JOURNAL OF MATERIALS SCIENCE **35** (2000) 127–131

High-pressure AB_2 metal hydrides with low hysteresis

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The effect of minor substitution for Mn on the basic hydriding properties of $Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.7}X_{0.1}$ (X = Mn, Fe, Co or V) has been studied at 20 and 60 °C in order to find alloy-hydrogen systems for high-pressure applications in which high capacity, low hysteresis and flat pressure-composition-isotherm (PCI) plateaus are required. Samples have been synthesized by arc melting, and characterized by X-ray diffraction (XRD) and volumetric PCI measurements. Experimental evidence shows that even a small amount of V practically eliminates hysteresis while at the same time the PCI plateau slopes increase. Co-substitution also decreases hysteresis and keeps the PCI plateaus flat, but Fe-substitution does not seem to have any favourable effect on the basic hydriding properties. Possibility to study the relationship between hysteresis effect of high-pressure hydrides and their crystal structure is discussed. *© 2000 Kluwer Academic Publishers*

1. Introduction

The feasibility of metal hydride devices in many applications depends, in addition to the efficiency of heat and mass transfer solutions, on the basic hydriding-dehydriding properties of the selected alloys: hydrogen absorption capacity, hysteresis and pressure-composition-isotherm (PCI) plateau slopes. This is especially the case in applications with strict thermal boundary conditions, such as thermally driven heat pumps and compressors that are to work on a low-temperature heat source (70–80 °C) and ambient cooling (10–25 °C). Such working conditions could be expected e.g. in self-sufficient solar hydrogen energy systems where the heat source of a thermodynamic hydride device could be the waste heat of an electrolyzer or a fuel cell, or the heat from solar collectors [1].

In a previous study [2], AB_2 alloys with relatively good hydriding properties in the high-pressure range were synthesized. One of the most promising alloy-hydrogen systems, $Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.8}$-$H_2$, was characterised by good capacity and reasonably flat PCI plateaus but still unsatisfactory hysteresis, especially at room temperature. Another system, $TiCrMn_{0.55}Fe_{0.3}V_{0.15}$-$H_2$, on the other hand, showed notably decreasing capacity at increasing temperatures, but negligible hysteresis. On the basis of these observations, it was decided to study whether the best features of these systems could be combined by minor substitutions of Mn by Fe, Co or V in $Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.8}$. The experimental results of this study are reported here.

2. Experimental details

The alloy samples were prepared from pure elements by melting in an arc furnace with a non-consumable tungsten electrode and a water-cooled copper tray, under an argon atmosphere of 1 bar. Purities of the raw materials were as follows: Ti, Zr, Cr and Co 99.99%, Mn and Fe 99.98% and V 99.7%. Samples were turned over and remelted three times and annealed at 1000 °C for 10 days under vacuum of 10^{-2} mbar to enhance homogeneity. Both melting and annealing were carried out in the presence of titanium getter to ensure high-purity preparation environment. Chemical composition of the synthesized samples was not analysed, but the weight difference between the raw materials and a fully treated sample was less than 0.3% in all cases. Powder X-ray diffraction (XRD) measurements were done using CuK_α radiation with Si-filter in a DRON-2 diffractometer.

The PCI measurements at 20 and 60 °C were accomplished using a high-pressure volumetric apparatus described elsewhere [3]. The annealed samples were crushed (particle size of 1–5 mm) in air just before insertion into the high-pressure apparatus and degassed (10^{-2} mbar) at room temperature for 1–2 h before introducing hydrogen (purity: 99.9999%). The samples were then activated at a hydrogen pressure of 100–200 bar and 20 °C. After this initial activation, a couple of absorption-desorption cycles were performed before reproducible PCI curves could be measured.

3. Results and discussion

According to the XRD analysis, all prepared samples were hexagonal C14, single phase alloys. The lattice parameters and unit cell volumes are listed in Table I. It can be seen that V as a substitution element enlarges the unit cell in the a-direction while the c-direction remains unchanged. Fe and Co, on the other hand, contract the unit cell in both directions. These observations are in line with the general trend that if a substitution element has a larger atomic radius than the substituted one, unit cell volume is increased, and vice versa (atomic radii of the B-elements: Mn-0.129 nm, V-0.132 nm, Fe-0.126 nm and Co-0.126 nm).

