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THERMODYNAMICS OF HYDROGEN GAS–SOLID REACTION

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Today materials for hydrogen storage might be divided into two families: (i) hydrides where atomic hydrogen resides mainly in the bulk of the material (alloys, molecular hydride complexes and molecular covalent compounds) and (ii) physisorbed high-surface-area materials where molecular hydrogen resides on the surface of the material (carbon fullerenes, nano-tubes and highly porous media). First group of hydrogen storage materials uptake hydrogen by chemical sorption when the interaction forces between a surface and an adsorbate are of the same general strength as found in chemical bonding in bulk compounds. It is useful to make a distinction between physisorption (H-H bond in the gas phase is preserved in the sorbed state) and chemisorption (H-H bond is broken during the sorption process). Also chemisorption may occur only in a monolayer on a surface, whereas physisorption is usually accompanied by multilayer adsorption depending upon the temperature. Therefore description of atomic hydrogen chemisorption becomes dissimilar to molecular hydrogen physisorption. Present work contains general thermodynamic characteristics of well-known metal hydrides. It is a short review where hydrogenation is discussed as a complex process through chemisorbed hydrogen at the surface, hydrogen under surface and finally hydrogen in the bulk.

Keywords: metal hydride, enthalpy, PC isotherm, entropy.

1. Introduction

Various metal hydrides are currently being studied for use as a means of hydrogen storage in fuel cell-powered electric cars and in batteries. They also have important uses in organic chemistry as powerful reducing agents, and many promising uses in a hydrogen economy. Practically, the term «hydride» has two distinct but overlapping meanings. The first meaning of hydride refers to any compounds hydrogen forms with other elements, ranging over most of the periodic table (groups 1–16) and deals with only in terms of formal nomenclature. The second meaning refers to a hydrogen atom that formally reacts as a hydrogen anion (H^{-}) as well as hydrogen atoms directly bonded to metal atoms regardless of their reactivity. Chemical bonds in hydrides range from very covalent to very ionic as well as multi-centered bonds and metallic bonding. Therefore hydrides can be components of discrete molecules, oligomers or polymers, ionic solids, chemisorbed monolayers, bulk metals, and other modern nanomaterials. Traditionally hydrides react as Lewis bases or reducing agents and it is also common for some metal hydrides to react as hydrogen radicals or as protonic acids. Hydrogen has a relatively low electron affinity, 72.77 kJ/mol and reacts exothermically with protons:

$$H^- + H^+ \rightarrow H_2; \quad \Delta H = -1676 \text{ kJ/mol} \tag{1}$$

This powerful Lewis base confirms that the hydride ion is a strong reducing agent:

$$H_2 + 2e \rightarrow 2H^-; \quad E° = -2.25 \text{ V} \tag{2}$$

The interstitial hydrides are distinct from ionic or covalent hydrides, in that they may form where H atoms allocate in tetrahedral or octahedral interstices within the metal framework. Solid solution formation with hydrogen is common too. The bonding between the metal atom and atomic hydrogen is highly delocalized, with multi-center, multi-electron bonding similar to that in metals occurring. Most interstitial hydrides can exist as (i) discrete molecules or metal clusters; or (ii) within bulk metals or alloys. In the first case they are atomic centers in a defined multi-centered, multi-electron bonds, in the second – their bonding is considered as metallic. Formally interstitial hydrides are separated into two groups: (i) metal/alloy hydrides and (ii) intermetallic hydrides.

Thermodynamic properties of interstitial hydrides was observed at the beginning of 70-th when metal hydrides where the first hydrogen storage materials that were used in practice. The present review organizes the main thermodynamic parameters in a one description and might be applied to the all solid materials which absorb hydrogen into the bulk.

2. Enthalpy of metal hydride formation

2. 1. Classical thermodynamic model

One of the well-known models to estimate the enthalpy of metal hydride formation and heat of metal/alloys formation was proposed by A.R. Miedema [1]. The main idea he was following: metal atoms in a binary AB alloy keep their identity, in other words it is possible to shown Wigner-Seitz-type atomic cells for the alloy which are quite similar to the cells for the two types of metal in the pure metallic lattice. In this case atomic volume for A component must be the same as for B component. Unless it is the same for metals A and B, the form for example B cells should be modified to fill the whole space, however until its volume is the same, and it can be done by cost of a small energy only. The changes in boundary conditions, which appear when A and B cells are not longer surrounded by the similar neighbors, are schematically shown in fig. 1.

