



TITANIUM-BASED LAVES PHASE HYDRIDES WITH HIGH DISSOCIATION PRESSURE

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Abstract—The results of the investigation of the hydrogen interaction with Laves phases having general composition $Ti_{1-x}Zr_xMn_{2-y-z}Cr_yFe_z$ are presented. The hydride phases are characterized by the rather high dissociation pressure of hydrogen at ambient temperature. The experiments were staged in standard Sieverts apparatus at pressures up to 100 atm and in a special apparatus which permitted the measurement of the quantities of absorbed and desorbed hydrogen up to pressures of 2000 atm. The thermodynamic characteristics of the obtained hydride phases were determined. Copyright © 1997 International Association for Hydrogen Energy

INTRODUCTION

The problem of finding the appropriate alloys with high hydrogen dissociation pressure at ambient temperature often rises while designing metal-hydride accumulators for various purposes. Multicomponent alloys on the basis of Laves phases $TiCr_2$ and $TiMn_2$ can be rather useful for solving this problem.

The analysis of the experimental literature data on the interaction of hydrogen with such multicomponent alloys shows that thermodynamic properties of these reactions and the absorption characteristics of alloys change monotonously with alloy composition within the boundaries of solid solution. This fact made the basis for the attempts to find out qualitative empirical “rules for designing” such alloys.

In present work on the basis of the well-known rules formulated in [1] we attempted to determine and to check experimentally the quantitative dependencies between the alloy composition and the absorption properties.

EXPERIMENTAL PART

Let us briefly state the main empirical rules proposed in [1] for the hexagonal Laves phases. If the cell volume of the alloy is about $160\text{--}165 \text{ \AA}^3$ then at 253 K the hydride dissociation pressure is about 1 atm. Moreover, the value of d-electron concentration of an alloy (the sum of d-electrons divided by the total number of components) allows one to evaluate the alloy absorption capacity ($H/M \approx 5\text{-DEC}$) and the width of the α -region (if $DEC \approx 4$, then the width is minimal).

Obviously, the elementary cell volume can be cal-

culated from the cell parameters which can be approximately determined using, for example, the Vegard rule for solid solutions. Dissociation pressure is determined from the van Hoff equation. In case of solid solutions the reaction enthalpy changes monotonously with composition also. Therefore, having enough experimental data for the mentioned parameters and using mathematical methods one can approximate this data with a function.

In the simplest case such a function of the monotonous dependence of absorption property from alloy composition can be presented as a second power equation:

$$F(x) = y_0 + \sum a_i x_i + \sum b_{ij} x_i x_j, \quad (i \leq j), \quad (1)$$

where x -metal atomic concentration, y_0 , a , b -coefficients. Knowing the coefficients of this equation, looking over the solutions of the equations for different parameters, and taking into account the value of d-electron concentration, one can determine the optimal alloy composition with pre-set characteristics.

In the present work we used the known literature data for the cell parameters, enthalpies and entropies of reaction with hydrogen of 38 hexagonal titanium and zirconium Laves phases. As the result of the determination of functions we obtained the following coefficients for equation (1) (indices 1–6 refer to metals zirconium, titanium, vanadium, chromium, iron and nickel, the manganese concentration determined as $(1 - \sum x_i)$). For a -parameter function:

$$y_0 = 4.93; \quad a_1 = 0.35; \quad a_2 = -0.29; \quad a_3 = 0.33;$$

$$a_4 = 0.10; \quad a_5 = 0.04; \quad a_6 = -0.04; \quad b_{11} = -0.17;$$

$$\begin{aligned}
 b_{12} &= 0.17; & b_{13} &= -0.15; & b_{14} &= 0.01; & b_{15} &= -0.14; \\
 b_{16} &= 0.00; & b_{22} &= -0.17; & b_{23} &= 0.15; & b_{24} &= -0.01; \\
 b_{25} &= -0.14; & b_{26} &= 0.00; & b_{33} &= -0.36; & b_{34} &= 0.00; \\
 b_{35} &= 0.27; & b_{36} &= 0.00; & b_{44} &= -0.29; & b_{45} &= 0.17; \\
 b_{46} &= 0.00; & b_{55} &= -0.17; & b_{56} &= 0.00; & b_{66} &= 0.01;
 \end{aligned}$$

for c -parameter function:

