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AN ANALYSIS OF THERMODYNAMIC CHARACTERISTICS OF METAL-HYDRIDE SYSTEMS FOR HYDROGEN STORAGE, USING A MODIFIED SCHEME OF THE PERTURBATION THEORY

Viktor V. Solovei

solovey@ipmach.kharkov.ua

ORCID: 0000-0002-5444-8922

Andrii M. Avramenko

an0100@ukr.net

ORCID: 0000-0003-1993-6311

Kseniia R. Umerenkova

ORCID: 0000-0002-3654-4814

A. Podgorny Institute of Mechanical Engineering Problems of NASU, 2/10, Pozharskyi Str., Kharkiv, 61046, Ukraine

The use of hydrides of intermetallic compounds (IMC) to implement the working processes of thermo sorption compressors, heat pumps, storage systems, cleaning, and programmable supply of hydrogen is due to a number of unique properties of these hydrogen sorbents. These include, first of all, the fact that the saturation of IMCs with a large sorption capacity occurs under relatively "mild" thermodynamic conditions, as well as the selectivity of sorption processes and the presence of the effect of thermodesorptional activation of atoms and molecules of hydrogen isotopes. The work is devoted to the description of phase equilibria in IMC hydrides. The proposed approach to the problem of calculating phase equilibria in metal hydrides consists in determining the properties of the lattice gas of H atoms and the H₂ molecular phase (which is in equilibrium with it) within the framework of a single method, the modified perturbation theory. The thermodynamic description of the hydrogen subsystem in the region of disordered α -, β -phases is carried out on the basis of the model of the non-ideal (interacting) lattice gas of hydrogen atoms. In this case, both the direct interaction between hydrogen atoms and the indirect "deformation" contributions to the potential energy due to the expansion of the lattice during hydrogen dissolution are taken into account. Simulation of phase transitions in IMC-hydrogen systems based on the modified perturbation theory scheme gives a correct description of the main features of phase diagrams in a wide range of hydrogen pressures. From the condition of the equality of the chemical potentials of the H-subsystem of the hydride and H₂-phase (calculated on the H atom), equations are obtained, relating the pressure of the gaseous H₂ phase to the hydride parameters c and T (phase diagrams). The proposed computational procedure does not use adjustable parameters or empirical correlations. It relies on the atomic characteristics of the hydrogen subsystem and metal matrix, which have an unambiguous physical meaning. The object of this research is the LaNi₅ intermetallic hydride. Of particular interest is the position of the critical point of the $\beta \rightarrow \alpha$ -transition in the LaNi₅-hydrogen system, for which there are no experimentally obtained parameter values. The paper presents the calculated values of the $\beta \rightarrow \alpha$ -transition critical parameters $T_c=445$ K, $p_c=87$ atm. The calculated data on the thermodynamic parameters of the $\alpha \rightarrow \beta$ -transition (enthalpy, entropy, and pressure on the isotherm plateau) make it possible to describe the solubility of hydrogen in LaNi₅ at pressures up to 500 atm and are in good agreement with the available experimental data in the literature.

Keywords: hydrogen, metal hydrides, intermetallic compounds, phase diagrams, lattice gas.

Introduction

Mathematical modeling of phase equilibria in hydrogen-metal hydride systems makes it possible to limit or eliminate expensive and lengthy experimental studies. However, until recently, methods for calculating the thermophysical properties of metal and IMC hydrides have mainly been empirical, which made it difficult to design and create elements of metal-hydride systems, since in this case it is impossible to predict their characteristics.

Article [1], devoted to the use of the thermodynamic perturbation theory for the description of phase equilibria in metal and IMC hydrides, shows the following. The model of the non-ideal lattice gas of hydrogen atoms, which is based on the perturbation theory method, makes it possible to reproduce the main features of the phase diagrams of IMC hydrogen systems. The calculations were performed in the region of disordered α - and β -phases, using the Pd-H₂ system as an example. The results obtained for PCT-dependencies (pressure-composition-temperature) of this system are consistent with experimental data.

