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Neutron diffraction study of the new hexagonal Laves phase (Hf,Ti)(Ni,V)$_2$ and its deuteride

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Abstract

A new hexagonal C14 Laves phase hydrogen storage alloy and its deuteride has been studied with neutron diffraction. The new Laves phase precipitated as a second phase when a vanadium-based solid solution, $TiV_3Ni_{0.56}$, was alloyed with hafnium. From the structural refinements it was suggested that Hf is situated at the A site and Ni at the B sites. The Ti and V occupancy could not be ascertained, but from structural consideration of related alloys, supported by EDS analysis, we suggest that they occupy the A and B site, respectively. The deuterium atoms were located to mainly occupy one of the tetrahedral A_2B_2 interstices, resulting in the formula unit (Hf,Ti)(Ni,V)$_2$ D_2.

Keywords: Laves phase (Hf,Ti)(Ni,V)$_2$; Deuterium positions; Neutron diffraction

1. Introduction

Investigation of intermetallic compounds with respect to their hydrogen storage properties is important in the future development of rechargeable Ni–MH batteries. They have proved to have several advantages over conventional secondary batteries, such as high energy density, better durability against overcharge and overdischarge, and also being more environmental friendly.

So far mainly $MmNi_5$-based alloys have been used in conventional batteries. To improve the battery performance further, development of new systems (AB, AB_2 and A_2B) that fulfils the future demands on high power and low weight batteries with high capacity is in progress. Lately, the interest in AB_2 Laves-type systems has increased due to their higher capacity. Besides characterising the phases with respect to the battery performance, the crystallographic information, i.e. hydrogen sites and bonding features, can be helpful in the search for new metal hydrogen compounds.

We have in a previous paper [1] reported a new Laves phase alloy (Hf,Ti)(Ni,V)$_2$ precipitating when a vanadium-based solid solution, $TiV_3Ni_{0.56}$, was alloyed with hafnium. It was recently shown that V-based solid solutions can be applied in rechargeable Ni–MH batteries [2,3]. The theoretical storage capacity of the solid solutions are almost three times higher than AB_5 systems. Since activation and kinetics were inferior to conventional AB_5-type alloys, attempts were made to alloy with different metals. When hafnium was added, the activation and kinetics improved coincidentally with the appearance of the new Laves phase [1,4]. The new Laves phase hydride is very stable and it does not participate in the hydrogen–dehydrogen cycling. Its role is to improve the activation and kinetics for the V-based solid solution alloy $TiV_3Ni_{0.56}$ by forming a second hydride phase which disintegrates the main alloy into a very fine powder with a high surface area.

In the structure refinements on X-ray diffraction data we found Hf to occupy the A site and Ni the two B sites with Ti (or V) possibly substituted in all the three sites [1]. The number of hydrogen atoms was estimated to be two per formula unit, if a volume expansion of about 2.9 Å^3 per hydrogen atom is assumed.

In this following paper, we use neutron diffraction to better characterise the new Laves phase and its deuteride in

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order to further improve the understanding of these potentially very high capacity systems.

2. Experimental

2.1. Sample preparation

The sample preparation of $TiV_3Ni_{0.56}$ and $TiV_3Ni_{0.56}Hf_{0.24}$ was described in the previous paper [1]. In order to facilitate the structural determination of the Laves phase, the sample composition was adjusted to maximise the content of the Laves phase which was attained to a metal ratio corresponding to the composition $TiV_{0.59}Ni_{1.33}Hf_{0.50}$.

To decrease the incoherent scattering in the neutron diffraction experiment, deuterium was used instead of hydrogen. The ingot was heat treated at 350°C under 30 bar D_2 pressure. We observed different cell parameters depending on the temperature and D_2 pressure and therefore tried to get a deuteride with a deuterium content corresponding to the previously investigated hydride.

