

STRUCTURE OF $Ti_{0.9}Zr_{0.1}Mn_{1.5}V_{0.3}Ti_{0.2}D_{2.8}$

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Abstract

The structure of $Ti_{0.9}Zr_{0.1}Mn_{1.5}V_{0.3}Ti_{0.2}$ alloy and its deuteride was studied using methods of X-ray analysis and time-of-flight neutron diffraction (TOFND). The refinement of diffraction profiles was performed using Rietveld method. The refinement of the diffraction profile of the starting alloy showed, that the vanadium atoms are situated in 2(a) sites and titanium atoms in 6(h) sites. That 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 R-factor showed that the best fit is achieved for the model of deuterium location in 3 sites, 24(l), 12(k), and 6(h). However, at low temperature approximately 0.11 deuterium atoms relocate from 24(l) to 12(k) position. The analysis of alloy and deuteride structure obtained 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.

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 $TiMn_{1.5}D_{1.15}$ [1], $ZrMn_{2.5}$ [2] and $TiMn_{1.12}V_{0.3}D_{1.9}$ [3].

In present work we studied the structure of nonstoichiometric $(\text{Ti}_{0.9}\text{Zr}_{0.1})(\text{Mn}_{0.75}\text{V}_{0.15}\text{Ti}_{0.1})_2$ and its deuteride.

2. Experimental part

The structure of alloy and its deuteride was studied using methods of X-ray analysis and time-of-flight neutron diffraction (TOFND). The refinement of diffraction profiles was performed using Rietveld method. The main goal was to solve the structure of AB_2 Laves phase in which A-components is presented by two atoms ($\text{A}=\text{Ti}_{0.9}\text{Zr}_{0.1}$) and B-component – by three atoms ($\text{B}=\text{Mn}_{0.75}\text{V}_{0.15}\text{Ti}_{0.1}$), that is to determine the occupancy of A-sites by titanium and zirconium, and, secondly, to determine whether the distribution of manganese and vanadium atoms in B^1 and B^2 sites is random or ordered. All possible positions of atoms were considered while refinement procedure.

It should be noted, that the alloy structure is rather difficult to refine. This is due to the practically equal values of amplitudes of coherent diffusion of neutrons for titanium and manganese ($b_{\text{Ti}}=3.438 \cdot 10^{-12}$ cm, $b_{\text{Mn}}=3.73 \cdot 10^{-12}$ cm) which makes it impossible to distinguish these two atoms in the same position.

3. Results and discussion

The refinement of the diffraction profile of the starting alloy showed, that the vanadium atoms are situated in 2(a) sites and titanium atoms in 6(h) sites. Fig. 1 and 2 show the X-ray and neutron diffraction patterns together with refined calculated profiles.

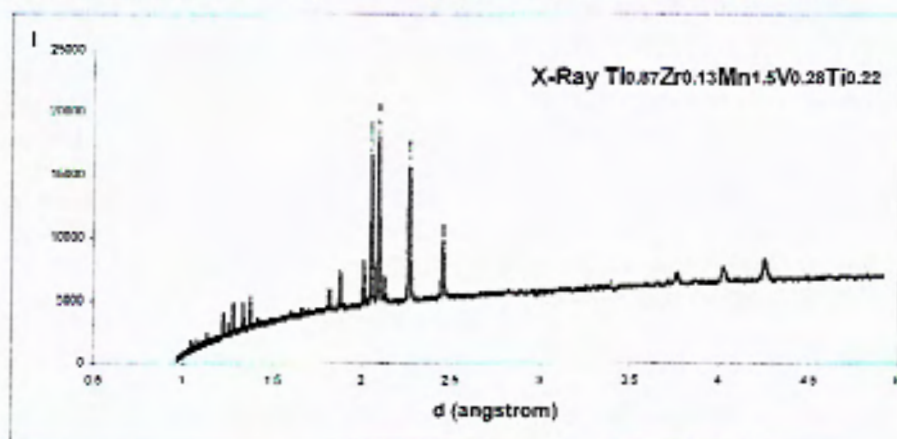


Figure 1. X-ray diffraction pattern of the starting alloy

The results obtained by X-ray and TOFND – cell parameters, atom coordinates, thermal factors, shown in Table 1 are in good agreement between each other. The refined composition also fits well to that obtained from electron-probe microanalysis.