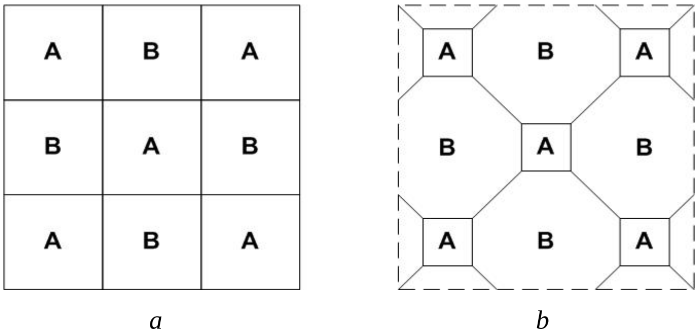

Fig. 1. Electron transfer in an alloy of two metals A and B: (*a*) Wigner-Seitz-type atomic cells for A and B atoms with parent dimension; (*b*) A and B atoms after charge transfer [1].

At the boundary between dissimilar cells there will be a discontinuity in the chemical potential for electrons and in the density of electrons. Firstly, that interruption will lead to electron transfer from the electropositive to the more electronegative metal, which transfer of charge should be lower than the energy of the alloy. And the second, the discontinuity in electron density will leads to a positive contribution to the alloy energy. Miedema had determined that the heat of formation of binary alloys could be described by following:

$$\Delta H = f(c)\,[-P_e\,(\Delta\varphi^*)^2 + Q\,(\Delta n_w)^2], \qquad (3)$$

where f(c) – is the function of concentration; φ^* – the parameter of electronegativity, which is similar to electron work function of pure metals; and n_w can be derived from compressibility data for pure metals.

F(c) function, φ^* and n_w parameters for element (including hydrogen) had been tabulated in [1]. The values for P_e and Q constants were derived from experimental heat of formation data: $P_e = 0.85\ V^{-1}$; $Q = 0.23\ eV/(dens.un.)^2$.

Miedema model was applied for any binary AB_n alloy very successfully. For example we can schematically show the structure of the imaginary compound AB_n (fig. 2).

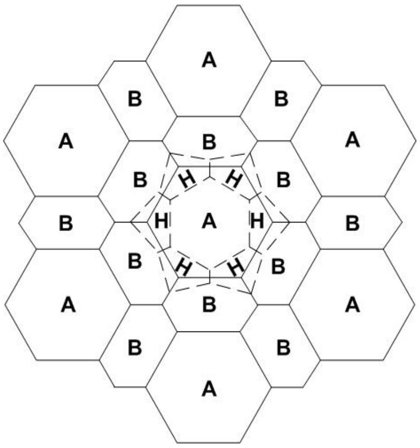

Fig. 2. Presentation of atomic cells in an intermetallic compound AB_n with and without hydrogen. The atomic cells of hydrogen are indicated by broken lines [1].

There are no A–A nearest neighbors, in other words, A-type atomic cells do not have any mutual contacts. And when the compound absorbs hydrogen in order to form a metal hydride, hydrogen atoms will occupy the interstitial positions in the AB_n lattice as showed by the dashed lines in fig. 2. If hydrogen is considered as metal, the atomic cells around a center proton must be drawn. And when A atoms attract hydrogen while B atoms do not, the hydrogen cells will start to separate A-type from B-type cells. Thus the area of contact between A and B cells will be reduced while the large areas of contact between A cells and H cells and, obviously, of B cells and H cells will be appeared.

