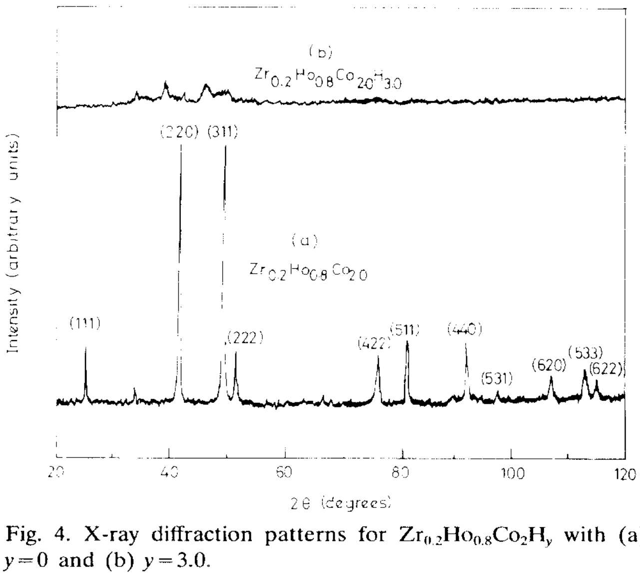

Fig. 4. X-ray diffraction patterns for $Zr_{0.2}Ho_{0.8}Co_2H_y$ with (a) $y=0$ and (b) $y=3.0$.

TABLE 2. Relative partial molar enthalpies ($\Delta\bar{H}_H$) and entropies ($\Delta\bar{S}_H$) for $Zr_{0.6}Ho_{0.4}Co_2H_y$. Standard deviations are given in parentheses

y	$-\Delta\bar{H}_H$ (kJ (mol H)$^{-1}$)	$-\Delta\bar{S}_H$ (J K^{-1} (mol H)$^{-1}$)
α phase		
0.05	13.9 (0.7)	35.2 (1.7)
0.06	15.8 (0.6)	40.5 (1.3)
0.07	16.9 (0.9)	43.9 (2.1)
0.08	18.6 (1.0)	48.5 (2.3)
0.09	18.4 (1.2)	49.0 (2.9)
α + β phase		
0.4	27.7 (0.3)	90.7 (0.8)
0.6	28.0 (0.7)	93.1 (2.1)
0.8	29.3 (0.7)	97.0 (2.0)
1.0	29.5 (0.8)	98.5 (2.2)
1.2	31.8 (1.0)	105.8 (3.0)

TABLE 3. Relative partial molar enthalpies ($\Delta\bar{H}_H$) and entropies ($\Delta\bar{S}_H$) for $Zr_{0.4}Ho_{0.6}Co_2H_y$. Standard deviations are given in parentheses

y	$-\Delta\bar{H}_H$ (kJ (mol H)$^{-1}$)	$-\Delta\bar{S}_H$ (J K^{-1} (mol H)$^{-1}$)
α phase		
0.06	9.1 (0.5)	18.5 (1.2)
0.08	8.4 (0.5)	18.0 (1.1)
0.10	9.9 (0.8)	22.4 (2.1)
α + β phase		
0.5	16.1 (0.9)	42.1 (2.7)
0.75	15.8 (0.8)	41.6 (2.4)
1.0	17.8 (0.7)	48.2 (2.3)
1.25	17.2 (0.6)	46.6 (1.9)
β phase		
1.5	31.3 (0.5)	89.2 (1.4)
1.6	32.7 (1.2)	94.0 (3.1)
1.7	32.8 (1.1)	95.7 (3.0)
1.8	33.6 (0.8)	99.6 (2.3)
1.9	33.3 (0.1)	100.1 (0.2)

