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Effect of alloying element on the sloping hydrogen plateaux in zirconium-based Laves phase systems

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Abstract

The hydriding and dehydriding properties of the quarternary $Zr_{1-x}Ti_xMnFe$ and $Zr_{1-x}Ti_xV_{0.5}Fe_{1.5}$ Laves phase alloys for the range $0 \leqslant x \leqslant 0.3$ were investigated as a function of alloy concentration. In addition, by comparing previously reported data on the $Zr_{1-x}Ti_xCr_{1-y}Fe_{1+y}$ system with those of the above two systems, the effect of alloying elements (*e.g.* titanium and iron) on the behaviour of the plateau slope was systematically analysed in order to understand the origin of sloping plateaux in the zirconium-based Laves phase. As titanium substitutes for zirconium in the $Zr_{1-x}Ti_xMnFe$ alloys, the slopes of the linearly increasing plateaux become lower with increasing hydrogen concentration. Unlike the $ZrCr_2$-base system, well-defined plateaux appear at $x = 0.2$ and a further increase in x to 0.3 produces an increase in the plateau slope. However, in the $Zr_{1-x}Ti_xV_{0.5}Fe_{1.5}$ system, titanium substitution does not cause any significant change in the plateau slope. From investigations of the lattice strain of each type of alloy system, it is found that the variations in the degree of slope with alloy composition is closely associated with the lattice strain of alloy caused by elemental substitution. It is suggested from the above results that the sloping plateaux in the zirconium-based Laves phase originates from the difference between the energy levels of various interstitial sites with respect to hydrogen where the energy level of each site is determined from the combined effects of two factors: a chemical energy and a strain energy.

1. Introduction

It is well known that AB_2 Laves phase alloys are potential hydrogen storage materials because of their large hydrogen capacity and rapid reaction rate with hydrogen [1]. AB_2 alloys consist of rare earth (R) or R-like elements (zirconium or titanium) and late transition elements (vanadium, chromium, manganese, iron etc.). The interactions of the zirconium-based Laves phases such as ZrV_2, $ZrCr_2$, $ZrFe_2$ and $ZrCo_2$ with hydrogen were first studied by Pebler and Gulbransen [2] and the hydriding properties of $ZrMn_2$ were investigated by Shaltiel *et al.* [3] and their pseudobinaries have been developed in order to adjust the hydride stability of the alloy without markedly reducing the hydrogen storage capacity [1]. In many cases, titanium and iron have

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been used for substitution of A and B elements respectively. Many modifications involving partial substitution in zirconium-based Laves phases have been usually investigated in $ZrMn_2$-type and $ZrCr_2$-type alloy systems.

However, it has been revealed that the plateau slope and hysteresis in the Laves phase are strongly affected by alloying elements and their concentrations. Because systems with low hysteresis and flat plateaux are required for practical applications such as heat pumps, one should examine the nature of the two factors, slope and hysteresis, and search for improved materials in the zirconium-based Laves phase alloys. However, there are only very limited data on *P–C* isotherms available concerning hysteresis and plateau slope as affected by alloying elements and their concentrations.

In the $ZrMn_2$-type alloys, it has been reported that the degree of slope and the extent of hysteresis in the *P–C–T* curves are very high and large respectively [4–8]. Iron substitution with manganese in $Zr(Mn_xFe_{1-x})_2$ [5] does not change the degree of slope of plateaux while there is some compositional dependence on the plateau slopes in the $Zr_{1-x}Ti_xMnFe$ alloys ($x = 0.2$ and 0.3) [6]. However, the origin of the sloping plateaux in the $ZrMn_2$-type alloys is still unclear. Wallace and coworkers [6] reported $Zr_{0.8}Ti_{0.2}MnFe$ to be the best of the Laves phases owing to its good hydrogenation characteristics, but this alloy still exhibits a large hysteresis.

On the contrary, $ZrCr_2$-type systems such as $Zr(Cr_{1-x}Fe_x)_2$ [9–11] exhibit a moderate hysteresis and a somewhat lower plateau slope than the $Zr(Mn_{1-x}Fe_x)_2$ system does [5]. There is no apparent dependence of the plateau slopes on iron concentration. Recently, it has been observed from the $Zr_{1-x}Ti_xCr_{1-y}Fe_{1+y}$ system [12] that titanium substitution for zirconium plays an important role in determining the degree of slope of the *P–C–T* curve and replacement of iron by chromium affects only the stabilities of hydrides and the extent of hysteresis. Well-defined plateaux are observed for $Zr_{0.9}Ti_{0.1}Cr_{1-y}Fe_{1+y}$ alloys (*i.e.* $x = 0.1$). It was suggested that the hydrogen site occupancy in the lattice is altered by titanium substitution and not by the replacement of chromium by iron [12].

