J Mater Sci (2007) 42:3645–3650
DOI 10.1007/s10853-006-1377-9

Prediction of enthalpy of formation and Gibbs energy change in pseudo-binary (Ti–Zr)(Fe–Cr)$_2$ and pseudo-ternary (Ti–Zr)(Fe–Cr)$_2$-H system using extended Miedema model

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Received: 25 September 2005 / Accepted: 22 February 2006 / Published online: 30 January 2007

Abstract The thermodynamic model proposed by Miedema is capable of predicting the enthalpy of formation (ΔH) and relative stability of phases in binary but not in ternary or multi-component systems. While developing nanocrystalline binary/ternary metal hydrides for compressor-driven reversible heating–cooling applications, it is necessary to identify appropriate alloy compositions with suitable hydrogen storage capacity and reversible hydrogen absorption–desorption capability. Accordingly, a suitable modification of the Miedema model is proposed in the present study for calculating ΔH of AB$_2$ type of pseudo-binary (Ti–Zr)(Fe–Cr)$_2$ and pseudo-ternary (Ti–Zr)(Fe–Cr)$_2$-H alloys. Subsequently, Gibbs energy (ΔG) of the possible phases is estimated to predict relative phase stability/equilibrium in a given system. It is shown that grain size or interfacial energy contribution exerts a significant influence on ΔG and relative stability of the phases beyond a critical value/limit. Finally, the predicted phase equilibrium from this model-based calculation is validated by suitable comparison with relevant experimental data reported in the literature.

Introduction

Metal hydrides are a new set of functional materials for multipurpose applications including hydrogen-storage cells, electrodes in batteries, heat pumps, gas sensors and actuators. Among various metal hydrides, Mg-based alloys offer greater storage capacity, while Ti/Zr-based AB$_2$-type of alloys are better suited for applications based on reversible hydrogen absorption/desorption characteristics [1, 2]. The present study is aimed at estimating the enthalpy (ΔH) and Gibbs energy changes (ΔG) for the Ti/Zr-based AB$_2$ type alloys and their hydrides, and thereby, predicting the microstructure and hydrogen storage capacity of these interstitial compounds/alloys. ΔH of binary alloys with at least one transition metal component can be calculated by the model developed by Miedema and his co-workers [3]. The same model can also predict ΔH of binary metal hydrides of known hydrogen concentration [4–8]. A complementary exercise can enable determination of hydrogen content in binary and ternary hydrides of known ΔH or ΔG values [8]. Similar attempt has also been made to estimate ΔH and hydrogen content of quaternary hydrides [9]. These mathematical models can determine ΔH for hydride formation in AB$_2$ type hydrogen storage alloys, but not ΔG [10, 11]. One of the main objectives of this paper is to develop a simple model to determine the ΔH and ΔG of the pseudo-binary AB$_2$ type intermetallic (Ti–Zr)(Fe–Cr)$_2$ alloys and their pseudo-ternary hydride counterparts so that the maximum hydrogen content or storage capacity in these alloys could be estimated. In addition, the influence of grain size (d_c) on phase stability/evolution and hydrogen storage capacity is

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also investigated for both the binary and ternary intermetallic alloys.

Miedema model for binary alloys and hydrides

The enthalpy (ΔH) of formation of a binary intermetallic alloy with components A and B in x_A and x_B mole fractions as per Miedema's model [3] is expressed as

$$\Delta H(\mathrm{A}_{x_A}\mathrm{B}_{x_B}) = \Delta H'(\mathrm{A}_{x_A}\mathrm{B}_{x_B}) + x_A \Delta H_{\mathrm{trans}}(\mathrm{A}) + x_B \Delta H_{\mathrm{trans}}(\mathrm{B}) \quad (1)$$