The PCI curves of the studied alloy-hydrogen systems are shown in Figs 1–4. The calculated values for average and minimum PCI plateau slopes ($d \ln p/d(H/M)$; hydrogen to metal atom ratio) as well as hysteresis factor (the ratio between absorption and desorption pressure at constant temperature: $p_{\mathrm{abs}}/p_{\mathrm{des}}$

TABLE I Lattice parameters and unit cell volumes of the synthesized samples

Alloy composition	a (nm)	c (nm)	c/a	V (10^3 nm^3)
$Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.8}$	0.4873(2)	0.7993(5)	1.640	164.38
$Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.7}V_{0.1}$	0.4882(1)	0.7992(3)	1.637	164.94
$Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.7}Co_{0.1}$	0.4867(2)	0.7973(4)	1.638	163.59
$Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.7}Fe_{0.1}$	0.4866(1)	0.7974(2)	1.639	163.51

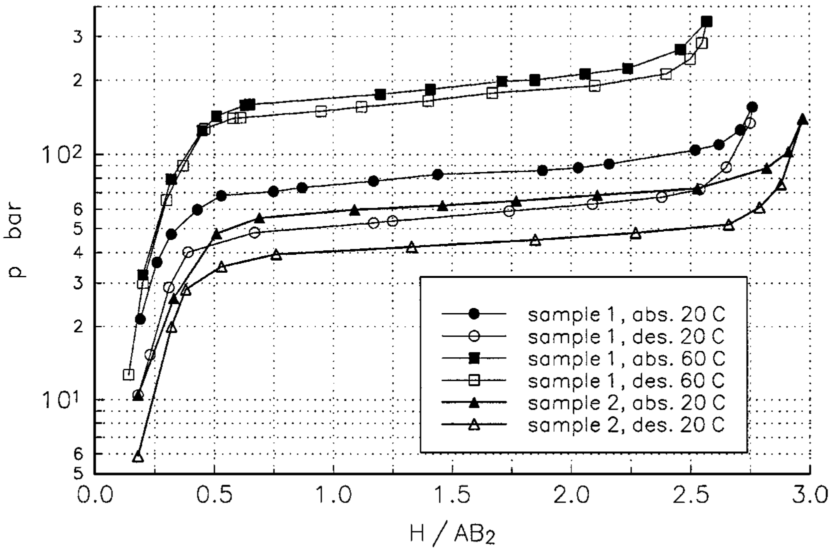

Figure 1 PCI curves of the $Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.8}$-$H_2$ system at 20 and 60 °C (sample 1, Ref. [2]; sample 2, the present study).

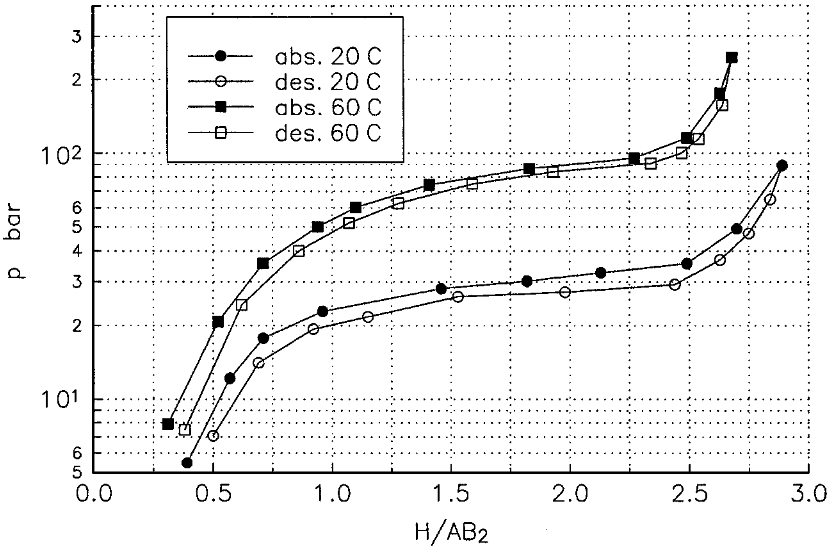

Figure 2 PCI curves of the $Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.7}V_{0.1}$-$H_2$ system at 20 and 60 °C.