The structure of deuteride phase was studied by TOFND. The obtained data shows that introduction of hydrogen does not change the metal matrix structure and the

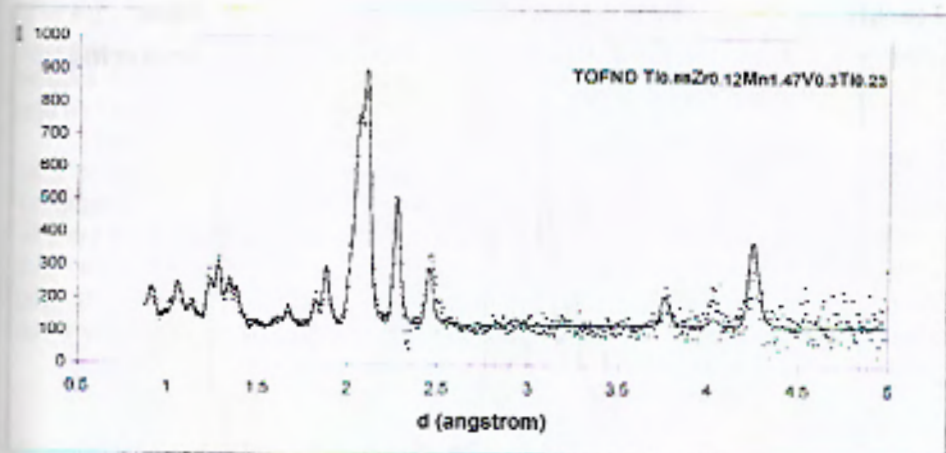


Figure 2. TOFND patterns of starting alloy

TABLE I. Structural parameters for $Ti_{0.88}Zr_{0.12}Mn_{1.47}V_{0.3}Ti_{0.23}$

Method	X-ray	TOFND
cell parameters (Å)	a=4,915	a=4,906
	c=8,056	c=8,062
	V=168.57	V=168.30
A-component		
4f (1/3,2/3,z)	z=0.0639	z=0.059
Ti:Zr	0.87:0.13	0.88:0.12
thermal factor (Å ²)	0.5	1.5
B-component		
2a (0,0,0)		
Mn:V	0.425:0.572	0.392:0.608
thermal factor (Å ²)	0.5	1.5
6h (x,2x,1/4)	x=0.830	x=0.827
Mn:Ti	0.85:0.15	0.85:0.15
Thermal factor (Å ²)	0.5	1.5
Refined composition	$Ti_{0.87}Zr_{0.13}(Mn_{1.49}V_{0.29}Ti_{0.22})$	$Ti_{0.88}Zr_{0.12}(Mn_{1.47}V_{0.3}Ti_{0.23})$

hydriding is accompanied by isotropic increase of cell volume by 20%. So, the pattern exhibits the same diffraction maximums, which positions and intensities are somewhat changed due to the increase of cell parameters and contribution of deuterium atoms (Fig.3).

The comparison of the diffraction patterns obtained at 295 K for alloy and its deuteride in the same conditions shows the appearance of so-called "halo" in the case of deuteride phase (Fig.3). This can be connected with the formation of short range order in deuteride phase thus attesting some ordering in the range of interstitial distances