$$\begin{aligned}
 y_0 &= 32.40; & a_1 &= 16.46; & a_2 &= -16.76; & a_3 &= 108.89; \\
 a_4 &= 1.24; & a_5 &= -71.65; & a_6 &= -13.25; & b_{11} &= 86.84; \\
 b_{12} &= -86.84; & b_{13} &= -1.56; & b_{14} &= 51.09; & b_{15} &= -8.13; \\
 b_{16} &= 0.00; & b_{22} &= 86.84; & b_{23} &= 41.56; & b_{24} &= -51.09; \\
 b_{25} &= 8.13; & b_{26} &= 0.00; & b_{33} &= -106.70; & b_{34} &= 0.00; \\
 b_{35} &= 92.16; & b_{36} &= 0.00; & b_{44} &= 24.20; & b_{45} &= 82.93; \\
 b_{46} &= 0.00; & b_{55} &= 43.60; & b_{56} &= 0.00; & b_{66} &= -4.41;
 \end{aligned}$$

for ΔH -function:

$$\begin{aligned}
 y_0 &= 103.66; & a_1 &= -54.98; & a_2 &= -51.91; & a_3 &= 234.06; \\
 a_4 &= 39.10; & a_5 &= -247.06; & a_6 &= -56.77; & b_{11} &= 320.03; \\
 b_{12} &= -320.03; & b_{13} &= -165.89; & b_{14} &= 133.67; \\
 b_{15} &= -344.93; & b_{16} &= 0.00; & b_{22} &= 320.03; \\
 b_{23} &= 165.89; & b_{24} &= -133.67; & b_{25} &= 344.93; \\
 b_{26} &= 0.00; & b_{33} &= -181.60; & b_{34} &= 0.00; \\
 b_{35} &= 10.07; & b_{36} &= 0.00; & b_{44} &= 74.41; & b_{45} &= 118.01; \\
 b_{46} &= 0.00; & b_{55} &= 496.86; & b_{56} &= 0.00; & b_{66} &= -18.90;
 \end{aligned}$$

for ΔS -function

$$\begin{aligned}
 y_0 &= 8.13; & a_1 &= 0.64; & a_2 &= -0.38; & a_3 &= 0.39; \\
 a_4 &= 0.11; & a_5 &= -0.12; & a_6 &= -0.12; & b_{11} &= -0.79; \\
 b_{12} &= 0.79; & b_{13} &= -0.11; & b_{14} &= 0.08; & b_{15} &= 0.11; \\
 b_{16} &= 0.00; & b_{22} &= -0.79; & b_{23} &= 0.11; & b_{24} &= -0.08; \\
 b_{25} &= -0.11; & b_{26} &= 0.00; & b_{33} &= -1.30; & b_{34} &= 0.00; \\
 b_{35} &= 1.32; & b_{36} &= 0.00; & b_{44} &= -0.66; & b_{45} &= 0.78; \\
 b_{46} &= 0.00; & b_{55} &= -0.49; & b_{56} &= 0.00; & b_{66} &= -0.04.
 \end{aligned}$$

The chosen alloys were prepared by the standard method of melting in an arc furnace in an atmosphere of purified argon. The starting metals were of purity higher than 99.9%. Because of high volatility of manganese this metal was taken with a surplus of 3–7 at.%. The composition of the obtained alloys was controlled by X-ray and in some cases by atomic absorption analysis and also by weighing before and after melting. The experiments were performed in standard Sieverts apparatus in a temperature range of 253–293 K and under a pressure of 0.01–150 atm.

RESULTS AND DISCUSSION

Table 1 shows the characteristics of the investigated alloys. The alloy compositions according to the atomic adsorption analysis correlate quite well with those taken for the schist. In general the cell parameters increase with decreasing manganese and zirconium content (metal radii are Ti, 1.46; Zr, 1.60; Mn, 1.30; Cr, 1.25; Fe, 1.26 Å).

Hydrogen desorption isotherms for studied alloys at 293 K are shown in Figs 1 and 2. As it can be seen most of the selected alloys are characterized by rather high desorption pressures. It should be noted that comparatively small absorption capacity in some cases ($< 180 \text{ cm}^3/\text{g}$) can be accounted for by the extremely large value of absorption-desorption pressure hysteresis and for the impossibility to perform full hydriding under pressure below 150 atm even at a temperature about 253 K.

