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Structure and hydrogen sorption properties of (Ti,Zr)–Mn–V alloys

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Abstract

The present investigation is a part of the series of works on the development of new materials as highly efficient hydrogen accumulating media. Earlier we reported on the investigation of Ti–Mn–V alloys of Laves phase type. This work is the continuation of these studies. The work was aimed on the determination of concentration boundaries of Laves phase and investigation of hydrogen sorption properties of alloys. Using X-ray, EDXA and electron microscopy methods the phase compositions of over 50 alloys were studied. The Laves phase concentration boundaries were determined to extend up to 26 at.% of vanadium. Compared to ternary Ti–Mn–V system the region of λ_1-phase is about 2 at.% wider for Ti–Mn side of concentration triangle. Depending on metal concentrations lattice parameters were determined to increase proportionally with increasing titanium or vanadium concentration according to Vegard rule. The interaction of alloys with hydrogen was studied by PC-isotherm method. The isotherms were measured at three different temperatures and thermodynamic parameters of reaction were calculated using the vant Hoff equation. The hydrogen sorption properties were analysed in view of overall alloy composition. The enthalpy of desorption was found to depend proportionally on unit cell volume of alloy.

Keywords: Hydrides; Alloys; Structure; Properties

1. Introduction

Intensive development of the chemistry of intermetallic hydrides in the past two decades is stipulated by the scientific aspect as well as by perspectives of practical application of these compounds in different fields of technique. Such a possibility of use of intermetallic hydrides for storage, transportation and purification of hydrogen is closely connected with the task of obtaining new hydrides with wide range of controlled absorption properties.

Progress in investigation of metal hydrides of λ_1 Laves phase and $CaCu_5$ types allows us to select for various hydrogen energy applications particular compositions with preset properties. Still the problem of research of new metallic compositions for highly effective hydrogen storage media is a typical question up to now.

The present study is a part of a series of works on research and investigation of new materials for highly effective hydrogen accumulators based on intemetallic compounds of Laves phase type. This type is one of the most prevalent intermetallic types and much work was connected with investigation of hydrogen interaction with these alloys and feasibility of development of low- and high-temperature hydrogen accumulators was shown.

Earlier we reported on the investigation of Ti–Mn–V system [1] where a considerably wide homogeneity range was found for Laves phase (38–63 at.% Mn, 0–25 at.% V) and hydrogen absorption properties of some λ_1-alloys were determined. Present work continues the investigation of hydrogen interaction with Ti–Mn-based Laves phase alloys, particularly with alloys of (Ti,Zr)–Mn–V system with Zr-content of 3–6 at.%.

Two compounds are known to form in the binary Ti–Mn system. TiMn compound is stable at 930°C and belongs to tetragonal structure type with lattice parameters $a = 8.19$ Å, $c = 12.81$ Å [2]. Laves phase $TiMn_2$ compound belongs to λ_1-structure type. The homogeneity range of $TiMn_2$ compound is rather wide solid solution range (64–70 at.% Mn) with lattice parameters in the range of $a = 4.857–4.818$ Å, $c = 8.017–7.879$ Å [3].

Available data for Zr–Mn system is summarised [4]. $ZrMn_2$ compound crystallises in λ_1 structure type with homogeneity range of 65.6–74.4 at.% Mn [5].

In the classic case of binary Laves phase AB_2 formation its stability is determined to a considerable extent by the dimension factor $r_A/r_B = 1.225$. Since for the overwhelming number of compounds they do not exhibit a noticeable homogeneity range, there was no detailed consideration of

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the existence of nonstoichiometric compositions. In our case wide homogeneity ranges for both Ti–Mn and Zr–Mn systems provoke speculation over the reasons for stability of these compositions. It was proposed that for the Zr–Mn compositions with excess manganese this reason could well be the change of the manganese valence state and consequent change of the atomic radius while filling the crystallographic positions of zirconium [6]. As an oblique confirmation of this can serve the results of neutron diffraction experiments for $ZrMn_2Fe_{0.8}$ and $ZrMn_2Co_{0.8}$ showing that excess manganese and iron (cobalt) fill in zirconium positions in the ratio Mn:Fe(Co) = 9:1 [7].

