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Structural study of hyperstoichiometric alloys $ZrMn_{2+x}$ and their hydrides

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Abstract

A neutron diffraction study of selected "hyperstoichiometric" alloys in the system $ZrMn_{2+x}$ and of their corresponding hydrides (deuterides) is presented. Mn–Zr substitution as well as the hydrogen location and distribution have been carefully analysed. Some questionable features are discussed in the light of additional experiments such as quantitative X-ray analysis.

1. Introduction

The Laves-phase-type compound $ZrMn_2$ is known to absorb a significant amount of hydrogen, leading to a very stable hydride which is not technologically interesting. Since a fair reversibility is required for storage applications, "hyperstoichiometry" has been designed as a route to modulate the dissociation pressure of the hydrides.

In spite of the various studies devoted to this class of compounds, no detailed structural characterization is so far available regarding "hyperstoichiometric" compounds of either system (alloy or hydride). The models for substitution were mainly based upon routine X-ray characterization, which showed that the substituted compounds retain the C14 structure, and the conclusion that the "hyperstoichiometric" manganese replaces zirconium was established from density measurements on the $ZrMn_{2+x}$ alloys [1, 2].

In the course of a study on the scope of these hyperstoichiometric compounds and their hydrides [3], it appeared, however, that a careful knowledge of the hydride structure was required in order to account for some features revealed by perturbed angular correlation (PAC) measurements [4]. The quadrupole-coupling parameters measured by PAC on the ^{181}Hf probe in substitution for zirconium indicated the existence of several distinct hafnium environments in the stoichiometric alloy $(Zr_{0.95}Hf_{0.05})Mn_2$. The local observations are therefore not consistent with what would be expected for

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a C14 hexagonal structure. Closely similar PAC spectra were measured in the hyperstoichiometric alloys $(Zr_{0.95}Hf_{0.05})Mn_{2+x}$ with $x=0.2$ and 0.4. The quadrupole spectrum relative to $HfMn_2$ was also found to be a mixture of different quadrupole couplings. These results suggest that local deviations of the average composition and/or C14 structure may occur.

We have thus undertaken a structural study of some $ZrMn_{2+x}$ compounds and their corresponding hydrides by means of neutron powder diffraction.

2. Experimental details

The starting elements (3N purity) were melted in a high frequency induction furnace and subsequently annealed in evacuated fused silica tubes at temperatures of about 900 °C. The nominal compositions $ZrMn_{2+x}$ with $x=0.5$ and 0.75 were thus prepared. A slight amount of hafnium was incorporated in order to reach the composition $(Zr_{0.95}Hf_{0.05})Mn_{2+x}$. This hafnium substitution was required for the spectroscopy experiments that were carried out in the meantime using the PAC technique; in such experiments hafnium acts as a quadrupolar probe sensitive to the electric field gradient created by the asymmetric charge environment.

The X-ray patterns revealed single-phase materials; however, the patterns corresponding to "hyperstoichiometric" alloys exhibited a significant broadening despite the heat treatment. Half of each sample batch was then hydrogenated. Hydrogenation (deuteration) was performed at room temperature and at pressures ranging from 32 to 50 bar in designed stainless steel autoclaves.

Attempts to initiate low pressure reactions were unsuccessful even after thermal activation up to 300 °C. It is our knowledge that such reactions can actually be initiated depending on the sample surface quality. The deuterium uptake was determined by volumetric and gravimetric methods. The rather exothermal reactions led to fully deuterated compounds with no X-ray-detectable unreacted α phase.

The neutron diffraction experiments were carried out at the Institut Laue–Langevin on the high resolution diffractometer D2B operating at $\lambda=1.594$ Å. The diffraction patterns were recorded in the 2Θ range 6°–150° and were analysed using conventional profile refinement methods [5]. In the case of deuterated compounds, profile fitting was eventually performed using a modified Rietveld version which can take into account modulations of the background [6].