TABLE II PCI-properties of the studied alloy-hydrogen systems

	Hysteresis				PCI slopes				
Alloy composition	p_{abs}/p_{des} at $H/M = 0.5$		$\ln(p_{abs}/p_{des})$ at $H/M = 0.5$		$d \ln p/d(H/M)$ (20 °C)		min-ave (60 °C)		Compression ratio ($p_{des,60\,°C}/p_{abs,20\,°C}$ at $H/M = 0.5$)
	20 °C	60 °C	20 °C	60 °C	abs	des	abs	des	
$Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.8}$[a]	1.48	1.11	0.39	0.10	0.2–0.7	0.5–0.7	0.5–0.6	0.5–0.7	2.03
$Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.8}$[b]	1.45		0.37		0.3–0.5	0.4–0.4			
$Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.7}V_{0.1}$	1.10	1.08	0.10	0.08	0.6–0.9	0.3–0.8	0.7–1.5	0.6–1.3	2.51
$Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.7}Co_{0.1}$	1.35	1.07	0.30	0.07	0.2–0.4	0.3–0.6	0.4–0.5	0.5–0.6	2.19
$Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.7}Fe_{0.1}$	1.51	1.09	0.41	0.08	0.6–0.7	0.3–0.6	0.4–0.6	0.3–0.6	2.02

[a] Sample 1 (previous study) [2].

[b] Sample 2 (this study).

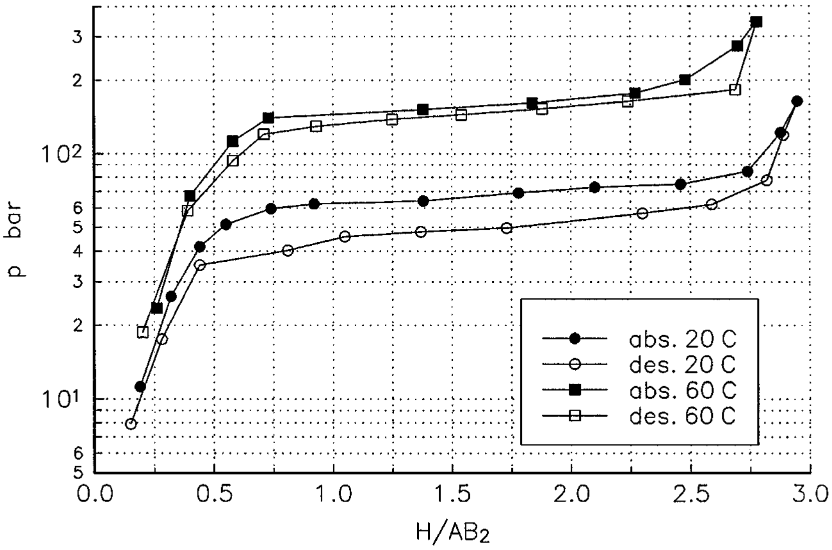

Figure 3 PCI curves of the $Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.7}Co_{0.1}$-$H_2$ system at 20 and 60 °C.

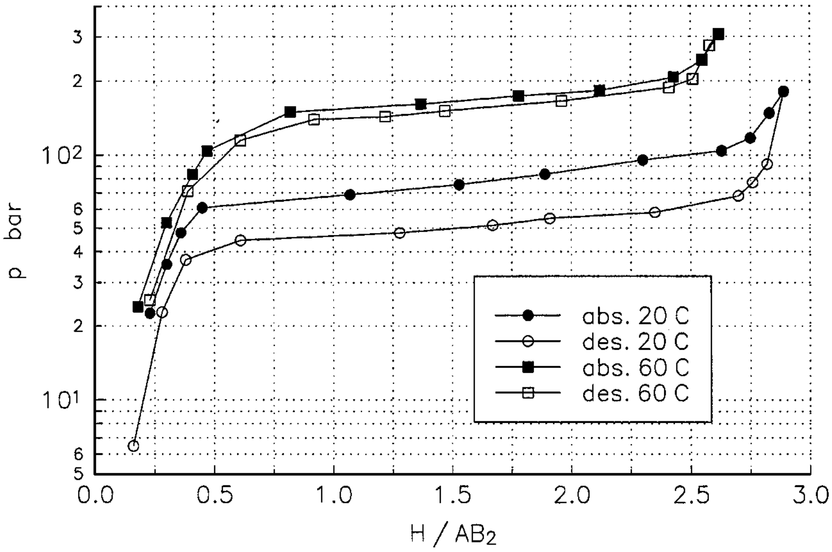

Figure 4 PCI curves of the $Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.7}Fe_{0.1}$-$H_2$ system at 20 and 60 °C.

or $\ln(p_{abs}/p_{des})$) and compression ratio ($p_{des,60\,°C}/p_{abs,20\,°C}$) are presented in Table II, all at 1.5 hydrogen atoms per formula unit ($H/AB_2 = 1.5$, equal to $H/M = 0.5$).