2.2. X-ray diffraction analysis

The unit cell dimensions for the alloy were determined to be $a=5.024(7)$ and $c=8.194(4)$ Å and for the deuteride they were determined to be $a=5.174(2)$ and $c=8.491(6)$ Å by indexing the diffraction pattern from a subtraction geometry Guinier-Hägg camera, using monochromatized $CuK\alpha_1$ ($\lambda=1.54060$ Å) and silicon as internal standard. Four reflexes are broader than the ones belonging to the $MgZn_2$-type phase: $d=2.68$ ($I=2.0$), 2.38 ($I=5.4$), 2.25 ($I=6.4$), 2.22 ($I=2.5$) Å; intensities are shown within the brackets. These d values also increases upon hydriding. Although searching for a phase with this d values in the JCPDS data base [10], for example comparing with the metals themselves (Hf,Ti,Ni,V), other alloys consisting of combinations between the metals, or oxides, they still remain unidentified. The $d=2.25$ Å reflex is however the strongest reflex in Ti and the $d=2.22$ Å reflex is the strongest reflex in HfV_2. They both form hydrides.

2.3. SEM analysis

The alloy was investigated with a JEOL820 scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDS) was performed to determine the surface contents.

The surface of the alloy can be seen in Fig. 1. The light-coloured phase is the Laves phase and the dark-coloured minor phase, about 10% of the total surface area, is a second phase. The compositions were estimated to be $TiV_{1.7}Ni_{1.6}Hf_{0.9}$ and $TiV_{0.5}Ni_{0.86}Hf_{0.28}$, respectively. The white dots in the picture with a radii less than 1 µm consist mainly of hafnium.

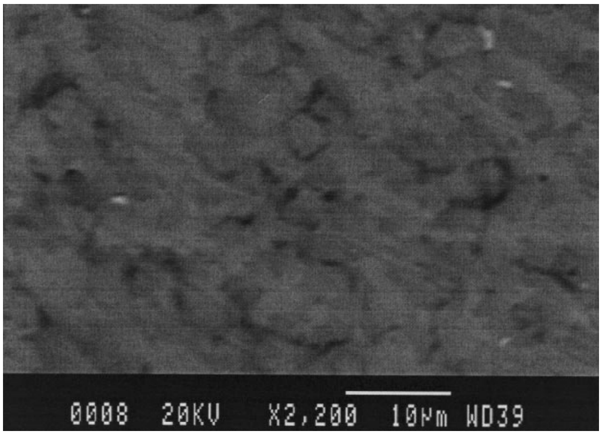

Fig. 1. SEM picture of the alloy showing the light-grey Laves phase $TiV_{1.7}Ni_{1.6}Hf_{0.9}$ and the dark-grey second phase $TiV_{0.5}Ni_{0.86}Hf_{0.28}$.

2.4. Neutron diffraction data collection

We first collected a neutron diffraction pattern of the alloy at the powder diffractometer in Studsvik ($\lambda=1.47$ Å, step length $\Delta 2\theta=0.08°$).

The deuterated sample exhibited a much poorer crystallinity compared to the alloy, with a 'wave-like' background usually connected with amorphous samples. But in this case it is probably connected to deuterium disorder on not fully occupied sites. We therefore used the diffractometer for liquid and amorphous materials in Studsvik for improving the statistics of the data collection. The scanning was performed at $\lambda=1.11$ Å with a step length $\Delta 2\theta=0.1°$.

3. Structure refinements

3.1. Refinement of the alloy

Both structures in the present paper were refined using the Rietveld program FULLPROF [5].

In the refinement of the undeuterated alloy, Hf was put in the 4f position and nickel in the 2a and 6h positions. Different combinations of Ti and V atoms as substituents for Hf and Ni were tested. It was not possible to differentiate between Ti and V, but the lowest criteria of fit were obtained with Ti in the 4f position and V in the 2a and 6h positions; $R_B=10.2$; $R_F=7.2$; $R_W=5.1\%$; GOF=1.4. The two non-overlapping impurity peaks were excluded form the refinement. The atomic parameters are summarised in Table 1 and the observed and calculated diffraction plot from the Rietveld refinement is shown in Fig. 2. The number of resolved and observed reflections was 34 and the number of refined parameters was 9, including cell parameters, coordinates, occupancy factors and half-width parameters (U,V,W). The background was described by interpolating between points. The displacement factors

Table 1
Atomic parameters for the alloy (Hf,Ti)(Ni,V)$_2$, space group P6$_3$/mmc (Z=4), refined from neutron diffraction data[a]

