Experimental and computational modelling study of Ni substitution for Fe in Zr_3Fe and its hydride

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Abstract

Zr_3Fe and Ni-substituted Zr_3Fe alloys with 30 and 50 at.% Ni were synthesized and their hydrogen absorption/desorption characteristics were compared experimentally (pressure–composition isotherms, thermal desorption spectroscopy, *in-situ* neutron diffraction) and by computational methods (*ab-initio* molecular dynamics (AMD), nudged elastic band theory (NEB)). All the alloys absorbed hydrogen to a hydrogen-to-metal atomic ratio of about 1.7, but the hydrides formed were stable at room temperature. The $Zr_3Fe_{0.5}Ni_{0.5}$ alloy and its hydrided form were multi-phase. The $Zr_3Fe_{0.7}Ni_{0.3}$ alloy was single-phase and retained the *Cmcm* structure of the parent intermetallic. *In-situ* neutron diffraction with D_2 in place of H_2 showed that the hydride formed in the isotherm measurements, $Zr_3Fe_{0.7}Ni_{0.3}H_{6.88}$, had the same structure (*Cmcm*) as Zr_3FeH_7 , while disproportionation was observed in the hydrogenation of Zr_3Fe . The kinetics of hydride formation was slower in both the Ni-

substituted alloys. Thermal desorption spectroscopy showed that substitution of 0.3Ni significantly destabilized the hydride, lowering the temperature of the principal desorption peak by about 300 K relative to $\text{Zr}_3\text{Fe-H}_2$, without loss of hydrogen capacity, and avoiding disproportionation. Based on the structures determined by neutron diffraction, AMD and NEB calculations were conducted to compare Zr_3Fe and $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}$ and their hydrides. The AMD calculations predicted that H diffusion was slower in Ni-substituted Zr_3Fe , in agreement with the experimental observation of slower kinetics, implying a higher activation energy for H migration. The NEB calculations also predicted a higher energy barrier for H migration in Ni-substituted Zr_3Fe .

Keywords: Zr_3Fe , Ni substitution, hydride, hydrogen storage, neutron powder diffraction, *ab initio* molecular dynamics simulations, nudged elastic band, density functional theory

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Introduction

Zr₃Fe absorbs 2 wt% H (Zr₃FeH_{6.7}) at room temperature under low pressure and would be a candidate for stationary hydrogen storage applications, except that complete desorption of the H requires a temperature of about 900 K [1]. Thus, how to modify Zr₃Fe and improve its hydrogen storage performance are important questions.

Substitution of the A or B element in an intermetallic compound of A_xB_y form is an effective technique to modify its hydrogen storage performance [2]. One good example of this approach is partial substitution of Mg for La in LaNi₃ [3], which improves the hydrogen storage performance of the compound. In this work, 30 and 50 at.% Ni substitutions were made for Fe in Zr₃Fe (Zr₃Fe_{0.7}Ni_{0.3} and Zr₃Fe_{0.5}Ni_{0.5}). To the authors' knowledge, these alloys had not been made previously. The goal of the work was to use experiments and computational modelling to study the effect of Ni substitution, looking for any improvement in the hydrogen storage performance relative to Zr₃Fe. The hydrogen storage properties of Zr₃Fe_{0.7}Ni_{0.3} and Zr₃Fe_{0.5}Ni_{0.5} were compared to those of Zr₃Fe. Zr₃Fe_{0.7}Ni_{0.3} and its hydride were studied in detail using thermal desorption spectroscopy, neutron diffraction and theoretical simulations, in order to understand its hydrogen storage properties.

The two aspects of concern were the crystal structure and the H migration mechanism. In-situ neutron powder diffraction (NPD) was employed to determine the D locations and occupancies, which were fed into calculations employing Density Functional Theory (DFT) [4]. To investigate H migration, which relates fundamentally to the temperature(s) at which hydrogen desorption occurs, a DFT-based approach including *ab-initio* molecular dynamics (AMD) [5] and nudged elastic band (NEB) [6-8] calculations was followed. In the present context, *ab-initio* MD is a method that advances the positions of nuclei along trajectories defined by classical mechanics, based on forces calculated using DFT. Here it was used to calculate the diffusion constants for H in Zr₃Fe and Zr₃Fe_{0.7}Ni_{0.3} at temperatures up to 1200

K. The NEB technique, which may be used to calculate the rate of a chemical process based on transition-state theory, was applied to calculate the energy barriers encountered by a migrating H atom. The computational results helped to explain the experimental results.

