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Structure of (Ti,Zr)–Mn–V nonstoichiometric Laves phases and $(Ti_{0.9}Zr_{0.1})(Mn_{0.75}V_{0.15}Ti_{0.1})_2D_{2.8}$ deuteride

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Abstract

The structure of several Laves phase alloys and deuteride was studied using methods of X-ray analysis and time-of-flight neutron diffraction. The refinement of diffraction profiles was performed using the Rietveld method. Introduction of hydrogen does not change the metal matrix structure and the hydriding is accompanied by isotropic increase of cell volume by 20%. The minimisation of the *R*-factor showed that the best fit is achieved for the model of deuterium location in three sites, *24(l)*, $12(k)_1$ and $6(h)_1$. However, at low temperature approximately 0.11 deuterium atoms relocate from the *24(l)* to the $12(k)_1$ position. The analysis of alloy and deuteride structure performed in this work as well as the reference data allow to draw a conclusion, that the set of sites in hexagonal Laves phase structure which are occupied by deuterium is a stable one and does not depend on temperature or alloy composition.

Keywords: Hydrogen storage materials; Crystal structure and symmetry

1. Introduction

The prediction of hydrogen absorption properties of potential hydrogen storage materials is impossible without the knowledge of structural peculiarities of metal matrix and relevant hydride phase. In most number of works the structure of stoichiometric Laves phases and hydrides, such as $TiMn_2$ and $ZrMn_2$ was studied. These compounds are known to have a large homogeneity region. This region characterises the range of stable existence of nonstoichiometric compositions with deviations from stoichiometry ($B/A=2\pm x$). This stability is stipulated by the ability of one of the components to occupy the crystallographic positions of the other component. Earlier we showed that the addition of zirconium and vanadium to Ti–Mn alloys leads to some enlargement of the homogeneity region. Still the crystal chemistry of these phases is studied insufficiently. Structural investigations were only completed for $TiMn_{1.5}D_{3.13}$ [1], $ZrMn_{2.5}$ [2] and $TiMn_{1.12}V_{0.75}D_{1.9}$ [3].

In the present work we studied the structure of $TiMn_{1.5}V_{0.5}$, $Ti_{0.9}Zr_{0.1}(Mn_{0.58}V_{0.35}Ti_{0.07})_2$, $(Ti_{0.9}Zr_{0.1})(Mn_{0.75}V_{0.15}Ti_{0.1})_2$ and its deuteride. The main goal was to determine the occupancy of A-sites by titanium and zirconium, and, secondly, to determine whether the distribution of manganese, vanadium and titanium atoms in B^1 and B^2 sites is random or ordered.

2. Experimental

The structure of alloys and deuteride was studied using methods of X-ray analysis and time-of-flight neutron diffraction (TOFND). X-Ray analysis was performed on a DRON-2 diffractometer (Cu Kα, Ni-filter). TOFND was carried out on a DN-12 spectrometer (Channel 12 of IBR-2 reactor at Joint Institute of Nuclear Research, Dubna, Russia). Measurements were done at two rings with $\theta=45°$ (time-of-flight=26.4 m) and $\theta=69.2°$ (time-of-flight=26.55 m).

It should be noted, that the alloy structure is rather difficult to refine. This is due to the practically equal values of neutron scattering lengths for titanium and manganese ($b_{Ti}=3.438\cdot10^{-12}$ cm, $b_{Mn}=-3.73\cdot10^{-12}$ cm,

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$b_{Zr}=7.16\cdot10^{-12}$ cm, $b_V=-0.3824\cdot10^{-12}$ cm, $b_D=6.671\cdot10^{-12}$ cm) making it impossible to distinguish these two atoms in the same position. The Rietveld refinement of diffraction profiles was performed using MRIA program. All theoretically possible positions of deuterium atoms were considered with the refinement procedure. Occupation factors of titanium and manganese atoms in the same crystallographic position and all thermal parameters were always fixed.

3. Results and discussion

The refinement of the diffraction profiles of the starting alloys showed, that in all cases various metallic atoms of B-component do not show preference in occupation of two possible sites—*2(a)* or *6(h)*. Table 1 shows the structure parameters for studied alloys.