TABLE 4. Relative partial molar enthalpies ($\Delta\bar{H}_H$) and entropies ($\Delta\bar{S}_H$) for $Zr_{0.2}Ho_{0.8}Co_2H_y$. Standard deviations are given in parentheses

y	$-\Delta\bar{H}_H$ (kJ (mol H)$^{-1}$)	$-\Delta\bar{S}_H$ (J K^{-1} (mol H)$^{-1}$)
α phase		
0.035	7.6 (0.3)	12.5 (0.8)
0.04	8.2 (0.5)	14.2 (1.2)
0.045	9.3 (0.6)	17.3 (1.4)
α + β phase		
0.2	12.0 (0.1)	21.3 (0.3)
0.4	12.0 (0.3)	22.3 (0.7)
0.6	12.4 (0.3)	24.1 (0.9)
0.8	12.9 (0.4)	25.9 (1.0)
β phase		
1.6	39.3 (0.5)	98.3 (1.2)
1.7	38.4 (1.8)	98.5 (4.4)
1.8	40.4 (1.4)	105.1 (3.5)
1.9	40.2 (1.7)	106.4 (4.4)
2.0	42.8 (2.0)	114.8 (5.0)

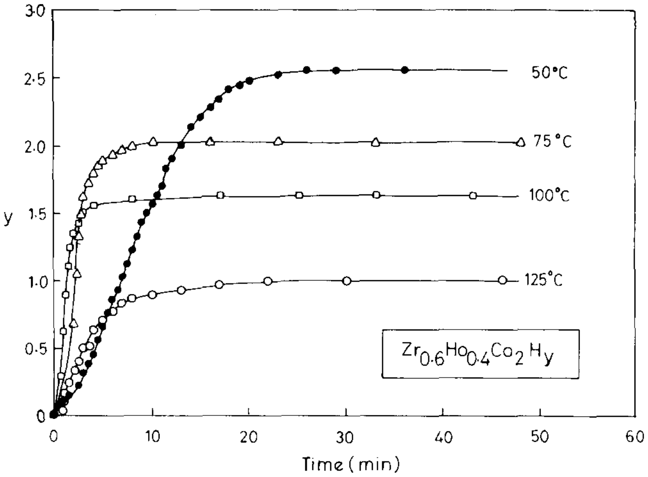

Fig. 5. Hydrogen absorption kinetics for $Zr_{0.6}Ho_{0.4}Co_2H_y$.

marize the values of relative partial molar enthalpy ($\Delta\bar{H}_H = 2\bar{H}_H - H^\circ_{H_2}$) and relative partial molar entropy ($\Delta\bar{S}_H = 2\bar{S}_H - S^\circ_{H_2}$) evaluated for the samples $Zr_{0.6}Ho_{0.4}Co_2H_y$, $Zr_{0.4}Ho_{0.6}Co_2H_y$ and $Zr_{0.2}Ho_{0.8}Co_2H_y$ respectively for different values of y which lie in the α, $\alpha+\beta$ and β phases.

It can be seen from the tables that both $\Delta\bar{H}_H$ and $\Delta\bar{S}_H$ increase slightly with increasing y in all phases. The average values of $\Delta\bar{H}_H$ and $\Delta\bar{S}_H$ in the $\alpha+\beta$ phase for $Zr_{0.6}Ho_{0.4}Co_2H_y$ are 29.3 kJ (mol H)$^{-1}$ and 97.0 J K^{-1} (mol H)$^{-1}$, for $Zr_{0.4}Ho_{0.6}Co_2H_y$ are 16.7 kJ (mol H)$^{-1}$ and 44.6 J K^{-1} (mol H)$^{-1}$ and for $Zr_{0.2}Ho_{0.8}Co_2H_y$ are 12.3 kJ (mol H)$^{-1}$ and 23.4 J K^{-1} (mol H)$^{-1}$ respectively. Both $\Delta\bar{H}_H$ and $\Delta\bar{S}_H$ decrease with increasing Ho concentration. This suggests that the energy released owing to the absorption of hydrogen is low for Ho-rich compounds. The effective entropy of hydrogen in the hydride phase ($\bar{S}_H$), computed from the $\Delta\bar{S}_H$ values using the entropy of hydrogen gas ($S^\circ_{H_2} = 130.5$ J K^{-1} (mol H)$^{-1}$), increases with increasing Ho concentration (x). This can be attributed to the increase in configurational entropy of hydrogen in Ho-rich compounds.

Figures 5–7 show the hydrogen absorption kinetics plotted at temperatures ranging from 50 to 200 °C for the compounds $Zr_{1-x}Ho_xCo_2H_y$, where $x = 0.4$, 0.6 and 0.8 respectively. It can be seen from the figures that the kinetics are fast for lower x. At higher Ho concentrations the higher hydrogen intake is compensated for by slower kinetics and this may be a consequence of the poisoning nature of the Ho-rich compounds during repeated hydriding–dehydriding cycles.

