Hydrogen storage properties of non-stoichiometric AB$_2$-type metal hydride [①]

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Abstract: Hydrogen storage properties of non-stoichiometric AB$_2$-type alloys, Ti$_{0.8}$Zr$_{0.2}$(MnCrVFe)$_{2-x}$($x = 0$, 0.1, 0.2, 0.3), have been studied. The results show that the structures of the substoichiometric alloys can be described using the replacement model, that is, some A-side atoms occupy the primary B-side atom positions. The equilibrium pressures of the alloys decrease gradually and the hysteresis effect between hydriding and dehydriding process decreases with the increase of x value. The free-energy change (ΔG) between hydriding and dehydriding process has a significant effect on the hysteresis of the alloys. The p-c-t plateau region becomes narrow and the reversible hydrogen capacity decreases with the increase of x value ($x > 0.1$), although the hydrogen absorption capacity increases. The alloy with $x = 0.1$ shows the optimum hydrogen storage properties.

Key words: hydrogen storage property; substoichiometric alloy; hysteresis effect   **Document code:** A

1   INTRODUCTION

Ti-based hydrogen storage alloys became attractive because of their large hydrogen capacities. Bernauer et al[1] and Li et al[2] pointed out that multi-element Ti-based hydrogen storage alloys are more promising materials for practical applications. (TiZr) (MnCrVFe)$_2$ alloy is a commonly used hydrogen storage alloy and mainly used in hydrogen compressor and hydrogen storage devices[3]. Our earlier research[4] shows that this alloy has a large hydrogen capacity, wide p-c-t plateau region, small plateau slope and hysteresis effect. But its application is limited due to the high equilibrium pressure. In the present work, non-stoichiometric alloys Ti$_{0.8}$Zr$_{0.2}$(MnCrVFe)$_{2-x}$ were selected and their equilibrium pressures and hydrogen storage properties were investigated.

2   EXPERIMENTAL

2.1   Preparation of alloy samples

The Ti$_{0.8}$Zr$_{0.2}$(MnCrVFe)$_{2-x}$($x = 0$, 0.1, 0.2, 0.3) alloys were prepared by melting together 99.8% sponge Ti, 99.8% sponge Zr, 99.6% electrolytic Mn, 99.0% electrolytic Cr, 99.8% sponge V and 99.9% pure Fe in a non-consumable arc melting furnace under an argon atmosphere. In order to obtain the designed alloys, the raw materials with approximately 4% excess Mn were melted in two stages, firstly under a small electric current (200 A) and subsequently under a large electric current (300 A) for three times to ensure homogeneity. The mass loss of the alloys after melting was about 3%.

2.2   Measurement of hydrogen storage properties

Hydrogen storage properties of the tested alloys were measured using a home-made p-c-t curve measuring apparatus. Fig.1 shows the schematic diagram of the apparatus. Particle size of the alloy samples was less than 174 μm with a mass of 10 g. Prior to measuring, the sample was activated and the activating process parameters are listed in Table 1. p-c-t curve plateau slope factor (S) and hysteresis factor (h) are determined using the following expressions:

$$S = \ln(p_{H/M=0.7}/ p_{H/M=0.3})/ 0.4 \qquad (1)$$
$$h = \ln(p_a/ p_d) \qquad (2)$$

where p_a and p_d represent hydriding and dehydriding equilibrium pressures near mid-plateau respectively. Thermodynamic properties, such as enthalpy change ΔH and entropy change ΔS, are determined in direct relationship to Van't Hoff equation:

$$\ln p = \Delta H/ RT - \Delta S/ R \qquad (3)$$

Table 1   Activating process parameters of hydrogen storage alloy

Degassing process			Hydriding process		Activating number
Temperature	Time	Vacuum	Pressure	Temperature	
90 ℃	3 h	1 Pa	3 MPa	26 ℃	5