The data obtained for deuteride phase shows that introduction of hydrogen does not change the metal matrix structure and that the hydriding is accompanied by isotropic increase of cell volume by 20%. So, the pattern exhibits the same diffraction maximums, whose positions and intensities are somewhat changed due to the increase of cell parameters and contribution of deuterium atoms.

The comparison of the diffraction patterns obtained at 295 K for alloy and its deuteride under the same conditions shows the appearance of so-called ‘halo’ in the case of deuteride phase (Figs. 1 and 2). This can be connected with the formation of short range order in deuteride phase thus attesting some ordering in the range of interstitial distances $d=2.3$–2.4 Å. It is known [4], that short-range order is revealed in the pattern as a background modulation. Therefore, wide diffusion maximums arise in the patterns, besides the Bragg maximums. The preservation of the ‘halo’ at low temperature shows, that no long-range ordering of the interstitials atoms takes place.

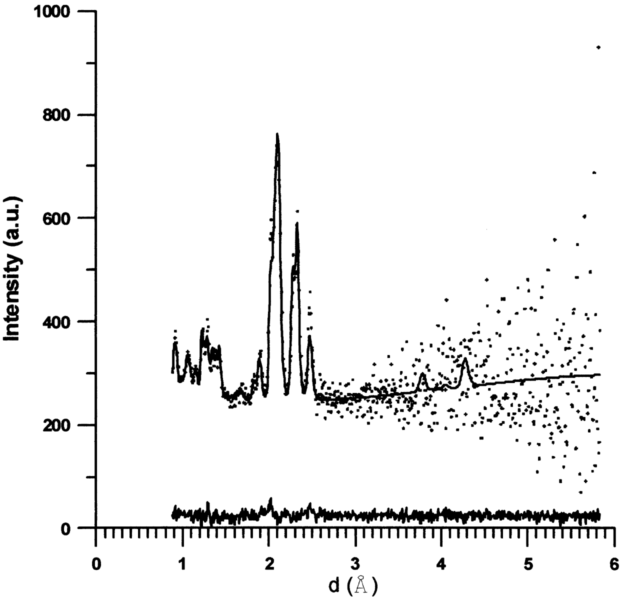

Fig. 1. TOFND pattern for the $Ti_{0.9}Zr_{0.1}Mn_{1.5}V_{0.3}Ti_{0.2}$ alloy.

The Laves phase hexagonal structure is characterised by seven types of tetrahedral sites suitable for hydrogen occupation. Since the alloy composition is a nonstoichiometric one, it is rather difficult to determine the dimensions of these sites and to assume, which one will be more preferable for hydrogen.

Still, it is clear that two of the sites with maximum contribution of B-component *4(f)* [AB_3] and *4(e)* [B_4] are the most unfavourable for hydrogen occupation. In fact, the attempt to locate deuterium atoms in these sites gave the zero or negative occupancy with refinement.

The results of *R*-factor minimisation showed that the best fit is achieved for the model of deuterium location in three sites, *24(l)*, *12(k)*$_1$ and *6(h)*$_1$. However, at low temperature approximately 0.11 deuterium atoms relocate from the *24(l)* to the *12(k)*$_1$ position. It is interesting that the same reordering at 80 K (~0.25D) was found for $TiMn_{1.5}D_3$ [1]. The structural parameters of deuteride

Table 1
Structure parameters of starting 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)	$a=4.894(2)$	$a=4.906(1)$	$a=4.915(3)$
	$c=8.020(5)$	$c=8.062(5)$	$c=8.085(6)$
A-component			
4(f)	$z=0.064(4)$	$z=0.059(3)$	$z=0.057(3)$
(1/3, 2/3, *z*)	Ti	0.88(1)Ti:0.12(1)Zr	0.87(2)Ti:0.13(1)Zr
B-component			
2(a)	0.60(2)Mn:0.4(2)V	0.39(1)Mn:0.61(1)V	0.73(1)V:0.27(1)Ti
(0,0,0)			
6(h)	$x=0.829(6)$	$x=0.827(3)$	$x=0.827(4)$
(*x*, 2*x*, 1/4)	0.79(2)Mn:0.21(2)V	0.85Mn:0.15Ti	0.81(2)Mn:0.19(1)V
R_w	1.1	6.2	5.6
Refined composition	$TiMn_{1.48}V_{0.52}$	$Ti_{0.88}Zr_{0.12}(Mn_{0.74}V_{0.15}Ti_{0.11})_2$	$Ti_{0.87}Zr_{0.13}(Mn_{0.61}V_{0.32}Ti_{0.07})_2$

