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A microscopic study of absorption and desorption of hydrogen in $LaNi_{4.85}Al_{0.15}$ using the grand canonical ensemble of statistical physics

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ABSTRACT

Modeling of absorption and desorption isotherms of hydrogen on $LaNi_{4.85}Al_{0.15}$ alloy at 298 K, 303 K and 313 K has been achieved through the use of grand canonical ensemble in statistical physics. In fact, a monolayer model with two levels of energy has been adopted to better fit the experimental data. Besides, six physicochemical parameters have been used to better describe the absorption and desorption processes from the point of view of α and β phases. These parameters are divided into two types. The first type of parameters contains four main parameters, namely the number of atoms per site, n_α and n_β, and the densities of hydrogen receptor sites $N_{m\alpha}$ as well as $N_{m\beta}$. The second type of parameters are mainly the two energetic parameters P_α and P_β which respectively refer to the pressures at half saturations for the α phase and the β phase. Thanks to these steric and energetic parameters, we could compare the absorption and desorption processes to highlight the evolution of these parameters during hysteresis encountered in the desorption isotherms.

1. Introduction

The decrease in oil reserves and the respect for ecology as well as environmental problems related to an exclusive and intensive use of oil have urged researchers to consider hydrogen as a real promising energy source. As a matter of fact, hydrogen is a clean fuel, whose combustion generates just pure water. It is neither expensive nor abundant. Moreover, Yes, we mean that hydrogen has a high energy density per unit of mass (34 k Wh kg^{-1}) [1]. Despite its advantages, hydrogen presents a few storage related problems. In this respect, hydrogen could be stored either at a gaseous state at a high pressure (700 bars), in fairly heavy bottles, or at a liquid state which requires a temperature of 20 K and hence the need for expensive cooling-devices, in addition to the significant loss through evaporation (phenomenon of boil-off). These two storage methods show important safety problems, linked on the one hand to the storage under pressure and to the high explosive potential of hydrogen in air on the other hand. A promising alternative for the above mentioned methods of storage consists in storing hydrogen at a solid state. For these storing method, a various kinds of hydrogen storage materials have been used such as metal organic frameworks (MOF, Zr-MOF) [2,3], the graphitic nanotubes/nanofibres, lithium amides materials [4], chemical hydrides [5–11] and carbon-related materials [12–14]. For these high-surface-area substrates hydrogen gas is physisorbed, so these aren't secure methods. The best and securest storage method consists in storing hydrogen at a low pressure, chemisorbed [15] in atomic form into the crystal structure of metals, forming the so called metal hydrides. Among these metals hydrides, $LaNi_5$ and its derivates exhibit excellent hydrogen storage characteristics [16]. Such as high volumetric storage density, easy activation, moderate kinetics [17], high capacity to absorb hydrogen rapidly which attains more than 6 hydrogen atoms per molecule of $LaNi_5$ [18] and reversibly nears the atmospheric pressure at room temperature [18–20]. To this criterion we can add the conditions of use as well as other criteria given by Sandrock [21], such as versatility, sensitivity to impurities, cyclic stability and easiness of manufacturing. As far as composition is concerned, $LaNi_5$ is among the most interesting and promising intermetallic metals [18,22,23]. Moreover, it's the only metal that hydrides at less than 10 MPa [24]. Several substitutions at the La and Ni sites have been widely used so as to improve their absorption and desorption of hydrogen [25,26]

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as well as the absorption and desorption capacity and their life cycle [27,28]. Generally, Al substituted alloys exhibited excellent resistance to oxygen [29] and enhanced hydrogen storage capacity [30–34]. Mendelson et al. [35] showed that a partial doping of Ni by Al considerably modifies the equilibrium pressure of hydrogen on the alloy. Moreover, the partial doping of Ni by Al enhanced the reaction kinetics [36] and the resistance of the $LaNi_5$-based materials to both intrinsic and extrinsic degradation [37]. Also it leads to an increase in discharge capacity of the $LaNi_5$ [38], increases in both the cell volume and the hydride stability [39] and greatly improved the cycle life of the $LaNi_5$ [38]. The storage of hydrogen in the $LaNi_5$ matrix through the phenomenon of absorption and it is released by desorption. This phenomenon is characterized, according to literature, by a phase transformation between the diluted solid solution and the concentrated solution. Hence, knowing the mechanism of transformation is of crucial importance. In fact, in literature, hydrogen absorption and desorption isotherms indicate the presence of two phases [40,41]. A α phase, which indicates a weak dissolution of hydrogen in the intermetallic compound and a β phase where the amount of hydrogen increases with pressures to form the hydride [42].

