ELSEVIER

Journal of Alloys and Compounds 404–406 (2005) 384–387

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

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.

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:

$$4\mathrm{Mg}\ \text{in}\ 4(f)\frac{1}{3}, \frac{2}{3}, z; \quad 2\mathrm{Zn}^1\ \text{in}\ 2(a)0, 0, 0;$$

$$6\mathrm{Zn}^2\ \text{in}\ 6(h)x, 2x, \frac{1}{4};$$

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).

0925-8388/$ – see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.jallcom.2005.02.078

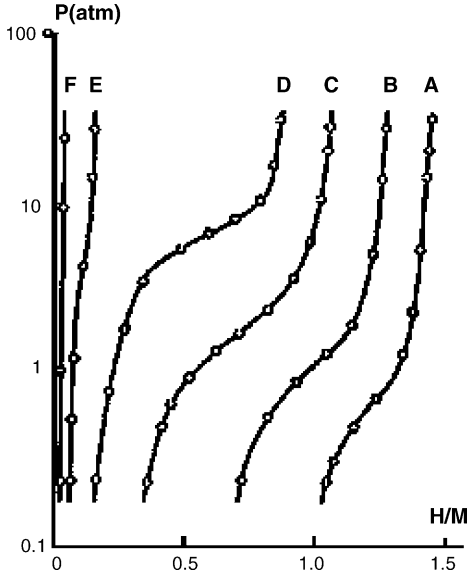

Fig. 1. Desorption isotherms for $TiMn_x$–H_2 systems at 20 °C ($x = 0.75$ (A); 1.0 (B); 1.25 (C); 1.5 (D); 1.75 (E) and 2.0 (F)).

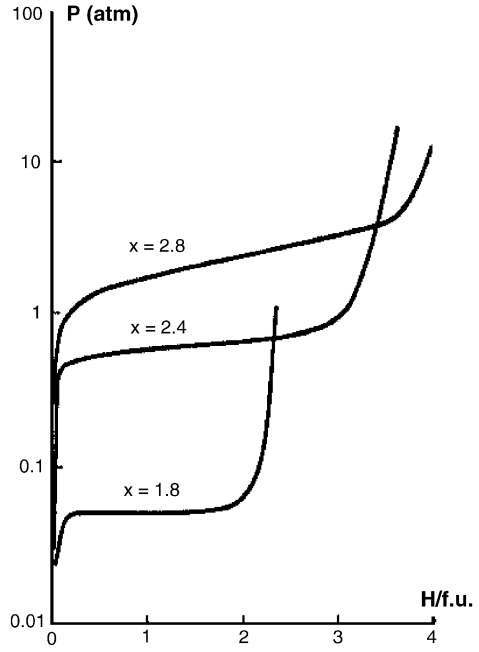

Fig. 2. Desorption isotherms for $ZrMn_x$–H_2 systems at 50 °C.

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 $TiMn_{1.5}$ and $ZrMn_{2.8}$ in conventional Laves phase form as $Ti(Mn_{0.9}Ti_{0.1})_2$ and $(Zr_{0.79}Mn_{0.21})Mn_2$.

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 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

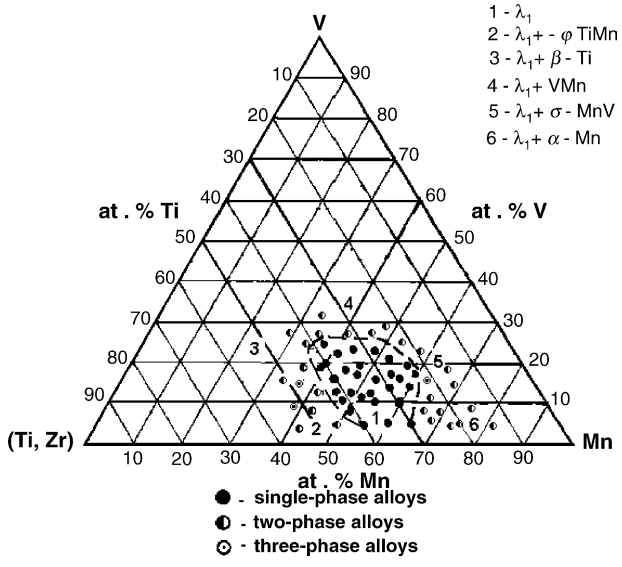

Fig. 3. State diagram for Ti(Zr)–Mn–V system.