EasyChair Preprint

№ 423

Estimation of Enthalpy of formation of metal hydrides – Effect of Different Measurement Parameters

Anil Kumar Emadabathuni, Dhananjay Mishra and Vinor Kumar Sharma

August 13, 2018

Estimation of Enthalpy of formation of metal hydrides – Effect of Different Measurement Parameters

Anil Kumar [a,b*], Dhananjay Mishra [a], Vinod Kumar Sharma[c]

[a]Discipline of Mechanical Engineering, Indian Institute of Technology Indore, Indore - 453 552, Inadia
[b]Department of Mechanical Engineering, Indian institute of Technology Tirupai, Tirupati – 517506, India
[c]Division of Thermal and Automotive, VIT University Vellore, State of Tamil Nadu, India
[*]Corresponding author Phone: +91-8772500387 E-mail address: anil@iittp.ac.in

***Abstract**: The enthalpy of formation of metal hydrides is estimated by van't Hoff equation. Pressure Concentration Isotherms (PCIs) at different temperatures are used to obtain van't Hoff plot. Enthalpy of formation is an important input in simulation and performance estimation of metal hydride based engineering devices. The absolute error in the measurement of enthalpy of formation depends upon the relative error of PCI measurements. The error in the estimation of this quantity depends upon the number of temperature points used for obtaining van't Hoff plot and temperature range and size of the range. In the present study PCIs of $MmNi_{3.5}Co_{0.8}Al_{0.7}$ hydride were measured in the temperature range of 20 to 240°C. The effect of number of temperature points, temperature range and size of the range on the estimation of enthalpy of formation is studied. The effect of the temperature range and size of the range is found to be more sensitive in the estimation of enthalpy of formation.*

Keywords: Enthalpy of formation, Van't Hoff plot, PCIs, Metal hydride.

1. INTRODUCTION

When directly exposed many metals directly react with hydrogen to form a group of new compounds called metal hydrides. Metal hydrides absorb and desorb hydrogen reversibly. Absorption is an exothermic reaction and desorption is an endothermic reaction. As absorption and desorption involves heat interactions these compounds found many technical applications like heat pump, heat transformer, hydrogen compressor and energy storage etc. Hydriding materials can be synthesized with different metals with varying composition to suit hydriding and dehydriding characteristics as required by the applications. But selection of a suitable metal hydride for a particular application is vital for successful performance of the system. This demands for a representative characterization of metal alloys. Pressure concentration isotherms are one, which provides such representative characterization for metal hydrides. They represent hydrogen gas pressure in thermodynamic equilibrium with a metal and its hydride as a function of hydrogen concentration at a given temperature. To design and estimate the performance of metal hydride based energy conversion processes enthalpy of formation is an important input parameter. The thermodynamic properties enthalpy of formation (ΔH) and entropy of formation (ΔS) can be estimated by calorimetric approach or using van't Hoff analysis. Using multiple PCI data, by plotting Ln (P_{H2}) Vs. 1/T, ΔH and ΔS are calculated by comparing equation of fit with van't Hoff equation

$$\mathrm{Ln}(P_e) = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \qquad (1)$$

In general PCI exhibits slop during α to β conversion and shows hysteresis between absorption and desorption, thermodynamic parameters ΔH and ΔS are calculated using mid plateau pressure values. Enthalpy of formation values reported in the literature by different authors are found to be different for the same material estimated using van't Hoff equation. This difference may be expected due to the error involved in the measurement of P_e, which would lead to error in the estimation of ΔH. However, based on their statistical analysis [1] showed that the error in the estimation of ΔH is independent of absolute error involved in P_e measurements. [4] and [5] showed that ΔH is a function of hydrogen concentration. In many cases the heat capacity of the alloy may change, leading to possible curvature in van't Hoff plots. In those cases the calculated value of ΔH majorly depends upon temperature range and number of temperature points used for the estimation. With this point in view, ΔH of a commercially used metal hydride $MmNi_{3.5}Co_{0.8}Al_{0.5}H_x$ is estimated using wide range of PCIs, the effects of temperature range and number of temperature points are studied.

