CRYSTAL STRUCTURE ANALYSIS OF $Ti_{4-x}Zr_xFe_2O_y$ DEUTERIDES

Zavaliy I.Yu., Denys R.V., Koval'chuck I.V., Delaplane R.G.[1], Marchuk I.[2]

(1) Physico-Mechanical Institute of NAS of Ukraine, 5 Naukovaz Str., 79601 Lviv, Ukraine
Studsvik Neutron Research Laboratory, Uppsala University, SE-611 82 Nyköping, Sweden
(2) Institute of Physical Chemistry, PAS, Warsaw, Poland

Introduction

The $Zr_4Fe_2O_x$ and $Ti_4Fe_2O_x$ oxygen-stabilised η-phases with the filled-Ti_2Ni type of crystal structure show interesting hydrogenation properties. The hydrogenation behaviour of Zr_2Fe ($CuAl_2$-type) and η-$Zr_4Fe_2O_{0.6}$ compounds is considerably different with respect to their disproportionation; both are characterised by getter properties during the interaction with hydrogen and other active gases. In contrast, $Ti_{4-x}Fe_{2+x}O_y$ alloys behave as typical materials for reversible hydrogen storage and are characterised by enhanced activation in comparison with oxygen-free Ti-Fe alloys. It has been shown that $(Zr,Ti)_4Ni_2O_{0.3}$ alloys annealed at 1000°C contain the η-phase with the filled Ti_2Ni-type of structure as dominant in the whole range of substitution [1]. In our work the continuous solid solution between Ti- and Zr-based η-phases was determined also in the Ti-Zr-Fe-O system. The synthesised deuterides $Ti_{4-x}Zr_xFe_2O_{(0.3\text{-}0.5)}$ have been investigated by neutron diffraction to determine the distribution of deuterium atoms depending on the Ti/Zr ratio and to explain the peculiarities of hydrogenation properties.

Results and discussion

We prepared the samples with the different Ti/Zr ratios: $Ti_4Fe_2O_{0.5}D_{3.5}$, $Ti_3ZrFe_2O_{0.3}D_{6.4}$, $Ti_2Zr_2Fe_2O_{0.5}D_{5.8}$, $TiZr_3Fe_2O_{0.3}D_{7.3}$, $Zr_4Fe_2O_{0.5}D_{8.1}$. The deuterides were synthesised by deuterium gas charging. Their absorption capacity has been determined by a standard volumetric technique. Powder neutron diffraction data were collected on the NPD (λ=1.47 Å) and R2D2 (λ=1.55 Å) instruments at the Studsvik Neutron Research Laboratory. Obtained neutron diffraction data were refined (for some deuterides jointly with X-ray diffraction data) by the Rietveld method using GSAS software. The observed, calculated and difference profiles of the $Ti_4Fe_2O_{0.5}D_{3.5}$ and $Ti_2Zr_2Fe_2O_{0.5}D_{5.8}$ deuterides are shown as an examples in Fig.1 (a, b), respectively. The crystallographic data for both compounds are collected in the Table 1.

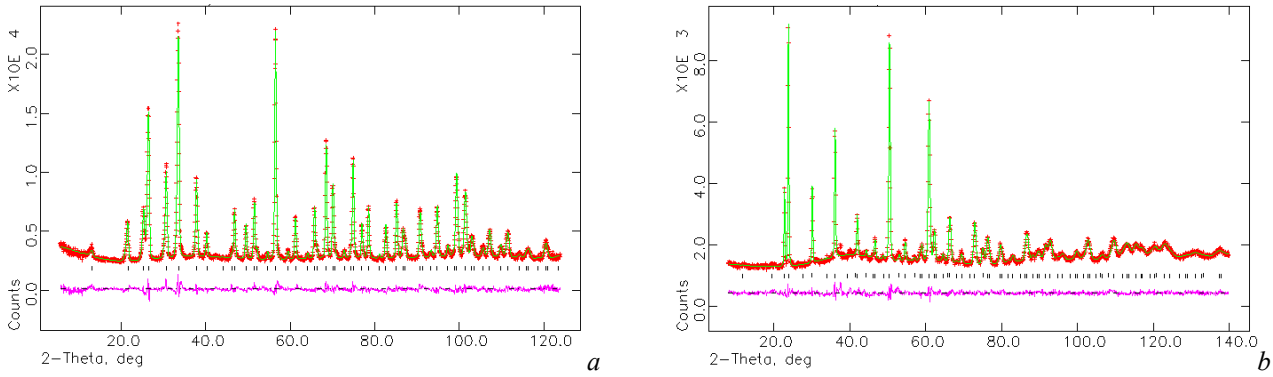

Fig. 1. The observed (+), calculated (line) and difference (lower line) neutron powder diffraction profiles for (a) $Ti_4Fe_2O_{0.5}D_{3.5}$ and (b) $Ti_2Zr_2Fe_2O_{0.5}D_{5.8}$