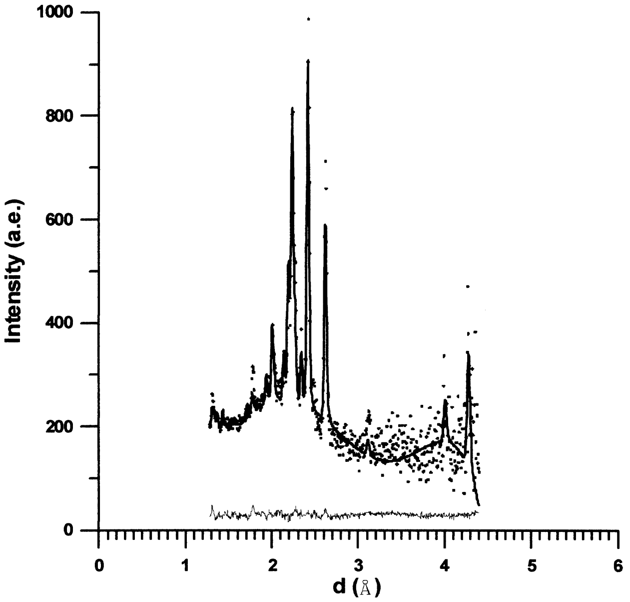

Fig. 2. TOFND pattern for the $Ti_{0.9}Zr_{0.1}Mn_{1.5}V_{0.3}Ti_{0.2}D_{2.8}$ deuteride.

Table 3
Interatomic distances for $Ti_{0.9}Zr_{0.1}Mn_{1.5}V_{0.3}Ti_{0.2}D^{*}_{2.8}$

Atom	*d* (Å) (±0.001)	Atom	*d* (Å) (±0.001)
A–A	3.174	B_1–D_3	3.377
A–B_1	3.058	B_2–D_1	1.649
A–B_2	3.023	B_2–D_2	2.011
B_1–B_2	2.622	B_2–D_3	1.473
B_1–B_1	4.270	D_1–D_1	2.286
B_2–B_2	2.595	D_1–D_2	1.356
A–D_1	1.727	D_1–D_3	2.264
A–D_2	1.589	D_2–D_2	1.589
A–D_3	2.274	D_2–D_3	1.342
B_1–D_1	1.694	D_3–D_3	2.504
B_1–D_2	2.734		

* $A=Ti_{0.89}Zr_{0.11}$, $B_1=Mn_{0.39}V_{0.61}$, $B_2=Mn_{0.85}Ti_{0.15}$

phase are summarised in Table 2. Interatomic distances are presented in Table 3.

4. Conclusions

The analysis of alloy and deuteride structure performed in this work as well as the reference data allows to draw a conclusion, that the set of sites in hexagonal Laves phase structure which are occupied by deuterium is a stable one and does not depend on temperature or alloy composition (Table 4). In all cases the $[A_2B_2]$ sites occupied by deuterium—*24(l)*, *12(k)$_1$*, *6(h)$_1$* and *6(h)$_2$*, contain maximum numbers of A-component, which is active to hydrogen. However, equal occupation is not observed in any case.

Nevertheless, it is possible to make an assumption, that in the intermetallic hydrides, where a considerable part of hydrogen-inactive B-atoms is substituted by hydride-forming metal, the occupancy factor for the *24(l)* site is higher.

Acknowledgements

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Table 2
Structural parameters for $Ti_{0.9}Zr_{0.1}Mn_{1.5}V_{0.3}Ti_{0.2}D_{2.8}$