Fig. 1 shows the PCI curves of the $Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.8}$-$H_2$ system (sample 1 from the previous study [2] and sample 2, the present study). Although the composition of the samples is nominally the same, the equilibrium plateau pressures differ quite remarkably from each other. This may be caused by slight differences in true compositions of the alloys: according to the chemical analysis, the previously studied alloy was in fact $Ti_{0.95}Zr_{0.05}Cr_{1.17}Mn_{0.81}$ [2]. The effect of impurities on the equilibrium plateau pressures is not clear, but differences in the maximum hydrogen storage capacity and the width of the α-solid solution phase can probably be attributed to higher impurity levels in sample 1 (purities: 99.5–99.8% [2]) than in sample 2 (99.98–99.99%).

Fig. 2 shows the PCI curves of the $Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.7}V_{0.1}$-$H_2$ system at 20 and 60 °C. The effect of partial substitution of Mn by V can be summarized as follows. Hysteresis is practically eliminated already at 20 °C but unfortunately, this major achievement is accompanied by a wider α-phase (which could be expected from the model of Bernauer *et al.* [4]) and increased slopes of the PCI plateaus near the α-phase. In addition, the equilibrium plateau pressures are significantly decreased, but this effect—stabilization of the hydride—can be at least partly compensated for by decreasing the Zr-content of the alloy. Furthermore, it could be worth studying whether still smaller amounts of V would result in practically hysteresis free alloy-hydrogen systems—with less unwanted side effects.

The PCI curves of the $Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.7}Co_{0.1}$-$H_2$ system at 20 and 60 °C are presented in Fig. 3. Comparison with Fig. 1 (sample 2) shows that partial substitution of Mn by Co reduces hysteresis a little (see also Table II) and keeps the PCI plateaus wide and flat. The high equilibrium pressures are also maintained (comparison with sample 2). The only drawback appears to be the modesty of the improvement, but—as Co does not seem to have any negative effects on the PCI-properties, bigger improvements might be achieved with increased Co-substitution.

Fig. 4 shows the PCI curves of the $Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.7}Fe_{0.1}$-$H_2$ system at 20 and 60 °C. On the basis of Figs 1 and 4, it can be stated that Fe does not have any significant positive impact on the PCI-properties of the studied base system (see also Table II). However, the amount of Fe used was small, only 5 at % of B-element.

Fig. 5 illustrates that even though the common trend between unit cell volume and Gibbs free energy (ΔG) of metal hydrides (increasing unit cell volume decreases ΔG and equilibrium plateau pressures) is valid for the studied systems, the scattering of the data is quite remarkable already among four examples. This implies that it is not possible to predict accurately the PCI plateau pressures of an alloy-hydrogen system with new element(s) merely on the basis of geometric factors, such as unit cell volumes. Obviously, even small amounts of a substitution element may modify the electronic environment of the host lattice to such an extent that the binding energy of hydrogen atoms to the interstitial lattice sites and thus, the hydride stability is changed in a way very difficult to predict. This has to be taken into account when tailoring alloys for specific applications with strict boundary conditions. Suitable alloys—as far as the equilibrium pressure levels are concerned—may be found by interpolation (and to some extent by extrapolation) of data among alloys composed of *same elements*, but if new elements are added, experimental work is indispensable.

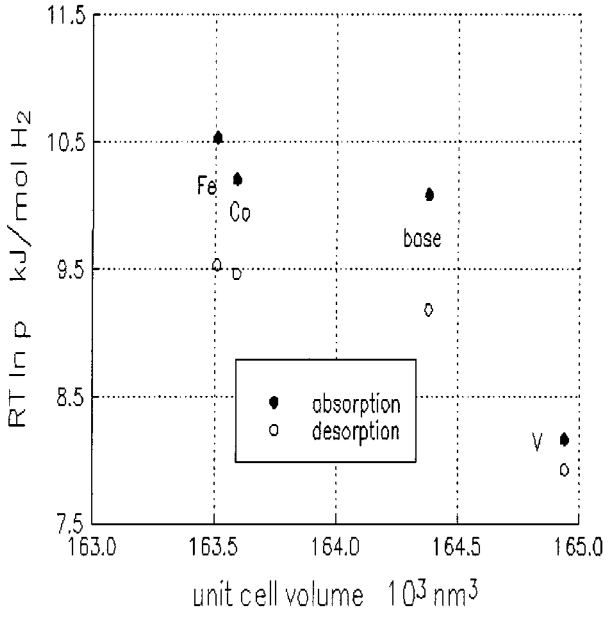

Figure 5 Gibbs free energy ($\Delta G = RT \ln p$) at 20 °C vs. unit cell volume (base: $Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.8}$; others: $Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.7}X_{0.1}$; X = V, Co or Fe).

