

Letter

Thermodynamics of hydride formation and decomposition for TiMn₂-H₂ system at pressure up to 2000 atm

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In our recent paper [1] we presented the first results obtained from a new apparatus for metal-hydrogen system studies with pressures up to 2500 atm. A special interest to such studies is connected with the possibility of technological applications of hydride systems having very high dissociation pressures, tens or hundreds of atmospheres at room temperature. For such applications one would need the accurate thermodynamic data of these hydride materials. The Ti-Mn system has been employed in a series of effective multicomponent alloys for hydrogen storage and it has been studied in detail by many authors (see, for example, ref. 2). However, the stoichiometric TiMn₂ compound (MgZn₂-type Laves phase) and TiMn_α alloys with α > 1.75 had been considered to be non-hydride-forming. By using high-pressure techniques we have been able to synthesize TiMn₂H_x (x is about 3) hydride and to determine the thermodynamic parameters of corresponding hydriding and dehydriding reactions.

Experimental details were described in ref. 1. The sample was prepared by arc melting from starting metals of at least 99.9% purity and was studied in as-cast condition. X-ray analysis of sample indicated the presence of only one hexagonal phase with lattice constants a = 4.818(2) and c = 7.917(7) Å.

All results of the measurement were analyzed on the basis of the equation of state for hydrogen at pressures up to 1 MBar, as proposed by Hemmes *et al.* [3]:

$$[P + a(P)/V^\alpha] \times [V - b(P)] = RT \quad (1)$$

The coefficients a(P), b(P) and α(T) given in ref. 3 were determined from a wide range of experimental data on the hydrogen compressibility.

The enthalpy change ΔH and entropy change ΔS for the reactions studied were calculated from the linear

relation between the logarithm of the hydrogen fugacity f appropriate to the plateau pressure P and the reciprocal of absolute temperature T:

$$\ln f = \Delta H/RT - \Delta S/T \quad (2)$$

The fugacity in turn was obtained from eqn. (1) by using real molar hydrogen volume at the corresponding pressures:

$$\ln f = \ln P - 1/RT \int_0^P (V_{\text{ideal}} - V_{\text{real}}) dP \quad (3)$$

Gamo *et al.* [2] noted the absence of hydrogen absorption by TiMn₂ and attributed this phenomenon to the smaller lattice constants and Ti-content than in TiMn_{1.5}, leading to an increase of the dissociation pressure of the corresponding hydride phase. In reality we found that significant hydriding of TiMn₂ started only at a hydrogen pressure above 50 atm. The absorption isotherm in the first cycle (Fig. 1) indicated that there is a two-stage character of the hydriding process. In the pressure range from 50 to 70–80 atm the hydrogen absorption led to the formation of an α-solid solution with the composition TiMn₂H_{0.3}. This part of the first isotherm apparently could not be considered as representing equilibrium (since it was not reproduced at following cycles) and it characterized only the activation process. The α → β transition pro-

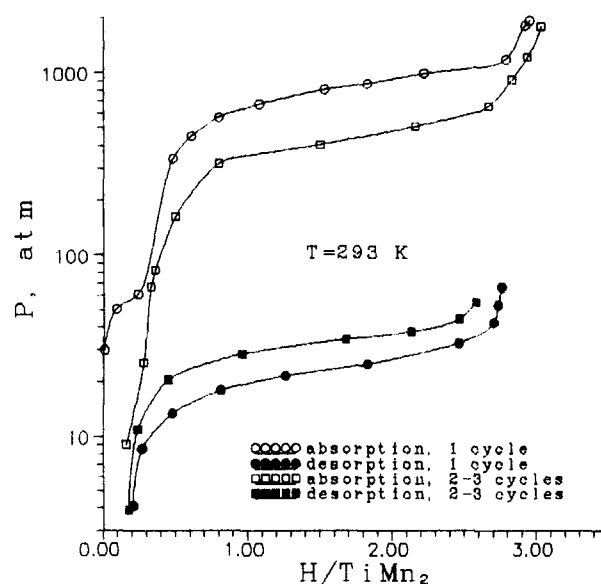
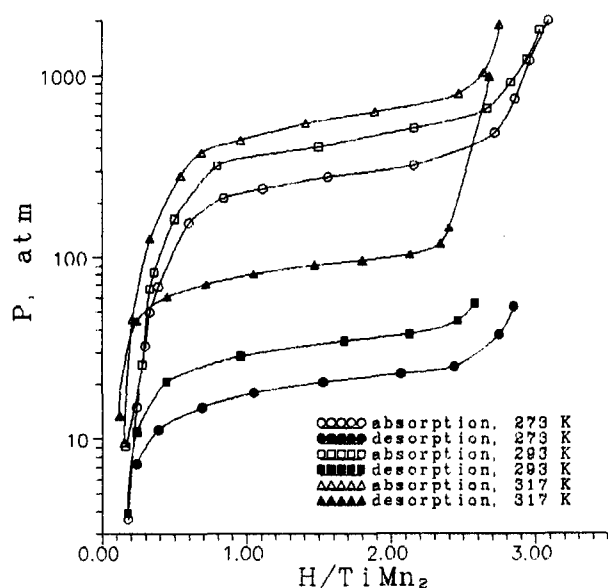