2. EXPERIMENTAL STUDIES

The alloy was synthesized at the Defence Metallurgical Research Laboratory, Hyderabad and delivered as powder with an average particle size of 50 µm. The synthesizing procedure is given elsewhere [3]. Alloy sample of 20 g was used for PCI measurements. The amounts of hydrogen absorbed and desorbed are calculated based on mass balance of hydrogen. An experimental setup with an operating temperature range between 253 and 573 K and maximum pressure of 100 bar is used in PCI measurements. The experimental setup and details of reactor, working procedure and data reduction are published in one of the author's paper [2].

3. Results and Discussion

The static PCI characteristics of $MmNi_{3.5}Co_{0.8}Al_{0.7}$ are shown in Figure 1 in the temperature range 20 to 240°C. All the isotherms show the three phases α (single phase solid solution), α+β (metal hydride formation) and β (second solid solution) in the test range indicating plateau pressure at 240°C is well below critical pressure. It is observed that the hydride is a low-pressure alloy as the mid plateau pressure is less than 1 bar up to 100^0C. $MmNi_{3.5}Co_{0.8}Al_{0.7}$ reached a maximum storage capacity of 1.2 wt% at 20^oC. Increase in temperature considerably reduces the storage capacity due to larger plateau slope. The isotherms showed a large plateau slope as pressure during absorption varies from sub atmospheric to 60 bar absolute at all temperatures which is a characteristic of all AB_5 materials.

Figure 2 shows van't Hoff plot in the temperature range of 20 to 240ºC with twelve temperature points. The van't Hoff fit showed curvature and is not linear in the complete temperature range, indicating that ΔH is not independent of temperature. However, in a narrow temperature range (20 to 80ºC, 60 to 120ºC, 100 to 160ºC, 140 to 200ºC and 180 to 240ºC) as shown by dotted lines in the Figure 2, van't Hoff fit is linear, ΔH is independent of temperature. The slope of the plot is increasing with increase in temperature indicating an increase in ΔH value with temperature. ΔH value decreased with increase in number of temperature points in the temperature range 20 to 240º as shown in Figure 3, indicating the estimated value is sensitive to number of temperature points used for van't Hoff plot. In a given temperature range using less number of temperature points for constructing van't Hoff plot leads to over estimation of ΔH value. Figure 4 shows the variation of ΔH with temperature range for the same number of temperature points; ΔH is increased linearly with increase in temperature range, this can be attributed to the increase in average temperature of the bed.

