ELSEVIER

Journal of Alloys and Compounds 293–295 (1999) 10–13

Journal of ALLOYS AND COMPOUNDS

Two mathematical models for the hydrogen storage properties of AB_2 type alloys

Shoushi Fang[a,*], Ziqiang Zhou[a], Jinlong Zhang[a], Meiyi Yao[a], Feng Feng[b], D.O. Northwood[b]

[a]*Institute of Hydrogen Storage Materials of Shanghai University, Shanghai 200072, PR China*
[b]*Department of Mechanical and Material Engineering, University of Windsor, Ontario, Canada N9B 3P4*

Abstract

Two semi-empirical models have been applied to AB_2 hydrogen storage alloys. One is concerned with the relation between formation enthalpy in hydriding and the atomic parameters of the alloys. The other is an expression for the *PCT* curves, which can be used for estimating some physical parameters of these compounds and their hydrides, calculating unknown *PC* isotherms at given temperatures and finding the relationship of hysteresis to temperature and hydrogen concentration.

Keywords: Mathematical model; Hydrogen storage alloy; *PCT* curve

1. Introduction

Hydrogen storage alloys are new functional materials for many applications, including electrode in a MH–Ni battery, catalyst, heat pump system and so on. The AB_2 type hydrogen storage alloys is now actively studied because of their potentially high hydrogen absorption capacity, fast hydrogen–desorption reaction and a suitable range of equilibrium plateau pressure for applications [1]. Although many properties such as crystal structure, phase composition, hydrogen absorption–desorption characteristics and self-discharge characteristics for AB_2 type alloys have been studied in recent years, relatively little work has been done about the mathematical models for the most important relationships of pressure, component and temperature (*PCT*) and the model of the formation enthalpy of metal hydride ΔH [2–4]. In order to predict or calculate the unknown formation enthalpy of metal hydride ΔH and/or the *PC* isotherms from the measured *PCT* curve data of hydrogen storage alloys, two models have been proposed and successfully applied to TiFe-based and $LaNi_5$-based hydrogen storage alloys [5–7]. One objective of this paper is to study if the two mathematical models can be applied to AB_2 type hydrogen storage alloys. The another objective of this paper is to study if the *PCT* model can be to find the hysteresis factor ($RT \ln P_a/P_d$) which is cumbersome to calculate from *PCT* data by a drawing method.

1.1. The model for the formation enthalpy of AB_2 type alloy hydrides

Presuming that the free energy change ΔG corresponding to the formation of an alloy hydride consists of three energy terms, i.e., chemical energy, elastic strain energy and electron Fermi energy, which are the functions of the average Pauling electronegativity difference ΔX among the elements included in the alloy, Goldschmidt atomic size parameter d and the electron concentration (e/a) of alloy respectively. The formation enthalpy in hydriding for the alloys can be described as follows [7]:

$$\Delta H = a_0 + a_1(\Delta X)^2 + a_2 d^2 + a_3(e/a)^{2/3} \quad (1)$$

Where a_0, a_1, a_2, a_3 are proportional coefficients which are different for different alloy systems. For AB_2 type alloys in the present study, they can be found from the data in Table 1 by a computer. The formation enthalpy in hydriding for the alloys can be described as:

$$H = -R[1.07\times10^4 - 4.27\times10^4(\Delta X)^2 + 2.25\times10^5 d^2 - 2.41\times10^3(e/a)^{2/3}] \quad (2)$$

Where R is the gas coefficient, which is equal to 8.314 J

*Corresponding author.