In ZrV_2-type materials, only very limited *P–C–T* data have been reported although a variety of modifications can be made [3].

Consequently, it can be said that the titanium substitution plays a key role in determining the behaviour of the plateau slope of Laves phases compared with the case of iron substitution, but the effect of titanium substitution on the sloping plateaux in all Laves phases, except in $ZrCr_2$-based systems, is still unclear.

In this paper, the thermodynamic properties of the $Zr_{1-x}Ti_xMnFe$–H_2 and $Zr_{1-x}Ti_xV_{0.5}Fe_{1.5}$–$H_2$ systems are investigated by measuring *P–C* isotherms as a function of x. The thermodynamic properties of the $Zr_{1-x}Ti_xCr_{1-y}Fe_{1+y}$–$H_2$ [12] are reanalysed to investigate the behaviour of the plateau slope. Using the above results, the effect of the alloying element, especially the effect of titanium substitution, on the properties of various systems will be compared. After analysis of the data it is hoped to obtain a better understanding of the origin of the sloping plateaux in the zirconium-based Laves phases.

2. Experimental details

The different compounds investigated in this study, $Zr_{1-x}Ti_xMnFe$ and $Zr_{1-x}Ti_xV_{0.5}Fe_{1.5}$ with various x, were prepared by arc melting appropriate proportions of zirconium (purity, 99.7%), manganese (purity, 99.9%), vanadium (purity, 99.9%) and iron (purity, 99.9%) in an argon atmosphere. The samples were turned over and remelted several times to ensure homogeneity of the alloy. In the $ZrMn_2$-type alloys, the manganese content was controlled to be within approximately 0.5% of the desired composition by adding appropriate excess manganese prior to melting, and these alloys were vacuum annealed at 950 °C for 1 day. All the alloys investigated in this work were in the single-phase range of C14 hexagonal Laves phase as verified by X-ray diffraction.

The lattice parameters of each sample calculated from the X-ray data are listed in Table 1. About 1 g of pulverized sample, with an initial size of $-100+325$ mesh, was placed into a copper tube reactor. A high pressure Sievert's-type hydrogen-charging apparatus was used to obtain the *P–C* isotherm curve.

In all cases, hydrogen was absorbed quite readily with no special activation treatment. *P–C* isotherms for absorption and desorption were measured at temperatures ranging from 20 to 60 °C to obtain thermodynamic parameters. From the *P–C–T* results, the changes in hydrogenation characteristics including plateau slope behaviour in each type of alloy system were investigated as a function of alloy concentration. The degree of slope was defined as $d(\ln P_f)/d([H]/[AB_2])$, where P_f is the equilibrium pressure for absorption and is obtained along the plateau region.

3. Results and discussion

3.1. *Thermodynamic properties*

Figure 1 shows the change in *P–C–T* curves in the $Zr_{1-x}Ti_xMnFe–H_2$ system as the titanium concentration increases ($x=0$, 0.1, 0.2 and 0.3). The hydrogen storage capacity $[H]/[AB_2]$ lies between 2.7 and 2.84 up to $x=0.2$ but suddenly decreases to about 2.0 at $x=0.3$. From the overall *P–C–T* curves in Fig. 1, it is of significance to note that the plateau slope as well as the hydride stability in $Zr_{1-x}Ti_xMnFe$ is greatly affected by x, in which the titanium effect on the *P–C–T* behaviour is similar to that in the $Zr_{1-x}Ti_xCr_{1-y}Fe_{1+y}$ system [12] but exhibits somewhat different trends.