Hysteresis values of high-pressure AB_2-H_2 systems have been reported rather scarcely but in many of the reported cases the hysteresis effect has been impractically high [5–8]. On the other hand, it is well-known that hysteresis can be effectively reduced, and even eliminated, e.g. in the case of $Ti_{1+x}Cr_{1.2}Mn_{0.8}$ by super-stoichiometry of Ti, and in the case of $Ti_{1.2}Cr_{2-y}Mn_y$ by increasing Cr-content [9]. Unfortunately, this seems to be achieved invariably with the cost of increased sloping and/or decreased length of the PCI plateaus, already at −10 °C [9]. Nevertheless, it appears to be possible to avoid these drawbacks to a large extent by carefully chosen minor substitutions of Ti or Mn [10], at least at somewhat lower pressure levels than in the present study. The hysteresis values reported here are among the small but not the smallest; PCI plateaus are among the flat (excluding the V-substituted alloy) but not the flattest, and the capacities are good, too. Altogether, the observed diversity of hysteresis and PCI plateau slope behaviour among these high-pressure hydrides is not fully understood. More light could be shed on these phenomena if the hydriding/dehydriding processes could be studied *in situ*, e.g. by high-pressure XRD or neutron diffraction. Near ambient pressure, *in situ* XRD has proven to be a useful tool to study hydride formation reactions [11, 12]. By using such methods, it should be possible to find out, whether the hydriding reaction occurs as an abrupt phase change from the solid solution (α) to the hydride phase (β), or as a more continuous increase of the hydrogen concentration in the host lattice. In the former case, the change in the lattice parameters would be discontinuous and the resulting stresses at the α-β interface would probably be proportional to the relative change of the unit cell volume (or lattice parameters). Hydriding reactions proceeding in such a way could be expected to result in a hysteresis effect proportional to the relative change of the unit cell volume between α- and β-phases, but possibly in flat PCI plateaus, too, if the interstitial lattice sites occupied by hydrogen atoms have the same binding energy. In the latter case, however, there would be no clear α-β interface under dynamic conditions and only a single phase could be detected under static pressure-temperature conditions (solid solution). The lattice parameters would change in a more or less continuous manner and the stresses and strains inside the lattice would be less pronounced and also more evenly distributed throughout the lattice during the hydriding process. This could be expected to result in a small or non-existing hysteresis effect, but probably in sloping PCI plateaus, as well. However, similar PCI behaviour—somewhat sloping plateaus and very small hysteresis—could be observed in the case of separate but coexisting hydrogen-poor and hydrogen-rich phases as well: firstly, if the alloy is not quite homogeneous, and secondly, if the hydriding reaction proceeds via (several) intermediate hydride phases with slightly different hydrogen content. Comparison of *in situ* structural information and hysteresis (and PCI plateau slope) data might help us understand better the reasons for the large variety of observed PCI properties, including hysteresis. But as long as such high-pressure *in situ* studies cannot be performed, the above outlined hypotheses are difficult to confirm. Probably the best approximation of *in situ* investigations can be achieved by hydriding the samples to different hydrogen concentrations, quenching them with liquid nitrogen and then poisoning with, e.g. SO_2, in order to get the XRD spectra of fully as well as partly hydrided samples. In addition, a correlation between the relative change of the unit cell volume in the α-β phase transformation and the hysteresis factor might be obtained. Such attempts are under way.

4. Conclusions

The main objective of this study was to find a way to combine the best PCI-features of $TiCrMn_{0.55}Fe_{0.3}V_{0.15}$-$H_2$ (almost hysteresis free) and $Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.8}$-$H_2$ (good capacity also at high temperatures) systems. The experimental approach chosen, minor substitutions of Mn in $Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.8}$ by V, Co and Fe, was partially successful: a completely satisfactory alloy-hydrogen system was not found, but Co- and V-substituted systems showed promising results. $Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.7}V_{0.1}$-$H_2$ system was practically hysteresis free but PCI plateau slopes were increased; $Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.7}Co_{0.1}$-$H_2$ system showed slightly decreased hysteresis and otherwise unchanged, relatively good PCI-properties. Thus, it was concluded that decreasing V-content in the former and increasing Co-content in the latter system deserve further attention. Substituting Fe alone for Mn does not seem to be an interesting option.

Acknowledgements

This work has been financed in part by the Technology Development Centre (TEKES), Finland, under the NEMO2 research programme.

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Received 14 April 1998
and accepted 15 June 1999