0925-8388/99/$ – see front matter
PII: S0925-8388(99)00380-1

Table 1
The initial data of $(\Delta X)^2$, $(\delta)^2$, $(e/a)^{2/3}$ and ΔH

Materials name	$(\Delta X)^2$ ($\times 10^{-2}$)	$(\delta)^2$ ($\times 10^{-3}$)	$(e/a)^{2/3}$	ΔH_{exp} (kJ/mol H_2)	ΔH_{cal} (kJ/mol H_2)	Ref.
$Zr_{1.0}Ti_{0.3}Ni_{1.4}Cr_{0.3}$	3.272	14.09	3.659	−30.39	−30.39	[8]
$Zr_{0.8}Ti_{0.4}Ni_{1.4}Cr_{0.4}$	2.996	12.99	3.683	−27.30	−28.82	[8]
$Zr_{1.0}Ti_{0.5}Ni_{1.2}Cr_{0.5}$	2.905	12.96	3.505	−30.22	−32.66	[8]
$Zr_{0.8}Ti_{0.3}Ni_{1.3}V_{0.6}$	2.846	11.61	3.589	−30.22	−28.66	[9]
$Zr_{0.8}Ti_{0.3}Ni_{1.1}Cr_{0.5}Mn_{0.1}$	2.852	12.91	3.597	−30.81	−30.91	[8]
$Zr_{0.8}Ti_{0.15}Cr_{0.15}Ni_{1.0}V_{0.8}$	2.527	11.00	3.464	−30.31	−31.16	[8]
$Zr_{0.7}Ti_{0.5}Ni_{1.3}Cr_{0.5}$	2.779	12.12	3.636	−27.25	−28.91	[8]
$Zr_{0.5}Ti_{0.3}Cr_{0.3}Ni_{0.7}V_{1.2}Cu_{0.1}$	1.765	7.71	3.512	−30.43	−26.75	[8]
$Zr_{0.5}Ti_{0.5}Ni_{1.1}V_{0.7}Cu_{0.2}$	2.432	9.12	3.648	−26.67	−24.29	[8]
$ZrMn_2$	0.222	9.45	3.302	−39.36	−39.69	[9]
$ZrFe_2$	3.556	12.71	3.542	−29.26	−29.14	[10]
$Zr(Fe_{0.5}Mn_{0.5})_2$	2.889	11.13	3.423	−30.10	−30.94	[13]
$Zr_{0.5}Ti_{0.3}Cr_{0.35}Ni_{1.0}V_{0.8}$	2.07	8.80	3.483	−26.88	−28.29	[8]
$Ti_{0.8}Zr_{0.2}Mn_{1.8}Mo_{0.2}$	0.649	4.28	3.277	−29.3	−29.00	[11]
$Ti_{0.9}Zr_{0.1}Mn_{1.4}V_{0.2}Cr_{0.4}$	0.206	3.94	3.203	−29.3	−31.42	[11]
$Ti_{0.8}Zr_{0.2}Cr_{0.4}Mn_{1.2}$	0.293	5.24	3.203	−28.84	−33.55	[12]
$Ti_{0.6}Zr_{0.5}Ni_{1.1}V_{0.8}$	2.293	8.86	3.471	−30.85	−27.85	[8]
$Ti_{0.7}Zr_{0.4}Ni_{1.3}V_{0.6}$	2.366	8.85	3.589	−27.71	−25.20	[8]
$Zr(Fe_{0.1}Mn_{0.9})_2$	2.512	10.809	3.370	−33	−32.74	[13]
$Zr(Fe_{0.75}V_{0.25})_2$	3.222	11.200	3.327	−32.2	−31.81	[14]
$Zr(Co_{0.5}Cr_{0.5})_2$	2.667	12.949	3.257	−40.2	−38.46	[14]
$(Zr_{0.6}Ti_{0.4})Mn_2$	0.16	7.176	3.279	−35.9	−36.12	[15]
$Zr(Fe_{0.8}Cr_{0.2})_2$	3.947	12.623	3.363	−28.20	−31.12	[16]
$Zr(Fe_{0.75}Cr_{0.25})_2$	3.222	12.59	3.327	−29.6	−34.41	[17]
$Zr(Fe_{0.7}Cr_{0.3})_2$	3.124	12.576	3.291	−31.00	−35.46	[16]
$Zr(Fe_{0.6}Cr_{0.4})_2$	2.92	12.529	3.22	−36.40	−37.51	[16]
$Zr(Fe_{0.55}Cr_{0.45})_2$	2.796	12.51	3.184	−37.40	−38.64	[17]
$Zr(Fe_{0.5}Cr_{0.5})_2$	2.667	12.491	3.148	−39.00	−39.78	[16]

K^{-1} mol^{-1}. The relation coefficient of Eq. (2) is 95%. Fig. 1 is a comparison of the regression and experimental values of ΔH. It indicates that the above model applies quite well to the data range in this paper.