2.3   Measurement of other properties

X-ray diffraction experiment was performed to determine whether the alloys were single-phase materials on a D/ max-RB type diffractometer. The sample size was less than 37 μm and the lattice constants were computed using high angle peak. Microhardness of the alloys was measured using HX-1 type microhardness instrument under 0.1 N loading. Each sample was measured 10 times and the average value was calculated. Densities of the samples were measured using water-draning method.
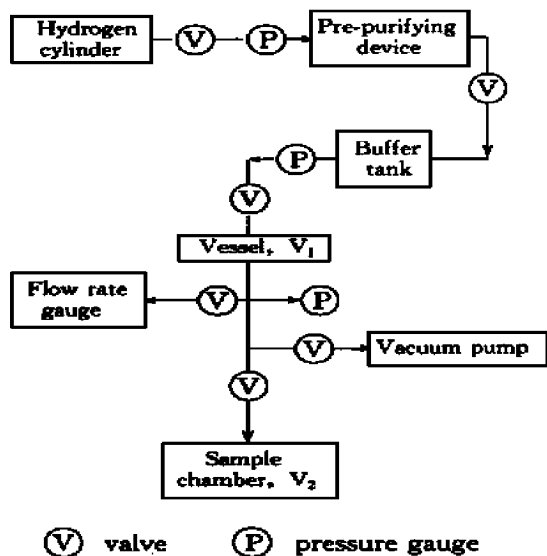
Fig .1　Schematic diagram of p-c-t
curve measuring apparatus

3　RESULTS

Fig .2 shows the p-c-t curves of $Ti_{0.8}Zr_{0.2}(MnCrVFe)_{2-x}$ alloys at 60 ℃ . It is observed that with the increase of substoichiometric degree (x) in B component, equilibrium pressures of the alloys decrease obviously, hydrogen absorption capacities increase and hysteresis effect between hydriding and dehydriding decreases, however, p-c-t curve plateau slope shows slight increase . The hydrogen storage property data, standard enthalpy change (ΔH^0) and entropy change (ΔS^0) of the alloys are listed in Table 2 and Table 3 respectively . The results show that p-c-t plateau region of the alloys becomes narrow in the case of x value larger than 0 .1 , especially when x value equals 0 .3 , which indicates the decrease in the

reversible hydrogen capacity of this alloy . Due to the increase of $c_{\alpha \to \beta}$, namely, hydrogen content corresponding to the starting point of $\alpha \to \beta$ phase transformation, the p-c-t plateau width decreases with the increase of x value although the hydrogen capacity of the alloy increases .
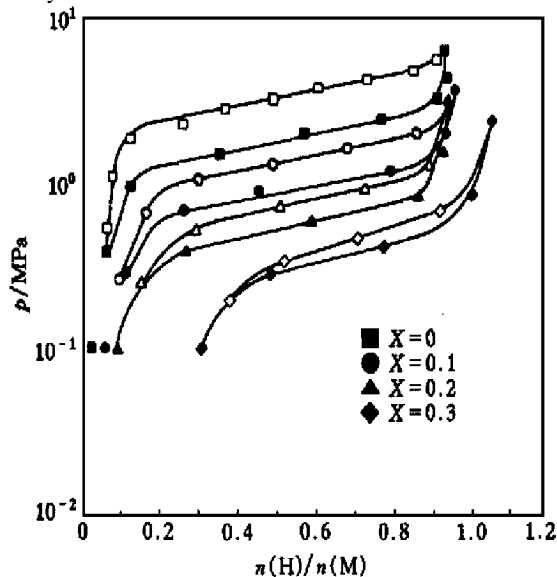

Fig .2　p-c-t curves of $Ti_{0.8}Zr_{0.2}(MnCrVFe)_{2-x}$ alloys (60 ℃)

Fig . 3 shows the relationship curve between $c_{\alpha \to \beta}$ and x value . It is of interest to note that the substoichiometric degree in B component has an obvious effect on increasing $c_{\alpha \to \beta}$. The reason will be discussed in detail in Section 4 . The effect of x value on $c_{\alpha \to \beta}$ was also observed earlier for $Ti_{1+x}Cr_{1.2}Mn_{0.8}$ alloys by Daikaku[6], however, the mechanism was not analyzed and just explained as the increase of stable hydride, which would not release hydrogen in the alloys .

The experimental results show that we can

Table 2　Hydrogen storage properties of $Ti_{0.8}Zr_{0.2}(MnCrVFe)_{2-x}$ alloys

Value of x	Equilibrium pressure/ MPa		Hydrogen capacity $n(H)/n(M)$	Plateau width $n(H)/n(M)$	S	h
	Hydriding	Dehydriding				
0	2 .49	1 .53	0 .94	0 .75 ~ 0 .8	1 .0	0 .5
0 .1	1 .27	0 .89	0 .96	0 .7 ~ 0 .75	1 .1	0 .4
0 .2	0 .70	0 .52	0 .96	0 .6 ~ 0 .7	1 .2	0 .3
0 .3	0 .32	0 .28	1 .04	0 .5 ~ 0 .6	1 .6	0 .1

