PHASE EQUILIBRIUM IN INTERMETALLIC HYDRIDES WITHIN THE MODEL OF NON-IDEAL (INTERACTING) LATTICE GAS

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Introduction

In the present paper the peculiarities of phase equilibrium in metal hydrides within the model of non-ideal lattice gas are described. $LaNi_5$ was chosen as the object for investigation. Position of the critical point of α–β-transition is of a particular interest as the experimental data on its parameters are absent.

Results and discussion

Application of intermetallic compounds (IMC) as working bodies for thermosorption compressors, thermal pumps, systems for storing, purification and enrichment of hydrogen is based on the fact that the IMC hydrides having high sorption ability are formed under rather mild thermodynamic conditions.

The new approach [1] to this problem lies both in determination of the hydrogen subsystem of the hydride and in H_2 molecular phase equilibrium with the hydride in the frames of modified scheme of the perturbation theory (MPT) [2].

Thermodynamic description of the hydrogen subsystem was carried out on the model of non-ideal (interacting) lattice gas of hydrogen atoms. Both direct interaction between hydrogen atoms and indirect deformation contributions to potential energy due to the lattice widening with the solution of hydrogen were taken into consideration.

We should notice that the initial crystalline structure of IMCs does not differ considerably from the structure of the metallic matrix in hydride phases of the IMC–hydrogen systems in the region of disordered α- and β-phases. In this case, the chemical potential $\mu_H=G_H/N_H$ of the H-component of IMC hydride (i.e. specific Gibbs energy, per an H atom) has the following form:

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

where $\beta=1/kT$; $\mu_H^+=\mu_H-\mu_H^{st}$; $\mu_H^{st}(T)$ – chemical potential in the standard state [1]; $\theta=C/C_s$ – specific hydrogen concentration (the degree of occupation of the interstices available for H-atoms adoption); $C=n_{IMC}\cdot c$ – hydrogen concentration in the form of the H/IMC relation, i.e. per the formulary unity; n_{IMC} – the number of atoms in the formulary unity; c – hydrogen concentration in H/Me units, i.e. per an atom of the matrix.; $\alpha=c^{-1}(\Delta V(c)/V)$ – dilatation coefficient of the IMC lattice with hydrogen solution. The value C_s in (1) (IMC sorption capacity) and c_s (maximum concentration of the occupied interstices) are related by the $c_s=C_s/n_{IMC}$.

The constants W_1 and W_2 which give the relation between macroscopic properties of IMC-hydrogen interstitial solutions and microscopic (atomic) characteristics of the hydrogen subsystem and metallic matrix are following:

$$W_1=2I_1n_M(\sigma_1^3/v_0)E_1c_s\ ,\quad W_2=(3I_2/4I_1^2)W_1^2\ , \quad (2)$$

where $I_1=-5{,}585$, $I_2=1{,}262$ – MPT parameters for H-gas [1]; n_M – the number of metal atoms (per unit cell); v_o – the unit cell volume at C=0; E_1 [K], σ_1[m] – the parameters of the (H–H)-interaction potential $u_H(r)=kE_1\varphi(r/\sigma_1)$.

Let us consider phase equilibriums in IMC hydride $LaNi_5$ that has the hexagonal structure of $CaCu_5$ type. For $LaNi_5$ system with $a_0=5{,}015\cdot10^{-10}$ m, $c_0=3{,}987\cdot10^{-10}$ m of the elementary cell which contains $n_M=n_{IMC}=6$ atoms, its volume is $v_0=86{,}84\cdot10^{-30}$ m^3. In the region of α–β-transitions between disordered α- and β-phases which is important from the practical viewpoint under mild thermodynamic conditions (~10^3 atm), when mostly T-interstices are occupied, $C_s=6{,}7$ (c_s=1,12). With that, the dilatation coefficient is $\alpha\cong2{,}9\cdot10^{-30}$ [m^3]$\cdot n_M/v_0=0{,}20$.

The $E_1\sigma_1^3$ member in (2) is responsible for the power constant of (H-H)–interaction in IMC lattice. For $LaNi_5$ it is estimated as 40-50% from the interaction constant of free H-atoms in singlet states (model for Pd hydride [1]); we will take $E_1\sigma_1^3=0{,}45(E_1\sigma_1^3)_{Pd}$, that result in $W_1=-2{,}52\cdot10^3$ K, $W_2=1{,}93\cdot10^5$ K^2.