Atom	Site	x	y	z	B_{iso}(Å^2)	Occupancy
Hf	4f	1/3	2/3	0.066(2)	0.02	2.81(4)
Ti	4f	1/3	2/3	0.066(2)	0.02	1.19(4)
Ni1	2a	0	0	0	1.4	0.26(4)
V1	2a	0	0	0	1.4	1.74(4)
Ni2	6h	0.831(1)	−0.831(1)	1/4	0.2	5.16
V2	6h	0.831(1)	−0.831(1)	1/4	0.2	0.84

[a] R_B=10.2, R_F=7.2 and R_{Wp}=5.1%. The refined parameters are represented with the estimated standard deviations within brackets.

could not be refined and were locked to reasonable values. Due to high correlation between the occupancy factors, the E.S.D.ś for Ni2 were abnormally high, but the best fit was obtained with the Nś locked to the values found in Table 1. Since hafnium is a strong absorber of thermal neutrons, absorption corrections were made, only decreasing the R_B value by less than 1%. From the occupancy factors (cf. Table 1) the AB$_2$-formula was calculated to be (Hf$_{0.70}$Ti$_{0.30}$)(Ni$_{0.50}$V$_{0.50}$)$_2$ which is in fairly good agreement with the synthesised composition (Hf$_{0.48}$Ti$_{0.52}$)(Ni$_{0.48}$V$_{0.52}$)$_2$ that was estimated from the EDS analysis.

3.2. Refinement of the deuteride

The Rietveld refinement of the deuteride was started with the metal atoms distribution locked to the same values as in the refinement of the undeuterated alloy. Then different combinations of tetrahedral sites for the deuterium atoms were tested, that is: A$_2$B$_2$ (24l, 12k, 6h (x=0.2), 6h (x=0.4)), AB$_3$ and B$_4$.

The derived Bragg R factor without deuterium included in the refinement was about 35%. When adding deuterium in the 24l site, the R values decreased to: R_B=20 and R_F=14%. Most of the deuterium atoms enter this site, but when adding the 6h site (x=0.23) the intensity of reflex *002* reaches full intensity and the calculated pattern fits the observed one better. The final criteria of fit were thus: R_B=16.7; R_F=11.9; R_W=4.1%; and GOF=1.6. The impurity peaks were excluded from the refinement. The refined atomic parameters can be found in Table 2 and the observed and calculated diffraction pattern are shown in Fig. 3. The number of resolved and observed reflections was 40, and 16 parameters were refined, including both atomic and instrumental parameters.

We also tried to refine deuterium in 6h (x=0.4) and 12k (x=0.4; z=0.6) but these sites have too low an occupancy and too low an accuracy to verify if they are significantly occupied. Moreover, the graphical fit was not improved. The R values decreased about 2% when refining all four D sites simultaneously, however. Refinement of the AB$_3$ and B$_4$ sites did not give R_F values below 20%.

It must be emphasised that the calculated pattern with D in the 24l and 6h (x=0.23) sites fits the observed pattern rather well and the best fit was obtained when the deuterium contents is two per formula unit, in agreement with the volume expansion upon hydriding, corresponding to about 2.9 Å^3.

