Journal of Alloys and Compounds 386 (2005) 26–34

Journal of
ALLOYS
AND COMPOUNDS

www.elsevier.com/locate/jallcom

Hydrogen-induced changes in crystal structure and magnetic properties of the Zr_3MO_x (M = Fe, Co) phases

I.Yu. Zavaliy [a,*], R.V. Denys [a], R. Černý [b], I.V. Koval'chuck [a], G. Wiesinger [c], G. Hilscher [c,1]

[a] *Physico-Mechanical Institute of the NAS of Ukraine, 5 Naukova Str., Lviv 79601, Ukraine*
[b] *Laboratory of Crystallography, University of Geneva, 24 Quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland*
[c] *Institute of Solid State Physics, TU Vienna, Wiedner Hauptstrasse 8-10, A-1040 Vienna, Austria*

Received 14 May 2004; accepted 16 May 2004

Abstract

It is shown that the oxygen-stabilised compounds $Zr_3Fe(Co)O_x$ ($x = 0$–1.0) interact with hydrogen at ambient temperature and pressure forming saturated hydrides with filled Re_3B type structure. The hydrogen storage capacity decreases with increasing oxygen content from 6.7 H/f.u. for Zr_3Fe down to 5.35 H/f.u. for $Zr_3FeO_{1.0}$ and from 6.9 H/f.u. for Zr_3Co down to 5.3 H/f.u. for $Zr_3CoO_{1.0}$. A small change of the unit cell volumes for the $Zr_3Fe(Co)O_x$ parent compounds and a substantial increase of these parameters for the corresponding saturated hydrides were observed with increasing oxygen content. The partial hydrogen-induced lattice expansion, ΔV/at. H, increases from 2.25 $Å^3$ for $Zr_3FeH_{6.7}$ up to 3.38 $Å^3$ for $Zr_3FeO_{1.0}H_{5.35}$ and from 2.08 $Å^3$ for $Zr_3CoH_{6.9}$ up to 3.25 $Å^3$ for $Zr_3CoO_{1.0}H_{5.3}$. Rietveld refinement using neutron powder diffraction data for $Zr_3FeO_{0.4}D_{6.25}$ showed a distribution of deuterium atoms and a redistribution of oxygen atoms from octahedral to tetrahedral sites in a similar way as in $Zr_3NiO_xD_y$. Both ^{57}Fe Mössbauer spectroscopy and magnetic susceptibility measurements of Fe-containing hydrides indicated weak hydrogen-induced magnetic ordering at low temperatures. The ordering temperatures of $Zr_3FeO_{0.2}H_{6.52}$ and $Zr_3FeO_{0.6}H_{6.25}$ are 105 and 140 K, respectively.

Keywords: Hydrogen storage materials; Zr-based alloys; X-ray diffraction; Neutron diffraction; Magnetic properties

1. Introduction

A_3B phases with the Re_3B type structure, formed in zirconium and hafnium-based systems dissolve oxygen up to the composition A_3BO (Zr_3Fe, Zr_3Co) [1] or can be stabilised by oxygen, when such compound does not exist in the binary system (Zr_3NiO and Hf_3NiO) [2]. The oxygen atom occupies the octahedral void in the Re_3B structure. Hydrogenation properties of $Zr_3Fe(Co)$ phases and their crystal structure were investigated in detail [3–5]. Studies of Zr_3FeH_x hydrides by Mössbauer spectroscopy performed previously by Aubertin et al. [6] showed the presence of hydrogen-induced magnetic ordering upon cooling to 4.2 K. However, neither the type of magnetic ordering nor the transition temperature has been determined.

Hydrogenation properties of an oxygen-stabilised compound and its crystal structure were studied recently for $Zr_3NiO_xD_y$ [7,8]. Reversible hydrogen-induced redistribution of oxygen atoms in the crystal structure and the inverse dependence of the hydrogen absorption capacity on the oxygen content were observed. The aim of this work was a study of the crystal structure and magnetic properties of oxygen-stabilised Zr_3MO_x compounds and their hydrides, for M = Fe, Co.