The authors of [2] described the heats of formation in binary metal hydrides based on energy effects which were associated with the boundaries between the transition metal and hydrogen metal atomic cells. This involved a decomposition of the heat of formation of the ternary hydride, AB_nH_{2m}, into two contributions:

$$\Delta H(AB_nH_{2m}) = \Delta H(AH_m) + \Delta H(B_nH_m). \tag{4}$$

Taking the same number of H atoms for the two binary hydrides to be equal was a somewhat arbitrary assumption. Since one has no key how to draw boundaries between atomic cells in a complex crystal structure this must be considered as the simplest assumption. If we make here another assumption, all ΔH values calculated below would change in the same direction. This may affect the quantitative agreement, but not the trends observed. In other words, if the heat of formation of the parent AB_n compound is only partially lost (as were assumed in [2]), the trends derived will not be affected. For hydrogen reaction which can be written in general as follows:

$$AB_n + mH_2 \rightarrow AB_nH_{2m} \tag{5}$$

the enthalpy of this reaction can be measured as:

$$\Delta H_{reaction} = \Delta H(AB_nH_{2m}) - \Delta H(AB_n). \tag{6}$$

For simplicity we can write $\Delta H\ (AB_nH_{2m})$ like that:

$$\Delta H\ (AB_nH_{2m}) = \Delta H(AB_nH_6) = \Delta H(AH_3) + \Delta H(B_nH_3). \tag{7}$$

When $2m = 6$ assumption has place, all metal bonds A–B in ternary AB_nH_6 metal hydride will be destroyed; and if $2m < 6$, A–B bonds coexist with A–H and B–H bonds, so the next valid relationship can be obtained:

$$\Delta H\ (AB_nH_{2m}) = m/3[\Delta H(AH_3)] + m/3[\Delta H\ B_nH_3)] + (3-m)/3[\Delta H(AB_n)]. \tag{8}$$

Under particular substitution some B atoms by C atoms the hydrogen reaction will be the next:

$$AB_{n-x}C_x + mH_2 \rightarrow AB_{n-x}C_xH_{2m}, \text{ or } A + (n-x)B + xC + mH_2 \rightarrow AB_{n-x}C_xH_{2m} \tag{9}$$

Then the enthalpy of metal hydride formation of $AB_{n-x}C_xH_{2m}$ hydride can be written as:

$$\Delta H(AB_{n-x}C_xH_{2m}) = m/3[\Delta H(AH_3)] + (m/3)(n-x)/n[\Delta H(B_nH_3)] + \\ + (m/3)(x/n)[\Delta H(C_nH_3)] + (3-m)/3[\Delta H(AB_{n-x}C_x)] + \Delta H_1. \tag{10}$$

ΔH_1 enthalpy shows the effect of mixing owing to replacing B atoms by C atoms and can be estimated as follows:

$$\Delta H_1 = \Delta H\ (AB_{n-x}C_x) - (n-x)/n\ [\Delta H\ (AB_n)] - x/n\ [\Delta H\ (AC_n)]. \tag{11}$$

Thus, one of the conclusions from this thermodynamic model, which was firstly presented by A. R. Miedema, will be the following: the more stable is IMC, the less stable is its intermetallic hydride. However, it was not experimentally confirmed, since different methods to estimate the enthalpy of metal hydride formation did not show an accurate common tendency. For example, even $LaNi_4M$ (M = Cu; Fe; Ni; Mn) compounds show very similar ΔH values, while their enthalpy of metal hydride formation were much different, especially for M = Mn [3]. Effects of substitution with foreign metals on the crystallographic, thermodynamic and electrochemical properties of AB_5-type hydrogen storage alloys were deeply investigated in [4].

2.2. Enthalpy determination by calorimetry

A method to obtain the heat of decomposition of metal hydrides is described in [5]. Calorimetrically measured enthalpies do not depend on the attainment of equilibrium hydrogen pressure (P_{H2}) but only on the heats evolved which are essentially independent of P_{H2}, provided that the gaseous hydrogen behaves ideally and hydrostatic effects are absent. Most calorimetric determinations of enthalpies of chemical reactions are carried out under irreversible conditions. If hydride formation and decomposition are reversible processes, their calorimetric ΔH values must be equal in magnitude. Of course, it is an assumption, because the phase boundaries are not the same for metal hydride formation and its decomposition, but this is generally a second order effect and the calorimetric enthalpy magnitudes are very close at moderate P_{H2}. High precision calorimetric method shows that for ZrNi–H, which has a large hysteresis, the hydride formation and decomposition values of $|\Delta H_{plateau}|$ are equal and the same is true for Pd–H and $LaNi_5$–H systems. The full explanation why hysteresis does not influence calorimetrically determined enthalpies one can find in [6]. An isothermal scheme exhibiting hysteresis where the phase boundaries α and β expressed as atom ratios (r) is presented in fig. 3.