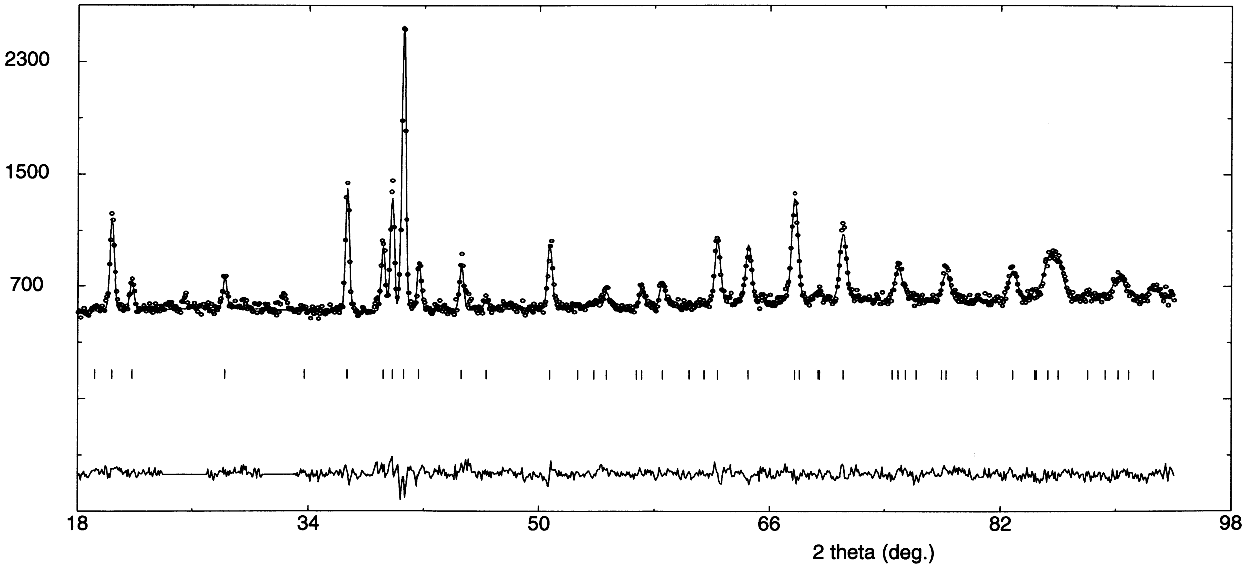

Fig. 2. The observed and calculated neutron diffraction pattern together with the difference plot from the Rietveld refinement on the alloy (Hf,Ti)(Ni,V)$_2$.

Table 2
Atomic parameters for the deuteride refined from neutron diffraction data[a]

Atom	Site	*x*	*y*	*z*	B_{iso}(Å^2)	Occupancy
Hf	4*f*	1/3	2/3	0.070(3)	1.7(6)	2.81
Ti	4*f*	1/3	2/3	0.070(3)	1.7(6)	1.19
Ni1	2*a*	0	0	0	0.0	0.26
V1	2*a*	0	0	0	0.0	1.74
Ni2	6*h*	0.832(2)	−0.832(2)	1/4	1.6(2)	5.16
V2	6*h*	0.832(2)	−0.832(2)	1/4	1.6(2)	0.84
D1	24*l*	0.049(6)	0.372(6)	0.562(3)	2.8(7)	7.3(6)
D2	6*h*	0.23(2)	0.45(2)	1/4	2.8(7)	1.4(2)

[a] $R_B=16.7$, $R_F=11.9$ and $R_{Wp}=4.1\%$. The refined parameters are represented with the estimated standard deviations within brackets.

As can be seen in the neutron diffractogram of the deuterated sample (Fig. 3), the background has an amorphous-like character with a diffuse maximum at about $2\theta=30°$ where the maximum peak in the C14 phase is found. Since this liquidus-like structure is not observed in X-ray, it is attributed to the short-range order involving the D atoms.

4. Discussion

The first structural characterisation of a hexagonal Laves phase containing deuterium was done on $ZrMn_2D_3$ by Didisheim et al. [6], using the Rietveld method. They had different starting models for the D atom distribution, considering all tetrahedral interstices coordinated by three different metal atom arrangements: A_2B_2, AB_3 and B_4. However, they only found deuterium on four different A_2B_2 tetrahedral interstices: 24*l*, 12 *k*, 6h_1 ($x=0.4$), 6h_2 ($x=0.2$) all with lower occupancy factors than unity. Since they found a short nearest neighbour distance between the D atoms of 1.3 Å, they assumed that only next nearest neighbour sites can be occupied simultaneously. From geometrical considerations in a paper by Westlake [7], it was concluded that AB_3 and B_4 sites, although they are large enough, can not be occupied, because they block the occupancy of too many A_2B_2 sites which implies a too low hydrogen-to-metal ratio than was experimentally observed.