The plateau region of titanium-free ZrMnFe ($x=0$) shows linearly increasing plateau pressure with increasing $[H]/[AB_2]$ but the degree of plateau slope is higher than those in $Zr(Cr_{1-x}Fe_x)_2$ series [10]. As x increases to 0.2, the degree of slope is gradually reduced from a $d(\ln P_f)/d([H]/[AB_2])$

TABLE 1

Crystallographic and hydrogen storage data of $Zr_{1-x}Ti_xMnFe$ and $Zr_{1-x}Ti_xV_{0.5}Fe_{1.5}$ alloy systems

Alloy concentration	Lattice parameters (Å)		ΔH (kcal (mol H_2)$^{-1}$)		ΔS (cal (mol H_2)$^{-1}$ K^{-1})		[H]/[AB_2] at 30 atm	Degree of slope
x	a	c	Absorption	(Desorption)	Absorption	(Desorption)		
$Zr_{1-x}Ti_xMnFe$								
0	5.021	8.211	−5.59	(8.17)	−19.7	(24.7)	2.80	0.75
0.1	5.002	8.180	−5.45	(7.74)	−20.2	(24.6)	2.84	0.58
0.2	4.977	8.134	−5.17	(7.08)	−21.0	(24.2)	2.70	0.38
0.3	4.974	8.140	−5.21	(6.69)	−21.4	(23.9)	1.98	0.59
$Zr_{1-x}Ti_xV_{0.5}Fe_{1.5}$								
0	5.041	8.248					3.10	0.81
0.1	5.026	8.216					2.98	1.15
0.2	5.005	8.184					2.78	0.95
0.3	5.001	8.168					2.56	0.83

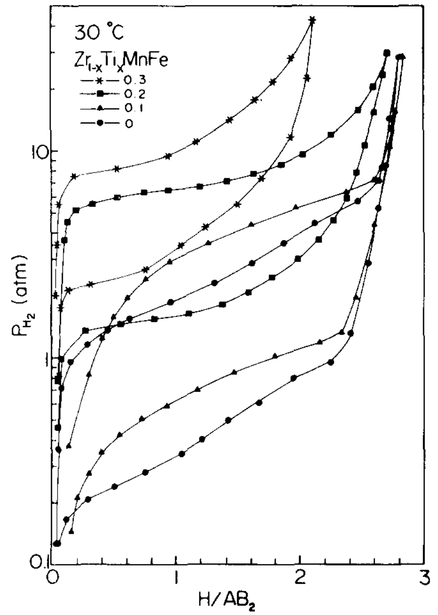


Fig. 1. *P–C–T* curves for the $Zr_{1-x}Ti_xMnFe$–H_2 system at 30 °C.

value of 0.75 for $x=0$ to 0.38 for $x=0.2$. These are caused by the greater increase in equilibrium pressures in the lower hydrogen content than in the high [H]/[M] range along the plateau region, which is nearly the same as for $Zr_{1-x}Ti_xCr_{1-y}Fe_{1+y}$ [12]. For $x=0.3$, the *P–C–T* curve exhibits no distinct plateau pressures in the two-phase region. It can be deduced from the above that the effect of titanium substitution for zirconium on the *P–C–T* behaviour on the $Zr_{1-x}Ti_xMnFe$, in particular on the slope and on the hydride stability, similar to that in the $ZrCr_2$-type pseudobinaries except in the presence of a well-defined plateau at $x=0.2$. All the alloys in Fig. 1 also exhibit a large hysteresis the values of which are in the range from 521 cal (mol $H_2)^{-1}$ for $x=0$ to 340 cal (mol $H_2)^{-1}$ for $x=0.3$ at room temperature while the values for $Zr_{1-x}Ti_xCr_{1-y}Fe_{1+y}$ are about 20–200 cal (mol $H)^{-1}$ [12].

The enthalpy ΔH and the entropy ΔS of the hydride formation and decomposition were computed using the least-squares method from the van't Hoff plot of ln P_{H2} *vs.* $1/T$ at $[H]/[AB_2]=1.0$ for $Zr_{1-x}Ti_xMnFe$ alloys. A good linear fit was observed in all cases. The results are summarized in Table 1 and plotted in Fig. 2. Also a linear dependence on x is obtained for thermodynamic parameters. The values of $|\Delta H|$ for hydride formation and decomposition decrease linearly with increasing x, but there exists more compositional dependence on $|\Delta H|$ in dehydriding than in hydriding. The measured enthalpy changes for hydriding and dehydriding range from -5.59 and 8.17 kcal (mol $H_2)^{-1}$ for $x=0$ to -5.21 and 6.69 kcal (mol $H_2)^{-1}$ respectively. The $|\Delta S|$ values increase with increasing x in the hydriding case but decrease with increasing x in the dehydriding case. The measured values