2. The mathematical model for *PCT* curves

For simplicity, the P–C isotherms at a given temperature can be separated into three line segments. We suppose both the first and third segments are controlled by the solubility of hydrogen atom in the alloy and its hydride respectively, and the second segment is controlled by the phase transition from α-phase into β-phase, a hydride of the intermetallic alloy: For the first and third segments, we assume the hydrogen concentration C_H (expressed in atomic ratio H/M) is a function of hydrogen pressure P and absolute temperature T, that is:

$$C_H = AP^{\gamma/2} \exp[-\gamma \times \bar{V}_H \times P/RT] \exp[-\gamma \times \Delta H_s/RT] \quad (3)$$

Where γ is the activity coefficient of hydrogen, $\bar{V}_H$ is the partial molar volume of hydrogen and ΔH_s is the solution heat of hydrogen. R is gas coefficient and A is a proportional coefficient.

For the second segment, the relation between the plateau pressure P and the hydrogen content C at a given temperature can be written as follows [5]:

$$\ln P = -\Delta H/RT + \Delta S/R + [(f_s)_{298} - 298k](C - C_m) + kT(C - C_m) \quad (4)$$

where ΔH and ΔS are the enthalpy and entropy of the formation of a hydride respectively. The $(f_s)_{298}$ means the slope factor of the plateau at 298 K and k stands for the variation rate of slope factor f_s with respect to temperature and C_m is the value of H/M at the midpoint of the pressure plateau in the *PCT* curve.

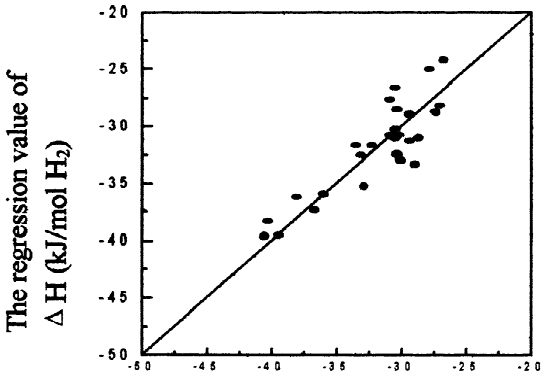

Fig. 1. A comparison of the regression and experimental values of ΔH (kJ/mol H_2).

Table 2
Physical coefficients for the segments 1 and 3 in *PCT* curves of Zr $(Fe_xCr_{1-x})_2$

x	Segments	A	γ	$\bar{V}_H$ (1/mol)	ΔH_s (kJ/mol H_2)
0.5	1	1.67×10^{-5}	1.03	−64.72	−23.99
	3	0.13	0.20	1.23	−25.93
0.55	1	4.45×10^{-4}	1.51	23.01	−12.16
	3	0.288	0.14	−0.82	−20.50
0.6	1	4.47×10^{-7}	2.04	−1.74	−17.03
	3	0.20	0.07	−6.97	−49.34
0.75	1	5.16×10^{-8}	2.32	−1.42	−15.66
	3	0.271	0.38	0.45	−5.69

