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HYDROGEN ABSORPTION-DESORPTION ISOTHERMS IN MAGNESIUM INTERMETALLIC COMPOUNDS

A statistical theory of hydrogen absorption-desorption in the system $CeMgCo_4$-H_2 was developed. The values of free energies of the two phases formed by dissolving hydrogen in a crystal $CeMgCo_4$ both $CeMgCo_4H_4$ and $CeMgCo_4H_6$ were calculated. The calculation was carried out using simplifying assumptions: the crystal lattice was assumed geometrically ideal, the interatomic interaction only for the nearest atom pairs was taken into account, and the correlation in the substitution position of the lattice atoms was not taken into account. The thermodynamic equilibrium conditions of these phases were determined. The minimizing of the free energy, which determines the equations of thermodynamic equilibrium, allowed studying the hydrogen sorption of crystals at different temperatures. The possibility of occurrence of the hysteresis effect, which disappears with increasing temperature, was shown. The absorption-desorption isotherms close to the real ones were obtained, and the appearance of these curves at the phase transition temperatures was explained. The calculations show that the experimental study of the sorption isotherms of hydrogen in the crystals can allow their mind to reveal the presence or absence of phase transformations in the system, as well as a possible phase transition temperature, if any. Comparison of experimental and calculated isotherms showed their similar nature.

Keywords: hydrogen sorption, isotherms, intermetallic compounds.

Разработана статистическая теория процесса абсорбции-десорбции водорода в системе $CeMgCo_4$-H_2. Рассчитаны свободные энергии двух фаз $CeMgCo_4H_4$ и $CeMgCo_4H_6$, формирующихся при растворении водорода в кристалле $CeMgCo_4$. Расчет проводился с упрощающими предположениями: кристаллическая решетка принималась геометрически идеальной, межатомные взаимодействия учитывались только для ближайших атомных пар, корреляция в замещении позиций решетки атомами не учитывалась. Определены условия термодинамического равновесия фаз. Минимизация свободных энергий, определяющая уравнения термодинамического равновесия, позволила изучить водородную сорбционность кристаллов для разных температур. Установлена возможность появления гистерезисного эффекта, который исчезает с повышением температуры. Построены близкие к реальным изотермы, объяснено появление на них изгибов в точках фазового перехода. Выполненный расчет показывает, что экспериментальное исследование изотерм водородной сорбции в кристаллах позволяет по их виду выявить наличие или отсутствие в системе фазовых превращений, а также определить возможную температуру фазового перехода при его наличии. Сравнение экспериментальных и расчетных изотерм показало их сходный характер.

Ключевые слова: водородная сорбция, изотермы, интерметаллиды.

Розроблена статистична теорія процесу абсорбції-десорбції гідрогену в системі $CeMgCo_4$-H_2. Розраховані вільні енергії двох фаз $CeMgCo_4H_4$ і $CeMgCo_4H_6$, що формуються при розчиненні водню в кристалі $CeMgCo_4$. Розрахунок вільних енергій проводився з використанням таких спрощень: кристалічна решітка вважалась геометрично ідеальною, міжатомні взаємодії враховувалися тільки для найближчих атомних пар, кореляція в заміщенні позицій решітки атомами не враховувалась. Визначено умови термодинамічної рівноваги фаз. Мінімізація вільних енергій, яка визначала рівняння термодинамічної рівноваги, дозволила вивчити сорбційність кристалів до водню при різних температурах. Показана можливість гістерезисного ефекту, який зникає з підвищенням температури. Побудовані близькі до реальних ізотерми і пояснена поява на них вигинів в точках фазового переходу. Виконаний розрахунок показав, що експериментальне дослідження ізотерм сорбції гідрогену в кристалах дозволяють за видом ізотерм виявити наявність або відсутність в системі фазових перетворень, а також визначити можливу температуру фазового переходу за його наявності. Порівняння результатів розрахунків та експериментальних ізотерм показало їх подібність.

Ключові слова: сорбція гідрогену, ізотерми, інтерметаліди.

Introduction

New perspective intermetallic hydride materials that proved to be attractive (because of their cheapness, non-toxicity, availability) for both the accumulation and storage of hydrogen and for practical use as battery electrodes supply [1] have been recently synthesized. Among the intermetallic compounds capable of absorbing hydrogen crystals are Mg_3MnNi_2, Mg_3TiNi_2, Mg_3AlNi_2, $LaMgNi_4$, $CeMgCo_4$ and also other ones [2,3]. Their hydrogen sorption capacity makes up 5.4 - 7.6 % weight of hydrogen.

