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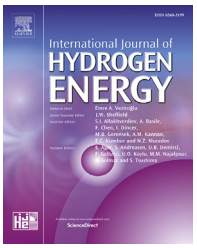

Investigations on calculation of heat of formation for multi-element AB_5-type hydrogen storage alloy

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ABSTRACT

With development in hydrogen energy research, more and more applications of hydrogen storage materials have been put forward. This requires synthesis of new materials for specific purpose. In context to designing of metal hydride bed, thermodynamic parameter 'Heat of formation' (ΔH) for hydrogen storage alloy is very important. Theoretical calculation of ΔH for binary compound or ternary hydride is accomplished by well known 'Miedema's Rule of Reverse Stability'. Experimentally ΔH may be determined using Van't Hoff Equation. So far, theoretical calculation of ΔH for multi-element alloy is not known. In the present investigation simple phenomenological formulae have been proposed to calculate ΔH for multi-element alloy including AH_m, BH_m, AB_n, AB_nH_{2m}, $AB_{n-x}C_x$, $AB_{n-x}C_xH_{2m}$, $AB_{n-x-y}C_xD_y$, $AB_{n-x-y}C_xD_yH_{2m}$ and so on. The calculated values of ΔH in present investigation have been compared with the experimental reported value or calculated by any other model reported in literature. An excellent agreement has been observed between the two.

Introduction

Hydrogen energy has evolved as one of the excellent energy options of renewable energy source. It offers clean and green fuel properties and when coupled with solar energy it becomes everlasting energy source. Hydrogen energy can be harnessed at its full potential only when it is stored properly. Hydrogen can be stored in gaseous, liquid and solid form. Among these, when stored in solid metal hydride, it offers maximum density of hydrogen storage and also the storage in solid metal hydride is the safest mode of hydrogen storage [1]. The important hydrogenation characteristics are activation time, p-c isotherm, hydrogen storage capacity, plateau pressure, operating temperature, thermodynamic parameter etc. The optimum combination of these properties is required for use of metal hydride in a particular application. In the applications like storage, gettering, purification and batteries, the most important property is hydrogen storage capacity. The knowledge of temperature-pressure characteristics (p-c isotherm) is necessary for the applications like, compressor, sensor and actuator. On the other hand thermodynamic parameters play an important role in the applications like heat storage, heat pumps and refrigerators [2].

Hydrogen absorption is an exothermic process. The amount of heat produced depends on the value of reaction enthalpy and subsequently heat has to be removed and can be utilized elsewhere. On the other hand hydrogen desorption is an endothermic reaction. In this case some amount of heat is added to the system to facilitate the reaction. Eventually, desorption leads to cooling effect in system. If more heat is not supplied to the system, it will stop due to cooling effect. It is

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beneficial to supply energy through waste heat. Hence a choice of specific metal hydride is necessary with knowledge of reaction enthalpy [3]. The application of metal hydride in heat pumps requires selection of two alloys. The values of reaction enthalpy and reaction entropy decide the efficiency and temperature difference between hot and cold reservoir [4]. An efficient metal hydride reactor or bed involves the mechanism of heat transfer through heat exchanger. Many researchers have reported their work on the process of heat transfer by including heat exchanger. A metal-hydride reactor equipped with a spiral heat exchanger containing fluid provides more heat transfer area; thus significantly reduces hydriding time [5]. In another work Belkhiria et al. have shown that a reactor surrounded by a small coil traversed by an alternative sinusoidal current and working as electromagnetic induction heater is more efficient in comparison to heat exchanger containing hot fluid [6]. Thermally driven metal hydride pump (MHP) system utilizing low-grade heat and equipped with a phase change heat exchanger is developed by Miled et al. [7]. This system is developed to store the heat of reaction during absorption and to release it during desorption process by using a Phase Change Material (PCM). It is noticed that the integration of a PCM reduces the pumping time by about 88% and provides efficiency nearly 8 times higher than the case without PCM.