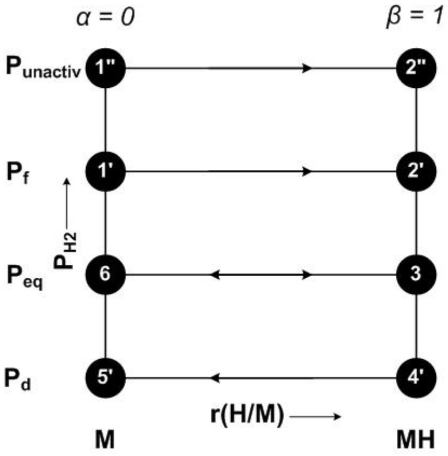

Fig. 3. The isothermal scheme of reversible and irreversible processes for metal hydride formation/decomposition [6].

There is an assumption that hysteresis does not influence on the phase boundaries, which was taken for convenience as 0 and 1, respectively. The equilibrium pathway (P_{eq}) was shown in the center of the normal hysteresis gap; it cannot be located above formation pathway (P_f) or below decomposition pathway (P_d), because then, the assumed (1'→2') and (4'→5') irreversible steps would not generate entropy. The hypothetical reversible step (6↔3), which does not have to exist in a real system, corresponds to reversible metal hydride formation/decomposition according to reaction:

$$M + ½\,H_2 \leftrightarrow MH \quad (\text{at } P_{eq}). \qquad (12)$$

Since the enthalpy is not dependent on pathway, it is obviously that, if H_2 is ideal gas and the process is isothermal then:

$$\Delta H(1'\to 6) = \Delta H(3\to 2') = 0,\ \text{then}\ \Delta H(1'\to 2') = \Delta H(6\to 3) = (\Delta H_{\text{plateau, eq}})^{f}. \quad (13)$$

Similar equation can be derived for metal hydride decomposition:

$$\Delta H(4'\to 5') = \Delta H(3\to 6) = (\Delta H_{\text{plateau, eq}})^{d}. \quad (14)$$

Since metal hydride formation and decomposition processes are absolutely reversible, their enthalpies should have the same magnitude, in other words:

$$|\Delta H(6\to 3)| = |\Delta H(3\to 6)| = |\Delta H_{\text{plateau, eq}}|. \quad (15)$$

It is also possible to consider the heats for metal hydride formation/decomposition using the reversible steps. The sum of the heats (per mol of H_2) for hydride formation (1'→2') from the reversible pathways (fig. 3) can be written as:

$$\begin{aligned}\Delta H\ (1'\to 2')_{\text{rev.paths}} &= \Delta H\ (1'\to 6) + \Delta H\ (6\to 3) + \Delta H\ (3\to 2') = \\ &= RT\ \ln(P_f/P_{eq})^{½} + q_{eq} + 0,\end{aligned} \quad (16)$$

where $q_{eq} = -|\Delta H_{\text{plateau, eq}}|$.

The irreversible step (1'→2') goes with heat evolution from the conversion driving force into the heat, ($-RT\ \ln(P_f/P_d)^{½}$), which enters in the surrounding and cancelling the heat for reversible step (1'→6). Thus the total heat change for the irreversible metal hydride formation (1'→2') is q_{eq} and equal on magnitude to $|\Delta H_{\text{plateau, eq}}|$. This indicates that driving force is evaluated as heat from the overcoming of barriers causing the hysteresis. Similar arguments can be made for the metal hydride decomposition step where there is also a driving force converted to a heat. That force can be used for the first hydrogenation (activation), where P_f is much bigger with respect to subsequent cycles of hydrogenation. But the calorimetric enthalpy for the initial hydrogenation is the same as for the next ones. The heat for the step (1"→2") by reversible paths can be written as:

$$\Delta H\ (1''\to 2'') = RT\ \ln(P_{f,\ init}/P_{eq})^{½} - |\Delta H_{\text{plateau, eq}}|, \quad (17)$$

which is dissipated by driving force ($RT\ \ln(P_{f,init}/P_{eq})^{½}$) and taking place at the initial high pressure of metal hydride formation (($P_{f,init}$), equals to q_{eq} or $-|\Delta H_{\text{plateau, eq}}|$, in spide of the initial hydrogenation results to solid disintegration into smaller particles.

2.3. Plateau enthalpies from van't Hoff plots

Hydrogen, that can be absorbed by solid may existence in three different forms, which are in dynamical equilibrium: adsorbed hydrogen, hydrogen under surface and hydrogen in the bulk. The content of adsorbed hydrogen strongly depends on the surface conditions while that influence is absent for hydrogen under surface. Hydrogen absorption into the bulk is accompanied by phase transitions – formation of hydride phases. Hydrogen solid solution is initiated at small hydrogen concentrations, which are called as α-phase. When hydrogen activity is increased by specific critical amount (xa), the formation of a new β-phase is initiated. Thus we obtain the coexistence of two phases (α and β). After reaching another critical amount (xβ) α→β phase transition is finished and a new solid solution but now called as solid solution in β-phase is formed. Since there is no long order of metallic atoms in amorphous alloys, their hydrogenation does not result in inner tensions due to volume changes in α/β phase borders, therefore only gradual change of hydrogen content takes place [7, 8]. Isotherms «hydrogen pressure – hydrogen content» or simply «pressure-composition» (often called as PC curves) are usually used to determine thermodynamic equilibrium between hydrogenated phases (fig. 4) [9, 10].

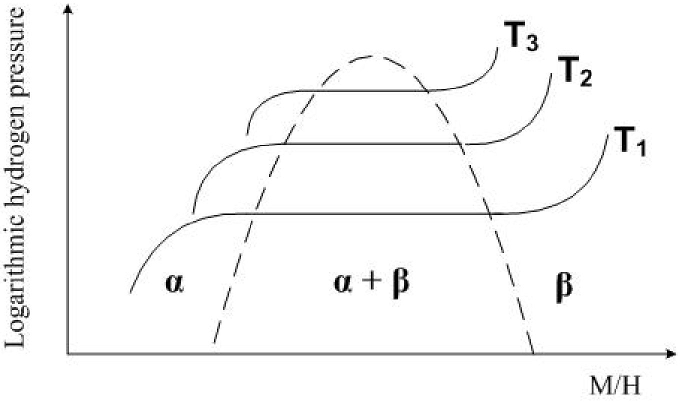

Fig. 4. The temperature dependency for the PC isotherms (T1<T2<T3).

Strictly speaking, based on PC-isotherms we can draw the first conclusions about ability of hydrogen absorbing alloy for their application. In fact, the main requirements for metal hydrides as reversible hydrogen storage are as follows: high hydrogen storage capacity; moderate thermodynamic stability for metal hydride; constant equilibrium hydrogen pressure under $MH_\alpha \rightarrow MH_\beta$ solid phase transition; low hysteresis of hydrogen absorption-desorption cycle. It is defined that equilibrium hydrogen pressure plateau increases with temperature. This temperature dependency is described by van’t Hoff equation:

$$\ln[P_{eq}/P^\circ] = \Delta H^\circ/RT - \Delta S^\circ/R, \tag{18}$$

where P_{eq} – is equilibrium hydrogen pressure at $\alpha \rightarrow \beta$ phase transition; P° – standard hydrogen pressure; R – gas constant; ΔH° and ΔS° – molar heat of metal hydride formation and entropy, respectively.

