HYDROGEN SORPTION PROPERTIES OF HEXAGONAL LAVES PHASE TiMn$_{1,5}$ INTERMETALLIC COMPOUND

Marinin V.S.[*]**, Umerenkova K.R., <u>Volovchuk O.V.</u>**
A.Podgorny Institute for Machine Building Problems
National Academy of Science of Ukraine,
2/10 Pozharskogo st., Kharkov, 61046 Ukraine
[*]*Fax: 38 (0572) 944 635*   *E-mail: ifk@sa.net.ua*

Introduction

In the paper [1] the main peculiarities of phase equilibriums in 'intermetallic compounds (IMC)-hydrogen' systems were described within the method of thermodynamic perturbation theory (MPT) through account of hydrogen-hydrogen interaction and the lattice dilatation. The calculations for compounds of CaCu$_5$ structural type in the region of disordered α-, β-phases were performed with the model of non-ideal lattice gas (case study: LaNi$_5$–H$_2$(D$_2$) systems).

In the present paper sorption properties of TiMn$_{1,5}$ IMC having hexagonal structure of C14 type or MgZn$_2$ (Laves phase) were determined using the proposed method. TiMn$_{1,5}$ possesses [2] one of the best combinations of hydrogen capacity and kinetics of sorption-desorption in soft (that is, actually significant) ranges of thermodynamic states among the other IMC. Phase diagrams for the TiMn$_{1,5}$–H$_2$ system were calculated for the first time both in two-phase (α+β) region and under overcritical parameters.

Results and discussion

Elementary cells of the metallic matrix of hydride phases on the basis of intermetallic compounds with the structure of MgZn$_2$ type which contain Ti, Zr, Er, Lu and Th as the first component retain initial symmetry of the IMC hexagonal Laves phases. In this case, excessive chemical potential of the hydrogen component of IMC hydride in the basic case of interstitial solutions with a single type of equivalent interstices has the following form [2]:

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

where β=1/kT; θ=C/C$_s$; C = n$_{IMC}$·c – hydrogen concentration as a H/IMC ratio, that is, per the formular unit of IMC; n$_{IMC}$ – the number of atoms in the formular unit; c – concentration of H in H/Me unit (per one atom of the matrix); α = c^{-1}(ΔV(c)/V) – dilatation coefficient of the IMC lattice on solving hydrogen; c$_s$=C$_s$/n$_{IMC}$, C$_s$ – sorption capacity of IMC, c$_s$ – the maximum concentration of the occupied interstices.

The constants W_1, W_2 in the model of non-ideal (interacting) lattice H-gas provide correlation between macroscopic properties of hydrides and microscopic (atomic) characteristics of hydrogen subsystem and metallic IMC matrix:

$$W_1 = 2I_1n_M(E_1\sigma_1^3)c_s/v_0, \ W_2 = (3I_2/4I_1^2)W_1^2, \quad (2)$$

where $I_1 = -5.585$, $I_2 = 1.262$ – MPT parameters for the lattice gas [2]; n_M – the number of matrix atoms in the elementary cell of v_0 (c=0); E_1 [K] and σ_1 [м] – parameters of (H–H)-interaction potential $u_H(r) = kE_1\varphi(r/\sigma_1)$.

For TiMn$_{1,5}$H$_x$, hydrides the maximum amount of absorbed hydrogen corresponds to the stoichiometric composition TiMn$_{1,5}$H$_{2,5}$ [3, 4], that is, the value of $C_s = 2,5$ ($c_s = 1$). With the parameters (in Å) $a_0 = 4.859$, $c_0 = 7.967$ of the elementary TiMn$_{1,5}$ cell containing [3] $n_M = 12$ atoms, and parameters of hydride matrix $a_x = 5.271$, $c_x = 8.579$ [2], with concentration $c_x=c_s=1$ the value of dilatation coefficient for TiMn$_{1,5}$ lattice is α = 0.267.