2. Experimental

Zr_3MO_x (M = Fe, Co; $x = 0.2, 0.4, 0.6, 0.8, 1.0$) alloys were prepared from pure metals by arc melting in a purified argon atmosphere on a water-cooled copper hearth. Oxygen was introduced into the alloys in the form of the oxide ZrO_2. Further homogenisation of the as-cast samples was performed by annealing at 800 °C for 400 h. Two batches of samples were prepared: first, for hydrogenation and X-ray

---

[*] Corresponding author. Tel.: +380-322-654833; fax: +380-322-649427.
E-mail address: zavaliy@ipm.lviv.ua (I.Yu. Zavaliy).
[1] Tel.: +43-1-58801-13130; fax: +43-1-58801-13199.

0925-8388/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2004.05.064

diffraction characterisation of $Zr_3Fe(Co)O_x$ (∼2 g each), and second, for neutron diffraction studies of $Zr_3FeO_{0.4}$ (∼6 g). Characterisation of the parent alloys and their hydrides was carried out by the X-ray powder diffraction (diffractometer DRON-3.0; Cu Kα radiation) and by high resolution X-ray powder diffraction (Bruker D8 diffractometer; Cu $K\alpha_1$ radiation). Crystal structure studies of the $Zr_3FeO_{0.4}D_{6.52}$ deuteride were performed using X-ray as well as neutron powder diffraction (Paul Scherrer Institute, diffractometer HRPT, high resolution mode, wavelength 1.494 Å). The lattice parameters were refined using the program CSD [9]. The crystal structure of the selected hydrides and the $Zr_3FeO_{0.4}D_{6.52}$ deuteride was refined by Rietveld method using the program FullProf [10].

The hydrogen/deuterium absorption characteristics were determined by a standard volumetric technique. Hydrogen/deuterium was injected into a stainless steel reactor containing a preliminary activated sample (300–400 °C for 0.5 h in ∼1 Pa vacuum). An exposure of the samples to a hydrogen/deuterium pressure of 0.1–0.12 MPa for 5−10 h was sufficient for achieving saturation of the alloys with hydrogen/deuterium.

The ^{57}Fe Mössbauer spectra were recorded in transmission geometry at room and liquid helium temperatures using a conventional constant acceleration type spectrometer with a ^{57}Co source in a Rh matrix. The data were analysed by fitting sets of Lorentzian lines to the experimental points. The isomer shift values are given relative to the source material. Magnetisation measurements have been performed on powdered specimens with a SQUID magnetometer in fields up to 6 T.

3. Results and discussion

3.1. Synthesis and crystal structure of parent compounds and their hydrides

The formation of the intermetallic phases Zr_3FeO_x and Zr_3CoO_x was confirmed in the homogeneity range of $x = 0$–1.0. Only traces of α-Zr and $Zr_4Fe_2O_x$ (in Fe-containing alloys) and α-Zr and ZrCo (in Co-containing alloys) were observed in the synthesised samples. The refinement of the crystal structure of the parent compounds $Zr_3Fe(Co)O_x$ (samples from the first batch, $x = 0.2$, 0.4, 0.6, 0.8, 1.0) has confirmed the partially filled Re_3B type structure. The lattice parameters of the main phase (weight fraction higher than 90 %) for all studied samples are presented in Table 1. Hydrides of these samples were characterised by the partially filled Re_3B type structure of the metal–oxygen sublattice. The corresponding lattice parameters as well as hydrogen storage capacity are collected in Table 1. It has been observed that the insertion of oxygen atoms leads to a very slight decrease (∼0.5%) of the cell volume of the parent phase Zr_3CoO_x in the range $x = 0$–1.0 and small changes (without monotonic tendency) of the cell volume for Zr_3FeO_x (Fig. 1b). It has been observed that the hydrogen-induced lattice expansion of the saturated hydrides increases substantially with the increasing oxygen content while the hydrogen content decreases, which is demonstrated in Fig. 1 by the plots of V_{parent}, V_{hydride}, H/M and ΔV/at.H as a function of the O content. The oxygen dependence observed for the $Zr_3Fe(Co)O_xH_y$ hydrides is the same as that obtained for $Zr_3NiO_xH_y$ [7,8].