When A and B are both transition metals and P, Q, R are empirical constants,

$$\Delta H'(\mathrm{A}_{x_A}\mathrm{B}_{x_B}) = 2fg\left[-P\Big((\phi^*)^2 + Q\left(\Delta n_{\mathrm{WS}}^{1/3}\right)^2 - R\right], \quad (2)$$

where ϕ^* is the effective chemical potential, Δn_{WS} represents the electron density at the boundary of the Wigner–Seitz (WS) cell, and V expresses the molar volume such that:

$$\phi^* = \phi^*_A - \phi^*_B, \quad (3a)$$

$$\Delta n_{\mathrm{WS}}^{1/3} = \left(\Delta n_{\mathrm{WS}}^{A}\right)^{1/3} - \left(\Delta n_{\mathrm{WS}}^{B}\right)^{1/3}, \quad (3b)$$

$$f = x_A^S x_B^S \left[1 + 8\left(x_A^S x_B^S\right)\right] \quad (3c)$$

$$g = \frac{1}{\left(\Delta n_{\mathrm{WS}}^{A}\right)^{-1/3} + \left(\Delta n_{\mathrm{WS}}^{B}\right)^{-1/3}}, \quad (3d)$$

$$x_A^S = \frac{x_A V_A^{2/3}}{x_A V_A^{2/3} + x_B V_B^{2/3}}, \text{ and} \quad (3e)$$

$$x_B^S = \frac{x_B V_B^{2/3}}{x_A V_A^{2/3} + x_B V_B^{2/3}}. \quad (3f)$$

For metals, $\Delta H_{\mathrm{trans}} = 0$, and for hydrogen it is equal to 100 kJ/mol. $\Delta H_{\mathrm{trans}}$ represents the energy to transform hydrogen from its gaseous state to metallic state.

Modified Miedema model for calculation of enthalpy and Gibbs energy changes of pseudo-binary (Ti–Zr)(Fe–Cr)$_2$ and ternary (Ti–Zr)(Fe–Cr)$_2$-H

ΔH (kJ/mol) of a pseudo-binary intermetallic $(\mathrm{A_1A_2})(\mathrm{B_1B_2})_2$-type system ($\mathrm{A_1,A_2}$ or $\mathrm{B_1,B_2}$ are similar metallic elements with identical crystal structure and properties) may be expressed as

$$\Delta H^{\mathrm{intermetallic}} = \frac{1}{3(x_{A_1} + x_{A_2} + x_{B_1} + x_{B_2})} \Big[(x_{A_1} + x_{A_2})\Delta H^{(\mathrm{A_1A_2})} + \sum_{i=1}^{2}\sum_{j=1}^{2}\left(x_{A_{(i)}} + x_{B_{(j)}}\right)\Delta H^{\{\mathrm{A}_{(i)}\mathrm{B}_{(j)}\}} + (x_{B_1} + x_{B_2})\Delta H^{(\mathrm{B_1B_2})}\Big] \quad (4)$$

where x_{A_1}, x_{A_2}, x_{B_1}, and x_{B_2} are the mole fraction of the elements $\mathrm{A_1}$, $\mathrm{A_2}$, $\mathrm{B_1}$ and $\mathrm{B_2}$, respectively. Here $x_{A_1} + x_{A_2} = 1$ and $x_{B_1} + x_{B_2} = 2$. It may be pointed out that the ΔH values in Eq. (4) are computed using the weighted mean of the ΔH values for the formation of the concerned binary couples.

For the pseudo-ternary $(\mathrm{Ti}_{1-X}\mathrm{Zr}_X)(\mathrm{Fe}_{1-Y}\mathrm{Cr}_Y)_2\mathrm{H}$ system, it is assumed that distribution of hydrogen reacting with the individual metallic constituent, for a given H/M ratio (M = metal, H = hydrogen), is proportional to the atomic fraction of that particular metal in the alloy. Hence, the generalized equation for ΔH of the $(\mathrm{A_1A_2})(\mathrm{B_1B_2})_2$-H system is given by