Investigation of the kinetics of hydrogen absorption-desorption in $CeMgCo_4$ compound showed that the system $CeMgCo_4$-H_2 demonstrates the formation of two hydrides (deuterides): with a relatively small amount of hydrogen more stable α phase of $CeMgCo_4H_4$ is formed while with a higher concentration of hydrogen β phase of $CeMgCo_4H_6$ is formed. In the process of absorption crystal lattice expands so that its increase in volume makes 20%. Experimental absorption-desorption isotherms show hysteresis effect (Fig. 1) [1]. Bends in the curves indicate the hysteresis loop for the implementation of the phase transition α → β.

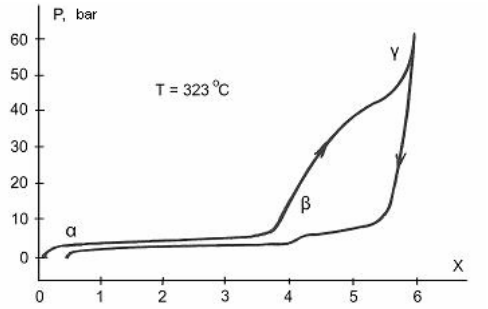

Fig.1. Experimental absorption-desorption isotherms for $CeMgCo_4$-H_2 system [1].

One may be interested in constructing the statistical theory for the hydrogen sorption processes in the $CeMgCo_4$-H_2 system, as well as ascertaining the conditions of thermodynamic equilibrium during phases formation process and describing isotherms of the process, identifying possible manifestations of the sorption hysteresis effect and the impact of α → β phase transition.

Theory. The comparison with experiment

To achieve the objectives we have calculated free energies F_i of hydride phases α = $CeMgCo_4H_4$ and β = $CeMgCo_4H_6$ using the known formula [4-8]

$$F_i = E_i - kT\ln W_i - kTN_H \ln\lambda_i \qquad (1)$$

where i = α, β; E_i – internal energy of the configuration for i-th phase, determined by the sum of the energy of interatomic interactions, W_i – thermodynamic probability of distribution of atoms in a crystal on their positions, calculated according to the rules of combinatorics, N_H – the number of hydrogen atoms in the crystal, λ_i – their activity, k – Boltzmann constant, T – absolute temperature.

The crystal structure of the intermetallic compound $CeMgCo_4$ is cubical. When forming the α and β phases hydrogen atoms first form octahedra around magnesium atoms, α phase occurs, aand further with hydrogen concentration increasing hydrogen atoms begin to fill more lattice cavities, for example, centers of some of the planar surfaces of the unit cell, β phase occurs. The lattice parameter equals to a = 7,501 Å. Hydrogenation (deuteration) of $CeMgCo_4$ crystal does not change the crystal lattice type, but causes its expansion by 20%.

The calculation of free energies has been performed using simplifying assumptions: the crystal lattice was taken geometrically ideal, interatomic interactions were taken into account only for the nearest atom pairs, correlation in substitution of atom positions in the lattice was not taken into account, the dependence of the energy of interatomic interactions on the hydrogen concentration was taken quadratic, the known dependence of the activity of atomic hydrogen in the crystal on external pressure was applied

$$\lambda_i = G_i p^{1/2} \tag{2}$$

where p – pressure; $G_i = const$ for each phase.

For calculation of internal configuration energy E_i terms with the energies of pairs of metals interaction are included in the constant term E_{oi} of this energy. Energy E_i is determined by the formula

$$E_i = E_{oi} + N_{CH}u_{CH} + N_{MH}u_{MH} + N_{KH}u_{KH} + N_{HH}u_{HH}$$

where N_{CH}, N_{MH}, N_{KH}, N_{HH} – numbers of the nearest atomic pairs *CeH*, *MgH*, *CoH*, *HH* (or *DD*), a u_{CH}, u_{MH}, u_{KH}, u_{HH} – energy of their interaction.