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In the present work, the proposed method determines the sorption characteristics of the LaNi₅ IMC with a hexagonal structure. For the first time, state diagrams of the LaNi₅-H₂ system have been constructed both in the two-phase region (α - β) and with supercritical parameters.

Chemical Potential of Lattice Gas in IMC Hydrides

The proposed approach to the problem of calculating phase equilibria in metal hydrides consists in determining the properties of the lattice gas of H atoms and the H₂ molecular phase (which is in equilibrium with it) in the framework of a single method, the modified perturbation theory (MTV) [2, 3]. The thermodynamic description of the hydrogen subsystem in the region of disordered phases is carried out on the basis of the model of the non-ideal lattice gas of hydrogen atoms. In this case, both the direct interaction between hydrogen atoms and the indirect "deformation" contributions to the potential energy due to the expansion of the lattice during hydrogen dissolution are taken into account.

We note an important fact: in the majority of cases, the initial crystal structure of an ICM is not different from the structure of the metal matrix in the hydride phases of the hydrogen-ICM systems in the region of disordered phases.

In this case, the chemical potential μ_H of the hydrogen component of ICM hydrides for the basic case of interstitial solutions with a single type of equivalent interstices, when limited to the components of the second-order perturbation theory, has the form [1]

$$\beta\mu_H^+(\theta, T) = \ln \frac{\theta}{1-\theta} + \frac{W_1\theta}{T(1+\alpha c_s\theta)} + \frac{W_2\theta^2}{T^2(1+\alpha c_s\theta)^2}, \quad (1)$$

where $\beta=1/kT$; $\mu_H^+ = \mu_H - \mu_H^{st}$; $\mu_H^{st}(T)$ is the chemical potential in the standard state [1]; $\theta=C/C_s$ is the relative concentration of hydrogen; $n_{IMC} \cdot c$ is the hydrogen concentration in the form of the H/IMC ratio, i.e. per formula unit of the IMC; n_{IMC} is the number of atoms in the formula unit; c is the concentration of hydrogen in units of H/Me, i.e. on one atom of the matrix; $\alpha=c^{-1}(\Delta V(c)/V)$ is the IMC lattice dilatation coefficient for the case when the hydrogen is dissolved. The values C_s [H/IMC], the sorption capacity of the IMC or the maximum number of H-atom insertion positions in the phase region under study and c_s [H/Me], the maximum concentration c , are connected by the relation $C_s=n_{IMC} \cdot c_s$.

The constants W_1 and W_2 , which provide the connection between the macroscopic properties of the IMC-hydrogen interstitial solutions and the microscopic (atomic) characteristics of the hydrogen subsystem of the IMC metal matrix, are equal to

$$W_1 = 2I_1 n_M (\sigma_1^3 / v_0) E_1 c_s, \quad W_2 = (3I_2 / 4I_1^2) W_1^2, \quad (2)$$

where $I_1 = -5.585$; $I_2 = 1.262$ are the MTV parameters for the H-gas [1]; n_M is the number of matrix atoms in a unit cell; v_0 is the cell volume at $C=0$; E_1 [K] and σ_1 [m] are the (H-H)-interaction potential parameters $u_H(r) = kE_1\phi(r/\sigma_1)$.

Boundaries of the α - and β -phases of the LaNi₅-H₂ system

For the LaNi₅-H₂ system in the α - β -equilibrium region, the maximum amount of absorbed hydrogen corresponds to the stoichiometric composition of LaNi₅H_{2.5}, i.e. the value $C_s=6.7$ ($c_s=1.12$). With the parameters (in Å) $a_0=5.015$, $c_0=3.987$ [4] of the LaNi₅ unit cell containing $n_M=n_{IMC}=6$ atoms, its volume is $v_0=86.84 \cdot 10^{-30}$ m³. With the hydride matrix parameters $a_x=5.426$, $c_x=4.269$ and concentration values $c_x=c_s=1$, we obtain, for the dilatation coefficient of the LaNi₅ lattice, the value $\alpha \approx 2.9 \cdot 10^{-30}$ [m³] $\cdot n_M/v_0=0.20$ [5].