Fig. 1. Pressure-composition isotherms during activation cycling for the TiMn₂-H₂ system.

TABLE 1. Equilibrium pressures, fugacities and thermodynamic parameters for hydrogenation and dehydrogenation of the $\text{TiMn}_2\text{-H}_2$ system

T (K)	Absorption		Desorption		Hysteresis factor $\ln(P_{\text{abs}}/P_{\text{des}})$
	P (atm)	f (atm)	P (atm)	f (atm)	
273	276	304	18.2	18.2	2.72
293	415	472	34.1	34.4	2.50
317	568	678	82.0	83.7	1.94
ΔH , kJ/mol H_2	11.8 ± 1.5	13.1 ± 0.8	24.6 ± 2.1	24.7 ± 1.8	
ΔS , J/(K mol H_2)	90.1 ± 3.5	95.7 ± 1.8	114.1 ± 3.1	114.3 ± 2.0	

Fig. 2. Pressure-composition isotherms for activated $\text{TiMn}_2\text{-H}_2$ system.

ceeded at considerably higher pressures – 700–800 atm during the first cycling.

It should be noted that the activation of the $\text{TiMn}_2\text{-H}_2$ system does not only lead to changes of the absorption pressure (that is notorious for many intermetallic compounds) but also the changes of the desorption pressure. In the second cycle P_{abs} decreased to 400 atm and P_{des} increased from 18 to 34 atm, *i.e.* pressure change by nearly a factor of 2. After the third cycle the activation could be regarded as being completed and the isotherms retained their shape.

The values of plateau pressures and the corresponding hydrogen fugacities are presented in Table 1. One can see from these data that the hysteresis for TiMn_2 is exceptionally large compared with other known inter-

metallic compound-hydrogen systems. The hysteresis factor $\ln(P_{\text{abs}}/P_{\text{des}})$ is approximately three times greater than that determined for $\text{TiMn}_{1.5}$ [2], though both alloys belong to the homogeneity region of the same compound. A similar dependence of the hysteresis on Mn-content was described for the $\text{Ti}_{1-x}\text{Cr}_{2-y}\text{Mn}_y\text{-H}_2$ system in ref. 4.

The thermodynamic evaluation of the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ phase transitions were made by means of the van't Hoff equation by substitution of the fugacities for the corresponding absorption and desorption pressures (eqn. (2)). Since the plateaus had significant slopes the equilibrium values have been selected at the hydride composition $\text{TiMn}_2\text{H}_{1.5}$ (approximately in the centre of the plateau). Regarding the data shown in Table 1, it should be noted that such a large difference in absorption and desorption enthalpies might be useful in certain applications.

By comparing the results obtained from the fugacity values with those obtained without taking into account the deviation of the high pressure values from ideality (*i.e.* using the true pressure values) we were able to show that even at experimental pressures of about 300 atm, the error of the conventional determination of thermodynamic functions may become significant and would need the appropriate corrections.

References

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