Table 3　ΔH^0 and ΔS^0 of hyriding and dehydriding reaction

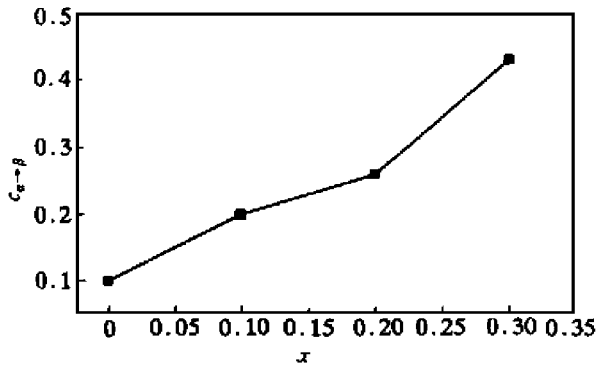| Value of x	$\Delta H^0/(kJ \cdot mol^{-1})$		$\Delta S^0(J \cdot K^{-1} \cdot mol^{-1})$		Inter-relative coefficient	
	Hydriding	Dehydriding	Hydriding	Dehydriding	Hydriding	Dehydriding
0	- 24 .5	27 .4	- 100 .3	104 .8	0 .99	0 .998
0 .1	- 28 .6	31 .2	- 106 .9	112 .2	0 .999	0 .999
0 .2	- 30 .1	35 .2	- 106 .4	- 120 .0	0 .999	0 .998
0 .3	- 29 .1	28 .3	- 96 .9	93 .6	0 .997	0 .995

Fig .3   Relationship between $c_{\alpha \to \beta}$ and x

decrease the equilibrium pressures of (TiZr) (Mn-Cr VFe)$_2$ series alloys through selecting substoichiometric AB$_{2-x}$ alloys . Simumtaneously , hysteresis effects of the alloys can be improved . It should be noted that , however , p-c-t plateau width will decrease , resulting in the decrease of reversible hydrogen capacity if substoichiometric degree in B component (x) is too large . The alloy shows optimum hydrogen storage properties in the case of x value equaling 0 .1 .

4   ANALYSIS AND DISCUSSION

4 .1   Structural changes of AB$_{2-x}$ alloys

There are three possible structures of the alloys when some B-type atoms are taken out of the stoichiometric alloys[7] : 1) being vacancies at primary B-side atom positions , called vacancy model ; 2) A-side atoms occupying primary B-side atom positions , called replacement model ; 3) some A-side atoms occupying B-side atom positions and partly being vacancies at primary B-side atom positions . The results of X-ray diffraction experiment show that all non-stoichiometric alloys involved in the present study are single-phase alloys . In order to determine the structures of the alloys , theoretical densities of the alloys were calculated according to the vacancy model and replacement model respectively and compared with the actual densities . Table 4 lists the lattice constants , crystal unit volumes , theoretical densities and actual densities of the alloys . The results show that the actual densities are very close to the theoretical densities deduced from the replacement model and far from that of the vacancy model . Moreover , the crystal unit volume in

creases with the increase of the x value . This indicates that the replacement model is more applicable for the Ti$_{0.8}$Zr$_{0.2}$(MnCr VFe)$_{2-x}$ alloys because the crystal unit volume will decrease if the vacancy model is tenable .

4 .2   Effect of substoichiometric ratio in B component (x) on $c_{\alpha \to \beta}$

All interstices in Laves phase structure alloys are quad-hedron interstices and divided into three types : 1) 2 A + 2 B , consisting of two A-side atoms and two B-side atoms and being 12 for one molecule ; 2) 1 A + 3 B , consisting of one A-side atom and three B-side atoms and being 4 for one molecule ; 3) 4 B , consisting of four B-side atoms and being 1 for one molecule . According to Shoemaker's exclusion principle[8] , two quad-hedron interstices having one common surface can not be occupied by hydrogen . So , most interstices can not be positioned by hydrogen . The research results from Didishmim et al[9] indicated that hydrogen atom occupies 2 A + 2 B interstice in the case of low hydrogen content while 1 A + 3 B interstice can also be occupied when the ratio of hydrogen atom to AB$_2$ molecule is larger than 0 .75 .