Figure 3 shows the absorption-desorption isotherms for the system alloy 3– H_2 measured in the superhigh pressure apparatus allowing to conduct the metal-hydrogen reactions under pressure up to 2000 atm [2]. Alloy 3 is characterized by a considerable hysteresis value, the hysteresis factor, $\ln(P_{\text{ab}}/P_{\text{des}})$, is 1.35, 1.68, 3.04 at 293, 273 and 195 K, correspondingly. Hysteresis factor is temperature dependent and increases approximately two times with 100° decrease of temperature. The thermodynamic parameters of reaction calculated from isothermal data were found to be: absorption- $\Delta H = -11.3 \pm 0.3 \text{ kJ/mol H}_2$, $\Delta S = -83 \pm 1 \text{ J/K} \cdot \text{mol H}_2$; “десорбция”- $\Delta H = 19.1 \pm 0.7 \text{ kJ/mol H}_2$, $\Delta S = 99 \pm 3 \text{ J/K} \cdot \text{mol H}_2$.

Figure 4 shows the desorption isotherms for the system alloy 5– H_2 . Though this alloy is characterized by a still higher desorption pressure it is possible to conduct its full hydriding without the use of super high pressures. The thermodynamic parameters of desorption calculated from isothermal data were found to be: $\Delta H = 28.7 \pm 0.7 \text{ kJ/mol H}_2$, $\Delta S = 133 \pm 2 \text{ J/K} \cdot \text{mol H}_2$.

Comparing the calculated from equation 1 and experimental values it should be noted that in some cases the coincidence is quite remarkable but in other, mainly for desorption pressures, the differences are far beyond the error limits. This fact can be connected with the following reasons. First, the proposed equations give a good agreement of theory and experiment only within the concentration range selected as a data base for computation

Table 1. X-ray characteristics of the starting alloys

Alloy	$a, \text{ \AA}$	$c, \text{ \AA}$	$V, \text{ \AA}^3$
1	4.886	7.993	165.3
2	4.856	7.952	162.4
3	4.85	8.058	164.2
4	4.85	7.957	162.1
5	4.905	8.075	168.2
6	4.844	7.957	161.7
7	4.862	7.962	163.0
8	4.867	7.977	163.6
9	4.878	7.992	164.7

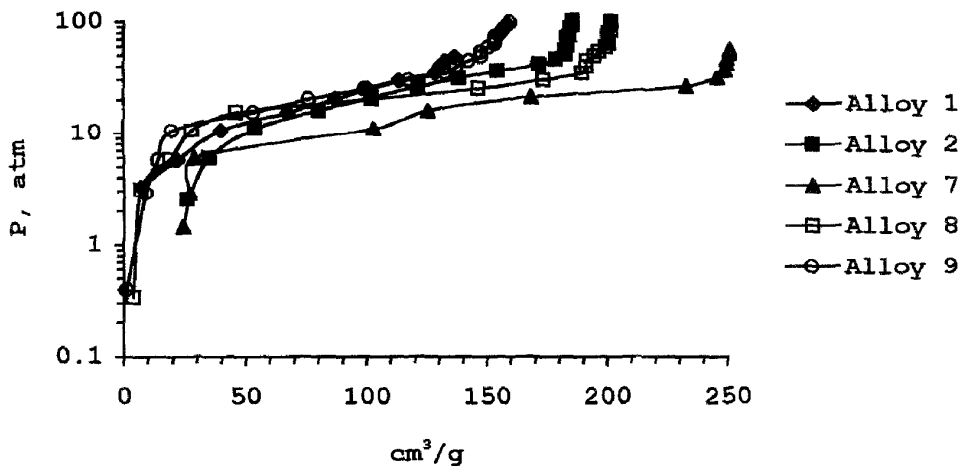


Fig. 1. Desorption isotherms for investigated alloys at 293 K.

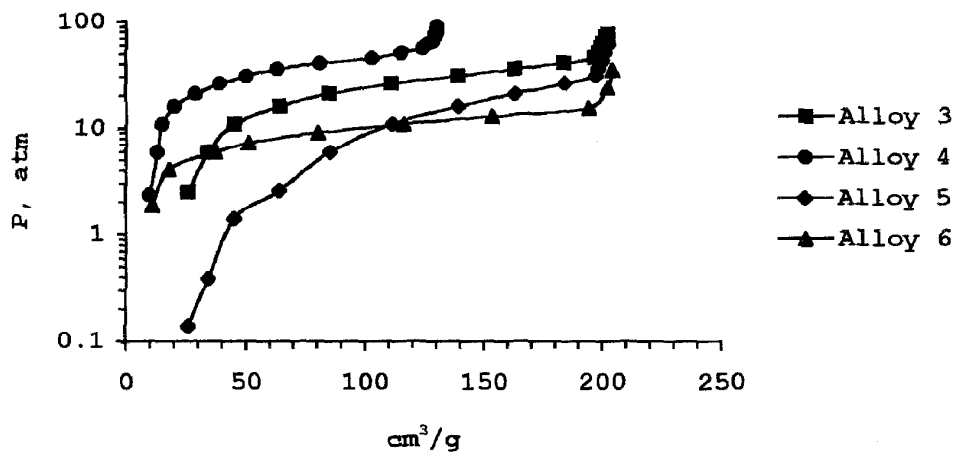


Fig. 2. Desorption isotherms for investigated alloys at 293 K.

