

## TITANIUM BASED LAVES PHASE HYDRIDES WITH HIGH DISSOCIATION PRESSURE

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**Abstract**—A method for quantitative prediction of the hydrogen sorption properties of Laves phases is proposed. It is based on the empirical rules formulated earlier by Bernauer. The investigation showed that the chosen alloys possess rather high hydrogen dissociation pressure. The isotherms and thermodynamic properties of the hydride phases were determined. The correlation between the experimental and calculated values is discussed. Copyright © 1996 International Association for Hydrogen Energy

### INTRODUCTION

One of the problems in the construction of metal-hydride hydrogen accumulators is the availability of alloys having rather high hydrogen dissociation pressures. Multicomponent alloys based on the Laves phases of  $\text{TiCr}_2$  and  $\text{TiMn}_2$  can be useful in the solution of this problem.

The analysis of the literature data on the interaction of hydrogen with such multicomponent alloys shows that the thermodynamic characteristics of these reactions and the alloy sorption properties change monotonously with the change of the alloy chemical composition within the limits of a solid solution. This fact served as a basis for attempts to propose qualitative empirical rules for the “construction” of such alloys. In this work we attempted to state and to experimentally test some quantitative relationships between alloy chemical compositions and their hydride phase properties. These relationships were based on well-known empirical rules proposed in [1].

### EXPERIMENTAL

The alloys for the investigation were chosen using the method which we proposed in [2] and developed in [3]. Here we will only briefly outline the main principles of the method.

In the simplest case, a function describing the monotonous dependence on a parameter can be represented by 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  $x$  is the atomic concentration of the metal, and  $y_0$ ,  $a$  and  $b$  are coefficients.

By determining the coefficients for cell parameters, and

the enthalpy and entropy of the reaction with hydrogen one can then calculate the alloy composition which suits the pretabulated criteria for all four characteristics.

The alloys were prepared by a standard method of arc melting. The starting metals were of a purity not less than 99.9%. The composition was controlled by means of X-ray analysis, and in some cases by atomic absorption spectroscopy, and also by weighing before and after the melting.

The experiments were performed in standard Sieverts apparatus in the range of pressures between 0.01–150 atm and temperatures between 253–293 K.

### RESULTS AND DISCUSSION

The characteristics of the alloys prepared are presented in Table 1. The parameters for alloy composition according to the results of the atomic absorption analysis are in good agreement with those calculated. The cell parameters decrease with decreasing manganese and zirconium content (the metal radii are Ti 1.46, Zr 1.60, Mn 1.30, Cr 1.25 and Fe 1.26 Å).

Figures 1 and 2 show the desorption isotherms for the hydride phases at 293 K. Almost all of the chosen alloys are characterised by rather high desorption pressures of the hydride phases. It should be noted that in some cases the relatively low absorption capacity ( $< 180 \text{ cm}^3/\text{g}$ ) can possibly account for the considerably large value of hysteresis which does not allow completion of the hydrogen absorption reaction at pressures below 150 atm at 250 K.

Figure 3 shows the absorption-desorption isotherms for Alloy 1, which were measured in a special high pressure hydrogen apparatus, which allows conduction of the metal-hydrogen reactions under a pressure of 2000 atm

Table 1. Experimental and calculated characteristics of alloys

Alloy	$a_{\text{exp}}$ (Å)	$a_{\text{calc}}$ (Å)	$c_{\text{exp}}$ (Å)	$c_{\text{calc}}$ (Å)	$V_{\text{exp}}$ (Å <sup>3</sup> )	$V_{\text{calc}}$ (Å <sup>3</sup> )	$P_{\text{exp}}$ , atm (293 K)	$P_{\text{calc}}$ , atm (293 K)
1	4.85	4.84	8.058	7.94	164.2	161.1	65.8	61.4
2	4.905	4.85	8.075	7.94	168.2	161.7	68.2	96.6
3	4.85	4.85	7.957	7.94	162.1	161.7	41.8	75.8
4	4.845	4.84	7.951	7.93	161.6	160.9	77.5	129.9
5	4.856	4.83	7.952	7.93	162.4	160.2	26.9	8.30
6	4.886	4.80	7.993	7.82	165.3	156.0	24.5	1965.0
7	4.862	4.86	7.962	7.96	163.0	162.8	11.7	19.7
8	4.878	4.86	7.992	7.98	164.7	163.7	26.3	19.8
9	4.880	4.86	8.021	7.97	165.4	163.0	9.6	26.1