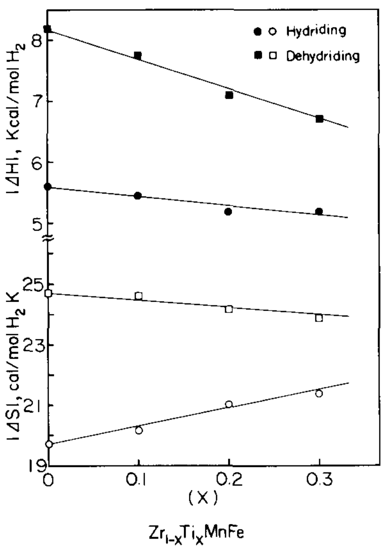


Fig. 2. The thermodynamic parameters ΔH and ΔS for hydride formation and decomposition calculated from the $Zr_{1-x}Ti_xMnFe$–H_2 system.

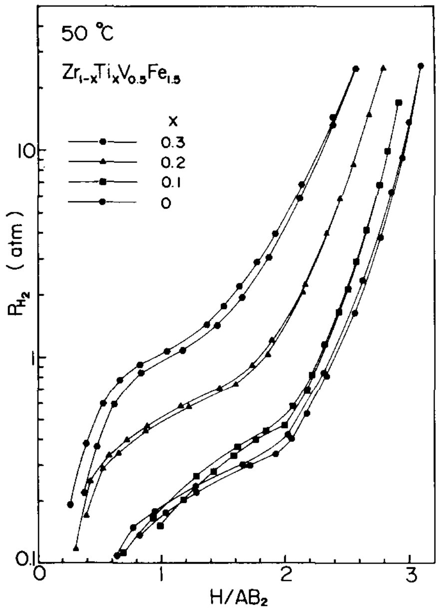


Fig. 3. *P–C–T* curves for the $Zr_{1-x}Ti_xV_{0.5}Fe_{1.5}$–$H_2$ system at 50 °C.

for hydride formation and decomposition are from -19.7 and 24.7 cal (mol $H_2)^{-1}$ K^{-1} for $x=0$ to -21.4 and 23.9 cal (mol $H_2)^{-1}$ K^{-1} for $x=0.3$ respectively. According to Wallace and coworkers [6], 20% substitution of titanium in the $Zr_{1-x}Ti_xMnFe$ system raises the vapour pressure approximately fivefold and 30% substitution increases it more than tenfold. However, in this work, the measured equilibrium pressures for hydride formation (at $[H]/[AB_2]=1.0$) are 1.88 atm for $x=0$, 3.0 atm for $x=0.1$, 6.5 atm for $x=0.2$, and 10.0 atm for $x=0.3$, indicating that the vapour pressure increases with a ratio of about 1.6-fold per 10% titanium substitution. This may be attributed to the differences in experimental conditions such as sample preparation and measuring technique.

The effect of titanium concentration in the $Zr_{1-x}Ti_xV_{0.5}Fe_{1.5}$–$H_2$ system on the *P–C–T* curve is represented in Fig. 3. As x increases, the hydrogen storage capacity decreases gradually from 3.1 for $x=0$ to 2.56 for $x=0.3$. In contrast with other alloy systems such as $ZrCr_2$-based alloys [12] and $ZrMn_2$-based alloys (Fig. 1), the $Zr_{1-x}Ti_xV_{0.5}Fe_{1.5}$ alloys do not cause any significant change in the plateau slopes as x varies. The detailed discussion for the plateau slope behaviour will be discussed later. It is also of significance to note that ZrV_2-based alloys in Fig. 3 have extremely low hysteresis energies, in the range of 17–30 cal (mol $H_2)^{-1}$. Thus it can be said from the *P–C–T* behaviours of the various types of alloy system that the hysteresis effects in Laves phase differ greatly in magnitude for different alloy systems. We are now investigating the hysteresis in the Laves phase of different alloy systems and will report this in another paper.

