

Journal of Alloys and Compounds 393 (2005) 231-238

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Crystal structure and hydrogen absorption of $Ti_x Zr_{1-x} Mn_2$

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Received 26 December 2003; received in revised form 4 June 2004; accepted 17 August 2004 Available online 23 November 2004

Abstract

 $Ti_xZr_{1-x}Mn_2$ alloys and their hydrides with x=0, 0.1, 0.2 and 0.3 were characterized by the XRD Rietveld analysis and isothermal measurement. Introduction of hydrogen did not change the crystal structure type (C14 Laves phase) but led to significant lattice expansion. The best fitting in the Rietveld analysis revealed that titanium atoms preferentially occupied the zirconium sites. Direct comparison of equilibrium pressures of $Ti_xZr_{1-x}Mn_2-H_2$ system at 269, 298 and 323 K showed that the pressure increased with the titanium content. The absolute values of ΔH and ΔS in $\alpha + \beta$ two-phase regions monotonously decreased with the titanium content. The variation of ΔS with the titanium content was interpretable by taking into account increased freedom of configuration of hydrogen atoms among various interstitial sites. As for the variation of ΔS with the hydrogen concentration, an unexpected decrease of the absolute value was found for $T_{0.3}Zr_{0.7}Mn_2-H_2$ system. We further detected an unusually small size of hydrogen-saturated α phase for $T_{0.3}Zr_{0.7}Mn_2-H_2$ system. Those two phenomena would be a symptom of some phase separation on hydriding.

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Keywords: Hydrogen storage materials; Intermetallics; X-ray diffraction; Phase transitions; Thermodynamic properties

1. Introduction

Zirconium-based AB₂ alloys with the Laves phase have attracted a great deal of attention as hydrogen storage materials because of their substantial hydrogen storage capacity [1–3]. ZrMn₂ is a representative one among them, but its hydride is too stable to be of practical significance owing to low equilibrium pressures. Therefore many studies have paid attention to increasing the equilibrium pressures of zirconium-based Laves phase alloys without reducing the absorption capacity by partial substitution of the A or B element by other elements [4]. Partial substitution of zirconium by titanium in ZrMn₂ increases equilibrium pressures to satisfy technological interests [5–7], and further substitution of manganese by iron to form Ti_xZr_{1-x}(Fe_yMn_{1-y})_z alloys varies equilibrium pressures in a wider range [8,9].

It has been found in our previous work [10] that $Zr(Fe_{0.2}Mn_{0.8})_2$ unexpectedly had lower equilibrium pressures than $ZrMn_2$ although the equilibrium pressures in the

Zr(Fe_xMn_{1-x})₂–H₂ systems essentially increased with the iron contents as a whole. The increasing order of the equilibrium pressures for the Zr(Fe_xMn_{1-x})₂–H₂ systems before the α (primary solid solution phase) $\rightarrow \beta$ (hydride phase) transition somewhat differed from that after the transition. Thus the $\alpha \rightarrow \beta$ phase transition should be carefully treated when the variation of equilibrium pressures with substitution is discussed. Since it is inaccurate to extrapolate the equilibrium pressures to some common temperatures without knowing where the $\alpha \rightarrow \beta$ phase transition is, it is advisable to directly compare the pressures at the common temperatures.

Although crystal structures and thermodynamic features of Ti_xZr_{1-x}Mn₂ system have been studied by Oesterreicher and Bittner [5] and Pourarian et al. [7], comparison of equilibrium pressures was based upon extrapolation of the van't Hoff plots without knowing at what temperature and at what hydrogen concentration the $\alpha \rightarrow \beta$ phase transition occurred. Thus in order to compare the stability of the hydrides in the Ti_xZr_{1-x}Mn₂-H₂ systems without inaccurate extrapolation, we planned systematic measurement of hydrogen absorption isotherms at selected common temperatures. This will offer an experimental basis for discussing stability of the hydride

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^{0925-8388/\$ –} see front matter 2004 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2004.08.097

in terms of the electronic structures. Since the zero concentration of hydrogen in the solid phase is confirmed by evacuation at elevated temperatures to assure the accuracy of hydrogen concentrations of each isotherm, absorption branch will be measured and discussed.

Another purpose of this study is to obtain accurate knowledge of structural characteristics of the alloys and relevant hydrides based upon the X-ray diffraction (XRD) Rietveld analysis. This is necessary to understand the phase stability of $Ti_xZr_{1-x}Mn_2$ hydrides by, for example, the DV-X_{\alpha} cluster method. The results predicted from the DV-X_{\alpha} cluster method will be attested in the forthcoming paper using the experimental data of the equilibrium pressures in this work.