$$\Delta H^{\mathrm{hydride}} = \frac{1}{x_{A_1} + x_{A_2} + x_{B_1} + x_{B_2} + x_H} \left[\sum_{i=1}^{2}\left(x_{A_1} + x_{A_2} + x_{H_{A_{(i)}}}\right)\Delta H^{\{\mathrm{A}_{(i)}\mathrm{H}\}} + \sum_{j=1}^{2}\left(x_{B_1} + x_{B_2} + x_{H_{B_{(j)}}}\right)\Delta H^{\{\mathrm{B}_{(j)}\mathrm{H}\}}\right] + \Delta H^{\mathrm{intermetallic}} \quad (5)$$

where

$$x_{H_{A_{(i)}}} = \frac{x_{A_{(i)}}}{x_{A_1} + x_{A_2} + x_{B_1} + x_{B_2} + x_H} x_H, \quad (6a)$$

$$x_{H_{B_{(j)}}} = \frac{x_{B_{(j)}}}{x_{A_1} + x_{A_2} + x_{B_1} + x_{B_2} + x_H} x_H, \quad (6b)$$

and x_{A_1}, x_{A_2}, x_{B_1}, x_{B_2} and x_H are the mole fraction of the elements $\mathrm{A_1}$, $\mathrm{A_2}$, $\mathrm{B_1}$, $\mathrm{B_2}$ and hydrogen, respectively.

Results and discussion

Table 1 summarizes ΔH values of some of the (Ti,Zr)(Fe,Cr)$_2$ alloys predicted by the present model (Eq. 4) and compares them with the relevant

Table 1 Summary of ΔH of the pseudo-ternary $(Ti_{1-X}Zr_X)(Fe_{1-Y}Cr_Y)_2$-H alloys predicted by present model and comparison with the relevant experimental data from the literature [12]

Alloy composition	Δ *H* from the literature (kJ/mol)	ΔH predicted by the present model (kJ/mol)	Reference
$Zr_{.7}Ti_{.3}CrFeH$	–30	–25.1	Yu et al. [13]
$Zr_{.5}Ti_{.5}CrFeH$	–27	–24.6	Yu et al. [13]
$Zr_{.9}Ti_{.1}Cr_{1-y}Fe_{1+y}H$ (y = 0–0.4)	–24 to –31	–24.4 to –24.6	Lee and Park [14]
$Zr_{.8}Ti_{.2}Cr_{1-y}Fe_{1+y}H$ (y = 0–0.4)	–26 to –29	–24.8 to –24.9	Lee and Park [14]
$Zr_{.8}Ti_{.2}Cr_{.6}Fe_{1.4}H$	–27	–24.9	Wallace and Pourarian [15]
$Zr_{.7}Ti_{.3}Cr_{.6}Fe_{1.4}H$	–22	–24.9	Wallace and Pourarian [15]
$Zr_{.9}Ti_{.1}Cr_{.55}Fe_{1.45}H$	–29	–24.6	Park et al. [16]

experimental data available in the database of Sandia National Laboratories [http://hydpark.ca.sandia.gov].

Figure 1 shows the variation of enthalpy of formation (ΔH) for $(Ti_{1-X}Zr_X)(Fe_{1-Y}Cr_Y)_2$ system as a function of composition (in terms of change in relative proportions of Ti:Zr = X and Fe:Cr = Y), calculated as per Eq. (4). Here, $(Ti_{1-X}Zr_X)(Fe_{1-Y}Cr_Y)_2$ is considered a pseudo-binary AB_2 type intermetallic alloy. It may be noted that ΔH is a strong function of composition; in other words, ΔH varies significantly with the Ti:Zr ratio in the A part/sub-lattice and Fe:Cr ratio in the B part/sub-lattice of the alloy. It is apparent that ΔH tends to attain a more negative value as Zr substitutes Ti in the Ti–Zr sub-lattice. Similarly, ΔH decreases and reaches the minimum at $2Y = 0.8$ as Cr increases in the Fe–Cr sub-lattice. Accordingly, the $(Ti_{1-X}Zr_X)(Fe_{1-Y}Cr_Y)_2$ intermetallic alloy/compound is most stable at $X = 0.6$ and $2Y = 0.8$ with the least ΔH (more negative) value than that in the rest of the composition range. Thus, it is expected that $(Ti_{0.4}Zr_{0.6})(Fe_{0.1}Cr_{0.4})_2$ should be most stable of equilibrium compound in the Ti–Zr–Fe–Cr system.