In case of excess A-component content in studied quaternary system one can assume that of two present metals (Ti and Zr) namely titanium will fill in the B-components positions because of smaller metallic radius ($r_{Ti} = 1.47$ Å, $r_{Zr} = 1.62$ Å). Besides, the lower boundary composition for Ti–Mn λ_1-alloys corresponds to Mn/Ti = 1.25, while for Zr–Mn system this value is Mn/Zr = 1.9. All these considerations allow to expect a wide homogeneity range for Laves phase in the (Ti,Zr)–Mn–V system.

Much work has been done on the investigation of hydrogen absorption properties of stoichiomentric λ_1-alloys of Ti–Zr–Mn–V system. Thus, hydrogen interaction with $Ti_{0.8}Zr_{0.2}Mn_{1.5}M_{0.5}$ (M = Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Al, Nb) pseudobinary compounds was studied [8]. $Ti_{0.8}Zr_{0.2}Mn_{1.5}V_{0.5}$ and $Ti_{0.8}Zr_{0.2}Mn_{1.5}Cr_{0.5}$ ($H/AB_2 = 3.3$) compounds showed the best absorption properties with most clearly pronounced isotherm patterns.

Akiba and co-workers studied hydrogen interaction with $Ti_{0.8}Zr_{0.2}MnV$ alloy [9]. According to microscopic and EDX analysis data this alloy consists of three phases: bcc main matrix, λ_1-phase and additions of α-ZrO_2. The relative amounts of each phase and their compositions were calculated using Rietveld method. The absorption capacity of the alloy was 1.95 mass.% at 373 K, but practically no reversible hydrogen desorption was noticed at this temperature.

However, there is practically no literary data on hydrogen absorption properties of nonstoichiometric alloys of Ti–Zr–Mn–V. Hence, present work aims to determine the phase boundaries of λ_1-phase in the Ti–Zr–Mn–V system and hydride formation peculiarities and hydrogen absorption properties of relevant alloys.

2. Experimental procedures

The following metals were used as starting components: Ti (99.99%), Zr (99.99%), electrolytic manganese (99.9%) and vanadium (99.9%). Alloys were prepared in arc furnace with tungsten nonconsumable electrode on a water-cooled hearth under purified argon pressure 1.5 atm. The samples were remelted three times to ensure their homogeneity. Manganese was taken in 4 mass.% excess to cover the losses while melting. Alloys were annealed at 1100–1150 K for 240 h in quartz ampoules under residual argon pressure 0.01 atm. After annealing procedure alloys were slowly cooled to room temperature at a rate of 0.5° min^{-1}. The samples were then studied by X-ray, electron microscopy, electron probe analysis and PC-isotherm methods. Hydriding and PC-isotherm measurements were performed in a standard Sieverts type device. Hydrogen was obtained by desorption from $LaNi_5$-hydride. X-ray studies of starting alloys and hydride phases were done in DRON-2 diffractometer (CuKa, Ni-filter) with silicon serving as an inner standard. Electron-probe analysis was performed on JXA-733 microanalyser complex with LINK-2 microanalytical system.

3. Results and discussion

3.1. (Ti,Zr)–Mn–V metallic system

We prepared 60 alloys for the investigation of the phase relations in the quaternary (Ti,Zr)–Mn–V system. Basing on the results of X-ray and electron-probe analysis the phase boundaries of λ_1-phase were determined as shown in Fig. 1: Ti–22–42 at.%, Mn–36–65 at.%, V–0–26 at.% (Fig. 1). The phases observed adjacent to λ_1-phase were also stated. Remarkable is rather high solubility of vanadium (up to 26 at.%) in $TiMn_2$ compound.