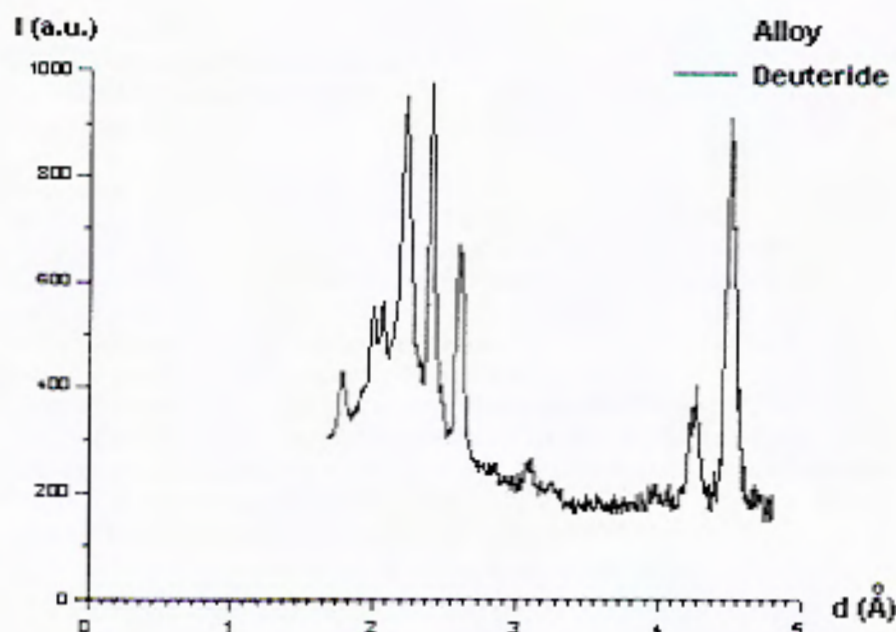


Figure 3 TOFND for deuteride phase with 'halo'

Table 2. Structural parameters for $Ti_{0.89}Zr_{0.11}Mn_{1.47}V_{0.11}Ti_{0.22}D_{2.8}$

Atom s	Atom positions	Crystal parameters at different temperature					
		295K			17K		
		Coord.	Occupancy	B (\AA^2)	Coord.	Occupancy	B (\AA^2)
Ti:Zr	4f 1/3,2/3,z	z=0.0721	0.89:0.11	1.5	z=0.0576	0.892:0.108	1.5
Mn:V	2a 0,0,0		0.387:0.613	1.5		0.392:0.608	1.5
Mn:Ti	6h x,2x,1/4	x=0.824	0.85:0.15	1.5	x=0.832	0.85:0.15	1.5
D ₁	24i x,y,z	x=0.089 y=0.391 z=0.565	0.310	2.0	x=0.149 y=0.356 z=0.558	0.291	2.0
D ₂	12k ₁ x,2x,z	x=0.472 z=0.607	0.230	2.0	x=0.499 z=0.593	0.294	2.0
D ₃	6h ₁ x,2x,1/4	x=0.444	0.168	2.0	x=0.507	0.114	2.0
Ref. composition		$Ti_{0.89}Zr_{0.11}Mn_{1.47}V_{0.11}Ti_{0.22}D_{2.8}$			$Ti_{0.89}Zr_{0.11}Mn_{1.47}V_{0.11}Ti_{0.22}D_{2.79}$		
Cell parameters (\AA)		a=5.228 c=8.553 V=202.7			a=5.232 c=8.540 V=201.8		

$\bar{d} = 3.24 \text{ \AA}$. 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.

The Laves phase hexagonal structure is characterised by 7 types of tetrahedral sites suitable for hydrogen occupation. They are shown in Fig.4. Since the alloy composition is nonstoichiometric one, it is rather difficult to determine the dimensions of these sites and to assume, which one will be 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 most unfavourable for hydrogen occupation. In fact, the attempt to locate deuterium atoms in these sites gave the zero or negative occupancy while refinement.

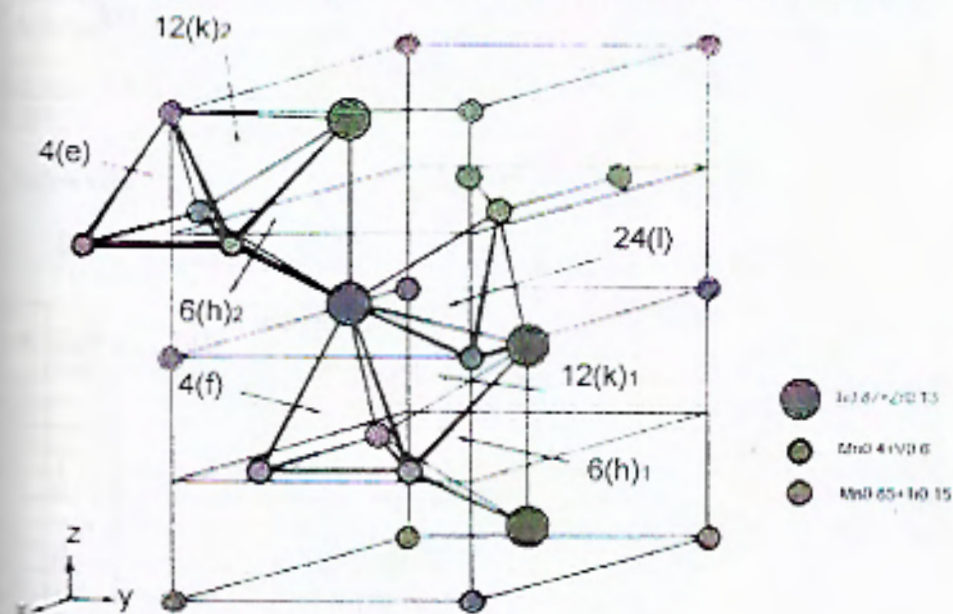


Figure 4. Interstitial sites in C14 Laves phase.