Figure 2 shows the variation of enthalpy of formation (ΔH) for $(Ti_{1-X}Zr_X)(Fe_{1-Y}Cr_Y)_2$-H system as a function of composition (in terms of Ti:Zr = X and Fe:Cr = Y), calculated as per Eq. (5). Taking H/M ratio equal to 1, ΔH as a function composition (i.e. X and Y) is estimated (Fig. 2). ΔH for the formation of hydride decreases (up to Zr = 0.7) as Zr content increases for a given H/M ratio and concentration of Fe and Cr (for lower amount of Cr). For higher amount of Cr, ΔH again increases for a given X and H/M ratio. Similarly ΔH reaches a minimum (~25 kJ/mol) at $2Y = 0.75$. Hence, ΔH is minimum for a combination of $X = 0.7$ and $2Y = 0.75$ at H/M = 1.

It may be pointed out that the values of ΔH as a function of Fe/Cr concentration, as predicted by the present model, are confined to a narrow range, unlike that shown by the concerned experimental results (Table 1). This difference may be attributed to the fact that Fe and Cr are less prone to hydride formation (magnitude of ΔH of Fe/Cr hydrides is quite small) than say Ti and Zr and ΔH for hydride formation is calculated using weighted mean of ΔH of the concerned binary hydrides. This is an inherent drawback of the extended Miedema model for calculation of the enthalpy of hydride formation for ternary or multi-component systems. Indeed, experimental data

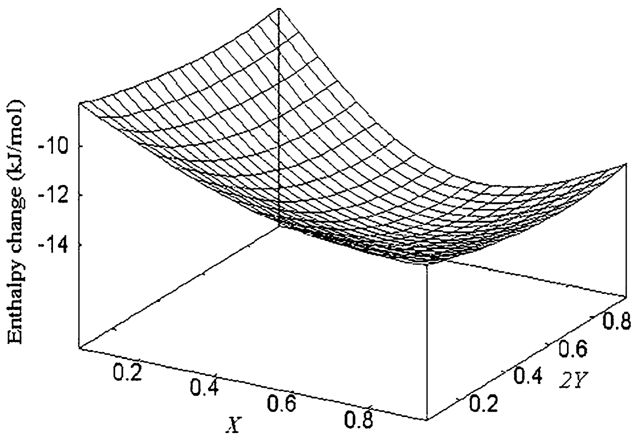

Fig. 1 Enthalpy of formation as a function of composition of pseudo-binary $(Ti_{1-X}Zr_X)(Fe_{1-Y}Cr_Y)_2$ alloys

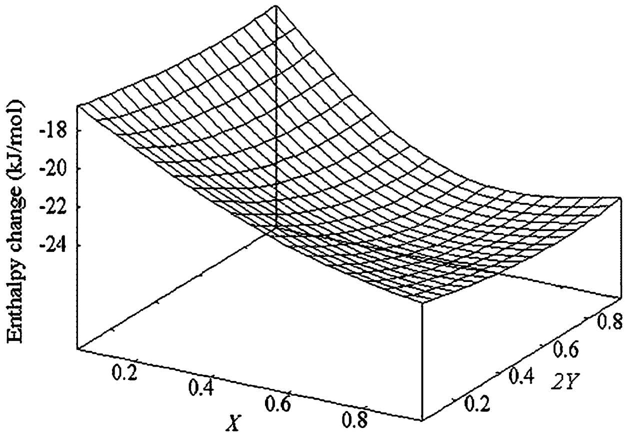

Fig. 2 Enthalpy of formation as a function of composition of pseudo-ternary $(Ti_{1-X}Zr_X)(Fe_{1-Y}Cr_Y)_2$-H alloys

reported in the literature show a considerable variation in ΔH for the hydrides for identical compositions (Table 1). Thus, the present exercise, despite the above limitations, is successful in predicting the trend of thermodynamic stability and composition of pseudo-binary/ternary alloys/hydrides with qualitative agreement with experimental data.