Alloys with more than 41 at.% of titanium contain also Φ-phase (~50 at.% Ti) with tetragonal structure ($a = 8.12$ Å, $c = 12.87$ Å) and bcc β-phase. Alloys containing more than 65 at.% Mn consist of λ_1-phase and also α-Mn and σ-phase with tetragonal structure. On the vanadium-rich

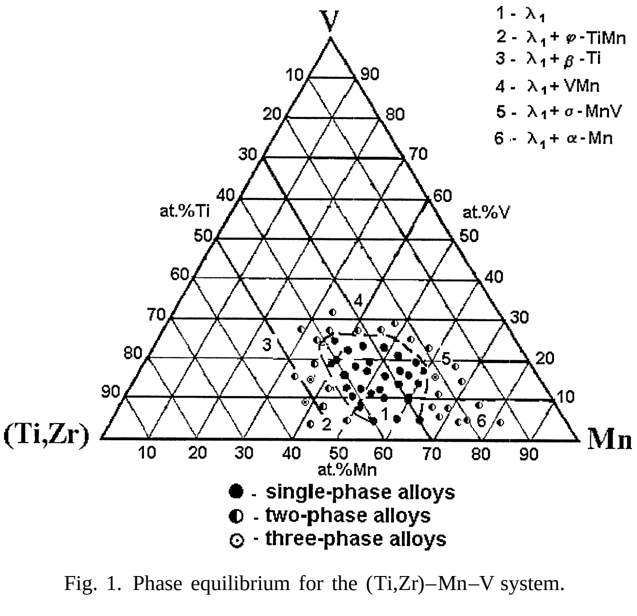

Fig. 1. Phase equilibrium for the (Ti,Zr)–Mn–V system.

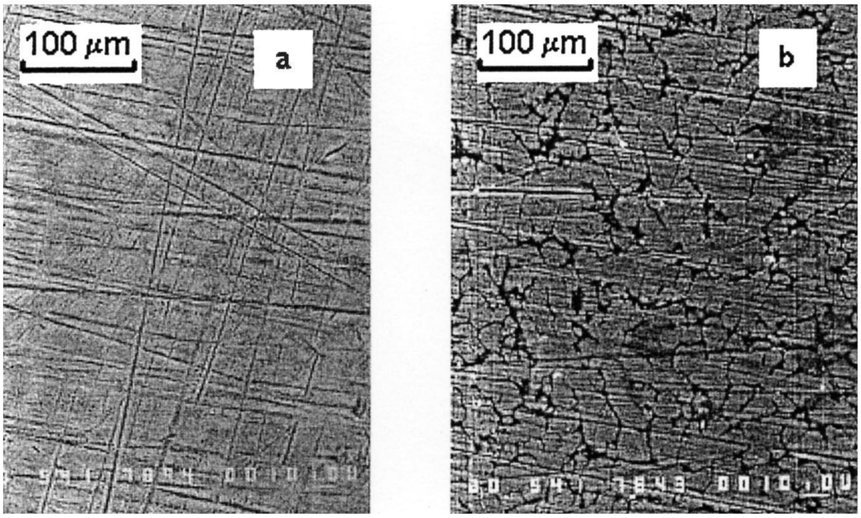

Fig. 2. SEM images for ternary alloys: a–single-phase alloy; b–two-phase alloys.

side λ_1-phase neighbours two-phase region consisting of λ_1-phase and VMn-phase with cubic structure ($a = 2.95$–3.01 Å). Fig. 2 shows images of single-phase λ_1-alloy and two-phase alloy from region 3 (Fig. 1) also containing β-titanium based phase.

Lattice parameters of single phase λ_1-alloys generally increase with increasing titanium and vanadium content. Compared to ternary Ti–Mn–V system, small additions of zirconium insignificantly expand the Laves phase boundaries.

3.2. Hydrogenation of λ_1-alloys

The character of hydride formation in the λ_1-alloys of (Ti,Zr)–Mn–V system was studied by PC-isotherm method. The obtained data is summarised in Table 1. The results showed that the hydriding reaction starts in rather mild conditions at room temperature without preliminary activation and resulting in hydrides which contained 1.8–2.0 mass.% H_2. In those cases, when we managed to prevent hydrogen desorption from hydride phase by its deactivation in an inert solvent at room temperature (if $P_{diss} \leq 1.5$ atm), X-ray data indicated that the hydrogen absorption takes place without any change of metal matrix structure and the relative increase of elementary cell volume amounts to 18%. Desorption isotherms for studied alloys are shown in Fig. 3 together with the isotherm for $TiMn_{1.5}$ compound which is considered as a model for the AB_2-type hydrogen storage materials [10]. Analysis of the obtained experimental data shows that substitution of titanium for its 4d analogue zirconium considerably increases the absorption capacity of Ti–Mn alloys. Isotherm patterns of studied alloys indicate that equilibrium pressure changes in wide range of values (0.1–10 atm) depending on component ratio.