In the $Zr_{1-x}Ho_xCo_2$ system the hydrogen intake increases, $\Delta\bar{H}_H$ decreases and the kinetics become slower

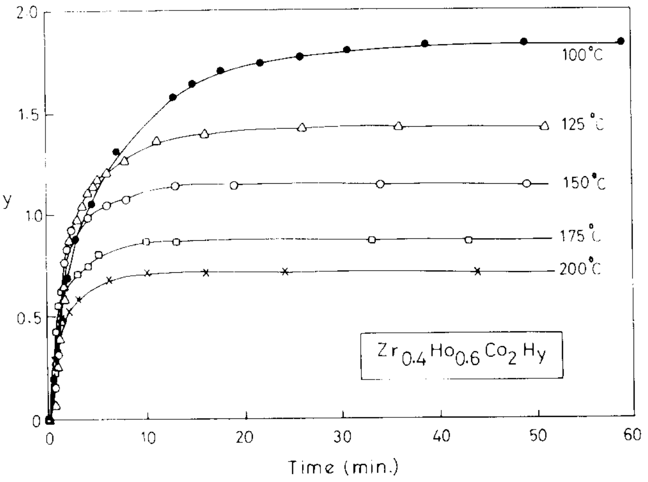

Fig. 6. Hydrogen absorption kinetics for $Zr_{0.4}Ho_{0.6}Co_2H_y$.

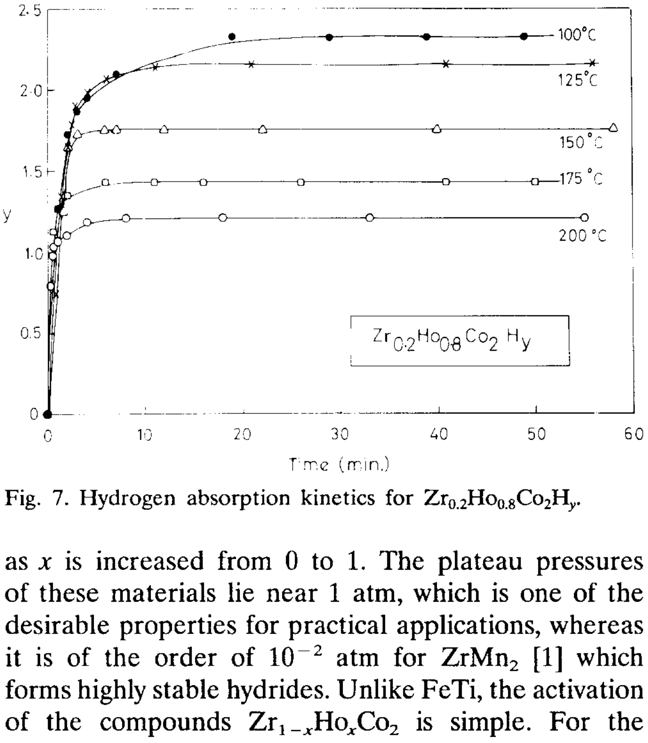

Fig. 7. Hydrogen absorption kinetics for $Zr_{0.2}Ho_{0.8}Co_2H_y$.

as x is increased from 0 to 1. The plateau pressures of these materials lie near 1 atm, which is one of the desirable properties for practical applications, whereas it is of the order of 10^{-2} atm for $ZrMn_2$ [1] which forms highly stable hydrides. Unlike FeTi, the activation of the compounds $Zr_{1-x}Ho_xCo_2$ is simple. For the concentration $x=0.6$ the average value of the enthalpy in the two-phase region is about 17 kJ (mol H)$^{-1}$, which is lower than that for conventional hydrogen storage materials such as FeTi and $LaNi_5$ where the enthalpy values are about 30 kJ (mol H)$^{-1}$ [16, 17] and $ZrMn_2$ where the value is about 53 kJ (mol H)$^{-1}$ [1]. This lower value of enthalpy is of technical significance with regard to practical applications, because it diminishes the problems associated with extensive heat flow in the hydride bed. This material possesses reasonably good values of hydrogen capacity, enthalpy and plateau pressure.

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