For the $E_1\sigma_1^3$ combination in (2) which is responsible for the energy of atom-atom attraction of hydrogen in TiMn$_{1,5}$H$_x$, as in the case of hexagonal matrix of LaNi$_5$H$_x$, let $E_1\sigma_1^3 = 0.45(E_1\sigma_1^3)_0$, where $(E_1\sigma_1^3)_0$ corresponds to interaction of free H-atoms [2]. This will give the values for constants $W_1 = -2.40\cdot10^3$ K, $W_2 = 1.748\cdot10^5$ K^2.

Preliminary parameters of the critical point of α–β transition according to (1) are: $T_c = -0.2163W_1/(1+\alpha c_s)$, $C_c = \theta_c \cdot C_s$, where $\theta_c = 0.46/(1+0.54\alpha c_s)$. For TiMn$_{1,5}$–H$_2$ system $T_c = 410$ K, $\theta_c = c_c = 0.402$ ($C_c = 1,0$ H/TiMn$_{1,5}$).

From the conditions for equilibrium α- and β-phases [1] boundaries of two-phase (α+β) region were determined, that is, curves of homogenous phase decomposition of TiMn$_{1,5}$H$_x$ hydrides.

Dependencies $p_{H_2}(\theta,T)$ in single– and two-phase regions at temperatures below T_c have the following form:

$$\ln p_{H_2}(\theta,T) = \ln p_{H_2}^{(PL)}(T) + 2\beta[\mu_H^+(\theta,T) - \mu_H^{+(PL)}(T)], \ (3)$$

where $\mu_H^{+(PL)}(T)$ – height of the "plateau" of dependencies (1) defined from the conditions of the phase equilibrium. Decomposition pressure of the β-phase may be presented in the Vant-Hoff form:

$$\ln p_{H_2}^{(PL)}(T) = -\frac{\Delta H_{\beta \to \alpha}}{RT} + \frac{\Delta S_{\beta \to \alpha}}{R} \quad . \qquad (4)$$

where enthalpy and entropy of the β-phase decomposition:

$$\Delta H_{\beta \to \alpha} \cong H_{H_2}^0 + 2RT\Delta_{\beta \to \alpha}, \quad \Delta S_{\beta \to \alpha} \cong S_{H_2}^0 - 2R\Delta_{\beta \to \alpha} \quad . (5)$$

The value $\Delta_{\beta \to \alpha}(T) = \beta(h_H^{+(\alpha)} - h_H^{+(\beta)})/(\theta_\beta - \theta_\alpha)$ corresponds to the relative difference of specific enthalpies of the lattice H-gas at the boundaries of homogenous phases $\theta_\alpha(T)$, $\theta_\beta(T)$:

$h_H^{(x)}(T) = h_H^{st}(T) + h_H^{+(x)}(T)$, where

$h_H^{+(x)} \equiv h_H^+(\theta_x, T)$.

For parameters of (β→α)-transition at T from 228 to 410 K (T_c) were obtained according to (5) the values $\Delta H_{\beta \to \alpha}$ = 26.04 kJ/moleH₂ and $\Delta S_{\beta \to \alpha}$ = 104.8 J/(K·mole H₂). The calculated data on decomposition pressure of TiMn₁,₅ β-phases were compared in the Fig.1 with the experimental data (○[3], ●[4]); the experiments were carried out in the limited temperature ranges.
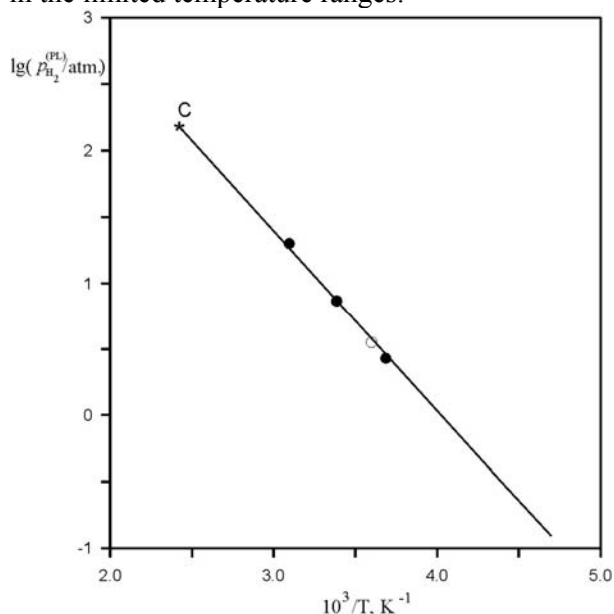