For the combination $E_1\sigma_1^3$ in (2) responsible for the energy of (H-H) hydrogen attraction in LaNi₅H_x, as in the case of the hexagonal PdH_x lattice [1], we take $E_1\sigma_1^3 = 0.45(E_1\sigma_1^3)_{Pd}$, where $(E_1\sigma_1^3)_0$ corresponds to the interaction of free H atoms. This gives the values of the constants $W_1 = -2.52 \cdot 10^3$ K, $W_2 = 1.93 \cdot 10^5$ K².

From expression (1), the values of temperature and concentration of hydrogen at the critical point of α - β -equilibria were obtained [6]: $T_c = -0.216 \cdot W_1 / (1 + \alpha c_s) = 445$ K, $C_c = \theta_c \cdot C_s = 2.75$ H/LaNi₅ ($\theta_c = 0.46 / (1 + 0.54\alpha c_s) = 0.41$). The pressure at the critical point $p_{H_2}^{(c)}$ is defined below. Experimental data on the position of the critical point of α - β -equilibria in the LaNi₅-H₂ system do not exist yet.

The $C_i(T)=C_s \cdot \theta_i(T)$ branches of the curve of decomposition of the homogeneous phases of the $\text{LaNi}_5\text{-H}_2$ system into the unordered phases $i=\alpha, \beta$ are determined by the equilibrium conditions

$$\begin{cases} p_H(\theta_\alpha, T) = p_H(\theta_\beta, T); \\ \mu_H^+(\theta_\alpha, T) = \mu_H^+(\theta_\beta, T), \end{cases} \quad (3)$$

where p_H is the pressure of the lattice H-gas.

The boundaries of the two-phase region ($\alpha+\beta$) are determined from the consequence of conditions (3), which are equal areas rules (bounded by the curve $\mu_H^+(\tilde{\theta})$ and the straight line $\mu_H^{+(PL)}$), which at temperature $T < T_c$ is implemented in the plane $(\mu_H^+ - \tilde{\theta})$ [1]

$$p_H^{(\beta)} - p_H^{(\alpha)} = \text{const} \int_{\tilde{\theta}_\alpha}^{\tilde{\theta}_\beta} [\mu_H^{+(PL)} - \mu_H^+(\tilde{\theta})] d\tilde{\theta} = 0. \quad (4)$$

Here the variable $\tilde{\theta} = \theta / (1 + \alpha c_s \theta)$; the dependencies $A^{(PL)} = A^{(\alpha)}(T) = A^{(\beta)}(T)$, where $A^{(i)}(T) \equiv A(\theta_i, T)$ are the values of the functions $A = p_H, \mu_H^+$ at the phase boundaries $i=\alpha, \beta$, i.e. on the "plateau" of pressure and the "plateau" of the chemical potential of the lattice H-gas.

Having determined the coordinates $\tilde{\theta}_i(T)$ from (4), we can obtain the branches of the curve of decomposition (CT) $\theta_i(T)$, i.e. the values $\theta_i = \tilde{\theta}_i / (1 - \alpha c_s \tilde{\theta}_i)$ that satisfy equations (3).

The Equilibrium Pressure of Hydrogen in the Two-Phase Region ($\alpha+\beta$)

The temperature dependence $p_{H_2}^{(PL)}(T)$ of the pressure of decomposition of the hydride β -phase, i.e. the hydrogen pressure on the plateau of isotherms $p_{H_2}(C)$ in the heterogeneous phase region ($\alpha+\beta$), can be represented by the traditional van't Hoff equation

$$\ln p_{H_2}^{(PL)}(T) = -\frac{\Delta H_{\beta \rightarrow \alpha}}{RT} + \frac{\Delta S_{\beta \rightarrow \alpha}}{R}, \quad (5)$$

where the parameters $\Delta H_{\beta \rightarrow \alpha}, \Delta S_{\beta \rightarrow \alpha}$, i.e. the enthalpy and entropy of the $\beta \rightarrow \alpha$ -transition, in the MTV scheme, have the form

$$\begin{aligned} \Delta H_{\beta \rightarrow \alpha} &\cong H_{H_2}^0 + 2RT\Delta_{\beta \rightarrow \alpha} \\ \Delta S_{\beta \rightarrow \alpha} &\cong S_{H_2}^0 - 2R\Delta_{\beta \rightarrow \alpha} \end{aligned} \quad (6)$$