Numbers of the nearest pairs of N_{CH}, N_{MH}, N_{KH}, N_{HH} can be found via considering the crystal lattice geometry. The unit cell of α phase contains four atoms of sodium and magnesium and 16 cobalt and hydrogen atoms. The connection between *MgH* atom pairs in octahedra is strong and short. *CeH* pairs exist at two distances r'_{CH} and r''_{CH}. Distances for the nearest atom pairs are $r'_{CH} = a / 2^{3/2} = 2{,}652$; $r''_{CH} = a \cdot 3^{1/2} / 4 = 3{,}248$; $r_{MH} = a / 4 = 1{,}875$; $r_{KH} = a \cdot 3^{1/2} / 8 = 1{,}624$; $r_{HH} = a / 2^{3/2} = 2{,}652$. Indicating the number of atoms' positions for metals *Ce*, *Mg*, *Co* as 6*N*, we get the number of *Ce*, *Mg*, *Co* atoms as *N*, *N*, 4*N* respectively. The numbers of positions of hydrogen atoms in α and β phases are, respectively, 4*N* and 6*N*. Some of these positions are vacant. Let assume c and c_v to be concentrations of hydrogen atoms and vacant positions.

Consider first α phase of $CeMgCo_4H_X$ ($0 \le x \le 4$). In this phase

$$c = \mathrm{N}_H / 4\mathrm{N} = x / 4, \quad c_v = 1 - c. \tag{3}$$

Calculating the numbers of the next atom pairs gives in result

$$N'_{CH} = N_{CH}(r'_{CH}) = 8N \cdot c; \qquad N''_{CH} = N_{CH}(r''_{CH}) = 4N \cdot c;$$

$$N_{MH}(r_{MH}) = 6N \cdot c; \qquad N_{KH}(r_{KH}) = 8N \cdot c; \qquad N_{HH}(r_{HH}) = 24N \cdot c^2.$$

With taking into account these formulas, the configuration energy E_α

$$E_\alpha = E_{o\alpha} + 4N(2u'_{CH} + u''_{CH} + 3/2u_{MH} + 2u_{KH} + 6cu_{HH})c. \tag{4}$$

Thermodynamic probability W_α defined by the formula

$$W_\alpha = \frac{(4\mathrm{N})!}{N_H!(4\mathrm{N} - N_H)!},$$

with using the Stirling formula $\ln(X!) = X(\ln(X) - 1)$, which is true for large numbers X, allows to obtain the natural logarithm

$$W_\alpha = 4N\ln(4N) - N_H\ln(N_H) - (4N - N_H)\ln(4N - N_H). \tag{5}$$

Substituting the expressions (4) and (5) in Eq. (1) with the formulas (3), we obtain the free energy of α phase

$$F_\alpha = E_{o\alpha} + 4\mathrm{N}\{U_\alpha(c) + kT[c\ln c + (1-c)\ln(1-c)] - kTc\lambda_\alpha\} \tag{6}$$

where $U_\alpha = U'_\alpha c + U''_\alpha c^2$, $\quad U'_\alpha = 2u'_{CH} + u''_{CH} + 3/2u_{MH} + 2u_{KH}$, $\quad U''_\alpha = 6u_{HH}$.

Energies U'_α and U''_α depend on the hydrogen concentration due to the significant expansion of the crystal lattice in the process of absorption. It increases the interatomic distances and interaction energies of atoms are reduced by the absolute value. Generally, this energy is determined by a fractional-rational function with polynomials of the fourth degree of concentration of hydrogen in the numerator and denominator of the works [4, 5, 8]. In our particular case, this dependence can be simplified and supposed to be quadratic. Thus, configuration energy E_α is of fourth degree of the hydrogen concentration.

The obtained formula (6) defines the dependence of the free energy of α phase on the temperature, pressure (taking into account (2)), the concentration of hydrogen atoms, their activity (G_α coefficient) and energy parameters of the interaction of atomic pairs.

The equilibrium concentration of hydrogen is defined by the minimal free energy

$$\partial F_\alpha / \partial c = 0 . \tag{7}$$

Substitution free energy F_α (6) into the condition (7) with accepting the quadratic dependence of the energies U'_α, U''_α on hydrogen concentration results in a formula

$$\ln P = 2\ln\frac{c}{G_\alpha(1-c)} + \frac{\Gamma_\alpha(c)}{kT} \tag{8}$$

where $\Gamma_\alpha(c) = \gamma_o c^3 + \gamma' c^2 + \gamma'' c + \gamma^*$, and constants γ_o, γ', γ'', γ^* are defined via u_{CH}, u_{MH}, u_{KH}, u_{HH}.