Atom	Atom positions	Crystal parameters at different temperature					
		295 K			17 K		
		Coordinates	Occupancy	B (Å^2)	Coordinates	Occupancy	B (Å^2)
Ti:Zr	*4(f)* 1/3, 2/3, *z*	$z=0.072(2)$	0.88(1):0.12(1)	1.5	$z=0.058(2)$	0.89(2):0.11(1)	1.5
Mn:V	*2(a)* 0, 0, 0		0.39(1):0.61(1)	1.5		0.39(1):0.69(1)	1.5
Mn:Ti	*6(h)* *x*, 2*x*, 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(l)* *x*, *y*, *z*	$x=0.089(4)$ $y=0.391(3)$ $z=0.565(4)$	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(k)$_1$* *x*, 2*x*, *z*	$x=0.472(6)$ $z=0.607(3)$	0.23(3)	2.0	$x=0.499(2)$ $z=0.593(7)$	0.29(4)	2.0
D_3	*6(h)$_1$* *x*, 2*x*, 1/4	$x=0.444(8)$	0.17(4)	2.0	$x=0.507(5)$	0.11(3)	2.0
Ref. composition		$Ti_{0.89}Zr_{0.11}Mn_{1.47}V_{0.31}Ti_{0.22}D_{2.8}$			$Ti_{0.89}Zr_{0.11}Mn_{1.47}V_{0.3}Ti_{0.23}D_{2.79}$		
Cell parameters (Å)		$a=5.228(2)$ $c=8.553(3)$ $V=202.7$			$a=5.232(1)$ $c=8.540(3)$ $V=201.8$		

Table 4
Deuterium occupation of sites in the AB_2 hexagonal structures

Deuteride	Sites and their occupancy							Ref.
	$[A_2B_2]$				$[AB_3]$		$[B_4]$	
	24(l)	*12(k)$_1$*	*6(h)$_1$*	*6(h)$_2$*	*12(k)$_2$*	*4(f)*	*4(e)*	
$ZrMoFeD_{2.6}$	0.275		0.63					[5]
$ZrVFeD_{3.6}$	0.312	0.275	0.530			0.1		[6]
$ZrVCuD_{4.0}$	0.342		1.0			0.175		[6]
$ZrVNbD_{5.4}$	0.25	0.792		0.917	0.05			[6]
$ZrMn_2D_{3.0}$	0.179	0.376	0.312	0.052				[7]
$ZrMn_2D_{3.04}$	0.211	0.372	0.369	0.079				[2]
$ZrMn_{2.5}D_{2.32}$	0.164	0.278	0.298	0.045				[2]
$ZrMn_{2.75}D_{2.12}$	0.14	0.247	0.286	0.045				[2]
$TiFe_{1.16}V_{0.84}D_{1.9}$	0.238			0.29				[8]
$TiV_{0.75}Mn_{1.12}D_{2.36}$	0.212	0.199	0.238			0.239		[3]
$TiAl_{0.4}Mn_{1.6}D_{2.5}$	0.25	0.23	0.32	0.07				[9]
$TiV_{0.4}Mn_{1.6}D_{3.5}$	0.25	0.43	0.33	0.19				[9]
$(Hf_{0.7}Ti_{0.3})(Ni_{0.5}V_{0.5})_2D_{2.2}$	0.304			0.23				[10]
$ZrCoVD_{3.4}$	0.403	0.226	0.187	0.02				[11]
$TiMn_{1.5}D_{3.13}$	0.223	0.386	0.22	0.204				[1]
$Zr_{0.642}Mn_{0.358}(Mn_{1.519}Fe_{0.471})D_{1.52}$	0.167	0.056	0.233	0.013				[12]
$Zr_{0.749}Mn_{0.251}(Mn_{1.487}Fe_{0.512})D_{4.08}$	0.236	0.388	0.527	0.468				[12]
$Zr(Cr_{0.6}Ni_{0.4})_2D_{3.3}$	0.257	0.334	0.128	0.382				[13]
$Zr(Cr_{0.6}Fe_{0.4})_2D_{2.5}$	0.202	0.329	0.05	0.359				[14]
$Zr(Cr_{0.6}Fe_{0.4})_2D_{2.97}$	0.227	0.327	0.09	0.372				[14]
$Zr(Cr_{0.25}Fe_{0.75})_2D_{2.2}$	0.156	0.274	0.027	0.318				[14]
$Zr(Cr_{0.25}Fe_{0.75})_2D_{2.5}$	0.177	0.288	0.033	0.323				[14]
$Ti_{0.89}Zr_{0.11}Mn_{1.47}V_{0.31}Ti_{0.22}D_{2.8}$	0.31	0.23	0.168					This work

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