

Regularities of hydrogen interaction with multicomponent Ti(Zr)–Mn–V Laves phase alloys

S.V. Mitrokhin*

Chemistry Department, Lomonosov Moscow State University, Moscow 119992, Russia

Received 6 September 2004; received in revised form 7 February 2005; accepted 14 February 2005

Available online 21 July 2005

Abstract

Titanium- and zirconium-based multicomponent Laves phases deriving from binary TiMn_2 and ZrMn_2 compounds are one of perspective groups of hydrogen-absorbing alloys for use in various hydrogen storage and energy conversion devices. Extensive systematic study of hydrogen sorption properties of nonstoichiometric alloys of Ti(Zr)–Mn–V system was performed in this work. Results of X-ray, neutron diffraction and PC-isotherm investigations are presented. Some useful regularities were found, which can be useful in prediction of hydrogen sorption properties of ternary alloys.

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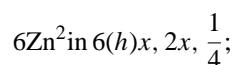
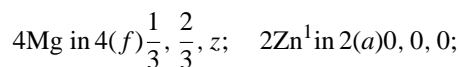
Keywords: Hydrogen storage materials

1. Introduction

Intermetallic compounds of AB_2 -type were first described by Friauf [1]. Later Laves [2] showed that these structures can exist only at particular ratio of component radii ($r_A/r_B = 1.225$). From that moment on three types of AB_2 compounds (MgZn_2 , MgCu_2 and MgNi_2) were named after him. One of the main regularities of their formation is the geometric factor. During years of investigation it was shown that Laves phases exist within a broad range of r_A/r_B —1.04–1.68 [3]. Laves phases are among the most numerous types of intermetallic compounds and since a lot of them are composed on base or from light hydride-forming transition metals, these compounds (especially hexagonal MgZn_2 -type) were thoroughly studied from the point of view of their application for hydrogen storage.

Compounds of MgZn_2 -type (Strukturbericht notation C14) crystallise in $P6_3/mmc$ with 4 formula units in the

elementary cell. Atoms occupy following positions:



where $x = 0.830$ and $z = 0.062$ for MgZn_2 . This structure type is characterised by presence of seven types of interstitials, which can be considered for location of hydrogen atoms while hydride formation.

One of the most interesting and important features of practically perspective Laves phases such as TiMn_2 and ZrMn_2 is the existence of wide ranges of homogeneity. There are at least three explanations of this phenomenon. Deviations from stoichiometry can take place as a result of:

1. Formation of vacancies in lattice (vacancy model).
2. Substitution by superstoichiometric atoms for substoichiometric atom positions in structure (substitution model).
3. Placement of superstoichiometric atoms in interstitial sites (interstitial model).

* Corresponding author. Tel.: +7 95 9391413; fax: +7 95 9328846.
E-mail address: mitrokhin@hydride.chem.msu.ru (S.V. Mitrokhin).

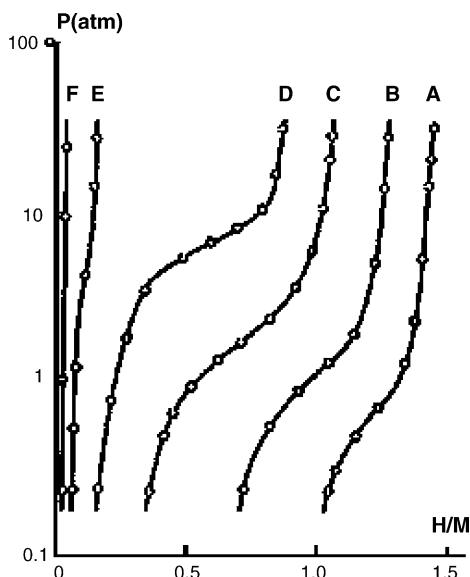


Fig. 1. Desorption isotherms for $\text{TiMn}_x\text{-H}_2$ systems at 20°C ($x = 0.75$ (A); 1.0 (B); 1.25 (C); 1.5 (D); 1.75 (E) and 2.0 (F)).

It was shown for both Ti–Mn system [4] and Zr–Mn system [5] that the calculated densities of compounds according to all three models correlate better with experimental values in case of substitution model. Structural investigations [6,7] also confirmed that the superstoichiometric component occupies in lattice the positions of substoichiometric component. In other words it is correct to represent alloys $\text{TiMn}_{1.5}$ and $\text{ZrMn}_{2.8}$ in conventional Laves phase form as $\text{Ti}(\text{Mn}_{0.9}\text{Ti}_{0.1})_2$ and $(\text{Zr}_{0.79}\text{Mn}_{0.21})\text{Mn}_2$.