Here, $H_{H_2}^0, S_{H_2}^0$ are the enthalpy and entropy of H_2 in the standard state of an ideal gas, the value $\Delta_{\beta \rightarrow \alpha}(T) = \beta(h_H^{+(\alpha)} - h_H^{+(\beta)}) / (\theta_\beta - \theta_\alpha)$ corresponds to the relative difference of the specific enthalpy h_H of the lattice H-gas $h_H^{(i)}(T) \equiv h_H^{st}(T) + h_H^+(\theta_i, T)$ at the boundaries of the homogeneous phases $\theta_\alpha(T)$ and $\theta_\beta(T)$.

For the working range of α - β -equilibria of a hydride, as before [2], we determine parameters (6) at the critical point of the $\beta \rightarrow \alpha$ -transition. Based on the expressions for the enthalpy of the non-ideal lattice H-gas [6] and for the critical concentration $\theta_c = 0.46 / (1 + 0.54\alpha c_s)$, for the system $\text{LaNi}_5\text{-H}_2$ ($\theta_c = 0.41$) we get

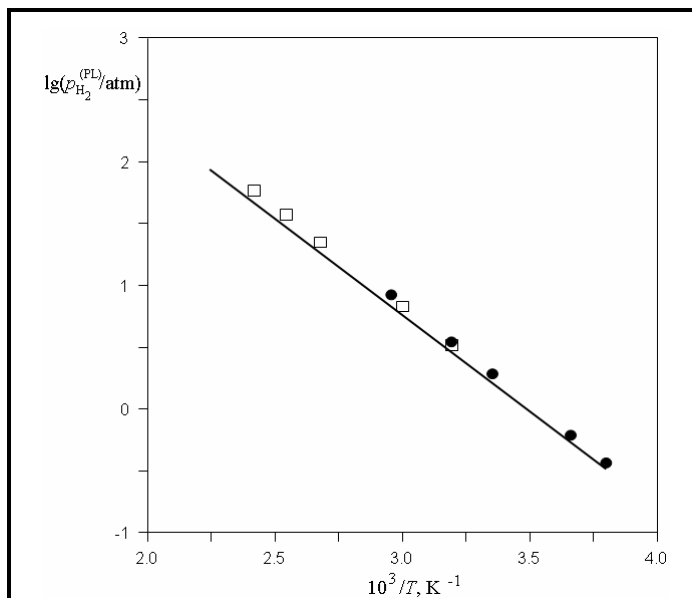


Fig. 1. Logarithm of the pressure of decomposition of the β -phase of LaNi_5 hydrides as a function of the reciprocal temperature:

— calculation according to (5) with $\Delta H_{\beta \rightarrow \alpha} = 29.8 \text{ kJ/mol H}_2$, $\Delta S_{\beta \rightarrow \alpha} = 104 \text{ J/(K}\cdot\text{mol H}_2)$; [7] and ● [8] are the experimental results on the desorption of H_2

$$-\Delta_{\beta \rightarrow \alpha}^{(c)} = \left. \frac{\partial(\beta h_H^+)}{\partial \theta} \right|_{\substack{T=T_c \\ \theta=\theta_c}} = \frac{1}{\theta_c(1-\theta_c)} + \frac{1}{\theta_c^2} \left[\ln(1-\theta_c) - \frac{0,63}{1+\alpha c_s} \right],$$

whence $\Delta_{\beta \rightarrow \alpha}^{(c)} = 2.3$. For the $\beta \rightarrow \alpha$ -transition parameters in the temperature range from 263 K to $T_c = 445$ K, according to (6), with $\Delta_{\beta \rightarrow \alpha} = 2.3$, we have the values $\Delta H_{\beta \rightarrow \alpha} = 29.8$ kJ/molH₂, $\Delta S_{\beta \rightarrow \alpha} = 104.0$ J/(K·mol H₂).