The minimisation of R-factor showed that the best fit is achieved for the model of deuterium location in 3 sites, 24(l), 12(k)₁ and 6(h)₁. However, at low temperature approximately 0.11 deuterium atoms relocate from 24(l) to 12(k)₁ position. It is interesting that the same reordering at 80 K ($-0.25D$) was found for $TiMn_{1.5}D_1$ [1]. The structural parameters of deuteride phase are summarised in Table 2. The interatomic distances are presented in Table 3.

Table 3. Interatomic distances for $Ti_{1-x}Zr_xMn_{1-y}V_xTi_{1-y}D_{2x}$ *

Atoms	d (Å)	Atoms	d (Å)
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_{1-x}Zr_x, B₁=Mn_{1-y}V_y, B₂=Mn_{1-y}V_y.Table 4. Deuterium occupation of sites in the AB₂ hexagonal structures.

Deuteride	Sites and their occupancy							Ref.
	[A ₂ B ₁]				[AB ₂]		[D ₂]	
	2d	12k ₁	6h ₁	6h ₂	12k ₂	4f	4c	
ZrMnFeD _{2.6}	0.275		0.63					[5]
ZrVFeD _{2.6}	0.312	0.275	0.530			0.1		[6]
ZrVCuD _{2.4}	0.342		1.0			0.175		[6]
ZrVNiD _{2.4}	0.25	0.792		0.917	0.05			[6]
ZrMnD _{2.0}	0.179	0.376	0.312	0.052				[7]
ZrMnD _{2.02}	0.211	0.372	0.369	0.079				[2]
ZrMn _{0.9} D _{2.02}	0.164	0.278	0.298	0.045				[2]
ZrMn _{0.8} D _{2.02}	0.14	0.247	0.286	0.045				[2]
TiFe _{1.15} V _{0.21} D _{1.9}	0.238			0.29				[8]
TiV _{0.98} Mn _{0.12} D _{1.9}	0.212	0.199	0.238			0.239		[3]
(Ti _{0.7} Y _{0.1})(Ni _{0.4} V _{0.1})D _{1.9}	0.304			0.23				[9]
ZrCoVD _{1.9}	0.403	0.226	0.187	0.07				[10]
TaMo _{1.5} D _{1.9}	0.223	0.386	0.22	0.204				[11]
Zr _{0.82} Mn _{0.18} (Mn _{0.12} Fe _{0.1})D _{1.92}	0.167	0.056	0.233	0.0129				[11]
Zr _{0.78} Mn _{0.22} (Mn _{0.22} Fe _{0.11})D _{1.93}	0.236	0.383	0.527	0.468				[11]
Zr(Cr _{0.2} Ni _{0.1})D _{1.9}	0.257	0.334	0.128	0.387				[12]
Zr(Cr _{0.4} Fe _{0.1})D _{1.9}	0.202	0.329	0.05	0.329				[13]
Zr(Cr _{0.6} Fe _{0.1})D _{1.9}	0.227	0.327	0.09	0.372				[13]
Zr(Cr _{0.8} Fe _{0.1})D _{1.9}	0.156	0.274	0.027	0.318				[13]
Zr(Cr _{0.9} Fe _{0.1})D _{1.9}	0.177	0.288	0.033	0.323				[13]
Ti _{0.22} Zr _{0.11} Mn _{0.67} V _{0.1} Ti _{0.27} D _{1.9}	0.31	0.23	0.168					this work

4. Conclusions

The analysis of alloy and deuteride structure obtained 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 [A2B2] sites occupied by deuterium - 24(l), 12(k)₁, 6(h)₁ and 6(h)₂, contain maximum number 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 24(l) site is higher.

5. Acknowledgement

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6. References

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