3.2. *The plateau slope behaviour*

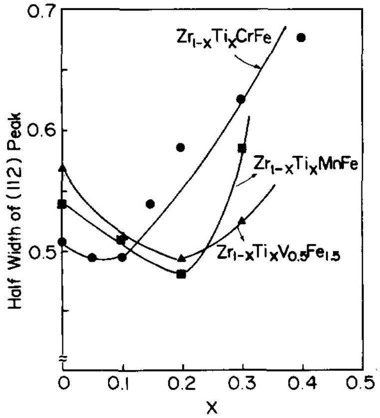
It is significant to note that the plateau slope in the zirconium-based Laves phase is not influenced by iron substitution with chromium (*e.g.* $Zr_{0.9}Ti_{0.1}Cr_{1-y}Fe_{1+y}$ [12] and $Zr(Cr_{1-x}Fe_x)_2$ [10]) or with manganese ($Zr(Mn_{1-x}Fe_x)_2$ [5]) but is greatly affected by titanium substitution for zirconium. Northwood *et al.* [9] explained the plateau slope behaviour in the $Zr(Cr_{1-x}Fe_x)_2$ alloys by a local environment model, in which hydrogen mainly occupies tetrahedral sites of Zr(2)Cr(2), Zr(2)Fe(2) and Zr(2)CrFe interstitial sites among A(2)B(2)-type sites and partially ZrCr(3), ZrFe(3), ZrCr(2)Fe and ZrCrFe(2) sites among AB(3)-type sites in the lattice. Each site has its own heat of hydride formation, which would lead to different local hydriding pressures — hence the sloping plateaux in the *P–C–T* curves. The local environment model cannot account for the well-defined plateaux in $Zr_{0.9}Ti_{0.1}Cr_{1-y}Fe_{1+y}$ alloys (Fig. 2 of ref. 12) and $Zr_{0.8}Ti_{0.2}MnFe$ (Fig. 1) because, according to the above model, there should exist more interstitial sites having different heats of formation owing to the presence of titanium in the lattice, and thus one would expect to enhance the plateau slope behaviour. The chemical energy between hydrogen and neighbouring metallic atoms is considered to be only one of contributing factors to the plateau slope behaviour. Other contributions, such as the size effect or electronic factors, are also to be considered.

In the hexagonal AB_2 Laves phases, there are two different sites, A(2)B(2) and AB(3)-type interstices, for hydrogen occupation and these sites are further classified, depending on the tetrahedron face shared, into four types of A(2)B(2) sites and two types of AB(3) site [1]. Several investigators observed, on the basis of neutron diffraction results, that hydrogen occupies predominantly A(2)B(2) interstitial sites although some hydrogen occupies the AB(3)-type sites [13–15]. Didisheim *et al.* [13] also observed different occupancies in the four types of A(2)B(2) site in which hydrogen occupies predominantly 12k and 6h (6h(1) or 6h(2)) sites compared with 24l sites. Sinha and Wallace [7] explained these preferred occupancies by strain energies associated with the occupancy of hydrogen in each site, where the larger sites (12k site) in the hole size among four types of A(2)B(2) site has a minimum strain energy.

Therefore the size effect of interstices, in addition to the chemical energy effect, can be of importance in determining the energy level of hydrogen occupation sites and then the size difference between interstitial sites may contribute to determining the plateau slope behaviour. To estimate the strain energies of each sites in the lattice, the hole radii of various interstices must be known. However, it is very hard to calculate the hole radii of each site in the lattice as the alloy concentration varies because the compounds investigated in this work are the quarternary alloy system. Hence we qualitatively estimated the strain energies of various interstitial sites from X-ray diffraction data of alloys as a function of alloy concentration. Because the atomic sizes of substituents (*e.g.* titanium and iron) are different from those of constituting elements of Laves phase such as zirconium, vanadium, chromium and manganese, the alloy itself is subjected into the lattice strain in order to retain the Laves phase structure when the alloy concentration varies. The lattice strain can be determined from the half-width of X-ray diffraction peaks which are associated with the particle size and with the lattice strain of alloy [16].