Nonstoichiometric compounds as media for hydrogen storage provided a good opportunity to modify the properties of intermetallic hydrides by means of substitution of components avoiding addition of another component to the alloy. Systematic studies of nonstoichiometric binary Ti–Mn and ternary Zr–Mn Laves phases were performed by Gamo et al. [8] (Fig. 1) and Pourarian [7] (Fig. 2).

One of the problems with application of binary metal alloys for hydrogen storage is the rapid change of properties connected with small changes of component ratio. This work was aimed on the systematic investigation of hydrogen absorption properties of C14 Laves phase alloys of Ti(Zr)–Mn–V system.

2. Results and discussion

Ti(Zr)–Mn–V metallic system was found to have rather large homogeneity range of Laves phase (36–65 at.% Mn) and vanadium is dissolved in TiMn_2 C14 phase without any structural change up to 26 at.% [9] (Fig. 3).

In view of such wide homogeneity region it was interesting to find out what changes take place in the structure of multicomponent nonstoichiometric alloys. In all cases, metallic atoms of B-component do not show preference in

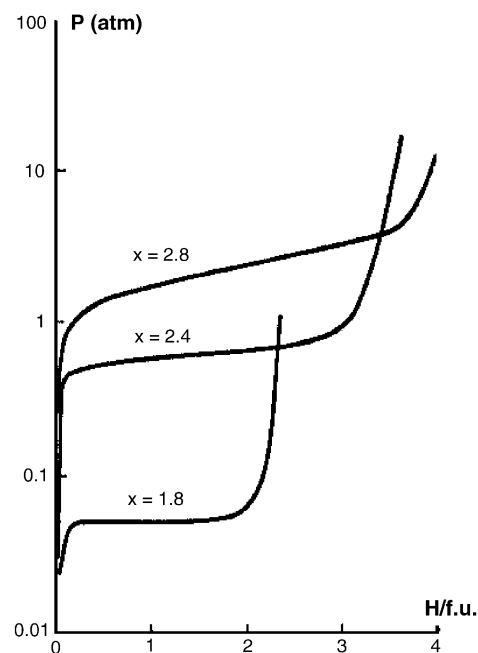


Fig. 2. Desorption isotherms for $\text{ZrMn}_x\text{-H}_2$ systems at 50°C .

occupation of two possible sites— $2(a)$ or $6(h)$ (Table 1). Though it is hard to distinguish manganese and titanium due to their close values of neutrons scattering lengths, the obtained R-factors allow to consider the proposed distribution of B-atoms as correct.

The interaction with hydrogen of multicomponent alloys usually starts without induction period after evacuation of sample to 10^{-2} mmHg at room temperature and full first absorption completes in 30 min.

Result for more than 50 different alloys showed that in the solid solution region main thermodynamic and structural parameters of alloys and hydrides change monotonously with

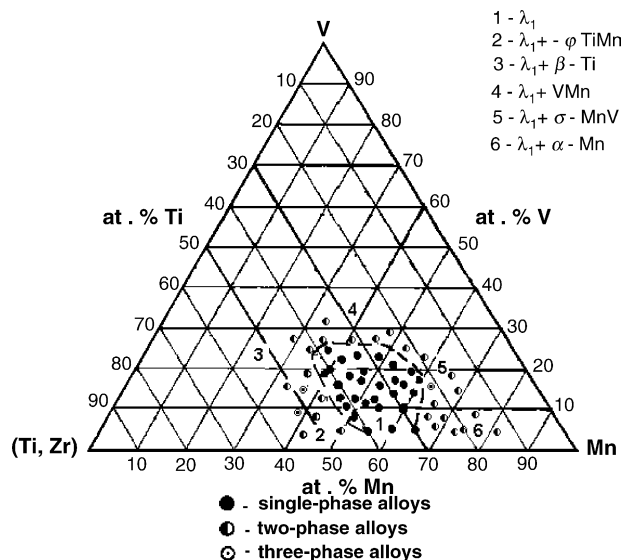


Fig. 3. State diagram for Ti(Zr)–Mn–V system.