2. Experimental

2.1. Sample preparation and powder X-ray diffraction

Ti_xZr_{1-x}Mn₂ (x=0, 0.1, 0.2, 0.3) alloys were prepared by melting the appropriate ratios of the constituent metals with purity better than 99.8% in a high-frequency induction furnace under an argon atmosphere. The whole ingots were used without any scraping or washing, but were mechanically crushed into coarse powders in a glove box filled with nitrogen prior to hydriding process. Each sample was placed into a stainless steel reactor and evacuated for 3 h by a mechanical pump at 623 K. Hydrogen gas (purity >99.99%) at a pressure of 4.5 MPa was then admitted into the reactor at room temperature. The evacuation-hydriding cycles were repeated until a steady amount of hydrogen was reproducibly occluded by fine powders.

All the samples were characterized by MAC Science MXP18V diffractometer under ambient air using Cu Ka radiation with power of $40 \text{ kV} \times 250 \text{ mA}$ and scanning steps of 0.04° (2 θ). The tested hydrides were withdrawn from pressureproof vessels after the line pressures remained constant, and the alloy samples were obtained by evacuating the hydrides at 623 K for 3 h until no further hydrogen was released. Prior to the measurements, the samples were slowly exposed to air at room temperature to prevent them from burning. In order to know whether there were any additional reflections after being exposed to air, other aliquots of the samples were sealed in a nitrogen-filled XRD holder with a nickel window and the crystal structures of them were characterized by Rigaku Rint 2000 diffractometer with a large sample holding space operated at $40 \text{ kV} \times 35 \text{ mA}$ with scanning steps of $0.04^{\circ} (2\theta).$

The XRD data collected by MXP18V diffractometer were analyzed by the Rietveld method using RIETAN 89 [11], with various *R* values used to assess the fitting. The most meaningful is R_{wp} (*R*-weighted pattern), which measures the weighted difference between the calculated and measured intensities. The R_e (*R* expected) value is an estimation of the minimum possible value of R_{wp} [12,13]. A reliable indicator of the goodness of the fit is the value $S = R_{wp}/R_e$ [12].

2.2. Hydrogen absorption isotherms

After completion of the cycling, about 0.7 g of hydrided samples were withdrawn in a nitrogen-filled glove box and were degassed again at 623 K by a mechanical pump to ensure complete desorption, and then the pressure-composition isotherm (PCT) measurements were performed under hydrogen up to 1 MPa using a conventional volumetric system. The sample holder was immersed in three kinds of baths. Water–ethyleneglycol bath was kept at 269.0 ± 0.2 K, water bath at 298.0 ± 0.2 K and silicone oil bath at 323.0 ± 0.5 K. The dead volume of the sample holder was 31 cm^3 and that of the upstream part equipped with a pressure gauge (full scale is 20 kg/cm^2 , $1 \text{ kgf/cm}^2 = 0.980665 \times 10^5 \text{ Pa}$) was 39 cm^3 .

3. Results

3.1. Preparative results

Each alloy used in this study showed reproducible time course of pressures on hydriding after 4 or 5 hydriding runs and residual line pressure kept a steady value characteristic of each system.

XRD results on $Ti_xZr_{1-x}Mn_2$ alloys and their hydrides are shown in Figs. 1 and 2. Almost all of the peaks were indexed to confirm the presence of C14 structure type (space group $P6_3/mmc$) of respective alloy or hydride, but some additional peaks marked by arrows were observed. A peak at $2\theta = 32.08^{\circ}$ in Fig. 1(a) was expected for manganese oxide. This peak was also found in nitrogen-filled XRD measurement. The number of diffraction peaks and the lattice parameters observed under air were the same as those under nitrogen. If we assume that the peaks marked by arrows in Fig. 2 might arise from a small quantity of corresponding α phases, they could be indexed as tabulated in Table 1. Since these extra peaks would not belong to the starting alloy or β hydride phases, they were excluded in the Rietveld analysis.

Table 1

Peak positions and assignments of extra peaks appearing in Fig. 2 $(1\,\text{\AA}\,{=}\,0.1\,\text{nm})$

| Sample | 2θ (°) | Assumed α phase | | |
|------------------------------------|---|---|-------|--------------|
| | | hkl | a (Å) | <i>c</i> (Å) |
| ZrMn ₂ H _{3.6} | 37.13 | 103 | 5.225 | 8.590 |
| $Ti_{0.1}Zr_{0.9}Mn_2H_{3.4}$ | 41.80 42.84 | $\begin{array}{c}112\\201\end{array}$ | 5.032 | 8.411 |
| $Ti_{0.2}Zr_{0.8}Mn_2H_{3.2}$ | 42.00 42.90 | $\begin{array}{c}1\ 1\ 2\\2\ 0\ 1\end{array}$ | 5.030 | 8.277 |
| $Ti_{0.3}Zr_{0.7}Mn_2H_{3.0}$ | 42.48 43.44 47.70 49.25 72.46 | 112 201 202 104 205 | 4.970 | 8.188 |

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