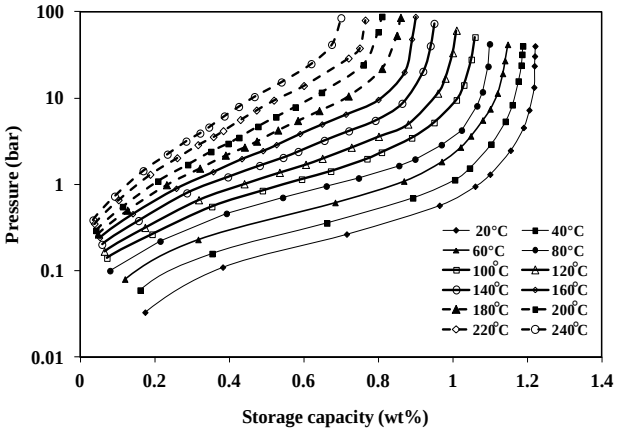


Fig. 1 Static PCI Characteristics of $MmNi_{3.5}Co_{0.8}Al_{0.7}$

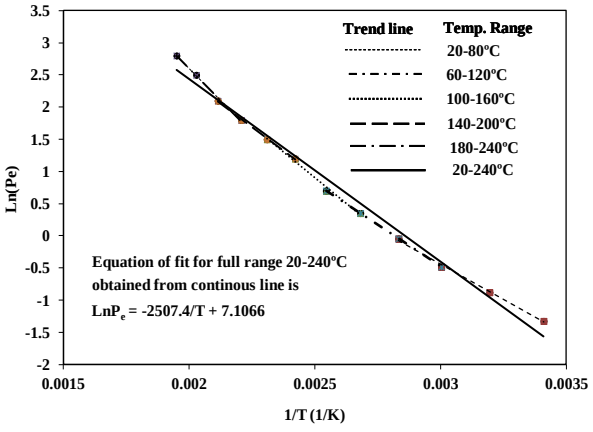
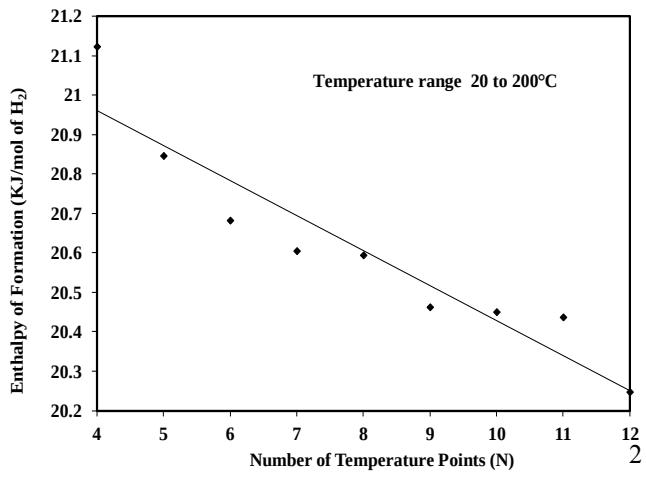


Fig. 2 Van't Hoff plots for $MmNi_{3.5}Co_{0.8}Al_{0.7}$



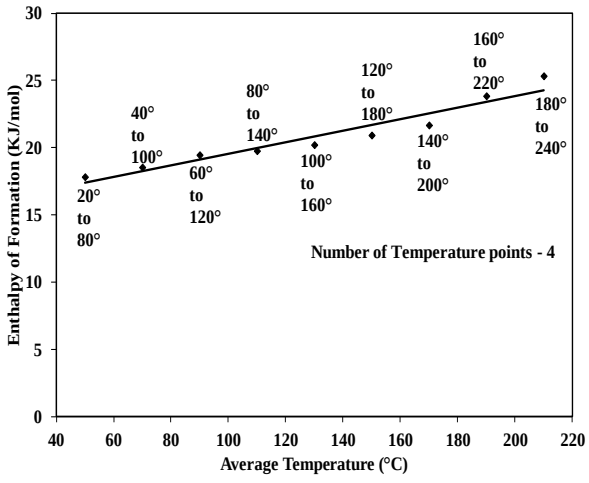


Fig. 3 Variation of Enthalpy of formation with number of temperature points in the same temperature range

Fig. 4 Variation of Enthalpy of formation with temperature range

4. Conclusions

1. In a narrow temperature range (80 to 100°C), van't Hoff plot is found to be linear, indicating ΔH is independent of temperature.
2. In a wide temperature range, van't Hoff plot showed a curvy nature and ΔH is dependent on temperature.
3. ΔH value is also found to be sensitive to number of temperature points in the broad range.
4. Enthalpy of formation increased with increase in temperature range for the same number of temperature points.
5. For any practical application like heat pump, heat transformer, refrigerator, etc. it is recommended to estimate ΔH in the appropriate temperature range with maximum possible number of temperature points.

5. REFERENCES

1. Andrei Zhukov and Robert Karlsson.: Statistical aspects of van't Hoff analysis: a simulation study, J. Mol. Recognit., (20), pp. 379–385 (2007).
2. E. Anil Kumar, M. Prakash Maiya and S. Srinivasa Murthy.: Influence of transient operating conditions on pressure-concentration isotherms and storage characteristics of hydriding alloys. International Journal of Hydrogen Energy, (32) pp. 2382-2389 (2007).
3. G. Balachandran, U. Krishna Prasad, M.V. Ananth and M.V.S. Suryanarayana.: Metallurgical Characteristics of AB_5 intermetallic alloys developed for hydrogen storage applications. International Conference on Solid State Hydrogen-Storage and Applications, Hyderabad, India (2005).
4. N Mani, S Ramaprabhu.: Effect of substitutional elements on hydrogen absorption properties in Mm-based AB_5 alloys. Journal of Alloys and Compounds, 363 (1–2), pp. 275-291 (2004).
5. P. Muthukumar, M. Linder, R. Mertz, E. Laurien.: Measurement of thermodynamic properties of some hydrogen absorbing alloys, International Journal of Hydrogen Energy, (34) pp. 1873-1879 (2009).