Further characterizations of the local chemical composition were carried out by X-ray fluorescence analysis using a Kevex probe attached to a Philips EM400T transmission electron microscope.

3. Results

3.1. *Structural parameters for $ZrMn_{2+x}$ alloys*

The structural refinements carried out on the starting alloys have confirmed that they retain the C14 structure and that the "hyperstoichiometric" manganese substitutes at the zirconium sites. Since only 5% atomic hafnium is accommodated in the zirconium sites and since the respective scattering lengths [7] are close to one another ($b_{Zr}=0.716$ fm, $b_{Hf}=0.777$ fm), it was not possible to distinguish hafnium from zirconium; attempts to do so did not yield significant improvements and increased the number of refined parameters instead.

The refined lattice parameters of "hyperstoichiometric" compounds were found to fall right on the early curve determined by Van Essen and Buschow [8], which shows the lattice parameter variation *vs.* the manganese concentration in the $ZrMn_{2+x}$ compounds. We report the neutron diffraction results in Table 1. We have confirmed that hyperstoichiometry corresponds to a substitution of manganese atoms on zirconium sites.

3.2. *Structural parameters for $ZrMn_{2+x}D_y$ samples*

In the deuterated compounds deuterium was located in the A_2B_2 tetrahedral holes of the C14 structure and in the AB_3 interstitial sites. The diffraction patterns corresponding to the deuterated compounds exhibited a wavy background, the modulation of which involves a distance of the order of 2.1 Å, which is roughly the H–H minimum distance of simultaneously occupied interstitial sites (Fig. 1).

In the stoichiometric $ZrMn_2D_y$ compound the distribution found by Didisheim *et al.* [9] was confirmed. It is worth emphasizing the remarkable agreement between the results presented herein and those from ref. 9 even though the preparation differs (the low pressure route was used in ref. 9).

It can be seen from Table 2 that in the deuterated "hyperstoichiometric" compounds the deuterium location is almost the same, with only minor changes in the distribution among the various sites. Attempts to accommodate deuterium in AB_3-type sites ($ZrMn_3$ tetrahedra) led to negative occupancy

TABLE 1

Refined structural parameters for the starting alloys (space group $P6_3/mmc$)

Formula	$Zr_{0.95}Hf_{0.05}Mn_{2.5}$	$Zr_{0.95}Hf_{0.05}Mn_{2.75}$
Cell parameters	$a=5.0210(7)$ Å $c=8.2526(9)$ Å	$a=5.0061(5)$ Å $c=8.2251(2)$ Å
Zr:Mn $4f$ ($\frac{1}{3}$, $\frac{2}{3}$, z)	0.860Zr + 0.140Mn $z=0.0625(3)$ $B=0.74(5)$ Å^2	0.801Zr + 0.199Mn $z=0.0632(2)$ $B=0.94(3)$ Å^2
Mn $2a$ (0, 0, 0)	$B=1.13(7)$ Å^2	$B=0.64(4)$ Å^2
Mn $6h$ (x, $2x$, $\frac{1}{4}$)	$x=-0.01701(3)$ $B=1.13(7)$ Å^2	$x=0.01705(6)$ $B=0.64(4)$ Å^2
R_w (%)	2.1	3.2
Refined formula	$(Zr_{0.860}Mn_{0.140})Mn_2$ $\rightarrow ZrMn_{2.488}$	$(Zr_{0.801}Mn_{0.199})Mn_2$ $\rightarrow ZrMn_{2.745}$