Fig. 1

Isotherms of hydrogen solvability in TiMn₁,₅ intermetallic compound are shown in the Fig. 2 in comparison with the experimental data on desorption (marks) [3, 4]. Temperature at experimental isotherms is given in °C. In the same figure predicted dependencies at elevated temperatures are shown both in two-phase and over-critical ($T>T_c$) regions.
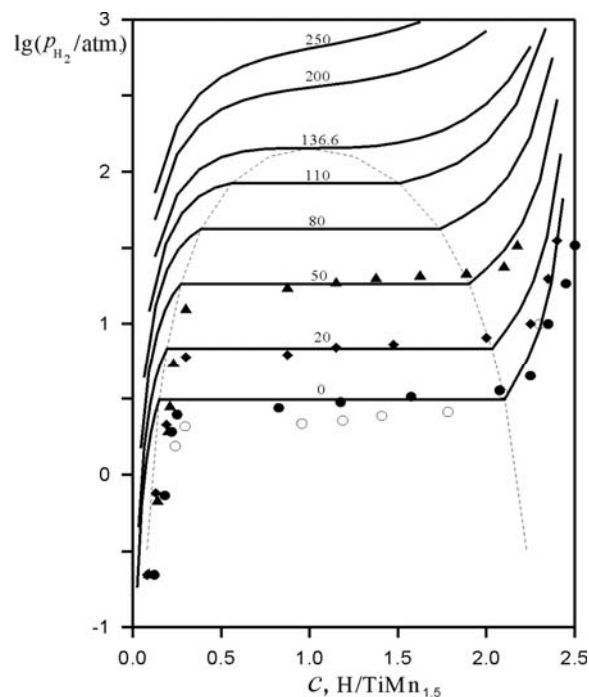

Fig. 2

Conclusions

Application of the method of perturbation theory to description of non-ideal lattice gas of hydrogen atoms in hydrides of intermetallic compounds gave a possibility to determine hydrogen sorption properties of the hexagonal Laves phase of TiMn₁,₅ in the region of α-, β-phases. Value of the critical point of α−β-transition in TiMn₁,₅H$_x$ hydride and behavior of solvability isotherms in over-critical region were predicted.

References
1. Marinin VS, Shmalko YuF, Umerenkova KR. Simulation of phase diagrams in LaNi₅−H₂(D₂) system and inversion of isotopic effect. Functional Materials 2007;14(4):492-497.
2. Shmalko YuF, Marinin VS, Umerenkova KR. Phase equilibriums in "hydrogen – metallic hydride" systems. Kharkov: KhNU–IMBP, 2007.
3. Andrejev BM, Dobrryanin OV, Magomedbekov EP, Pak YuS, Shitikov VV. Interaction of hydrogen with TiMn₁,₅ intermetallic compound. Journ. Phys. Chem.. 1982; 56(2): 463-465.
4. Gamo T, Moriwaki Y, Yanagihara N, Yamashita T, Iwaki T. In: Formation and properties of titanium – manganese alloy hydrides. Proc. 3rd World Hydrogen Energy Conf., Tokyo, 1980. Vol. 4. Oxford: 1981, p.2127-2143.