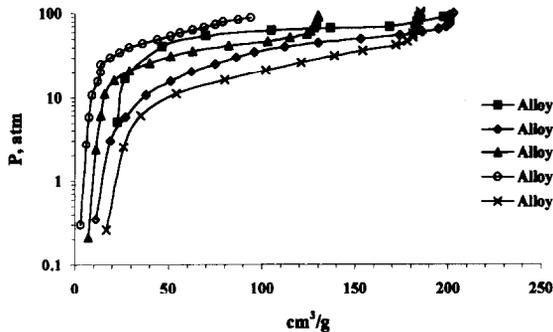


Fig. 1. Desorption isotherms for alloys 1–5 at 293 K.

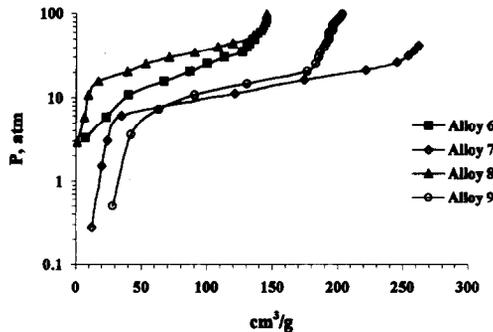
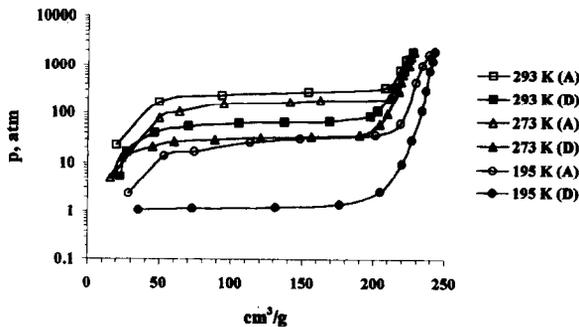


Fig. 2. Desorption isotherms for alloys 6–9 at 293 K.

Fig. 3. Absorption-desorption isotherms for system Alloy 1–H<sub>2</sub>.

[4]. This alloy is characterised by a considerable value of hysteresis: the hysteresis factor  $\ln(P_{\text{abs}}/P_{\text{des}})$  is 1.35, 1.68

and 3.04 at 293, 273 and 195 K respectively. This factor is temperature dependent and increases approximately two-fold with a temperature decrease of 100 K. The thermodynamic functions for this and some other alloys investigated are presented in Table 2.

The desorption isotherms for Alloy 2 are presented in Fig. 4. This alloy is characterised by a very interesting phenomenon, of an increase in the desorption plateau pressure after several absorption-desorption cycles.

The same phenomenon can also be observed for the reaction of Alloy 4 with hydrogen (Fig. 5). The plateau pressure after 3 cycles of absorption-desorption is about 15 atm higher than in the first absorption cycle at the same temperature. This is not the only intermetallic system possessing such properties. Similar behaviour was noted earlier for the system CeNi<sub>5</sub>-H<sub>2</sub> [5]. Alloy 4 has the highest desorption pressure among all the investigated alloys. Comparing it with Alloy 1 one can conclude that the hysteresis factor for Alloy 4 is also rather high. Under our experimental pressure (below 100 atm) it is not possible to obtain the pure hydride phase because the equilibrium absorption pressure is higher than 100 atm.

The desorption isotherms for Alloy 9 are presented in Fig. 6. This alloy is the richest in zirconium content and obviously the equilibrium pressure value is the lowest.