3.2.1. The $Zr_{1-x}Ti_xCr_{1-y}Fe_{1+y}$ system

Figure 4 shows the progressive change in the half-width of (112) diffraction peaks as a function of x for the $Zr_{1-x}Ti_xCrFe$, $Zr_{1-x}Ti_xMnFe$ and $Zr_{1-x}Ti_xV_{0.5}Fe_{1.5}$ systems respectively. Because all X-ray data were obtained from the same particle size distribution (−325 mesh), the change in half-width in Fig. 4 means the variation in the lattice strain as a function of x. Figure 5 represents the variations with x in the degree of slope for the above three alloy systems. On comparison of Fig. 4 and Fig. 5, both the change in the lattice strain and the change in the degree of slope in $Zr_{1-x}Ti_xCrFe$ show the same trend with titanium concentration, exhibiting minima at $x = 0.1$ at which concentration a well-defined plateau is formed. A similar relationship can be also obtained in the variation in *c*/*a* *vs.* x (Fig. 6). In contrast, as shown in Figs. 7 and 8, both the lattice strain and *c*/*a* in the $Zr_{0.9}Ti_{0.1}Cr_{1-y}Fe_{1+y}$ system, where the degree of slope is independent of y, exhibit nearly constant values as iron is replaced by chromium. The above results indicate that the sloping mechanism in the $Zr_{1-x}Ti_xCr_{1-y}Fe_{1+y}$ system can be closely correlated with the lattice strain (or with the strain energy of interstitial site associated with both the lattice strain and the structural change).



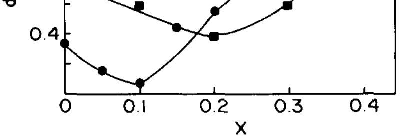
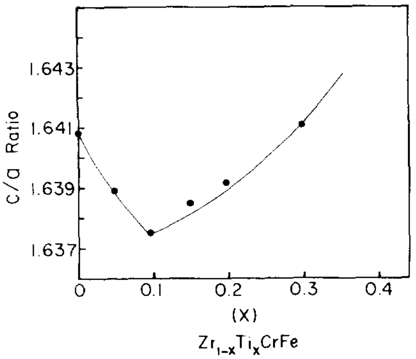


Fig. 4. The variation in half-width of (112) diffraction peaks *vs.* x in the $Zr_{1-x}Ti_xCrFe$, $Zr_{1-x}Ti_xMnFe$ and $Zr_{1-x}Ti_xV_{0.5}Fe_{1.5}$ alloys.

Fig. 5. The changes in the degree of slope *vs.* x for the $Zr_{1-x}Ti_xCrFe$, $Zr_{1-x}Ti_xMnFe$ and $Zr_{1-x}Ti_xV_{0.5}Fe_{1.5}$ systems.



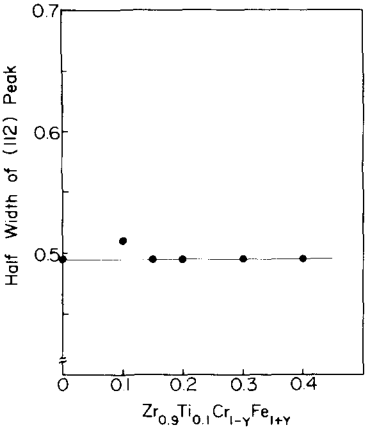
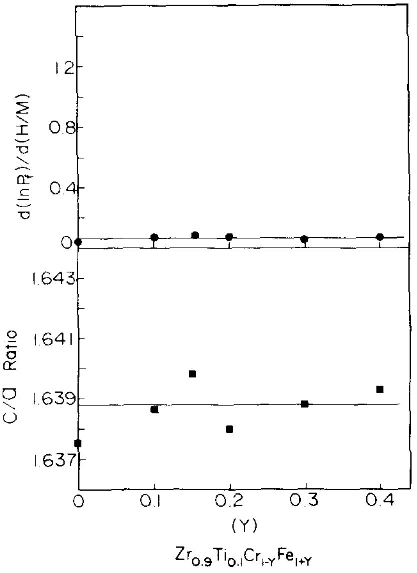


Fig. 6. The variation in the c/a ratio *vs.* x in $Zr_{1-x}Ti_xCrFe$.

Fig. 7. The variation in half-width of (112) diffraction peaks *vs.* y in the $Zr_{0.9}Ti_{0.1}Cr_{1-y}Fe_{1+y}$ system.



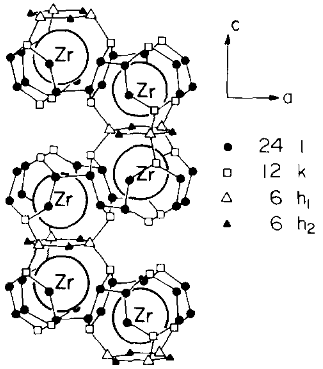


Fig. 8. The changes in the degree of slope and c/a ratio *vs.* y for the $Zr_{0.9}Ti_{0.1}Cr_{1-x}Fe_{1+y}$ system.