Table 1
Structure parameters of initial alloys

Method	X-ray	TOFND	TOFND
Alloy	TiMn _{1.5} V _{0.5}	Ti _{0.9} Zr _{0.1} (Mn _{0.75} V _{0.15} Ti _{0.1}) ₂	Ti _{0.9} Zr _{0.1} (Mn _{0.58} V _{0.35} Ti _{0.07}) ₂
Cell parameters (Å)	$a = 4.894(2)$ $c = 8.020(5)$	$a = 4.906(1)$ $c = 8.062(5)$	$a = 4.915(3)$ $c = 8.085(6)$
A-component			
4(<i>f</i>) (1/3, 2/3, <i>z</i>)	$z = 0.064(4)$ Ti	$z = 0.059(3)$ 0.88(1)Ti:0.12(1)Zr	$z = 0.057(3)$ 0.87(2)Ti:0.13(1)Zr
B-component			
2(<i>a</i>) (0, 0, 0)	0.60(2)Mn:0.4(2)V	0.39(1)Mn:0.61(1)V	0.73(1)V:0.27(1)Ti
6(<i>h</i>) (<i>x</i> , 2 <i>x</i> , 1/4)	$x = 0.829(6)$ 0.79(2)Mn:0.21(2)V	$x = 0.827(3)$ 0.85Mn:0.15Ti	$x = 0.827(4)$ 0.81(2)Mn:0.19(1)V
R_w	1.1	6.2	5.6
Refined composition	TiMn _{1.48} V _{0.52}	Ti _{0.88} Zr _{0.12} (Mn _{0.74} V _{0.15} Ti _{0.11}) ₂	Ti _{0.87} Zr _{0.13} (Mn _{0.61} V _{0.32} Ti _{0.07}) ₂

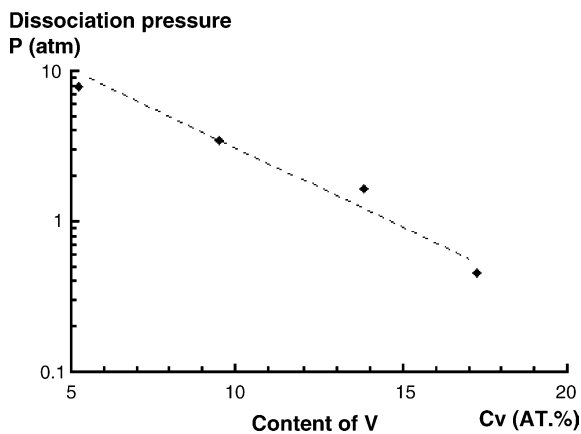


Fig. 4. Dependence of equilibrium desorption pressure vs. vanadium content in Ti(Zr)-Mn-V alloys.

concentration of components. The trends of such changes are identical to those observed for stoichiometric compound. For example, at constant titanium + zirconium content substitution of vanadium for manganese leads to decrease of equilibrium plateau pressure values (Figs. 4 and 5).

Other important dependences found in our works are shown in Figs. 6 and 7. The logarithmic plot of equilibrium plateau pressure versus cell volume for both stoichiometric and nonstoichiometric alloys exhibit almost linear trend.

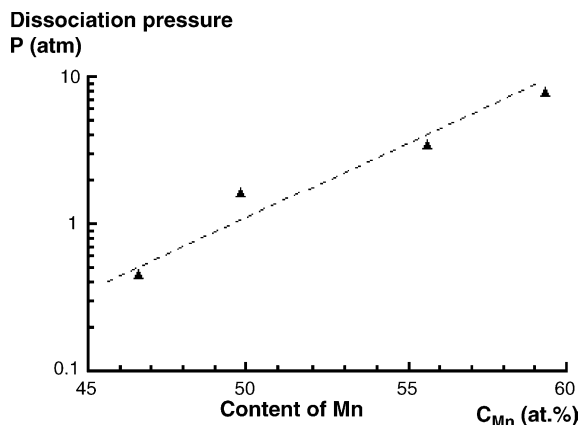


Fig. 5. Dependence of equilibrium desorption pressure vs. manganese content in Ti(Zr)-Mn-V alloys.

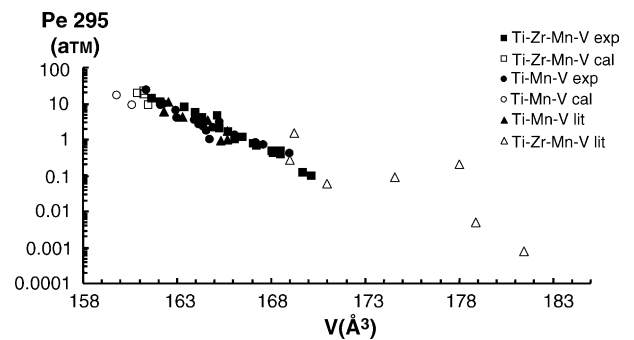


Fig. 6. Dependence of equilibrium desorption pressure vs. elementary cell volume.

The plot of desorption reaction enthalpy versus cell volume is also rather close to linear function. Nonlinearity of both plots at unit cell volume higher than 173 Å refers to the data obtained in one of the first works on stoichiometric ternary Ti_{1-x}Zr_xMn₂ alloys [10]. However, if taken separately, these data points can be considered as having their own linear dependence.