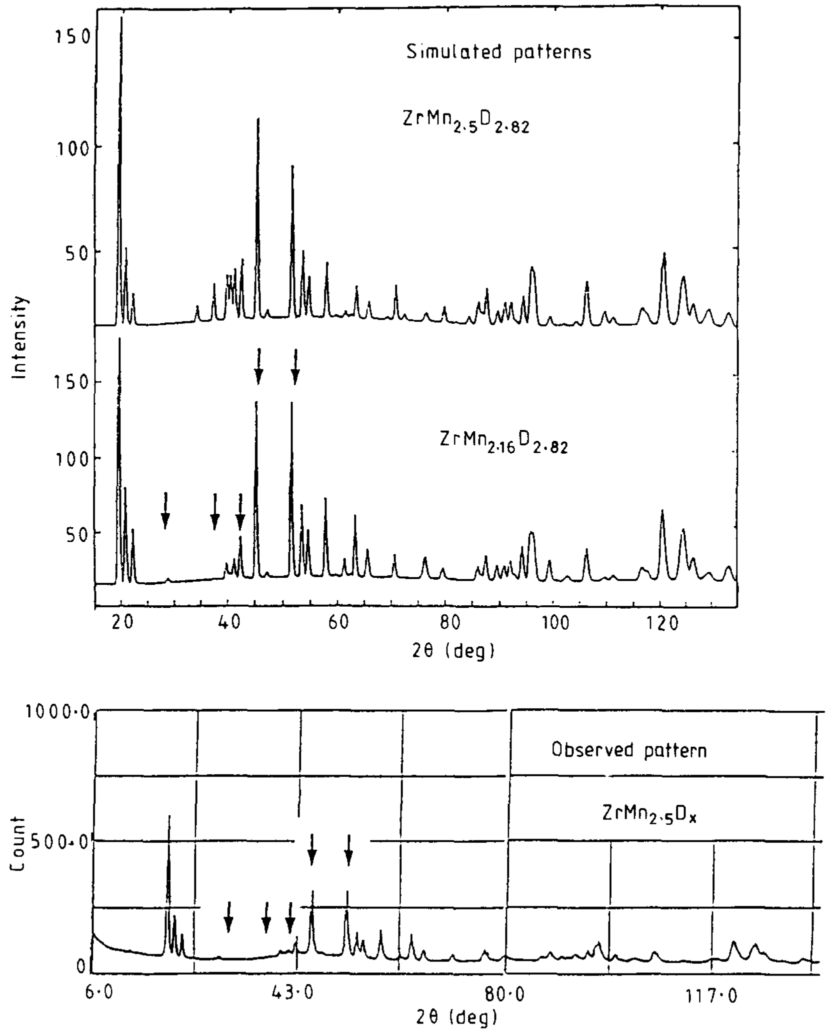

Fig. 1. Experimental neutron diffraction pattern of the deuteride with nominal composition $ZrMn_{2.5}D_x$ compared with calculated diffraction patterns for the compositions $ZrMn_{2.5}D_{2.82}$ and $ZrMn_{2.16}D_{2.82}$.

factors. Hydrogen accommodation of A_2B_2 sites in "hyperstoichiometric" compounds should not be surprising since they are the most attractive sites within the structure and because of the stronger binding of hydrogen to zirconium [10]; besides, "hyperstoichiometry" corresponds to a lowering of the zirconium concentration and therefore to a decrease in the chemical attractivity of the available sites in the structure.

It should be actually noted that throughout the refinements of the deuterated "hyperstoichiometric" compounds a large correlation between excess (hyperstoichiometric) manganese and deuterium occupancy developed:

TABLE 2

Refined structural parameters for the deuterated alloys (n is the occupancy factor)