The structural analysis results reveal that the structures of the Ti$_{0.8}$Zr$_{0.2}$(MnCr VFe)$_{2-x}$ alloys are similar to that of the substitution of B component by Ti elements . Obviously , primary some 1 A + 3 B interstices change into 2 A + 2 B interstices after some B components are substituted by Ti and this is just the reason why $c_{\beta \to \alpha}$(hydrogen content corresponding to the end point of $\alpha \to \beta$ phase transformation) and hydrogen absorption capacity of the alloy increase . Simultaneously , primary some 2 A + 2 B interstices change into 3 A + 1 B interstices which have strong affinity for hydrogen . The latter change results in the increase of $c_{\alpha \to \beta}$. This means that much more hydrogen atoms occupy the 3 A + 1 B interstices prior to the $\alpha \to \beta$ phase transformation . Because the number of the changed 3 A + 1 B interstices is two times of the changed 2 A + 2 B interstices ($x = 0 .3$) , the increment of $c_{\alpha \to \beta}$ is much larger than that of $c_{\beta \to \alpha}$, which results in the decrease of p-c-t plateau width .

A simple calculation was carried out to check the reasonableness of the above analysis . Some primary 2 A + 2 B interstices in stoichiometric alloy , exactly

Table 4   Crystallographic data and densities of Ti$_{0.8}$Zr$_{0.2}$(MnCr VFe)$_{2-x}$ alloys

Alloy	$a/$ Å	$c/$ Å	c/a	$V/$ Å^3	$d_{tv}/$ (g·cm^{-3})	$d_{tr}/$ (g·cm^{-3})	$d_a/$ (g·cm^{-3})
$x = 0$	4 .884	8 .056	1 .652	166 .2	-	-	-
$x = 0 .1$	4 .890	8 .050	1 .646	166 .7	6 .36	6 .56	6 .52
$x = 0 .2$	4 .900	8 .058	1 .647	167 .6	6 .12	6 .53	6 .50
$x = 0 .3$	4 .908	8 .082	1 .646	168 .6	5 .93	6 .49	6 .48

d_{tv} and d_{tr} represent theoretical density calculated according to the vacancy model and the replacement model respectively ; d_a represents actual density .

1 .32 , change into 3 A + 1 B interstices in the case of $x = 0 .3$ for $Ti_{0.8}Zr_{0.2}(MnCrVFe)_{2-x}$ alloy . If all 3 A +1 B interstices are occupied by hydrogen ,the hydrogen capacity of this alloy is 0 .44 $n(H)/n(M)$ and the value must be corrected as η 0 .44 $n(H)/n(M)$ taking exclusion principle into account[8] . The corrected value is corresponding to the increment of $c_{\alpha \to \beta}$ between stoichiometric alloy and substoichiometric alloy . The interstice distribution is the same for the alloys with different x values , that is , η value is the same for the alloy . We suppose that N_{3A+1B} represents the number of 3 A + 1 B interstices and $\Delta c_{\alpha \to \beta}$ is the difference of $c_{\alpha \to \beta}$ between stoichiometric alloy and substoichiometric alloy , the relationship between N_{3A+1B} and $\Delta c_{\alpha \to \beta}$ should be expressed as follows :

$$(\eta/3) N_{3A+1B} = \Delta c_{\alpha \to \beta} \qquad (4)$$

Fig .4 shows the relationship curve between N_{3A+1B} and $\Delta c_{\alpha \to \beta}$ and the result is in good agreement with our analysis . Linear relationship is very apparent and inter relative coefficient is 0 .98 .
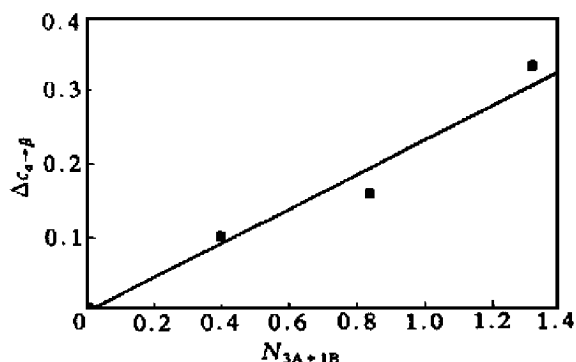

Fig .4   Relationship between N_{3A+1B} and $\Delta c_{\alpha \to \beta}$

4 .3   Hysteresis effects

It can be observed from Table 2 that substoichiometric alloy in B component has a profound effect on decreasing hysteresis between hydriding and dehydriding . At present , there have been many investigations to elucidate that the unreversible factors , such as plastic deformation , pulverization of particle size and shape , can affect the hysteresis remarkably[6,10] . Park et al[11] observed that the more easily the alloy pulverizes , the greater the hysteresis effect is . Elastic modulus , elastic limit and brittleness of the alloys are the most important data to study the hysteresis property .