It is possible to evaluate from data in Fig. 6 the approximate minimal value for alloy cell volume below which reaction with hydrogen does not start at pressures below 100 atm. Since the Laves phases containing manganese are usually characterised by rather big absorption-desorption hysteresis, then the absorption equilibrium pressure could be at least two

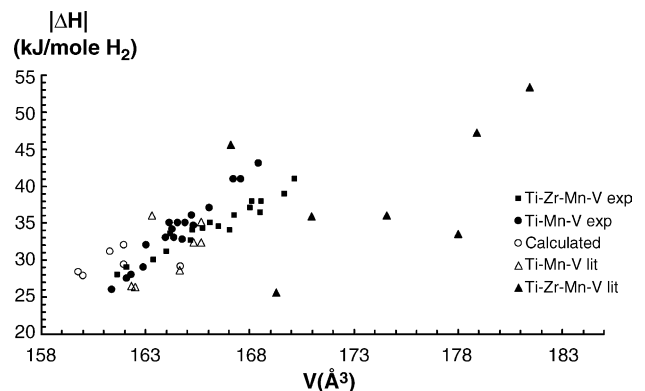


Fig. 7. Dependence of desorption enthalpy vs. elementary cell volume.

Table 2
Structural parameters for $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.5}\text{V}_{0.3}\text{Ti}_{0.2}\text{D}_{2.8}$

Atoms	Atom positions	Crystal parameters at different temperature					
		295 K			17 K		
		Coordinates	Occupancy	B (\AA^2)	Coordinates	Occupancy	B (\AA^2)
Ti:Zr	4(<i>f</i>) 1/3, 2/3, <i>z</i>	$z = 0.072(2)$	0.88(1):0.12(1)	1.5	$z = 0.058(2)$	0.89(2):0.11(1)	1.5
Mn:V	2(<i>a</i>) 0, 0, 0		0.39(1):0.61(1)	1.5		0.39(1):0.69(1)	1.5
Mn:Ti	6(<i>h</i>) <i>x</i> , 2 <i>x</i> , 1/4	$x = 0.824(3)$	0.85:0.15	1.5	$x = 0.832(2)$	0.85:0.15	1.5
D ₁	24(<i>l</i>) <i>x</i> , <i>y</i> , <i>z</i>	$x = 0.089(4)$, $y = 0.391(3)$, $z = 0.565(4)$	0.31(5)	2.0	$x = 0.149(3)$, $y = 0.356(1)$, $z = 0.558(2)$	0.29(2)	2.0
D ₂	12(<i>k</i>) ₁ <i>x</i> , 2 <i>x</i> , <i>z</i>	$x = 0.472(6)$, $z = 0.607(3)$	0.23(3)	2.0	$x = 0.499(2)$, $z = 0.593(7)$	0.29(4)	2.0
D ₃	6(<i>h</i>) ₁ <i>x</i> , 2 <i>x</i> , 1/4	$x = 0.444(8)$	0.17(4)	2.0	$x = 0.507(5)$	0.11(3)	2.0
Refined composition		$\text{Ti}_{0.89}\text{Zr}_{0.11}\text{Mn}_{1.47}\text{V}_{0.31}\text{Ti}_{0.22}\text{D}_{2.8}$			$\text{Ti}_{0.89}\text{Zr}_{0.11}\text{Mn}_{1.47}\text{V}_{0.3}\text{Ti}_{0.23}\text{D}_{2.79}$		
Cell parameters (\AA)		$a = 5.228(2)$, $c = 8.553(3)$, $V = 202.7$			$a = 5.232(1)$, $c = 8.540(3)$, $V = 201.8$		

times greater. Maximum experimentally achieved desorption pressure is about 30 atm. which corresponds to approximately cell volume 160\AA^3 .

Structural data for deuteride $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.5}\text{V}_{0.3}\text{Ti}_{0.2}\text{D}_{2.8}$ phase shows that introduction of hydrogen does not change the metal matrix structure. Hydride formation leads to isotropic increase of cell volume by 20%. Deuterium atoms occupy three of seven available types of interstitial tetrahedral sites—24(*l*), 12(*k*)₁ and 6(*h*)₁ (Table 2). At low temperature approximately 0.11 deuterium atoms relocate from 24(*l*) to 12(*k*)₁ position, which was also found for $\text{TiMn}_{1.5}\text{D}_3$ [6].

Useful and rather simple correlations found in this work favoured the attempt to summarise them in one empirical mathematical model. We assumed that important characteristics of Laves phase alloys such as thermodynamic functions of reaction with hydrogen and crystal parameters change monotonously within the region of solid solution. If in the case of binary alloy it is rather simple to obtain their values just by application of Vegard rule, in case of multicomponent alloys it practically impossible to take into account all the connected changes of concentrations of components. In its latest version our model was realised in a program which allow to calculate thermodynamic and structural characteristics for multicomponent alloys with any number of components.

Acknowledgements

This work was supported in part by RFBR Grant 02-02-17545 and General Motors Corp.

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