The regression results of the equation coefficients for the AB_2 type alloys $Zr(Fe_xCr_{1-x})_2$ ($x=0.5,0.55,0.6,0.75$) [16,17] are listed in Tables 2 and 3 according to the Eqs. (3) and (4). It is shown from Table 2 that with increasing amount of Fe, the activity coefficient of hydrogen γ in the alloys increases and that increases first and then decreases in the hydrides. From Table 3, it is clear that the formation enthalpy of hydrides decrease while the slope factor increases with increasing the iron amount. The hysteresis factor ($RT\ \ln P_a/P_d$, the subscript a and d stand for absorption and desorption respectively) can be described as a function of absolute temperature T and hydrogen content C (H/M) according to the Eq. (4):

$$T\ln P_a/P_d = B_0 + B_1T + B_2T(C - Cm) + B_3T^2(C - Cm) \quad (5)$$

where $B_0 = \Delta H_d + \Delta H_a$, $B_1 = -\Delta S_a - \Delta S_d$, $B_2 = R\{[(f_s)_a - (f_s)_d]_{298} + 298(k_d - k_a)\}$, $B_3 = (k_a - k_d)R$. Based on the Eq. (4), these parameters can be found from the *PCT* data for the absorption and desorption, respectively. They are shown in Table 3 for the $Zr(Fe_xCr_{1-x})_2$ ($x=0.5$, 0.55, 0.6, 0.75) alloys. The hysteresis at a given temperature and hydrogen concentration in the plateau can be calculated by inserting the value of these parameters based on the Eq. (5). For an example, the hysteresis factor for the $Zr(Fe_xCr_{1-x})_2$ ($x=0.75$) alloy is as follow:

$$RT\ln P_a/P_d = 7.72\times10^3 - 18.16T + 5.665T(C - Cm) - 0.016\,T^2(C - Cm) \quad (6)$$

As a result, the hysteresis of $Zr(Fe_xCr_{1-x})_2$ increases at a given temperature when C is equal to Cm with increasing the iron amount (see Table 4).

Table 4
The hysteresis factor ($RT\ \ln P_a/P_d$:kJ/mol H_2) of $Zr(Fe_xCr_{1-x})_2$ at different temperature when C equals to Cm

T (K) / x	318	353	370
0.5	0.828	0.276	0.009
0.55	0.905	0.824	0.785
0.6	1.136	0.902	0.788
0.75	1.945	1.310	1.001

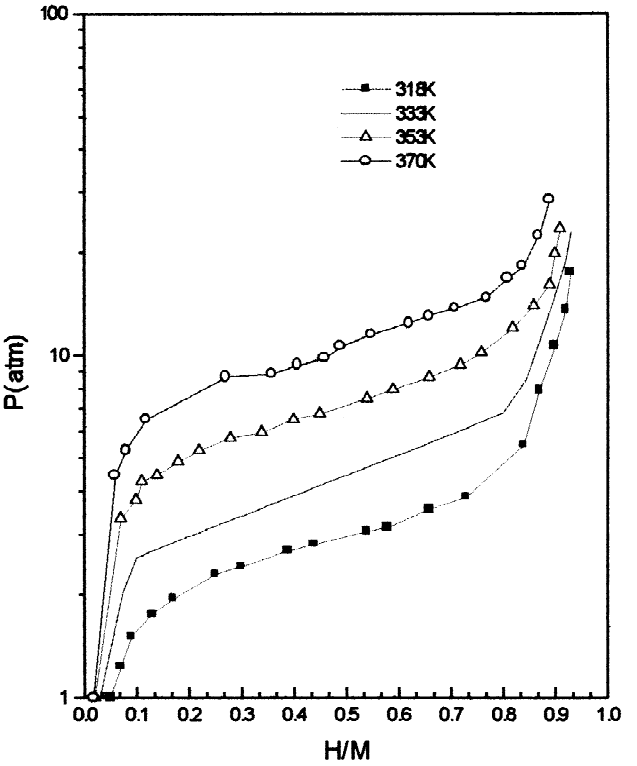

Fig. 2. A new P–C isotherms ($T=333$ K) calculated from the measured *PCT* curves of Zr $(Fe_{0.75}Cr_{0.25})_2$.

Fig. 2 is an example of calculating the unknown P–C isotherms at a given temperatures ($T=333$ K is calculated) from the data of measured *PCT* curves ($T=318$ K, 353 K, 370 K) of the alloy $Zr(Fe_{0.75}Cr_{0.25})_2$ according to Eqs. (3) and (4).