Among verities of hydrogen storage alloys, AB_5-type metal hydride is superior due to its easy activation and its operation at pressure and temperature close to atmospheric condition [8]. With the development in hydrogen energy research, more applications have been designed. In fact each application requires a specific set of properties. To fulfil these criteria multi-element alloys have been developed by substituting other elements at A and B site. In recent years many AB_5-type multi-element alloys have been synthesized for specific application and the effects of substituted elements have been studied [9–13]. AB_5-type alloys are applied very effectively to fabricate metal hydride electrode in Ni-MH battery [14–16]. The process of hydrogen absorption is not limited to only crystalline material, but also extended to amorphous material [17]. Hence hydrogen storage process has wide applications.

Few models have been proposed by researchers to calculate thermodynamic parameters of alloys. Ledovskikh et al. have developed a new mathematical model based on first principles chemical and statistical thermodynamics and involves many parameters [18]. In a separate study Kaabi et al. have experimentally determined the thermodynamic parameters of multi-element negative electrode materials in nickel-metal hydride batteries. They have obtained the thermodynamic parameters by converting electrochemical isotherm into pressure isotherm and then applying Van't-Hoff equation [19]. Prediction in the variation of enthalpy with hydrogen content at hydrogenation or dehydrogenation plateau for $LaNi_5$ based multi-element alloy has been discussed by Liu et al. [20].

From above discussion it is clear that thermodynamic parameters are important properties of metal hydrides. Till now, development of new materials for specific application is based on trial and error method. No model is available at present which can predict the thermodynamic parameter 'reaction's enthalpy of hydride formation' for multi-element alloy. In present investigation simple phenomenological model has been proposed to calculate 'reaction's enthalpy of hydride formation' for binary, ternary and multi-element AB_5-type metal hydride.

Methodology- formulation of new equations

For metal hydrides the equilibrium pressure (plateau pressure) is represented by Van't Hoff equation [21].

$$\ln P_{H_2} = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \tag{1}$$

Where ΔH and ΔS represent change in enthalpy and change in entropy during formation of metal hydride per mole of hydrogen (H_2). ΔS is almost constant for all metal hydrides due to high entropy of hydrogen as a gas which is lost upon entering the metal. Hence ΔH is more characteristic value than ΔS. ΔH represents the heat of formation of metal hydride and is the measure of stability of metal hydride. More negative be the value of ΔH, more will be the stability of metal hydride. In this regard Miedema has given "rule of reverse stability" to calculate ΔH [21].

$$\Delta H\,(AB_nH_{2m}) = \Delta H\,(AH_m) + \Delta H\,(B_nH_m) - \Delta H\,(AB_n) \tag{2}$$

From Eq. (2), it can be inferred that larger be the stability of (AB_n), less will be the stability of (AB_nH_{2m}) and vice versa. Therefore it is known as 'rule of reverse stability'. The last term on right hand side of Eq. (2) is kept for the reason that some energy is invested in breaking the bonds between A and B in parent alloy during formation of hydride.

When this equation is applied on AB_5-type metal hydride, it must be noted that in normal case of AB_5-type metal hydride, the maximum value of 2 m corresponds to 6. Hence, in the case when 2 m < 6, all the bonds between AB_5 are not broken and some of the bonds still coexist. Pasturel et al. have proposed an equation to calculate heat of formation for ternary metal hydride; however it has not been extended further [22]. In this connection, new equations have been proposed in present investigation to calculate heat of formation. It may be mentioned here that no synthesis of materials have been done in present investigation. Heat of formation has been calculated on the basis of proposed model and the obtained result has been compared with previously reported values.

ΔH of multi-element hydride

Eq. (2) given by Miedema can be applied only to the binary alloy (AB_n), however the state-of-the-art-alloys are multi-elemental. As plateau pressure is related to ΔH (Eq. (1)), knowledge of ΔH is very important. Hence simple and new equation has been proposed in the present investigation for ternary alloy, which can be extended further to multi-element alloy.

$$\Delta H\,(AB_{n-x}C_xH_{2m}) = \Delta H\,(AH_m) + \left(\frac{n-x}{n}\right)\Delta H\,(B_nH_m) + \frac{x}{n}\Delta H\,(C_nH_m) - \frac{m}{3}\Delta H\,(AB_{n-x}C_x) \tag{3}$$

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