According to (8), one can be calculate isotherms of hydrogen absorption-desorption in $CeMgCo_4H_X$ crystal with determining the dependence of P on the hydrogen concentration at different temperatures. Previously energy parameters γ_o, γ', γ'', γ^* and G_α coefficient must be evaluated. This evaluation was performed using the experimental data for the process of hydrogenation-dehydrogenation in $CeMgCo_4H_X$ crystal at temperature equal 323˚C (Fig.1). Evaluation showed that $G_\alpha = 1$ and the energy parameters are

$$\gamma_o = 4{,}16 \text{ eV}, \qquad \gamma' = -6{,}24 \text{ eV}, \qquad \gamma'' = 2{,}08 \text{ eV}, \qquad \gamma^* = 0{,}01 \text{ eV}. \tag{9}$$

Using the values calculated according to (8) the isotherms of hydrogen absorption - desorption in $CeMgCo_4H_X$ crystal were plotted for different temperatures (Fig. 2). As one can see, the graph has a certain degree of symmetry, so for $f = \ln P$ the following relation is true

$$f(c) = f(1-c). \tag{10}$$

Moreover, we see the sorption hysteresis effect appearance. The hysteresis loop narrows with increasing temperature, shortens and disappears.

There is no mentioned symmetry on an experimental graph (Fig. 1). Possible explanation is following: at $x \geq 3$ ($c \geq 3/4\ x$) the introduction of hydrogen atoms into the crystal is more intensive, hydrogen atoms begin to fill not only vertices of octahedra, but also other cavities of the crystal lattice, for example, the centers of the planar planes in the cell unit with coordinates $z = a/8$, $a/4$, $a/2$, $3a/4$, $7a/4$. It leads to the significant expansion of the crystal lattice and the implementation of the structural phase transition α → β.

The structure of β phase ($CeMgCo_4H_6$) is not yet clarified due to its instability. But it can be stated that the free energy of this phase will be similar to the F_α (6)

$$F_\beta = E_{o\beta} + 6N\{U_\beta(c) + kT[c\ln c + (1-c)\ln(1-c)] - kTc\lambda_\beta\}.$$

In β phase $c = N_H / 6N = x / 6$, $0 \leq c \leq 1$, $0 \leq x \leq 6$. The condition of thermodynamic equilibrium (7) also results in equation, similar to (8)

$$\ln P = 2\ln\frac{c}{G_\beta(1-c)} + \frac{\Gamma_\beta(c)}{kT}.$$

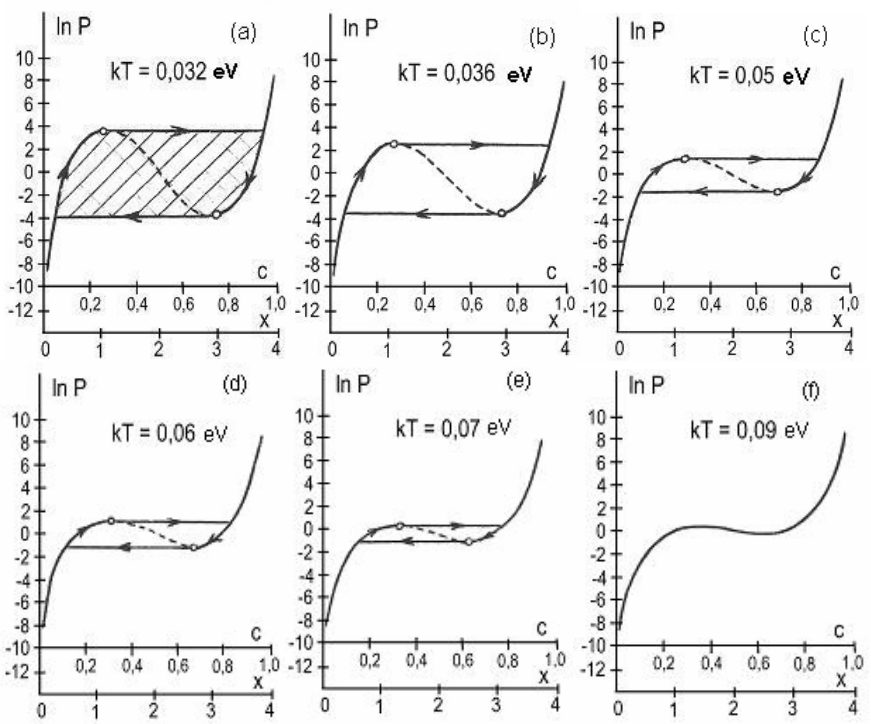

Fig.2. Estimated absorption-desorption isotherms of hydrogen in magnesium intermetallic compound $CeMgCo_4H_4$ according to (8) for the energy parameters (9) and for different temperatures equal to kT = 0.032, 0.036, 0.05, 0.06, 0.07, and 0.09 eV (curves *a*, *b*, *c*, *d*, *e*, *f*). Dashed parts correspond to the unstable state of the system. Circles on the curves mark the extreme points. Shaded area shows the sorption hysteresis effect. Coordinates *c*, *x* define hydrogen concentration in the intermetallic compound: $0 \le c \le 1$, $0 \le x \le 4$.