Experimental and calculation methods

The source materials were Zr foil (0.25 mm, 99.8%, supplied by Advent Research Materials), Fe chip (99.98%, supplied by Sigma-Aldrich) and Ni foil (0.5 mm, 99.99%, supplied by Advent Research Materials). Alloys with proportions Zr_3Fe , $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}$ and $\text{Zr}_3\text{Fe}_{0.5}\text{Ni}_{0.5}$ were synthesized by arc melting on a water-cooled copper hearth with a tungsten electrode. The chamber was first purged with ultra-high purity Ar gas several times. A Ti oxygen getter was pre-melted to further decrease the oxygen level inside the chamber. The button-shaped ingot was melted 5 times and flipped between meltings to obtain the best homogeneity. The buttons were sealed in a quartz tube under high vacuum, homogenized at 750 °C for 7 days and furnace cooled. Samples were made by manual grinding.

Laboratory XRD was performed to confirm that the samples were crystalline and, in the case of Zr_3Fe , had the reported structure (*Cmcm* [9]). XRD also showed that $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}$ had the *Cmcm* structure, whereas “ $\text{Zr}_3\text{Fe}_{0.5}\text{Ni}_{0.5}$ ” was multiphase, for which reason it was studied only to a limited degree.

SEM/EDX analysis was conducted to analyse the elemental composition of the alloys, using a JEOL JSM-6010 SEM with Oxford EDX detector.

Hydrogen absorption–desorption isotherms were measured with a Hiden Isochema HTP1 automated Sieverts (manometric) hydrogenator at pressures up to 80 bar. Thermal desorption spectroscopy (TDS) measurements were made using a Hiden Analytical DSMS quadrupole mass spectrometer attached to a quartz tube containing the sample and inserted into a tube

furnace. No carrier gas was used and the quartz tube was initially evacuated with a rotary vacuum pump.

In-situ NPD experiments were conducted with the high-resolution powder diffractometer, Echidna, at the Australian Centre for Neutron Scattering, Sydney: $\lambda = 2.439\text{\AA}$; 331 reflection from Ge crystal, 335 cut; range, $4 - 164^\circ$; step, $\Delta 2\theta = 0.05^\circ$. A thin-walled 316 stainless-steel pressure cell with internal diameter 10 mm was used and the deuterium uptake was managed with a Hiden IMI instrument similar to the HTP1. The samples were pulverized manually and sieved to $53 - 250\mu\text{m}$. The grinding was done in air but the sieved powders were stored in an Ar glove box before the experiments. About 10 g of powder was used for each sample.

The GSAS (General Structure Analysis System) II software was used for Rietveld refinement with the neutron diffraction patterns [10]. A Chebyshev function was used to model the background and the pressure cell was treated as three peaks in the background. The peak shapes were modelled with a mixed Gaussian-Lorentzian (pseudo-Voigt) function.

For the computational study, AMD calculations were conducted using the Vienna *Ab-initio* Simulation Package (VASP) [6, 11-13] with structural parameters determined by NPD. A supercell containing 132 atoms was built from the unit cell of each structure. The NVT simulations (ensemble constrained by constant number of atoms, constant volume and constant temperature) were carried out by means of a Nosé thermostat to control the temperature [14]. The equation of motion was solved via the velocity Verlet algorithm with a time step of 3 fs and 1 fs respectively.

NEB calculations were performed with the experimentally determined alloy structures and followed one migrating hydrogen atom. The hydrogen migration path was determined by consideration of the interstitial sites occupied by deuterium. The NEB calculations were

conducted with VASP. Once the NEB calculations were finished, energy barriers were calculated with VTST tools from the University of Texas at Austin [15].

Results and discussion

SEM/EDX

SEM/EDX analysis was conducted on samples of the homogenized alloys. The results are presented in Supplementary Information.