Analysing data in Table 1, it is clear that sample 11 with lowest titanium and zirconium content (27 at.% and 3 at.%) and high manganese content (65 at.%) does not absorb hydrogen up to 100 atm hydrogen pressure. On the other hand sample 1 with the same Ti/Zr ratio but with lower manganese content (57 at.%) and higher vanadium concentration absorbs a considerable amount of hydrogen (1.98 mass.%) with the equilibrium plateau pressure in the range of 12–7 atm. Comparison of absorption properties of samples 3 and 12 with the same A-component ratio as well as the samples with the same titanium and zirconium content (samples 5 and 8) shows that substitution of manganese for vanadium significantly decrease equilibrium pressure value. This decrement can possibly be accounted for the gradual increase of elementary cell volume by substitution, since the metallic radii of vanadium (1.36 Å) and titanium (1.47 Å) are both larger than that of manganese (1.12 Å).

Desorption isotherm for sample 6 with higher titanium and lower manganese content is characterised by a considerably lower equilibrium pressure (0.75 atm) than that for the sample 2 (8 atm). Sample 10 with maximum titanium (40 at.%) and zirconium (6 at.%) contents shows the lowest equilibrium pressure of all studied quaternary alloys.

The influence of alloy composition on the dissociation pressure value is shown in Figs. 4 and 5, where the dependencies of equilibrium pressure are plotted versus the vanadium and manganese content at the constant titanium content. Vanadium promotes the decrement of pressure, while manganese acts reciprocally and samples with manganese concentration of higher than 60 at.% do not absorb noticeable amounts of hydrogen up to the pressure of 100 atm.

So, the addition of zirconium and vanadium to Ti–Mn λ_1-alloys leads to decrease of equilibrium pressure as shown in the Fig. 6. The alloys with cell volume smaller

Table 1
Properties of quaternary alloys of (Ti,Zr)–Mn–V system

No.	Composition	Mass.% H_2 at 295 K	T, K	P_{diss}, atm	$\lvert\Delta H\rvert$, kJ mole^{-1} H_2	a, Å	c, Å	V, Å^3
1	$Ti_{27}Zr_3V_{13}Mn_{57}$	1.98	294	11	30±1	4.86	7.98	162.12
	$Ti_{0.9}Zr_{0.1}V_{0.4}Mn_{1.9}$		274	4.2				
			253	1.5				
2	$Ti_{32}Zr_4V_5Mn_{59}$	1.76	299	8	29±1	4.86	7.96	163.41
	$Ti_{0.9}Zr_{0.1}V_{0.1}Mn_{1.7}$		276	3				
			253	1				
3	$Ti_{31}Zr_4V_{10}Mn_{55}$	1.90	294	3.5	31±0.5	4.86	7.98	164.19
	$Ti_{0.9}Zr_{0.1}V_{0.3}Mn_{1.6}$		275	1.5				
			253	0.45				
4	$Ti_{28}Zr_3V_{20}Mn_{49}$	1.8	335	9.7	32±2	4.88	7.99	165.26
	$Ti_{0.9}Zr_{0.1}V_{0.7}Mn_{1.6}$		314	4.7				
			298	2				
5	$Ti_{32}Zr_4V_{14}Mn_{50}$	1.93	333	6.8	33±2	4.89	7.99	165.74
	$Ti_{0.9}Zr_{0.1}V_{0.4}Mn_{1.4}$		315	3.2				
			298	1.65				
6	$Ti_{36}Zr_4V_5Mn_{55}$	1.93	335	5	34±3	4.91	8.01	167.06
	$Ti_{0.9}Zr_{0.1}V_{0.1}Mn_{1.4}$		314	2				
			299	0.75				
7	$Ti_{34}Zr_5V_{11}Mn_{50}$	1.85	315	1.8	35±1	4.91	8.06	167.25
	$Ti_{0.9}Zr_{0.1}V_{0.3}Mn_{1.3}$		295	0.65				
			273.5	0.24				
8	$Ti_{32}Zr_4V_{18}Mn_{46}$	2.04	335	2.55	37±2	4.92	8.07	168.54
	$Ti_{0.9}Zr_{0.1}V_{0.5}Mn_{1.3}$		313	1.1				
			297	0.46				
9	$Ti_{36}Zr_4V_{10}Mn_{50}$	1.97	334	2.25	38±0.5	4.93	8.07	168.64
	$Ti_{0.9}Zr_{0.1}V_{0.2}Mn_{1.2}$		314	1				
			294	0.38				
10	$Ti_{40}Zr_6V_5Mn_{49}$	1.97	362	1.9	39±1	4.94	8.07	169.68
	$Ti_{0.9}Zr_{0.1}V_{0.1}Mn_{1.1}$		333	0.73				
			294	0.12				
11	$Ti_{27}Zr_3V_5Mn_{65}$	0.5	–	–	–	4.84	7.95	161.24
	$Ti_{0.9}Zr_{0.1}V_{0.1}Mn_{2.2}$							
12	$Ti_{31}Zr_4V_5Mn_{60}$	0.1	–	–	–	4.85	7.95	161.35
	$Ti_{0.9}Zr_{0.1}V_{0.1}Mn_{1.8}$							