Fig. 9. The structural arrangement of A(2)B(2)-type sites (24l, 12k, 6h(1) and 6h(2) sites) around zirconium atoms.

It is confirmed from the results described above that the strain effect in $Zr_{1-x}Ti_xCrFe$ is due to the presence of size differences among the various interstitial sites (*e.g.* size difference in 12k, 24l and 6h sites of A(2)B(2)-type sites) in the lattice, which arises from the non-ideal c/a ratio of the compound itself. The c/a ratio at $x=0$ is 1.641 (ZrCrFe) while that for the ideal case is 1.633 [17]. When the *c*/*a* ratio is larger than 1.633, as shown in Fig. 9, the 6h sites (6h(1) of 6h(2)) and the 12k sites lying in the *c* direction rather than in the *a* direction around the zirconium atoms can have a somewhat larger hole size than the 241 sites. Therefore, as the hydrogen occupies the A(2)B(2)-type sites in ZrCrFe ($x=0$), the larger sites such as the 6h or the 12k sites would be preferentially filled to minimize the strain energy of the lattice and hence the slope of the plateaux in ZrCrFe occurs.

At $x=0.1$, the lattice strain as well as the *c*/*a* ratio of the alloy exhibit a minimum value. This implies that the alloy becomes a more close-packed structure at 10% titanium substitution for zirconium and the size difference between various A(2)B(2)-type sites is minimized. This can cause a well-defined plateau in the *P*–*C* isotherm, but the *c*/*a* ratio at $x=0.1$ is 1.638, which is still higher than that of the ideal C14 structure. There can still be a strain energy effect due to the size difference between interstitial sites in the lattice, although somewhat lower than in the case of titanium-free alloys, where one would expect a sloping plateau. Hence the strain energy factor alone cannot explain the well-defined plateaux at $x=0.1$ in the $Zr_{1-x}Ti_xCrFe$ alloys. On the contrary, considering the chemical energy effect only, there should exist more interstitial sites for hydrogen occupation, *e.g.* Zr(2)B(2), ZrTiB(2) and Ti(2)B(2) (B ≡ Cr, Fe), having different affinities for hydrogen, which would also enhance the plateau slope behaviour.

It is very suggestive that the well-defined plateaux at $x=0.1$ are correlated with the combined effect of two energy factors for hydrogen occupation: a chemical energy effect and a strain energy effect. As shown in Table 2, because both the hydrogen affinity [18] and the atomic size of titanium are lower and smaller respectively than those of zirconium, a portion of the ZrTiB(2)-type and the Ti(2)B(2)-type sites has a lower chemical binding energy towards hydrogen and probably a somewhat larger hole size (*i.e.* smaller strain energy effect) than Zr(2)B(2)-type sites. Then the energy levels of sites occupied by hydrogen can be uniform and flat plateaux in the *P*–*C*–*T* curve would be produced.

For the $Zr_{0.9}Ti_{0.1}Cr_{1-y}Fe_{1+y}$ system, the variation in y, in contrast with the case of titanium substitution, does not cause any significant change in

TABLE 2

Goldschmit radii and heats of hydride formation of elements

	Goldschmit radius (Å)	ΔH_f [18]
Zr	1.602	−188 (ZrH_2) (kJ (mol hydride)$^{-1}$)
Ti	1.462	−136 (TiH_2) (kJ (mol hydride)$^{-1}$)
V	1.346	−37 ($V_{1-x}H_x$) (kJ (g atom H)$^{-1}$)
Cr	1.282	−7 ($Cr_{1-x}H_x$) (kJ (g atom H)$^{-1}$)
Mn	1.254	−5 ($Mn_{1-x}H_x$) (kJ (g atom H)$^{-1}$)
Fe	1.274	+7 ($Fe_{1-x}H_x$) (kJ (g atom H)$^{-1}$)

the lattice strain as well as the c/a ratio of alloy and therefore no change in the plateau slope occurs. These originate from the similarities in the atomic size as well as the hydrogen affinity between chromium and iron atoms. The iron substitution for chromium does not cause the size and the chemical binding energy of hydrogen of occupation sites to vary; thus the result is a nearly uniform increase (or decrease) in the energy levels of each site.