For Zr_3Fe , the SEM images (Figure S 3) showed that the synthesized intermetallic was homogeneous within resolution and the EDX results (Table S1) showed that the spatially averaged composition was close to the ideal 3 : 1 stoichiometry. NPD confirmed that the intermetallic was single-phase.

For $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}$, the SEM images (Figure S 4) showed that the synthesized alloy was homogeneous within resolution and the EDX results (Table S2) showed that the spatially averaged composition was close to the desired 3 : 0.7 : 0.3 proportions. NPD confirmed that the alloy was single-phase.

For $\text{Zr}_3\text{Fe}_{0.5}\text{Ni}_{0.5}$, the SEM images (Figure S 5) show that the synthesized alloy was homogeneous within resolution and the EDX results (Table S3) show that the spatially averaged composition was close to the desired 3 : 0.5 : 0.5 proportions. However, NPD showed that the alloy was multi-phase at the crystallite scale.

Isotherm analysis

Absorption–desorption isotherms were measured for all the synthesized alloys, as shown in Figure 1. After loading into the hydrogenator, and prior to hydrogenation, each sample was heated in situ under vacuum for 2 h at 200 °C to remove residual oxygen and water, then cooled to room temperature. The analysis was performed in three steps: 3 absorption–

desorption cycles at room temperature, followed by heating under vacuum for 3–4 h at 390 °C (the upper temperature limit of the HTP1) and cooling to room temperature, followed by 3 more absorption–desorption cycles at room temperature.

Figure 1 Absorption–desorption isotherms measured at room temperature before (left)

and after (right) heat treatment under vacuum for 3–4 h at 390 °C. Top: Zr_3Fe . Middle: $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}$. Bottom: $\text{Zr}_3\text{Fe}_{0.5}\text{Ni}_{0.5}$. Note that the zero of H/M was reset between cycles by the HTP1 instrument.

From Figure 1, Zr_3Fe formed $\text{Zr}_3\text{FeH}_{6.60}$ during the first hydrogen absorption cycle, but no desorption was observed, meaning that the hydride was stable at room temperature in agreement with previous work [1]. In the two following cycles, there was no significant hydrogen absorption, confirming that a stable hydride had been formed. Partial desorption equivalent to about 0.6 H/M occurred at 390 °C, but a stable hydride was again formed in the first subsequent absorption cycle. $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}$ and $\text{Zr}_3\text{Fe}_{0.5}\text{Ni}_{0.5}$ exhibited similar behaviour, forming stable hydrides $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}\text{H}_{6.88}$ and $\text{Zr}_3\text{Fe}_{0.5}\text{Ni}_{0.5}\text{H}_{6.96}$, but the $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}$ hydride released significantly more hydrogen (equivalent to about 0.9 H/M) at 390 °C, suggesting that Ni substitution had destabilized the hydride. This trend was reversed in the $\text{Zr}_3\text{Fe}_{0.5}\text{Ni}_{0.5}$ hydride, so attention was then focussed on $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}$.

The increased pressures at the start of the first absorption plateaux on the left side of Figure 1 indicate a kinetic limitation in starting the phase transformation to the hydride. This effect was not observed after heat treatment at 390 °C, suggesting that the limitation was caused by surface oxide rather than a difference in intrinsic kinetics related to hydrogen dissociation, phase nucleation or hydrogen diffusion.

Thermal desorption spectroscopy

TDS analysis was performed on $\text{Zr}_3\text{FeH}_{6.60}$ and $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}\text{H}_{6.88}$ with results shown in Figure 2.

Figure 2 Thermal desorption profiles for $\text{Zr}_3\text{FeH}_{6.6}$ and $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}\text{H}_{6.88}$ (heating rate: $2^\circ\text{C}/\text{min}$).

$\text{Zr}_3\text{FeH}_{6.60}$ desorbed hydrogen in the temperature range from about 200°C to 700°C , with the highest peaks occurring above 390°C , the temperature at which the sample was quasistatically desorbed between sets of absorption–desorption cycles as shown in Figure 1. The desorption peak at around 650°C corresponds to the dissociation of ZrH_2 , which is a disproportionation product in the formation of the Zr_3Fe hydride. This temperature agrees with that reported in Ref. [1]. $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}\text{H}_{6.88}$ desorbed in the range from about 200°C to 650°C , but the majority of hydrogen desorption occurred below 390°C . The TDS results are therefore qualitatively consistent with the right-hand column of Figure 1. Thus 0.3Ni substitution significantly lowered the stability of the hydride without decreasing the amount of hydrogen absorbed.