than 160 Å^3 do not absorb hydrogen at moderate pressure (up to 100 atm). It should be noted that obtained results for nonstoichiometric alloys agree in whole with the reported data for stoichiometric alloys [8]. In order to absorb hydrogen $Ti_{0.8}Zr_{0.2}Mn_{1.5}M_{0.5}$ alloys should possess elementary cell volume more than 165 Å^3.

Based on the experimental results it is possible to find a dependence of desorption reaction enthalpy on elementary cell volume as shown in Fig. 7. This dependence exhibits the increase of the absolute values of enthalpy with increasing cell volume. It is interesting to note that the experimental values for stoichiometric alloys of related $Ti_{1-x}Zr_xMn_2$system [11] and binary Ti–Mn alloys [10,12] fit well to this dependence.

4. Conclusions

In present work we determined the phase boundaries of λ_1-phase of (Ti,Zr)–Mn–V system by means of X-ray and electron-probe analysis. The phase boundaries of λ_1-phase were determined: Ti–22–42 at.%, Mn–36–65 at.%, V–0–26 at.%. Using PC-isotherm method the character of hydride formation for quaternary λ_1-alloys was studied.

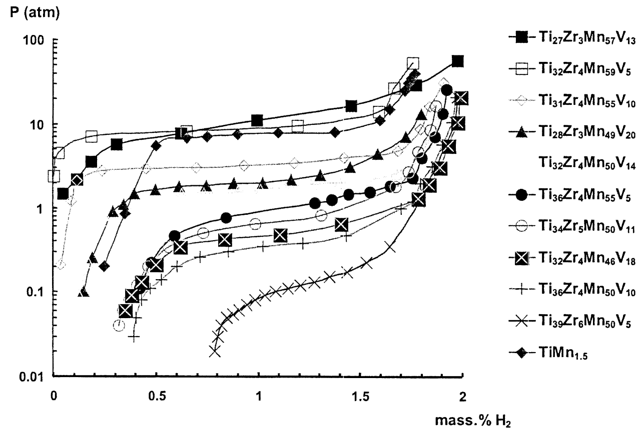

Fig. 3. Desorption isotherms for the alloys of (Ti,Zr)–Mn–V system at 295 K.

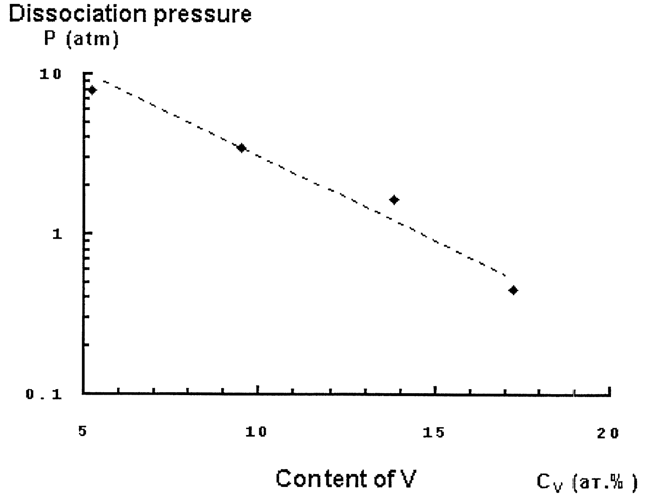

Fig. 4. Dissociation pressure vs. vanadium content for (Ti,Zr)–V–Mn alloys.