During adsorption and desorption, hysteresis phenomenon is encountered, in addition to the phenomenon of phase transformation. This is generally attributed to the excess of energy required to accommodate constraints associated with volume expansion during the formation of hydride [43,44]. This is also explained by several processes, especially the constraints generated during the insertion and dis-insertion of hydrogen from the solid matrix [45] and the creation of defects related to composition [46]. As well as the plastic deformations which may also explain this hysteresis [47]. Also, the nature of hydrogen bonding with the metal compound and the energies of the hydrogenation are of crucial importance. Therefore, they have been widely treated. As Eugenio Riccardo Pinatel et al. [48] used the AB initio to calculate energies of formation at 0 K for the hydrides $LaNi_5H_7$ and $LaAl_5H_7$. It is equal (modules value) to 291 kJ/mol-H_2 for $LaNi_5H_7$ and to 103 kJ/mol-H_2 for the $LaAl_5H_7$. Tatsumi et al. [49] investigated the energy of $LaNi_5H_7$ employing ultrasoft pseudopotentials and plane-wave basis. They found that the theoretical heat of solution using the $La_2Ni_{10}H_1$ (modeled value) is 33 kJ/mol-H_2 and the theoretical heat of formation of the $LaNi_5H_7$ is 45 kJ/mol-H_2. Also for the YNi_5H_x compounds (with x = 0.0, 0.25, 0.5, 1.0, 3.0, 3.5, 4.0), G.I. Miletić et al. [50] have investigated, using density functional theory with ultrasoft pseudopotentials and a plane wave basis set, the site preference of H atoms, the energetic of a hydride formation and the energetic of the α and β reaction. Moreover, Zhao Shuang et al. [51] used the stepwise regression method and atomic parameters to calculated the enthalpy of formation of the hydrides of $LaNi_{5-x}M_x$ (M stands for Mn, Fe, Co, Ni, Al, Ga, Ge and Si). They found that ΔH ($kJ.mol^{-1}H_2$) of $LaNi_5$ is 30.2 ($kJ.mol^{-1}H_2$), of $LaNi_{4.8}Al_{0.2}$ is 32.8 ($kJ.mol^{-1}H_2$), of $LaNi_{4.5}Al_{0.5}$ is 36.7 ($kJ.mol^{-1}H_2$) and of $LaNi_{4.6}Ge_{0.4}$ is 38.6 ($kJ.mol^{-1}H_2$) and that the amount of released hydrogen is controlled by electronegativity, charge-to-radius ratio, electron concentration and atomic size factor. Using the DFT, a pseudopotential (PP) method and an all-electron method, A.F. Al Alam et al. [52] have analyzed the energetic and magnetic ground state configuration of LaNi5 and its saturated hydrogen β solution. They also study the binding of hydrogen within the host lattice. Moreover by the DFT, L.G. Hector Jr.et al. [53] indicate that the H–Ni and H–La interactions in the $LaNi_5H_7$ hydride are primarily metallic with a small ionic component. Furthermore, Basing on the mean-field theory and Brrag Williams approximation, a new lattice gas model has been developed by A.Ledovskikh et al. [54]. The various host energies (L_i), hydrogen guest energies (E_i) and hydrogen interaction energies (U_i) are calculated for the hydrides $LaNi_4Cu_1$, $LaNi_{4.2}Cu_1$, $LaNi_{4.4}Cu_1$ and $LaNi_5Cu_1$. We take for example the $LaNi_4Cu_1$, its hydrogen guest energies (module) are equal to 3.32 $kJ.mol^{-1}H_2$ for α phase and 0.53 $kJ.mol^{-1}H_2$ for β phase, its hydrogen interaction energies (module) $U_{\alpha\alpha} = 3.81$ $kJ.mol^{-1}H_2$ and $U_{\beta\beta} = 1.27$ $kJ.mol^{-1}H_2$ and $U_{\beta\alpha} = 6.19$ $kJ.mol^{-1}H_2$ and its host energy (module) L = 0.47 $kJ.mol^{-1}H_2$.

In this context, our work is presented also to complement and enrich the theoretical investigation, to calculate the formation energies (absorption energies), the desorption energies and investigate the dynamic of formation and decomposition of the hydride ($LaNi_{4.85}Al_{0.15}$). This study is using the statistical physics. The experimental isotherms of absorption and desorption of hydrogen on $LaNi_{4.85}Al_{0.15}$ for T = 298 K, T = 303 K and T = 313 K are fitted by a model established by statistical physics treatment. In our theoretical development, certain hypotheses have been made in order to simplify theoretical calculation. The obtained model gives the expression of the absorbed amount in the case of absorption and the retained amount in the case of desorption in relation to the pressure of equilibrium. Thanks to this model, we could evaluate the dynamics of absorption and desorption in terms of phase transformation and hysteresis after steric and energetic studies. We have compared the adsorption and desorption processes, in order to find an explanation of the hysteresis encountered during desorption stage.

2. Experimental procedure

Hydrogen is the used gas of a UP type 99.99% [55]. The reactor and the reservoir are flooded in a bath with a thermostat to control temperature. We use a cylindrical reservoir composed of a cylindrical body and a lid, made of brass. The pressure in the reservoir is measured using a pressure gauge (type PA-21LC, 0–100 bar). The sensor of pressure is attached to a D.C constant voltage and to a data acquisition system. The reactor tightness for vacuum (10^{-3} bar) and for a hydrogen pressure of more than 16 bars was tested to determine the suitable amount of alloy introduced in the reactor. This latter authorizes the achievement of quasi-isothermal condition in the bed and the selection of suitable dimensions of the reactor like diameter, height and thickness. Firstly, a primary vacuum is generated in the reservoir and in the reactor. Secondly, an amount of hydrogen is put in the reservoir under a defined pressure. The reservoir is in contact with the reactor. Absorption of hydrogen starts and the pressure in the reservoir decreases until equilibrium. For the three experimental temperatures 298 K, 303 K and 313 K, this procedure using a higher initial reservoir pressure is repeated until the saturation of the hydride bed.

In case of desorption, the reservoir originally under a primary vacuum is placed in contact with the reactor. Then, the pressure in the reservoir rises until equilibrium is reached. For the three temperatures 298 K, 303 K and 313 K, this process is duplicated up to the end of desorption. The obtained isotherms are traced in Fig. 1(a)–(c).

3. Modeling of absorption and desorption isotherms

Absorption and desorption could be regarded as a process of interaction amidst the absorbate (molecule of hydrogen) and the absorbent (receptor site of $LaNi_{4.85}Al_{0.15}$) to obtain the complex formed between the absorbate and the receptor site. Such a site is at a state of equilibrium between a free state and an absorbed one. The study of particle exchange for the free state and the absorbed state requires a grand canonical ensemble in statistical physics [56] so as to take account of the variation of particle number during the process of absorption and desorption. This study is divided into three parts. The assumption of some hypotheses is necessary for