Table 1. Crystallographic data for $Ti_4Fe_2O_{0.5}D_{3.5}$ and $Ti_2Zr_2Fe_2O_{0.5}D_{5.8}$

Atom	Site	$Ti_4Fe_2O_{0.5}D_{3.5}$: sp. gr. *Fd3m*; *a*=11.6838(1) Å					$Ti_2Zr_2Fe_2O_{0.5}D_{5.8}$: sp. gr. *Fd3m*; *a*=12.2982(3) Å				
		x	*y*	*z*	U_{iso}×100	SOF	*x*	*y*	*z*	U_{iso}×100	SOF
*M1	48*f*	0.3166(2)	1/8	1/8	1.22(7)	1.0(–)	0.3143(5)	1/8	1/8	0.9(2)	1.0(–)
Ti2	16*d*	1/2	1/2	1/2	4.2(2)	1.0(–)	1/2	1/2	1/2	0.9(3)	1.0(–)
Fe	32*e*	0.70651(6)	0.70651(6)	0.70651(6)	0.92(3)	1.0(–)	0.7010(1)	0.7010(1)	0.7010(1)	1.42(8)	1.0(–)
O	16*c*	0	0	0	0.5(–)	0.553(6)	0	0	0	1.41(5)	0.54(3)
D1	32e_1	–	–	–	–	–	0.033(1)	0.217(1)	0.033(1)	2.6(1)	0.149(9)
T2	32e_3	–	–	–	–	–	0.062(4)	0.062(4)	0.062(4)	2.6(1)	0.048(9)
D2	192*i*	0.500(1)	0.560(2)	0.355(2)	1.5(–)	0.034(2)	0.4806(7)	0.5675(7)	0.3621(6)	2.6(1)	0.201(5)
D3	96g_1	0.2799(1)	0.2799(1)	0.1524(2)	1.3(1)	0.437(5)	0.4690(4)	0.4690(4)	0.1554(5)	2.6(1)	0.434(7)
D7	8*a*	1/8	1/8	1/8	3.7(2)	1.00(1)	1/8	1/8	1/8	5.7(6)	0.81(4)

*M1= Ti for $Ti_4Fe_2O_{0.5}D_{3.5}$ and M1= 0.331(7) Ti + 0.669(7) Zr for $Ti_2Zr_2Fe_2O_{0.5}D_{5.8}$.

The observed volumetric data showed a decrease of hydrogen storage capacity with the rise in oxygen content in the studied compounds, and the contrary, the increase of H-capacity with increase of the Zr/Ti ratio. We present in Table 2 the distribution of D-atoms among the interstitial sites and total number of deuterium atoms per unit cell for all studied deuterides in this work. We also included the literature values for $Ti_4Fe_2OD_{2.25}$ [2] and $Zr_4Fe_2O_{0.25}D_{9.9}$ [3] deuterides for comparison. In general the analysed deuterides retained the initial cubic Ti_2Ni-type of structure of metal matrix with the unit-cell volume expanded by 13-17%, which corresponds to 2.3-2.5 Å^3 per absorbed D atom. However, the authors of [3] observed some distortions of the metal matrix in the $Zr_4Fe_2O_{0.25}D_{9.9}$ deuteride, and therefore we can observe in the table below some peculiarities of D-distribution for this compound in comparison with others.