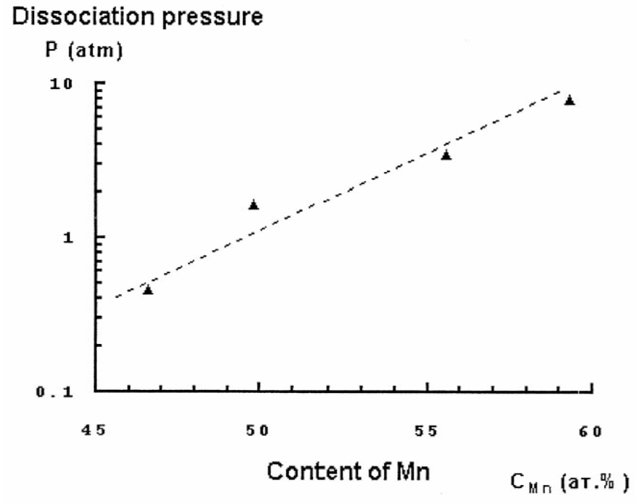

Fig. 5. Dissociation pressure vs. manganese content for (Ti,Zr)–V–Mn alloys.

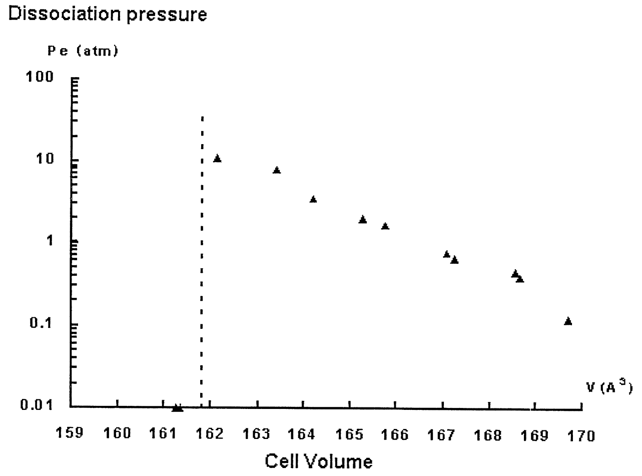

Fig. 6. Dissociation pressure vs. cell volume for (Ti,Zr)–V–Mn alloys.

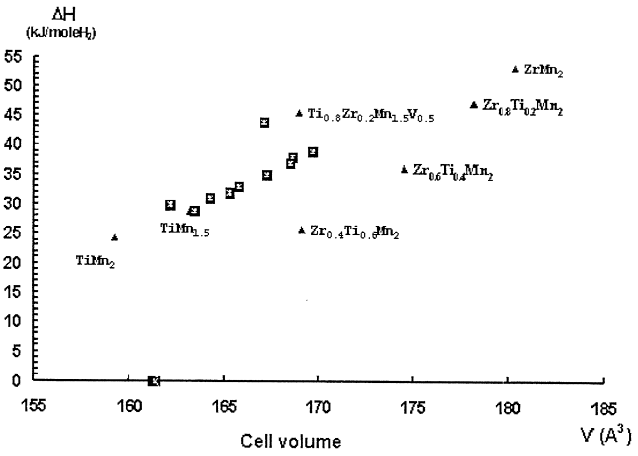

Fig. 7. Hydriding enthalpy vs. cell volume for (Ti,Zr)–V–Mn alloys.

Clearly marked dependencies of reaction enthalpy and equilibrium pressure on elementary cell volume allow to predict hydride properties. It was shown that these alloys could be perspective for the development of new materials for metal-hydride technology.

Acknowledgements

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