The relationship between microhardness and hysteresis of $Ti_{0.8}Zr_{0.2}(MnCrVFe)_{2-x}$ alloys , shown in Fig .5 , indicates that the microhardness alone can not reflect the relationship between mechanical properties and hysteresis of the alloys .

It may be noted that the enthalpy change and the entropy change during hydriding and dehydriding process affect the hysteresis inevitably . According to Van' t Hoff equation , the relationship between pres-
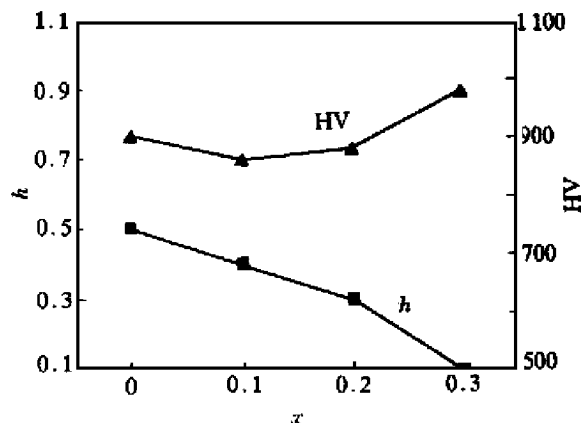

Fig .5   Microhardness (Hv) and hysteresis factor (h) of $Ti_{0.8}Zr_{0.2}(MnCrVFe)_{2-x}$ alloy

sure (p_a) and free-energy change (ΔG_a) during hydriding process can be expressed as

$$RTln\,p_a = \Delta G_a \qquad (5)$$

where ΔG_a can be deduced using the following expression

$$\Delta G = \Delta H - T\Delta S \qquad (6)$$

Under the similar circumstances for dehydriding process :

$$- RTln\,p_d = \Delta G_d \qquad (7)$$

where p_d and ΔG_d represent pressure and free-energy change during dehydriding process . The following equation can be obtained from Eqns .(5) and (7) :

$$RTln(p_a/p_d) = \Delta G_a + \Delta G_d \qquad (8)$$

where the left side of the equation is a multiplication of hysteresis factor ($ln(p_a/p_d)$) and RT , which can be approximately considered hysteresis energy . The free-energy change $\Delta G(\Delta G = \Delta G_a + \Delta G_d)$ during hydriding and dehydriding process are calculated and the results are shown in Fig .6 . It is observed that the hysteresis effect has a corresponding relationship with ΔG . With increase in x value , ΔG of the alloys decreases gradually and the hysteresis effect of the alloys decreases simultaneously .
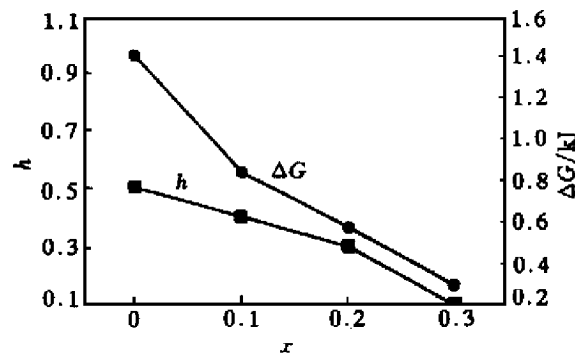

Fig .6 ΔG and hysteresis factor of $Ti_{0.8}Zr_{0.2}(MnCrVFe)_{2-x}$ alloys

5   CONCLUSIONS

1) The structures of the substoichiometric alloys can be described using the replacement model, that is, some of A-side atoms occupy the primary B-side atom positions.

2) The equilibrium pressures of the alloys decreases gradually and the hysteresis effect between hydriding and dehydriding process decreases with the increase of x value. The free-energy change between hydriding and dehydriding process has a great effect on hystereses of the alloys.

3) The p-c-t plateau region becomes narrow and the reversible hydrogen capacity decreases with the increase of x value ($x > 0.1$), although the hydrogen absorption capacity increases. The alloy with an x value equaling 0.1 shows the optimum hydrogen storage properties.

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