For a refined structure model to be physically relevant it is a rule-of-thumb to have a ratio of resolved and observed reflections to the number of refined parameters of at least 5 [8]. In both our experiments, the observed-to-parameter ratios are too low. It is therefore difficult to refine the structure especially with respect to the deuteride with enough precision to determine the exact positions and occupancies for the D atoms. Moreover, the (Hf,Ti)(Ni,V)$_2$ sample contains four unidentified impurity peaks which during the refinements were removed as excluded regions. These reflexes overlapped partially the C14 phase in both the alloy and in the deuterated sample, thus affecting the accuracy of the refined structural parameters. However, the

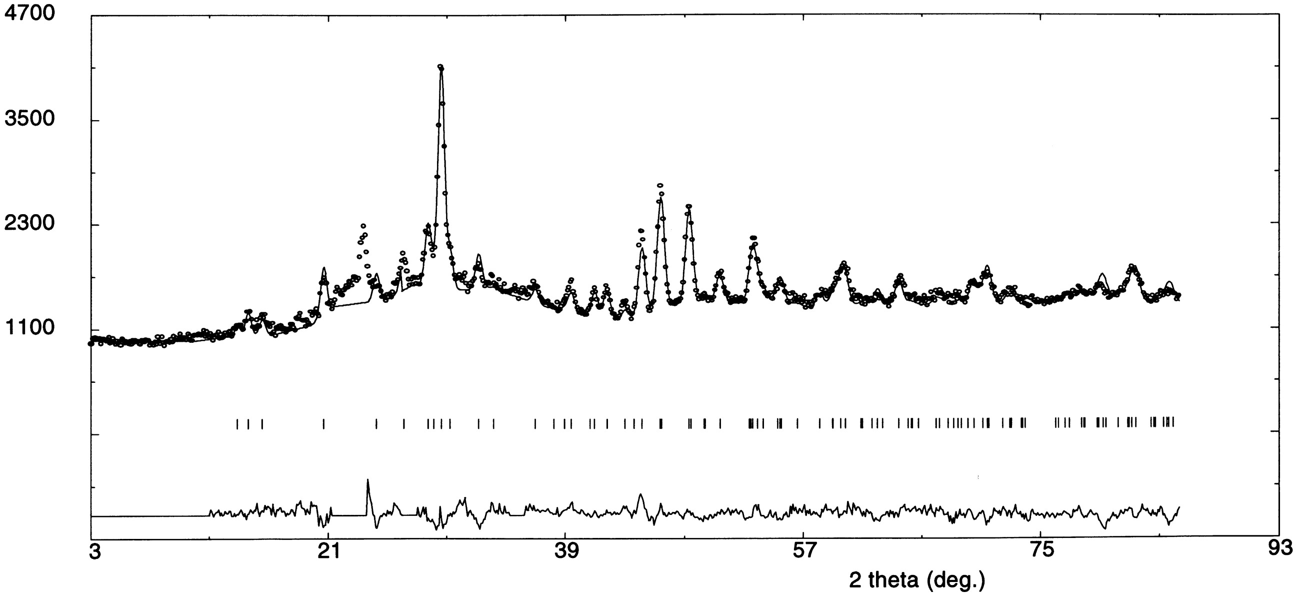

Fig. 3. The observed and calculated neutron diffraction pattern together with the difference plot from the Rietveld refinement on the deuteride.

calculated pattern fits the observed one rather well and among different models, the lowest criteria of fit was obtained when at least two of the four A_2B_2 sites were occupied.

As was discussed in the previous paper [1], comparing atomic radii and electronegativities, it can be presumed that titanium substitutes hafnium at the A site (4*f*) and vanadium substitutes nickel at the B sites (6*a* and 6*h*). This is supported by the atomic distribution found in the EDS analysis. It could be emphasised that among previously known Laves phases with similar compositions, Ti is found in the A site and V in the B sites as for example in $TiCr_2$, $TiZn_2$, $TiMe_{1.87}$ ($Me=V_{0.40}Mn_{0.60}$) and HfV_2, ZrV_2, respectively [9,10]. However, since Ti and V have very similar X-ray scattering factors, they could not be differentiated in the refinement procedure of the X-ray data. Vanadium has unfortunately also a very small neutron scattering length which makes it difficult to determine which sites it is substituting with neutron scattering.

From the structural refinements we thus found Hf at the A site and Ni at the B sites, and the Ti and V occupancies were supported from the EDS analysis. The formula was calculated to be $(Hf_{0.7}Ti_{0.3})(Ni_{0.5}V_{0.5})_2$. The deuteride contains about two deuterium atoms per formula unit and we suggest that they are situated mainly in the tetrahedral 24*l* site.

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