In Fig. 1, the dependence of the decomposition pressure of the β -phase of LaNi₅ hydrides on the reciprocal temperature obtained from expression (5), is compared with the experimental data on hydrogen desorption in [7] and [8], with the experiments carried out in limited operating temperature ranges.

From equation (5), with $T = T_c$ for the LaNi₅-H₂ system, it is possible to obtain the pressure at the critical point of α - β -equilibria: $p_{H_2}^{(c)} = 87$ atm. Experimental data on this parameter do not exist.

LaNi₅ Hydrogen Sorption Properties in the Single- and Two-Phase Regions at Pressures up to 500 atm

Phase diagrams connecting the pressure p_{H_2} of molecular hydrogen with the parameters c , T of the hydride can be obtained from the condition of equality of the lattice H-gas chemical potentials $\mu_H(c, T)$ and the gaseous phase H₂, $\mu_{H_2}(p_{H_2}, T)$ per the H atom

$$\frac{1}{2} \mu_{H_2}(p_{H_2}, T) = \mu_H(c, T). \quad (7)$$

If at the given c , T , the β -phase of the IMC hydride decomposes into the α - solid solution and H₂, plateaus appear on the PCT diagrams in the two-phase region ($\alpha + \beta$). These plateaus are segments of the constant pressure $p_{H_2}^{(PL)}(T)$ whose positions can be determined from the equality

$$\frac{c_\beta - c_\alpha}{2} \beta \mu_{H_2}^{(PL)} = \beta (h_{MH}^{(\beta)} - h_{MH}^{(\alpha)}) - (s_{MH}^{(\beta)} - s_{MH}^{(\alpha)}), \quad (8)$$

where $\mu_{H_2}^{(PL)} \equiv \mu_{H_2}(p_{H_2}^{(PL)}, T)$ is the chemical potential of H₂ on the "plateau"; $\beta h_{MH}^{(x)} \equiv H_{MH}(c_x, T)/RT$, $s_{MH}^{(x)} \equiv S_{MH}(c_x, T)/R$ are the specific enthalpy and entropy of the hydride at the phase boundaries $c_i(T) = c_s \theta_i(T)$. Upon transforming equalities (7) and (8) for the dependencies $p_{H_2}(\theta, T)$ intersecting one- and two-phase regions of IMC hydrides, we obtain

$$\ln p_{H_2}(\theta, T) = \ln p_{H_2}^{(PL)}(T) + 2\beta[\mu_H^+(\theta, T) - \mu_H^{+(PL)}(T)], \quad (9)$$

where $p_{H_2}^{(PL)}(T)$ is the decomposition pressure of the β -phase; $\mu_H^{+(PL)}(T)$ is the height of the "plateau" on the concentration dependencies of isotherms $\mu_H^+(\theta)$, with the height determined by the conditions of the phase gas-liquid transition in the hydrogen component of the hydride, i.e. in the lattice H-gas.

Expression (9) with $\theta < \theta_\alpha$ and $\theta > \theta_\beta$ describes the descending and ascending branches of the isotherms $p_{H_2}(C)$, respectively, and with $\theta_\alpha < \theta < \theta_\beta$ gives the value $p_{H_2}^{(PL)}(T)$ according to the van't Hoff equation (5).

For PCT-dependencies above the critical point of α - β -equilibria, taking into account the second virial coefficient correction for the chemical potential $\mu_{H_2}(p_{H_2}, T)$, we can obtain

$$\ln p_{H_2}(\theta, T) + 0,18 \frac{p_{H_2}(\theta, T)}{T} = Q + \frac{\Delta \Phi_{H_2}^0(T)}{R} + 2\beta[\mu_H^+(\theta, T) - \mu_H^{+(c)}], \quad (10)$$

where $\Delta \Phi_{H_2}^0(T) = \Phi_{H_2}^0(T) - \Phi_{H_2}^0(T_-)$; the values $Q = \ln p_{H_2}^{(c)} + 0,18 p_{H_2}^{(c)}/T_c$, $\Phi_{H_2}^0(T) = -G_{H_2}^0(T)/T$; $G_{H_2}^0$ is the Gibbs energy in an ideal gas state; the hydrogen pressure p_{H_2} is set in atm, the temperature T is set in K.