The curve for decomposition of the homogenous system $LaNi_5$-hydrogen in α-, β- phases is

determined; parameters of the critical point for α–β-transition are as follows: temperature $T_c = -0{,}2163 W_1/(1+\alpha c_s) = 445$ K, concentration $C_c = \theta_c \cdot C_s = 2{,}75$ H/LaNi$_5$ (where $\theta_c = 0{,}46/(1+0{,}54\alpha c_s) = 0{,}41$), H_2 pressure $p_{H_2}^{(c)} = 104$ atm. These values (experimental data on them are absent) match the shape of the phase diagram in this area of states much better than $T_c = 450$ K, $C_c = 3{,}3$ H/LaNi$_5$, and $p_{H_2}^{(c)} \sim 200$ atm, which were obtained in [3] within a rough model – Bragg-Williams approximation for the hard lattice ($C_c = 0{,}5C_s$). The isotherms of hydrogen solubility in LaNi$_5$ obtained on the base of MPT [1] below and above T_c are presented in the Fig.1 in comparison with different experimental data on desorption (A.Biris et.al., 1976 - marks). Temperatures at the calculated isotherms are given in °C.

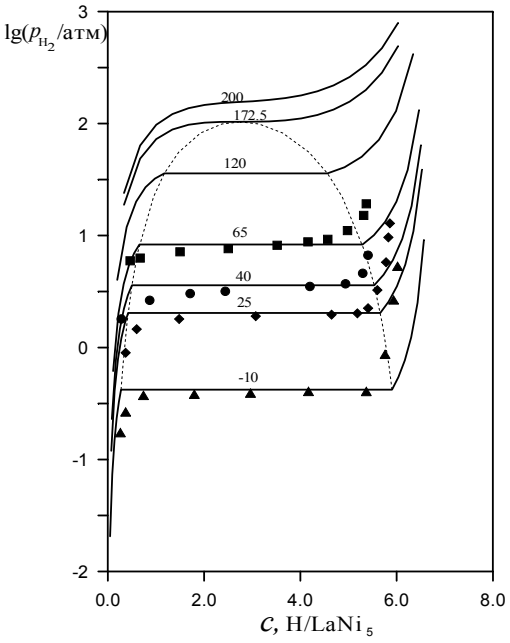

Fig. 1

The pressure of β-phase decomposition, i.e. the pressure at the 'plateau' of β→α transition may be presented by the van't Hoff equation

$$\ln p_{H_2}^{(PL)}(T) = -\frac{\Delta H_{\beta\to\alpha}}{RT} + \frac{\Delta S_{\beta\to\alpha}}{R}, \qquad (3)$$

where for enthalpy and entropy of β→α transition in the temperature range 263 K ... T_c (445 K) the values $\Delta H_{\beta\to\alpha} = 29{,}43$ kJ/moleH_2 and $\Delta S_{\beta\to\alpha} = 104{,}6$ J/(K · mole H_2) are obtained. The calculated data on the pressure of β-phase decomposition in LaNi$_5$ are compared in the Fig.2 with the experimental data (marks); the experiments were carried out within the limited temperature ranges.

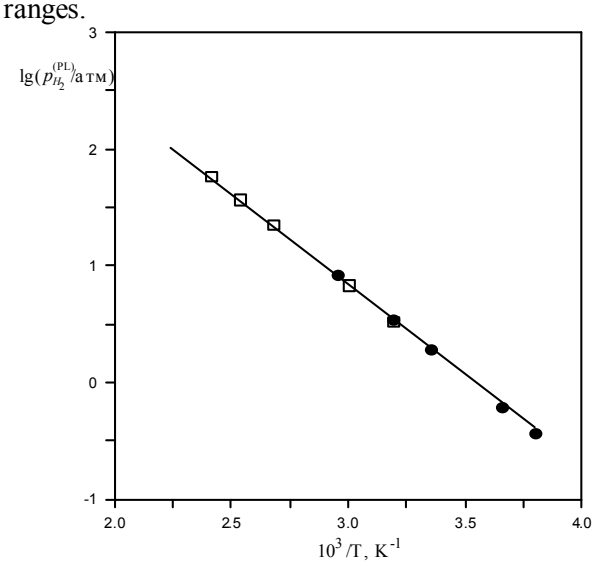

Fig. 2

Conclusions

Application of the model for the non-ideal gas of H-atoms for description of phase equilibriums in IMC hydrides allows reproducing the main peculiarities of IMC hydrogen phase diagrams in the region of disordered α- and β-phases. For LaNi$_5$ hydride the obtained diagrams of solubility within the wide range of pressures math the experimental data. The position of the critical point of α–β-transition in the LaNi$_5$ hydride is predicted.

References

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