Deuterium atoms in all studied deuterides partially occupy 2 types of $(Zr,Ti)_3Fe$ tetrahedra (192*i* and 96*g*). These interstices accumulate most of the D-atoms. The $(Zr,Ti)_6$ octahedra are occupied for Ti-based compounds up to composition $Ti_2Zr_2Fe_2O_{0.5}$. On the contrary, D1-site surrounded by other $(Zr,Ti)_3Fe$ tetrahedron (or T1 and T2 sites on $(Zr,Ti)_3$ triangular face of this tetrahedron) is occupied only for Zr-rich compounds and this occupation increases with the increase of Zr-content. Commonly, the occupancy and distribution of D-atoms in the structure of the studied deuterides depends strongly on the Zr:Ti ratio and oxygen content. We also found the hydrogen-induced redistribution of oxygen atoms between different types of $(Zr,Ti)_6$ octahedra in the $TiZr_3Fe_2O_{0.3}D_{7.3}$ and $Zr_4Fe_2O_{0.5}D_{8.1}$ deuterides. A similar phenomenon was observed recently for $Zr_3NiO_xD_y$ and $Zr_3V_3O_xD_y$ deuterides.

Table 2. Occupation of various interstitial sites by deuterium atoms in $Ti_{4-x}Zr_xFe_2O_y$ deuterides

Deuterium sites	Coordination	Number of deuterium atoms per unit cell						
		$Ti_4Fe_2OD_{2.25}$	**$Ti_4Fe_2O_{0.5}D_{3.53}$**	**$Ti_3ZrFe_2O_{0.3}D_{6.4}$**	**$Ti_2Zr_2Fe_2O_{0.5}D_{5.82}$**	**$TiZr_3Fe_2O_{0.3}D_{7.3}$**	**$Zr_4Fe_2O_{0.5}D_{8.1}$**	$Zr_4Fe_2O_{0.25}D_{9.9}$
D1 in 32e_1	$M1_3Fe$	–	–	–	**4.77**	–	**21.66**	22.11
T1 in 32e_2	$M1_3$	–	–	–	–	**16.96**	**7. 2**	6.46
T2 in 32e_3	$M1_3$	–	–	**5.12**	**1.54**	**2.69**	**11.94**	–
D2 in 192*i*	$M1_2M2Fe$	18.72	**6.53**	**21.89**	**38.59**	**35.33**	**58.75**	49.92
D3 in 96g_1	M_3Fe	8.72	**41.95**	**68.93**	**41.66**	**61.44**	**27.36**	45.02
D4 in 96g_2	$M1M2Fe_2$	–	–	–	–	–	–	6.86**
D5 in 8*b*	Fe_4	–	–	–	–	–	–	2.08
D6 in 32e_4	$M1Fe_3$	–	–	–	–	–	–	–
D7 in 8*a*	$M1_6$	8	**8**	**5.76**	**6.48**	–	–	–
D8 in 16*c*	$M1_6$	–	–	–	–	–	–	–
Total		35.44	**56.48**	**101.70**	**93.04**	**116.42**	**126.91**	132.45

* M corresponds to Ti and/or Zr;
** this site occupation corresponds to 48(f) position (0.7795,1/8,1/8), which is occupied only in $Zr_4Fe_2O_{0.25}D_{9.9}$.

Conclusions

The crystal structure of several saturated deuterides of oxygen-modified intermetallic compounds $(Ti,Zr)_4Fe_2O_x$ (x=0.3; 0.5) has been investigated by both X-ray and neutron powder diffraction. The distribution of D-atoms in the metal matrix has been determined and analysed in function of the Ti/Zr and oxygen content. The obtained crystallographic data were compared with the structural results for other oxygen-stabilised Ti/Zr-based η-phases.

Acknowledgements

Travel funds from the Visby Programme of the Swedish Institute are gratefully acknowledged. We thank H. Rundlöf and A. Wannberg for skilled assistance with data collection.

References

[1] Zavaliy I.Yu., Woicik G., Mlynarek G. *et al*. Phase-structural characteristics of $(Ti_{1-x}Zr_x)_4Ni_2O_{0.3}$ alloys and their hydrogen gas and electrochemical properties. J. Alloys Comp., **314**, 124 (2001).

[2] C.Stioui, D.Fruchart, A. Rouaut *et al.*, Crystal structure of the $Ti_4Fe_2OD_{2.25}$ deuteride. Mat. Res. Bull. **16**, 869 (1982).

[3] I.Yu. Zavaliy, A.O. Pecharsky, R. Cerny, *et al*. Crystal structure and properties of $Zr_4Fe_2O_xH_y$. Proc. of 20-th European Crystallographic Meeting (ECM'2001), Krakow, 2001, p.304.