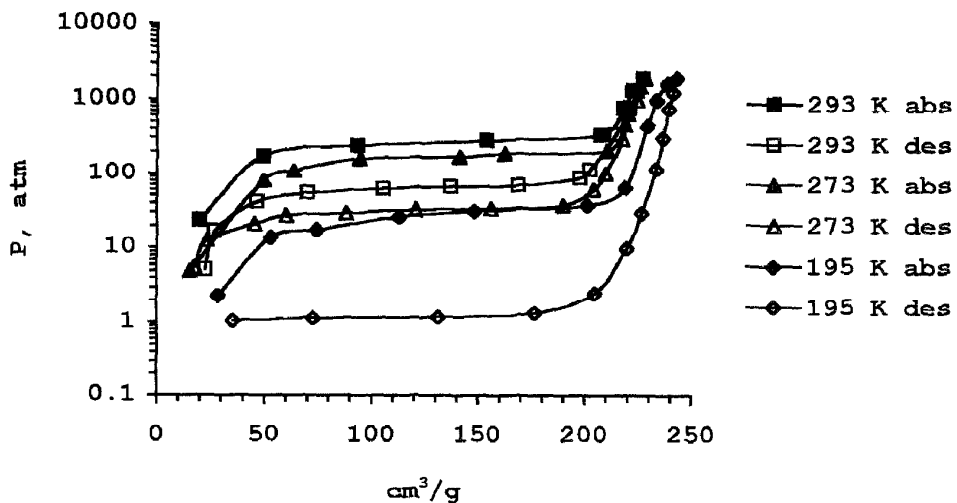


Fig. 3. Absorption-desorption isotherms for the system Alloy 3-H₂.

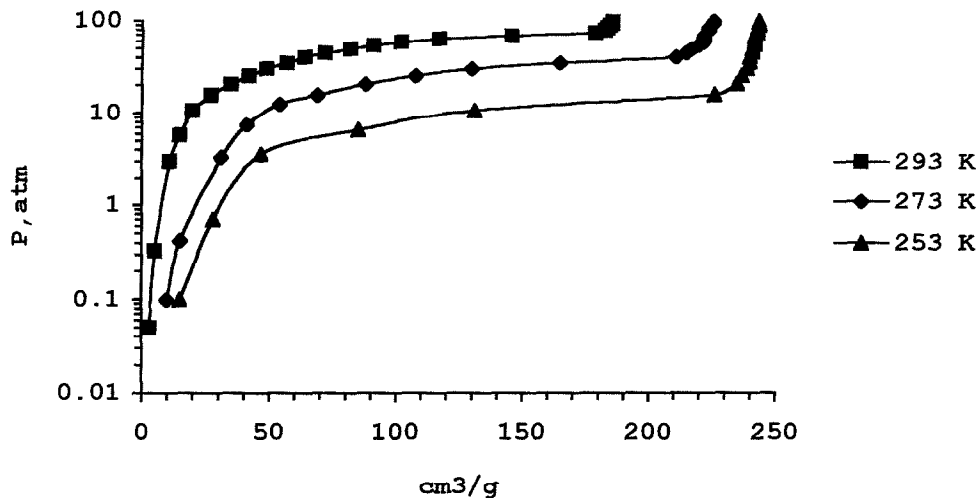


Fig. 4. Desorption isotherms for the system Alloy 5-H₂.

of the equation coefficients. If the component concentration value is out of the range than the alterations in calculated parameters are hardly predictable. Second, for a more precise prediction one should use the tabulated parameter values of samples which were previously standardized, their real chemical composition has been determined and the preliminary procedures such as annealing or quenching have been stated. Third, in present work we use the experimental data for 38 Laves phases. The enlargement of the data base will also make the predictions more precise.

Nevertheless, even in their present state the proposed functions are quite usable for the preliminary evaluation

of some absorption parameters of hexagonal Laves phases.

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