3.2.2. The $Zr_{1-x}Ti_xMnFe$ and $Zr_{1-x}Ti_xV_{0.5}Fe_{1.5}$ systems

On comparison of the changes in the lattice strain and in the degree of slope with increasing x (Fig. 4 and Fig. 5) in the various types of alloy system, the slope behaviour appears to have a different nature from one alloy system to another. In $Zr_{1-x}Ti_xCrFe$, as already noted above, the lattice strain as well as the degree of slope exhibit minimum values at $x=0.1$. Similar trends are also found in $Zr_{1-x}Ti_xMnFe$ but the minima of the above two factors, the lattice strain and the degree of slope, can be seen at $x=0.2$, where flat plateaux also exist, indicating that the slope behaviour of the $ZrMn_2$-based system is the same as that of the $ZrCr_2$-based system. However, in the case of the $Zr_{1-x}Ti_xV_{0.5}Fe_{1.5}$ alloys, there is no apparent improvement in the plateau slope as x varies although the lattice strain exhibits a minimum value at $x=0.2$.

It is suggested that the occurrence of flat plateaux at $x=0.2$ in $Zr_{1-x}Ti_xMnFe$ results from the larger initial lattice strain of ZrMnFe ($x=0$) than that of ZrCrFe ($x=0$) in $Zr_{1-x}Ti_xCrFe$. Because the difference between the atomic sizes of manganese and iron is, as shown in Table 2, somewhat larger than that between the atomic sizes of chromium and iron, ZrMnFe has a larger lattice strain when retaining the Laves phase structure. In addition, the hydrogen affinity of manganese is nearly the same as that of chromium, indicating the presence of a similar chemical energy effect between $Zr_{1-x}Ti_xCrFe$ and $Zr_{1-x}Ti_xMnFe$. These would cause a larger size difference in hydrogen occupation sites and thus a sloping plateau with a higher degree of slope in ZrMnFe would be produced. This size effect of ZrMnFe would not be minimized until the alloy concentration reaches $x=0.2$, explaining the flat plateaux in the *P–C–T* curve of $Zr_{0.8}Ti_{0.2}MnFe$ alloy.

The fact that the plateau slope is independent of the titanium concentration in $Zr_{1-x}Ti_xV_{0.5}Fe_{1.5}$ can be attributed to larger differences in atomic size as well as to the hydrogen affinity between vanadium and iron. As shown in Fig. 4, the lattice strain of $ZrV_{0.5}Fe_{1.5}$ ($x=0$) is largest among the three types of titanium-free alloys, which would produce a severely enlarged size difference of the interstices and enhance the slope. The lattice strain exhibits a minimum value at $x=0.2$ although there is no improvement in the plateau slope. This means that there exists a strong chemical energy effect in addition to strain energy effects in the sites occupied by hydrogen.

Consequently, it can be said that the strain energy effect, in addition to the chemical energy effect according to local environment model, is one of the contributing factors that cause the plateau slope behaviour. When designing hydride alloys of zirconium-based Laves phase with flat plateaux, one should consider both atomic size and hydrogen affinity of the late transition elements and the compound has to be alloyed with an appropriate amount of titanium. The more quantitative contribution to the hydrogen energy levels of each of the sites arising from the chemical energy factor and the strain energy factor cannot be determined. A more extensive study is required.

4. Conclusion

The $Zr_{1-x}Ti_xMnFe$ and $Zr_{1-x}Ti_xV_{0.5}Fe_{1.5}$ alloy systems exhibit many attractive thermodynamic characteristics compared with the $Zr_{1-x}Ti_xCr_{1-y}Fe_{1+y}$ system. In the $Zr_{1-x}Ti_xMnFe$ alloys, increasing x produces a decrease in the degree of slope as well as hydride stability. A well-defined plateau pressure is formed at $x = 0.2$, indicating that the slope behaviour in the $ZrMn_2$-based alloy system is nearly similar to that in the $ZrCr_2$-based alloy system. However, the titanium substitution in $Zr_{1-x}Ti_xV_{0.5}Fe_{1.5}$ does not cause any significant change in the plateau slope. The lattice strain of the alloy caused by elemental substitutions appears to have a close correlation with the slope behaviour and affects the strain energy of the sites occupied by hydrogen. It is suggested that the sloping plateaux in the zirconium-based Laves phase originate from the difference in energy levels of various interstitial sites towards hydrogen in the lattice where the energy level of each site is determined from the combined effects of two factors: a chemical energy and a strain energy.

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