Table 3
Physical coefficients for the second segment in *PCT* curves Zr $(Fe_xCr_{1-x})_2$ [a]

x	H_a	ΔH_d	ΔS_a	ΔS_d	$(f_s)_a$	$(f_s)_d$	k_a	k_d
0.5	−34.64	40.48	−98.6	114.36	1.368	0.88	−0.0039	0.0085
0.55	−32.35	33.99	−92.09	94.40	1.447	1.06	0.0035	0.0056
0.6	−30.38	33.64	−94.70	101.38	1.487	1.14	−0.0085	−0.0019
0.75	−17.89	25.61	−70.72	88.88	1.544	1.43	−0.0033	−0.0014

[a] Notes: ΔH: kJ mol^{-1}; ΔS: J K^{-1} mol^{-1}.

3. Conclusions

The following conclusions can be made from the above results that:

1. The relation between formation enthalpy in dehydriding for AB_2 type alloys and the atomic parameters can also be expressed as a semi-empirical model: $\Delta H = a_0 + a_1(\Delta X)^2 + a_2(d)^2 + a_3(e/a)^{2/3}$.
2. An unknown P–C isotherm at a given temperature can be calculated from the data of measured PCT curves using the mathematical model.
3. Hysteresis can be described as a function of temperature and the hydrogen concentration by the model.

Acknowledgements

This cooperative study was funded by the Natural Sciences and Engineering Research Council of Canada through a Research Grant awarded to Professor D.O. Northwood and the National Science Foundation of China by a grant awarded to Professor Ziqiang Zhou.

References

[1] H.-W. Lee, J.-Y. Lee, J. Alloys Comp. 202 (1993) 23–28.
[2] J. Huot, E. Akiba, H. Iba, J. Alloys Comp. 228 (1995) 69–75.
[3] H.W. Yang, S.N. Jeng, Y.Y. Wang, C.C. Wan, J. Alloys Comp. 227 (1995) 69–75.
[4] J.-H. Lee, K.-Y. Lee, S.-M. Lee, J.-Y. Lee, J. Alloys Comp. 221 (1995) 174–179.
[5] Z. Zhou, J. Zhang, J. Ge, F. Feng, Z. Dai, Int. J. Hydrogen Energy 19 (3) (1994) 269–273.
[6] Z. Zhou, F. Feng, J. Zhang, X. Ping, Materials Science Progress (In Chinese) 5 (2) (1991) 117–123.
[7] Z. Zhou, J. Zhang, J. Ge, X. Wu, T. Xie (Eds.), New Energy Systems and Conversions, Universal Academy Press, Inc, Yokohama, Japan, 1993, pp. 79–82.
[8] G. Hong, Chinese Patent, CN1043409A, Jun. 27, 1990
[9] S.H. Qian, D.O. Northwood, Int. J. Hydrogen Energy 13 (1) (1988) 25–35.
[10] H.H. Van Mal, K.H.J. Buschow, A.R. Miedema, J. Less-Common Met. 35 (1974) 65.
[11] T. Gamo, Y. Moriwaki, N. Yanagihara, T. Yamashita, T. Iwaki, Proc. 3rd World Hydrogen Energy Conference, 4 (1980) 2127
[12] H.W. Yang, S.N. Jeng, Y.Y. Wang, C.C. Wan, J. Alloys Comp. 227 (1995) 69–75.
[13] V. Shitikov, G. Hilscher, H. Stampfl, H. Kirchmayr, J. Less-Common Metal 102 (1984) 29.
[14] D. Shaltiel, I. Jacob, D. Davidov, J. Less-Common Metal 53 (1977) 117.
[15] H. Fujii, F. Pourarian, V.K. Sinka, W.E. Wallace, J. Phys. Chem. 85 (1981) 3112.
[16] S. Qian, Ph.D. Dissertation, University of Windsor, Canada, 1989, 106–121
[17] A. Esayed, Ph.D. Dissertation, University of Windsor, Canada, 1993, 69–85