Supposed formula	$Zr_{0.95}Hf_{0.05}Mn_2D_{3.26}$	$Zr_{0.95}Hf_{0.05}Mn_{2.5}D_{3.25}$		$Zr_{0.95}Hf_{0.05}Mn_{2.75}D_{3.10}$
Cell parameters	$a=5.4055(9)$ Å $c=8.7964(7)$ Å	$a=5.3889(10)$ Å $c=8.7660(11)$ Å		$a=5.3493(9)$ Å $c=8.6995(9)$ Å
Zr:Mn 4f ($\frac{1}{3}$, $\frac{2}{3}$, z)	Zr $z=0.0629(6)$ $B=0.6$ Å^2	0.85Zr+0.15Mn $z=0.0637(9)$ $B=0.6$ Å^2	Zr $z=0.0642(8)$ $B=0.6$ Å^2	0.772Zr+0.227Mn $z=0.0632(10)$ $B=0.6$ Å^2
Mn 2a (0, 0, 0)	Mn $B=1.1$ Å^2	Mn $B=1.1$ Å^2	Mn $B=1.2$ Å^2	Mn $B=1.4$ Å^2
Mn 6h (x, 2x, $\frac{1}{4}$)	$x=-0.1634(12)$ $B=1.1$ Å^2	$x=-0.1631(10)$ $B=1.1$ Å^2	$x=-0.1610(10)$ $B=1.1$ Å^2	$x=-0.1698(18)$ $B=1.1$ Å^2
D1 24l (x, y, z)	$x=0.0398(13)$ $y=0.3249(16)$ $z=0.5647(9)$ $B=1.5$ Å^2 $n=0.211(8)$	$x=0.0506(20)$ $y=0.3477(25)$ $z=0.5662(13)$ $B=1.5$ Å^2 $n=0.164(2)$	$x=0.0433(20)$ $y=0.3255(25)$ $z=0.5169(13)$ $B=1.5$ Å^2 $n=0.191(8)$	$x=0.0397(22)$ $y=0.3219(29)$ $z=0.5706(14)$ $B=1.5$ Å^2 $n=0.146(11)$
D2 12k (x, 2x, z)	$x=0.4594$ $z=0.6261$ $B=1.5$ Å^2 $n=0.372(6)$	$x=0.4524(30)$ $z=0.6352(16)$ $B=1.5$ Å^2 $n=0.278(2)$	$x=0.4633(13)$ $z=0.6263(12)$ $B=1.5$ Å^2 $n=0.353(6)$	$x=0.4478(30)$ $z=0.6254(10)$ $B=1.5$ Å^2 $n=0.247(8)$
D3 6h (x, 2x, $\frac{1}{4}$)	$x=0.4660(30)$ $B=1.5$ Å^2 $n=0.369(3)$	$x=0.4540(36)$ $B=1.5$ Å^2 $n=0.298(6)$	$x=0.4676(20)$ $B=1.5$ Å^2 $n=0.356(4)$	$x=0.4800(53)$ $B=1.5$ Å^2 $n=286(5)$
D4 6h (x, 2x, $\frac{1}{4}$)	$x=0.2021(30)$ $B=1.5$ Å^2 $n=0.079(3)$	$x=0.220$ $B=1.5$ Å^2 $n=0.045(9)$	$x=0.220$ $B=1.5$ Å^2 $n=0.061(5)$	$x=0.262$ $B=1.5$ Å^2 $n=0.045(6)$
Refined formula	$ZrMn_2D_{3.04}$	$Zr_{0.85}Mn_{0.15}Mn_2D_{2.32}$	$ZrMn_2D_{2.82}$	$Zr_{0.772}Mn_{0.227}Mn_2D_{2.12}$
R_w (%)	5.67	5.98	5.85	5.50
χ^2	2.8	3.5	3.0	8.0

besides, discarding the substituted manganese allowed us to better reconcile the refined deuterium concentration with that determined from volumetric measurements, which is generally found to be higher.

Table 2 allows us to compare the fully refined parameters with those refined while keeping the deuterium concentration fixed at the value determined by volumetric measurements. It is seen that for deuterated $ZrMn_{2.5}$ the refinements yield the formula $ZrMn_2D_{2.82}$ with a deuterium distribution very similar to that observed in $ZrMn_2D_3$.

As previously mentioned, the diffraction peaks were found to be rather broad and their linewidths could not be satisfactorily described using the diffractometer standard resolution function. In order to account for this feature, it was not possible to decide between a size or a strain effect; the latter effect would indicate a concentration distribution within a given sample.