Earlier, Herbst [8, 9] calculated the equilibrium hydrogen content in binary, ternary and quaternary hydrides using Miedema model. Following similar approach, hydrogen content in $(Ti_{1-X}Zr_X)(Fe_{1-Y}Cr_Y)_2$-H is determined in the present study from the composition that corresponds to the minimum enthalpy or Gibbs energy for the given system. Figure 3 shows the variation of ΔH as a function of H/M ratio of the pseudo-ternary hydrides of a particular Fe:Cr ratio. It appears that ΔH is the minimum for H/M = 1.6–1.9 (depending on the composition of the alloy) for all four compositions. Thus, it follows that the equilibrium hydrogen content (in terms of hydrogen atom per mol of hydride) in all four alloys will vary between 5.4 and 5.7 at the most stable constitutions of the pseudo-ternary alloy.

Stability of a given phase in terms of Gibbs energy (ΔG) is expressed as

$$\Delta G = \Delta H - T\Delta S + A\gamma, \tag{7}$$

where ΔS is the entropy change, A is the surface area, T is the temperature and γ is the surface energy. ΔS of the alloy can be easily calculated using an appropriate model (e.g., ideal solution model). For small particle size (at or sub-micron or nanometric level), the surface to volume ratio is large and hence the interfacial Gibbs energy ($A\gamma$) assumes significant magnitude. In the present case, we assume that all the particles are uniform spheres of sub-micron radius of R. These tiny particles are polycrystalline, i.e., contain a number of grains, which also are assumed (as further simplification) to be equal sized small spheres of radius r. Considering both the particle surface and grain boundary area, the effective contribution of interfacial Gibbs energy (ΔG_γ) of the alloy is expressed as

$$\Delta G_\gamma = 4\pi\left[N_{\text{particle}}R^2\sum_i x_i\sigma_i + N_{\text{grain}}r^2\sum_i x_i\gamma_i\right], \tag{8}$$

where σ_i is the surface free energy, γ_i is the grain boundary energy, N_{grain} is the number of the grains per particle, N_{particle} is the number of the particle per mol of the compound. N_{particle} is expressed as

$$N_{\text{particle}} = \frac{\text{molar volume of the alloy}}{4/3\pi R^3}, \tag{9}$$

and as R/r is considered extremely large. N_{grain} is expressed as

$$N_{\text{grain}} = \left(\frac{R}{r}\right)^3\prod. \tag{10}$$

Π is the packing density. We assume that the grains are of equal radius and packed with maximum packing density to accommodate maximum number of grains per particle (i.e. Π = 0.74). The surface free energy (σ_i) and the grain boundary free energy (γ_i) of the elements are taken from Murr [17]. An approximate value of σ_i and γ_i for Ti and Zr are assumed from the available data by considering their structure and melting point. In the present study, ΔG is calculated assuming that the average particle size is 40 μm.

ΔG as a function of composition (varying the Ti:Zr ratio and consequently the Fe:Cr ratio) is shown in Fig. 4. The effect of composition on ΔG is nearly the same as that on ΔH. As the concentration of Zr increases, ΔG primarily decreases and then again increases. Both at the Ti and Zr rich end, Cr concentration affect ΔG the same way as does Zr concentration. However, ΔG decreases continuously in equi-atomic Ti and Zr alloys with the increment of Cr. Only at $2Y = 0.9$, ΔH goes upwards. The most stable intermetallic (in terms of ΔG value) forms at $X = 0.6$ and $2Y = 0.85$ and the corresponding ΔG value is 17.85 kJ/mol.