So, thermodynamic data can be derived from van’t Hoff plots on equilibrium hydrogen pressure, which is affected by hysteresis. In some M–H systems hysteresis is quite large, for example for $CeNi_5$–H, $RT \ln(P_f/P_d)^{1/2} = 1.9$ kJ/mol H_2 and the plateau enthalpies obtained from the van’t Hoff plots are $\Delta H_{f,plateau} = -8.35$ kJ/mol H_2 and $\Delta H_{d,plateau} = 11.1$ kJ/mol H_2, in other words their magnitudes differ by ~25%. Thus, since equilibrium hydrogen pressure plateau is directly affected by hysteresis, it must be taken into account in van’t Hoff equation:

$$RT \ln(P_f)^{½} = RT \ln(P_f/P_d)^{½} + RT \ln(P_{eq})^{½}, \tag{19}$$

where the first term is hysteresis for metal hydride formation (1’→2’) (see fig. 3) and can be called as (hyster.×f_f), and f_f is a fraction of the total hysteresis due to metal hydride formation.

In addition, it is important to note, hysteresis does not change much with temperature unless the temperature range is significant enough to change the phase boundaries, for example, near the critical temperature. Since this is nearly temperature independent, last equation can be re-written after division by T and differentiation with respect to 1/T, as:

$$R\left(\frac{\partial \ln P_f^{1/2}}{\partial(1/T)}\right) = (\text{hyster.}\times f_\text{f}) + R\left(\frac{\partial \ln P_{eq}^{1/2}}{\partial(1/T)}\right), \tag{20}$$

or

$$(\Delta H_\text{plateau})^\text{f} = (\text{hyster.}\times f_\text{f}) + (\Delta H_\text{plateau, eq})^\text{f}. \tag{21}$$

Similar mathematical procedure can be carried out for $RT\ln(P_\text{d})^{½}$ to obtain $(\Delta H_\text{plateau})^\text{d}$ value:

$$(\Delta H_\text{plateau})^\text{d} = (\text{hyster.}\times f_\text{d}) + (\Delta H_\text{plateau, eq})^\text{d}. \tag{22}$$

Magnitude of $(\Delta H_\text{plateau})^\text{f}$ and $(\Delta H_\text{plateau})^\text{d}$ is equal but negative for hydride formation and positive – for decomposition. Obviously $(f_\text{f} + f_\text{d}) = 1$, thus combining (21) and (22) equations we can get the hysteresis expression:

$$(\Delta H_\text{plateau})^\text{f} + (\Delta H_\text{plateau})^\text{d} = \text{hysteresis} = RT \ln(P_\text{f}/P_\text{d})^{½}. \tag{23}$$

It should be noted, that absolute $(\Delta H_\text{plateau})^\text{f}$ value is always less than $(\Delta H_\text{plateau})^\text{d}$, since hysteresis term must be positive and $|(\Delta H_\text{plateau})^\text{f}| < |(\Delta H_\text{plateau})^\text{d}|$ inequality is really confirmed by experiments in [6].

3. Entropy of hydrogenation

Entropy usually is determined from van't Hoff plots, however, this is not the case when $P_{H2} = P_{H2,eq}$ (Eq. 12), but for $P_{H2} = 1$ bar. Molecular hydrogen is in its standard state for this entropy change, $\Delta S_\text{plateau,1bar}$, but since non-stoichiometric solid phases are not considered as standard states, $\Delta S_\text{plateau,1bar}$, would not be a standard value. In M–H solutions, the infinitely diluted solution is taken as the standard state. For hydrogenation under hydrogen pressure of 1 bar, $\Delta S_\text{plateau,1bar}$ can be estimated by calorimetric method:

$$\Delta S_\text{plateau,1bar} = (\Delta H_\text{plateau,cal}) / T - R \ln(P_\text{plateau,eq})^{½}, \tag{24}$$

where $P_\text{plateau,eq}$ is approximated by $(P_\text{f}/P_\text{d})^{½}$, and $\Delta H_\text{plateau, cal} = \Delta H_\text{plateau,eq}$. The last term in this equation is the entropy for changing from $P_\text{plateau,eq}$ to hydrogen pressure of 1 bar. $\Delta S_\text{plateau,1bar}$ values derived from van't Hoff plots are not affected by hysteresis while the $\Delta H_\text{plateau,cal}$ values are affected. If Eq. (19) is differentiated with respect to T, $\Delta S_\text{plateau,1bar}$ might be obtained, because $RT \ln(P_\text{f})^{½}$ is the Gibbs free energy change for (12) reaction, where $\alpha \neq 0$ and $\beta \neq 1$:

$$-\Delta S^{f}_{plateau,1bar} = R\left(\frac{d(T\ln p_f^{1/2})}{dT}\right) = R\ln(p_{plateau,eq})^{1/2} + RT\left(\frac{d(\ln p_{eq}^{1/2})}{dT}\right), \tag{25}$$

where $\Delta S^{f}_{plateau,1bar}$ corresponds to entropy change under 1 bar, which is not affected by hysteresis with respect to the value for (12) reaction under $P_\text{plateau,eq}$ and it has been assumed that:

$$d(\text{hyster.}\times f_\text{f})/dT = 0. \tag{26}$$

The same way it can be shown $\Delta S^{d}_{plateau,1bar}$ under metal hydride decomposition which is taken from van't Hoff plots and also is independent on hysteresis. Thus absolute $\Delta S_{plateau}$ values for metal hydride formation and decomposition should be equal to each other, while the $|\Delta H_{plateu}|$ should not be [6].

The entropy depends on temperature very strong, while total difference of standard entropy between solid and its hydride is insignificant and equal ~10 J/mol·K. First of all, the entropy change for metal hydride is provided by standard entropy loss of gaseous hydrogen, and in general does not depend on the chemical nature of solid. Therefore for specific group of hydrogen storage alloys entropy value can be colligated and lies in range of ~110–130 J/mol·K [11]. However higher entropy might be found for disintegrated solids (e.g. nanoparticles) that leads to increased P_{eq} and a destabilization of the hydrogenated sides in solid [12, 13]. Nanocrystalline solids are characterized by a higher degree of disorder due to the significantly larger contribution of phase boundaries to the overall volume [14, 15]. For a complex hydride this means that reaction entropy may be observed, which is larger than that of hydrogen in the system. In [16] an examination of difference in microstructure and the hydrogen gas – nanosolid reaction were proposed to study in details. Useful information may be obtained from the investigation of stability and bond energy of nanoparticles and their possible transformation during the reaction with hydrogen.

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РЕЗЮМЕ

Іван САЛДАН

ТЕРМОДИНАМІКА РЕАКЦІЇ ГАЗОПОДІБНИЙ ВОДЕНЬ–ТВЕРДЕ ТІЛО

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Сьогодні матеріали для зберігання водню можуть бути розділені на дві категорії: (i) гідриди, де атомарний водень в основному знаходиться в об’ємі даного матеріалу (сплави, молекулярні гідридні комплекси і молекулярні ковалентні сполуки), а також (ii) матеріали з великою площею поверхні, фізично сорбовані молекулярним воднем (вуглецеві фулерени, нанотрубки і дрібнопористі середовища). Перша група це воденьсорбційні матеріали, які поглинають водень шляхом хімічної сорбції, коли сили взаємодії між поверхнею та адсорбентом є загалом такої ж самої сили, як було знайдено для хімічного зв’язку в об’ємі сполук. Дуже важливо розрізняти фізичну сорбцію (зв'язок Н–Н в газовій фазі є збережений у стані сорбції) та хімічну сорбцію (зв'язок Н–Н є зруйнований протягом процесу сорбції). Крім того, хімічна сорбція може виникати на поверхні тільки в моношарах, в той час, як фізична сорбція зазвичай супроводжується багатошаровою адсорбцією і залежить від температури. Тому опис хімічної сорбції атомарним воднем виявляється відмінним від фізичної сорбції молекулярним воднем. Дана робота містить основні термодинамічні характеристики добре відомих металогідридів. Це короткий огляд, в якому гідрування розглядається як складний процес через хімічно сорбований водень на поверхні, водень під поверхнею і в кінцевому випадку водень в об’ємі.

Ключові слова: металогідриди, ентальпія, PC ізотерми, ентропія.

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