The phase diagram of the LaNi₅-H₂ system as a set of hydrogen solubility isotherms at temperatures below T_c is calculated according to expression (9), and in the supercritical single-phase region, $T \geq T_c$, according to expression (10).

The results are shown in Fig. 2 in comparison with the results of experiments on hydrogen desorption [7, 8]. The figure also shows the calculated dependencies at elevated temperatures and pressures up to about 500 atm, when in the virial decomposition of the chemical potential of the gaseous phases of hydrogen, it is permissible to be restricted to the term with the second virial coefficient B_{H_2} . There are no experimental data on hydrogen solubility in LaNi_5 in this state region. At the critical temperature $\mu_H^{+(c)} = \mu_H^{+(PL)}(T_c)$ and $\Delta\Phi_{H_2}^0 = 0$ and expression (10) describes the critical isotherm $p_{H_2}(\theta, T_c)$ LaNi_5 445 K (172.6 °C) with the inflection point $C_c = 2.75 \text{ H/LaNi}_5$; $p_{H_2}(\theta_c, T_c) \equiv p_{H_2}^{(c)} = p_{H_2}^{(PL)}(T_c) = 87 \text{ atm}$.

The results shown in Figs. 1 and 2, allow us to conclude that the model of the non-ideal lattice gas for the hydrogen subsystem of IMC hydrides provides a correct description of the main features of the PCT diagrams of the $\text{LaNi}_5\text{-H}_2$ system in the region of disordered phases in a wide pressure range. The difference between the calculated and experimental values does not exceed 7% in determining the pressure depending on the temperature in the two-phase region and 12% in calculating the values of the phase transition energy.

Conclusion

The application of perturbation theory for determining the thermodynamic properties of the non-ideal lattice gas of hydrogen atoms makes it possible to simulate phase equilibria in ICM hydrides in the region of disordered phases. The calculated enthalpy and entropy of the $\beta \rightarrow \alpha$ -transition in the $\text{LaNi}_5\text{-H}_2$ system and the pressure on the plateau of solubility isotherms are in good agreement with the available experimental data. In addition, data on the hydrogen sorption properties of LaNi_5 at elevated temperatures and pressures are obtained. There are no experimental data in this state area. The position of the transition critical point and the behavior of hydrogen isotherms in the supercritical region at pressures up to about 500 atm are predicted.

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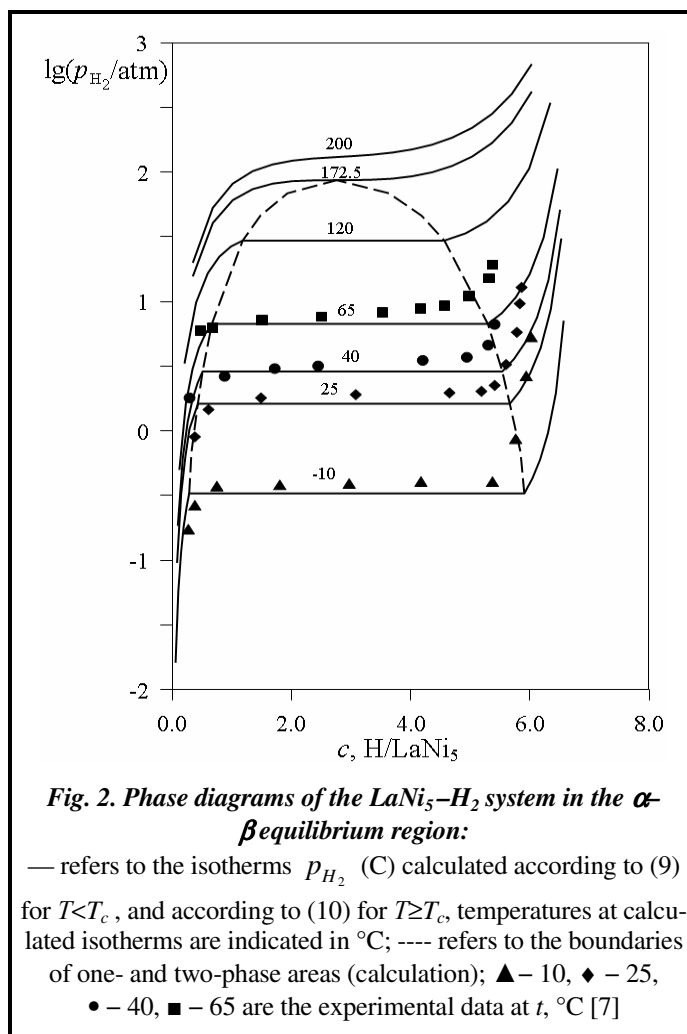