3.3. Simulation of neutron diffraction patterns

Diffraction patterns corresponding to deuterated "hyperstoichiometric" compounds with a fixed deuterium amount and various manganese substitution rates have been simulated. It can be seen from Fig. 1 that the best agreement with the observed patterns (which looked pretty much alike) was obtained for the composition $ZrMn_{2.16}D_{2.82}$. In the figure the arrows point to the region of the diffraction pattern which is sensitive to the substitution rate: a set of peaks around 25°–40° as well as the relative intensities of the two major peaks in the 2Θ range 45°–55°.

3.4. Chemical analysis

In addition, a quantitative analysis was undertaken by means of energy-dispersive X-rays. Analysis of a "hyperstoichiometric" alloy with nominal composition $Zr_{0.95}Hf_{0.05}Mn_{2.4}$ yielded the atomic percentage ratio Zr:Hf:Mn = 28.34:1.47:70.19 (standard deviation 0.7%). Analysis of the corresponding deuterated compound was made a little more difficult owing to the powdery character of the sample. However, analysis of a large number of individual grains yielded the atomic percentage ratios Mn:Zr = 66.53:33.47 (standard deviation 0.7%); moreover, hafnium was hardly detectable in most grains. Since deuterium cannot be detected, it is seen that the individual grains of the analysed sample had a composition close to $ZrMn_2D_y$.

4. Discussion

The prepared samples lie in a composition range where the lattice parameters are very sensitive to the manganese concentration. It is observed that this is indeed the case for the starting alloys, whereas for the corresponding deuterides the refined lattice parameter values (as seen from Table 2) are merely scattered around a mean value. Actually, a more pronounced effect

TABLE 3

Derived deuterium uptake from volumetric considerations

Formula	ΔV (Å^3) relative to the alloy	D number per formula	ΔV (Å^3) relative to $ZrMn_2$	D number per formula
$ZrMn_2D_{3.26}$	40.48	3.16	40.48	3.16
$ZrMn_{2.5}D_{3.25}$	40.28	3.14	38.34	2.99
$ZrMn_{2.75}D_{3.10}$	37.04	2.90	33.48	2.61

Volume 1D(H) → 3.2 Å^3.

is expected in the case of hydrided compounds considering the nominal compositions.

It can be seen from Table 2 that the refined deuterium amount and distribution in the deuterated "hyperstoichiometric" compounds are almost the same, yielding a deuterium-induced volume increase that turns out to be mainly sample independent, as seen from Table 3 in which a comparison with $ZrMn_2$ is also provided.

Finally, the hydrogen-induced volume increase found in the hyperstoichiometric compounds compares well with that derived by considering stoichiometric $ZrMn_2$ as being the main absorber.

The lattice parameters reported in earlier works [1, 8] for the compounds $ZrMn_{2+x}H_{3.6}$ with $x = 0.8$ and 1.8 are roughly those observed for $ZrMn_2D_{3.04}$ and $ZrMn_{2.16}D_{2.82}$ respectively. This rather small variation in the lattice parameters has been generally attributed to a balance effect between the Zr–Mn substitution on one hand and hydrogen insertion on the other.

These rather puzzling features prompt us to surmise that hydrogen absorption at high pressures (50 bar) in "hyperstoichiometric" materials might lead to a disproportionation reaction resulting in $ZrMn_2H_x$ as the main constituent.

The question of whether such a behaviour is due to the high stability of $ZrMn_2D_3$ is still open. Furthermore, it is known that surface segregation may occur when hydriding such compounds in an oxygen-poisoned atmosphere [10].

5. Conclusions

This neutron diffraction study of selected $ZrMn_{2+x}H_y$ compounds has shown that hydrogenation of "hyperstoichiometric" alloys under gas pressures of about 50 bar is very similar to that of stoichiometric compounds. It is seen that accurate investigations carried out by various techniques such as neutron diffraction and fluorescence analysis yield converging hints suggesting that a disproportionation reaction might take place upon hydrogenation in which stoichiometric $ZrMn_2$ is the main hydrogen absorber.

In order to have a full understanding of this phenomenon, a forthcoming paper will be devoted to a metallographic study of these alloys.

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