For $(Ti_{1-X}Zr_X)(Fe_{0.7}Cr_{0.3})_2$ system, ΔG values are calculated with varying X and grain size. There is no significant difference among the estimated values of

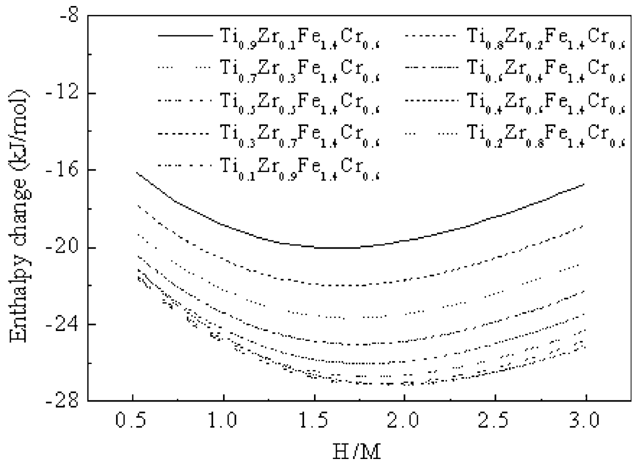

Fig. 3 Enthalpy of formation of pseudo-ternary $(Ti–Zr)(Fe_{1.4}–Cr_{0.6})$-H system as a function of H/M ratio

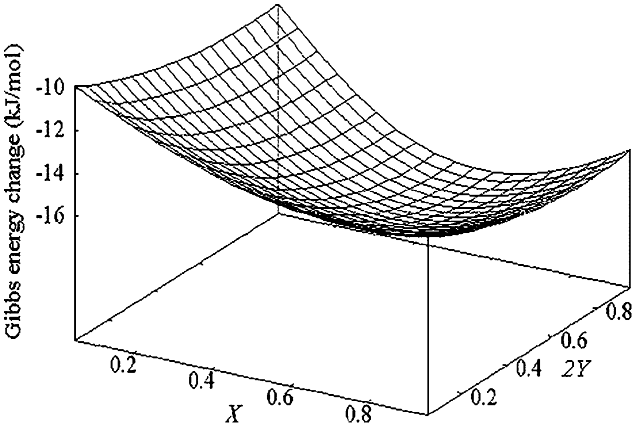

Fig. 4 Gibbs energy change as a function of composition of pseudo-binary $(Ti_{1-X}Zr_X)(Fe_{1-Y}Cr_Y)_2$ system

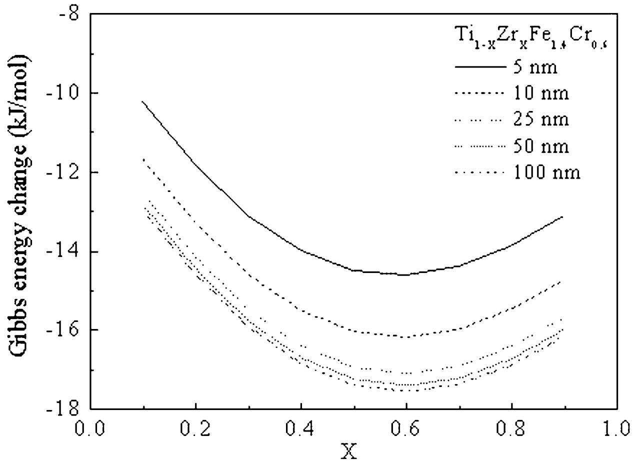

Fig. 5 Gibbs energy change as a function of composition of pseudo-binary $(Ti_{1-X}Zr_X)(Fe_{0.7}Cr_{0.3})_2$ system with different grain sizes

ΔG for $d_c = 100$, 50 and 25 nm. However, ΔG value increases sharply and ΔG vs. X plot drastically goes upwards for $d_c = 10$ nm (Fig. 5). Thus, the relative stability of the intermetallic alloys decreases beyond certain minimum value of d_c.