Table 1
Lattice parameters of parent and hydrogenated Zr_3FeO_x and Zr_3CoO_x compounds from Rietveld refinement (space group Cmcm)

Nominal composition	a (Å)	b (Å)	c (Å)	V (Å^3)	H/M ratio	ΔV/at.H (Å^3)
Zr_3Fe [4]	3.324(2)	10.974(5)	8.821(3)	321.7(1)		
$Zr_3FeH_{6.7}$ [4]	3.5803(3)	11.059(1)	9.6486(8)	382.03(9)	1.73	2.25
$Zr_3FeO_{0.2}$	3.3233(8)	11.028(3)	8.820(2)	323.2(2)		
$Zr_3FeO_{0.2}H_{6.52}$	3.5871(6)	11.123(2)	9.694(2)	386.8(2)	1.63	2.44
$Zr_3FeO_{0.4}$	3.31841(5)	11.0722(2)	8.7995(1)	323.311(8)		
$Zr_3FeO_{0.4}H_{6.40}$	3.56914(7)	11.2356(2)	9.7195(2)	389.76(1)	1.60	2.60
$Zr_3FeO_{0.6}$	3.31731(3)	11.0948(1)	8.78458(9)	323.315(5)		
$Zr_3FeO_{0.6}H_{6.25}$	3.5482(1)	11.3064(4)	9.7452(3)	390.95(2)	1.56	2.72
$Zr_3FeO_{0.8}$	3.3326(8)	11.134(1)	8.728(4)	323.8(1)		
$Zr_3FeO_{0.8}H_{5.68}$	3.527(1)	11.452(1)	9.745(3)	393.7(1)	1.42	3.08
$Zr_3FeO_{1.0}$	3.3228(5)	11.137(2)	8.723(2)	322.8(1)		
$Zr_3FeO_{1.0}H_{5.35}$	3.506(1)	11.504(2)	9.796(4)	395.1(2)	1.34	3.38
Zr_3Co [5]	3.277(3)	10.904(4)	8.990(2)	321.3(2)		
$Zr_3CoH_{6.9}$ [5]	3.5959(1)	10.9734(3)	9.5961(3)	378.65(3)	1.73	2.08
$Zr_3CoO_{0.2}$	3.2864(4)	10.947(1)	8.895(1)	321.0(1)		
$Zr_3CoO_{0.2}H_{6.60}$	3.559(1)	11.126(4)	9.572(4)	379.1(4)	1.65	2.20
$Zr_3CoO_{0.4}$	3.2960(2)	10.9872(6)	8.8575(6)	320.78(7)		
$Zr_3CoO_{0.4}H_{6.30}$	3.5479(3)	11.2006(9)	9.6243(7)	382.46(9)	1.58	2.45
$Zr_3CoO_{0.6}$	3.30541(3)	11.00988(9)	8.81106(8)	320.654(5)		
$Zr_3CoO_{0.6}H_{5.95}$	3.51600(9)	11.3388(3)	9.6590(3)	385.08(2)	1.49	2.71
$Zr_3CoO_{0.8}$	3.31021(4)	11.0204(1)	8.7790(1)	320.258(6)		
$Zr_3CoO_{0.8}H_{5.65}$	3.49761(4)	11.4103(1)	9.6881(1)	386.640(9)	1.41	2.94
$Zr_3CoO_{1.0}$	3.3132(2)	11.0285(5)	8.7449(4)	319.54(3)		
$Zr_3CoO_{1.0}H_{5.30}$	3.4813(3)	11.4729(9)	9.7254(7)	388.44(5)	1.33	3.25