The comparison of the experimental and calculated values of cell parameters and equilibrium pressures is presented in Table 1. For cell parameters our calculations show a good correlation with experimental data. Meanwhile the dissociation pressure values in some cases differ greatly. The following is an attempt to explain this phenomenon.

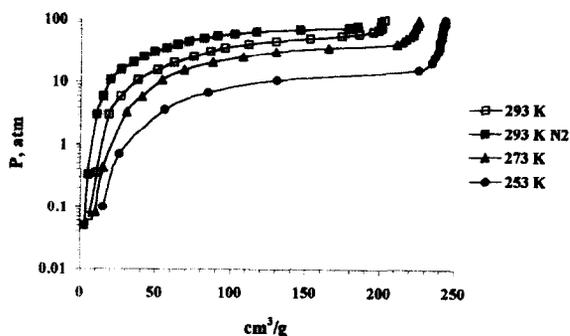
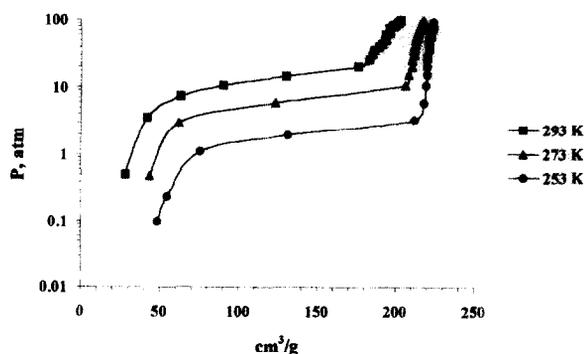
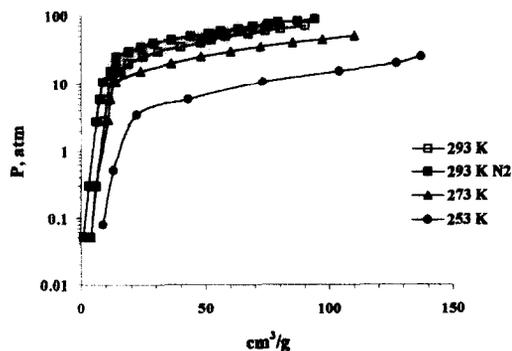
First, the proposed equation gives an approximate agreement of experimental and calculated parameters only within the concentration range of component metals taken as a computational base. Outside this range, as in the case of nonstoichiometric Alloy 6, one can get unpredictable deviations from the calculated values.

Second, for a more precise prognosis one should use as a data base only the tabulated values. This means that the alloys should be fully characterised before investigation, that is, the history of their preparation (quenching, annealing etc.) and chemical composition (taken from analysis) should be known and taken into account.

Nevertheless, even in its present form, the proposed

Table 2. Thermodynamic characteristics of hydrogen interaction with alloys

System	$\Delta H_{\text{abs}}$ (kJ/molH <sub>2</sub> )	$\Delta S_{\text{abs}}$ (J/KmolH <sub>2</sub> )	$\Delta H_{\text{des}}$ (kJ/molH <sub>2</sub> )	$\Delta S_{\text{des}}$ (J/KmolH <sub>2</sub> )
Alloy 1-H <sub>2</sub>	-11.3±0.3	-83±1	19.1±0.7	99±3
Alloy 2-H <sub>2</sub>	—	—	28.7±0.7	133±2
Alloy 4-H <sub>2</sub>	—	—	29.8±2.6	137.9±9.6
Alloy 9-H <sub>2</sub>	—	—	31.2±0.5	129±2

Fig. 4. Desorption isotherms for system Alloy 2-H<sub>2</sub>.Fig. 6. Desorption isotherms for system Alloy 9-H<sub>2</sub>.Fig. 5. Desorption isotherms for system Alloy 4-H<sub>2</sub>.

equation can be used for prediction and evaluation of the basic properties of Laves phase hydride phases.

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