Keeping the H/M ratio equal to 1, the ΔG values of varying atomic fraction of Zr and Cr are estimated and shown in Fig. 6. In the lower Cr concentration zone, ΔG values decreases continuously with decreasing Ti content. But ΔG values form a loop as a function of Zr content in the Cr-rich end. The effect of Cr is less intense than Zr. Most stable hydrides form at nearly equal atomic ratio of Ti and Zr and at the richer Cr content. The amount of probable hydrogen content of some $(Ti–Zr)(Fe–Cr)_2H$ alloys is estimated from their relative stability in terms of their respective ΔG values.

Figure 7 shows the variation of ΔG as a function of composition (different Ti:Zr ratios). The stability of

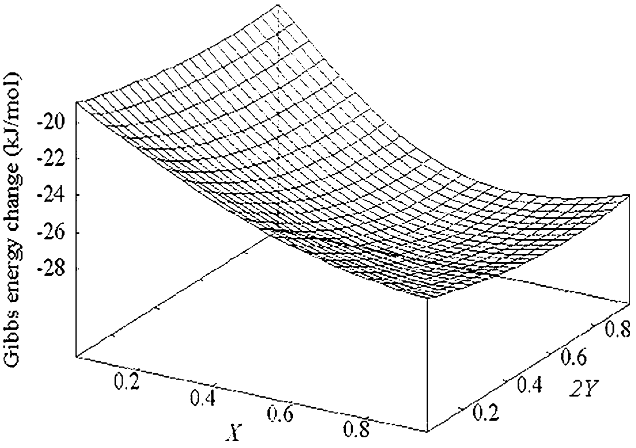

Fig. 6 Gibbs energy change as a function of composition of pseudo-ternary $(Ti_{1-X}Zr_X)(Fe_{1-Y}Cr_Y)_2$-H system

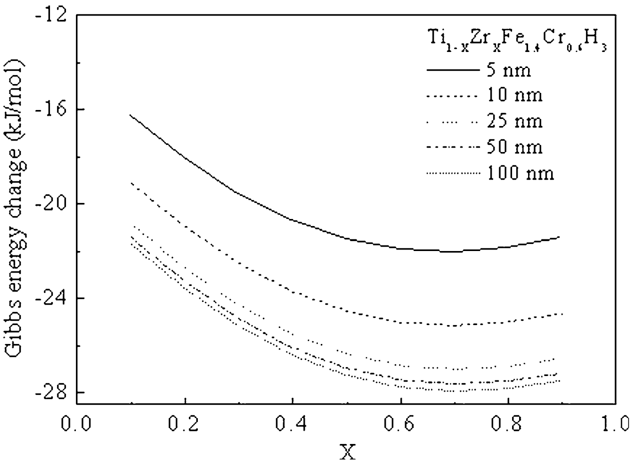

Fig. 7 Gibbs energy of Ti–Zr–Fe–Cr hydride as a function of composition for various grain sizes

the hydride increases with the increase of Zr atomic fraction (ΔG decreases with the increase of Zr:Ti ratio). There is no significant change in ΔG with the reduction in grain size up to a grain size of 25 nm. But after 25 nm the hydride becomes more and more unstable with grain refinement.

Conclusion

The following conclusions can be drawn from the above study

1. The proposed modified model can predict the ΔH and ΔG values of intermetallic AB_2 type pseudo-binary $(Ti–Zr)(Fe–Cr)_2$ and pseudo-ternary $(Ti–Zr)(Fe–Cr)_2$-H hydrides for the entire composition range.
2. Using the above analytical approach, the most stable or equilibrium composition of the given

pseudo-binary (Ti–Zr)(Fe–Cr)$_2$ and ternary (Ti–Zr)(Fe–Cr)$_2$-H alloys can be predicted.
3. The possible hydrogen storage capacity of the hydrides can be estimated from the most stable composition in terms of both ΔH and ΔG values.
4. The stability of a given hydride decreases with decrease in grain size, particularly below a grain size of 25 nm.

Acknowledgements Partial financial support from the Ministry of Non-conventional Energy Sources, New Delhi (Grant no.: 103/08/2001-NT) is gratefully acknowledged. Useful technical discussion with Prof. E. Rabkin and Prof. H. J. Fecht is deeply appreciated.

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