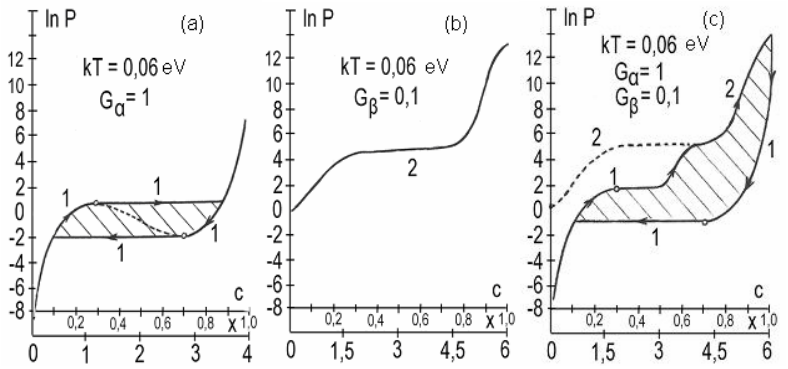

Fig.3. Estimated isotherms of hydrogen absorption-desorption: *a* – in $CeMgCo_4H_X$ crystal at $0 \le x \le 4$, $G\alpha = 1$, $\Gamma\alpha(c)$; *b* – in $CeMgCo_4H_X$ crystal at $0 \le x \le 6$, $G\alpha = 0{,}1$ and $|\Gamma\beta(c)| = 0{,}5\,|\Gamma\alpha(c)|$; *c* – in the system with $\alpha \rightarrow \beta$ phase transition at $x \approx 3$. Shaded area demonstrates the hysteresis effect.

Thus, due to the lattice expansion the absolute value of energy $\Gamma_\beta(c)$ is reduced in comparison with $\Gamma_\alpha(c)$ and activity of hydrogen atoms decreases (activity characterizes system energy changing simultaneously with changing number of hydrogen atoms entering the crystal)

$$|\Gamma_\alpha(c)| > |\Gamma_\beta(c)| \quad \text{and} \quad \lambda_\alpha > \lambda_\beta \quad (G_\alpha > G_\beta).$$

As an example, absorption-desorption isotherms were constructed in the α and β phases in the case of $G_\beta = 0{,}1G_\alpha$ and $\left|\Gamma_\beta(c)\right| = 0{,}5\left|\Gamma_\alpha(c)\right|$, which are shown in Fig. 3*a*, *b*.

According to Fig. 3*b*, the hysteresis effect in β phase at the selected temperature is absent. Fig. 3*c* is a superposition of graphs *a* and *b* taking implementation of the phase transition α → β at x ≈ 3 into account, when the curve 1 smoothly transforms into curve 2. Hydrogen atoms with increasing pressure (absorption) has been extensively introduced into the crystal while with decreasing pressure (desorption) intensively leave it. As a result of the phase transition α → β hysteresis loop is distorted in comparison to that one in Fig. 3 in the absence of transformation. The comparison of the calculated and experimental isotherms in Fig. 3 and 1 indicates their similar nature.

Conclusions

A statistical theory of the hydrogen absorption-desorption in $CeMgCo_4$ crystal with forming hydrides (deuterides), i.e. α and β $CeMgCo_4H_4$ phases, makes it possible to explain and justify the behavior of the isotherms of the process, observed experimentally. The free energies of phases determining their dependency on temperature, pressure, hydrogen concentration, and activity of the hydrogen atoms and energy constants have been calculated. Minimization of the free energy, which determines the thermodynamic equilibrium equation, allowed studying the hydrogen sorptivity of crystals at different temperatures. The possibility of the hysteresis effect that disappears with increasing temperature has been shown. Consideration of the phase transformation α → β allowed constructing the isotherms close to real ones and explaining the appearance of curves at the phase transition for them.

Performed calculations show that the experimental investigation of the hydrogen sorption isotherms in crystals can identify presence or absence of phase transformations in the system and also identify the possible phase transition temperature, if any. We should also note that the estimated energy parameters are not optimal. Summarizing results of independent experiments may allow using the above formulas to set the curves of absorption and desorption more clearly, as well as to estimate the temperature of phase transformations in the crystal.

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