Fig. 2. Phase diagrams of the $\text{LaNi}_5\text{-H}_2$ system in the α - β equilibrium region:

— refers to the isotherms $p_{H_2}(C)$ calculated according to (9) for $T < T_c$, and according to (10) for $T \geq T_c$, temperatures at calculated isotherms are indicated in °C; ---- refers to the boundaries of one- and two-phase areas (calculation); ▲ – 10, ◆ – 25, ● – 40, ■ – 65 are the experimental data at t , °C [7]

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Аналіз термодинамічних характеристик металогідридних систем для зберігання водню з використанням модифікованої схеми теорії збурень

В. В. Соловей, А. М. Авраменко, К. Р. Умеренкова

Інститут проблем машинобудування ім. А.М. Підгорного НАН України,
61046, Україна, м. Харків, вул. Пожарського, 2/10

Застосування гідридів інтерметалічних сполук (ІМС) для реалізації робочих процесів термосорбційних компресорів, теплових насосів, систем зберігання, очищення і програмованої подачі водню обумовлено низкою унікальних властивостей цих сорбентів водню. Це, перш за все, те, що насичення воднем ІМС з великою сорбційною ємністю відбувається за порівняно «м'яких» термодинамічних умов, а також вибірковість сорбційних процесів і наявність ефекту термодесорбційного активування атомів і молекул ізотопів водню. Робота присвячена опису фазових рівноваг в гідрідах ІМС. Запропонований підхід до проблеми розрахунку фазових рівноваг в металогідрідах полягає у визначенні властивостей решіткового газу атомів водню і рівноважної з ним молекулярної фази в рамках єдиного методу - модифікованої теорії збурень. Термодинамічний опис водневої підсистеми в області неспорядкованих α - β -фаз виконано на базі моделі неідеального (взаємодіючого) решіткового газу атомів водню. Водночас враховано як пряму взаємодію між атомами водню, так і непрямі «деформаційні» вклади в потенціальну енергію внаслідок розширення решітки під час розчинення водню. Моделювання фазових переходів в системах ІМС-водень на базі модифікованої схеми теорії збурень дає правильний опис основних особливостей фазових діаграм в широкому діапазоні тисків водню. За умови рівності хімічних потенціалів H -підсистеми гідриду та H_2 -фази (в розрахунку на атом H) отримані рівняння, що зв'язують тиск газоподібної фази H_2 з параметрами гідриду c і T (фазові діаграми). В запропонованій обчислювальній процедурі не використовуються підганні параметри або емпіричні кореляції, і вона спирається на атомні характеристики водневої підсистеми та металевої матриці, що мають однозначне фізичне значення. Як об'єкт дослідження обрано гідрід інтерметаліду LaNi_5 . Особливий інтерес викликає розташування критичної точки $\beta \rightarrow \alpha$ -переходу в системі LaNi_5 -водень, для якої відсутні значення параметрів, отриманих експериментально. В роботі наведені розрахункові значення критичних параметрів $\beta \rightarrow \alpha$ -переходу $T_c=445$ К, $p_c=87$ атм. Визначені розрахунковим шляхом дані про термодинамічні параметри $\alpha \rightarrow \beta$ -переходу (ентальпія, ентропія і тиск на плато ізотерм) дають можливість окреслити межі розчинності водню в LaNi_5 за тисків до 500 атм та добре узгоджуються з наявними в літературі експериментальними даними.

Ключові слова: водень, металогідріди, інтерметалеві сполуки, фазові діаграми, решітковий газ.

Література

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