Neutron diffraction

Zr_3Fe

Two neutron diffraction patterns were collected from Zr_3Fe . One 2-hour scan was done as

loaded, after evacuation. When the deuterium pressure was applied, the Zr_3Fe did not absorb instantly, most likely owing to surface oxide. The sample was activated in situ by heating the cell with a hot air gun under deuterium pressure. After about 20 minutes, the Zr_3Fe started to absorb deuterium. After equilibrium was achieved, indicated by the deuterium pressure stabilising, one 8-hour scan was collected from the deuterated Zr_3Fe .

NPD patterns and refinement results for the undeuterated and deuterated Zr_3Fe are shown in Figure 3 and Table 1. The Zr_3Fe structure in [9] was used as the model structure. The data residual R_w after the refinement was 6.7% (in this paper, the reported R_w is the weighted residual excluding the background). The refinement confirmed that the synthesized Zr_3Fe had the expected crystal structure ($Cmcm$) and the measured lattice parameters (Table 1) were close to the reported values ($a = 3.321\text{\AA}$; $b = 10.966\text{\AA}$; and $c = 8.825\text{\AA}$ [9]).

Deuterated Zr_3Fe is also shown in Figure 3. The deuterated sample was multi-phase, but with very little (if any) Zr_3Fe present. It was observed that the peaks at 52.7° and 92.9° in the deuterated Zr_3Fe were at the roughly correct 2θ positions for ZrD_2 , suggesting disproportionation to ZrD_2 and ZrFe_2 but the peaks were relatively broad, suggesting nanoscopic products. Disproportionation to ZrD_2 and ZrFe_2 was also reported by Yartys et al. [1]. Noting the relatively large volume of sample required for neutron diffraction, the high enthalpy of reaction to form the stable hydride appeared to generate sufficient heat to increase the temperature to the point where disproportionation of Zr_3Fe hydride could occur. ZrD_2 [16] and ZrFe_2 [17] structures were used to trial the disproportionation scheme proposed in ref. [1]. The relatively poor fit in the lower panel of Fig. 3 shows that the proposed disproportionation scheme is not supported by our results.

Figure 3 Rietveld refinement results for undeuterated (top) and deuterated (bottom) Zr_3Fe (red reflection markers: ZrD_2 ; blue reflection markers: ZrFe_2). Blue crosses: experimental data; red line: calculated profile; black line: calculated background, including peaks from the stainless-steel pressure cell; lower black line: difference between experimental data and model.

Table 1. Structure parameters of undeuterated Zr_3Fe from neutron diffraction.

a (Å)	3.3249(2)	b (Å)	10.9731(7)	c (Å)	8.8066(5)	
	Coordinates			Occupancy	U_{iso} (Å ²)	Multiplicity
Fe1	0	0.7398(2)	0.25	1.000	0.013(1)	4
Zr1	0	0.4308(3)	0.25	1.000	0.012(1)	4
Zr2	0	0.1378(2)	0.0573(2)	1.000	0.015(1)	8

 $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}$

One 2-hour neutron diffraction pattern was collected from $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}$ as loaded, after evacuation. As with Zr_3Fe , a hot air gun was then used to activate $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}$ for deuterium absorption. As Figure S 8 (Deuterium pressure vs time during NPD on $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}$) shows, the deuterium pressure did not settle within the experimental time owing to slow kinetics. Multiple deuterium charges were admitted to the sample and 1-hour patterns were collected to confirm that the diffraction pattern had stabilized. Note the decreasing rate of change of the pressure with time, indicating slower absorption kinetics despite the pressure being maintained at a high value compared to the equilibrium pressure. The final five 1-hour patterns were summed for Rietveld refinement.

The NPD patterns and Rietveld refinement results for the undeuterated and deuterated $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}$ are shown in Figure 4, Table 2 and Table 3. The Zr_3Fe structure in [9] was used to refine the undeuterated $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}$. Its data residual R_w after refinement was 9.3%. For deuterated $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}$, the deuterium absorption was not complete, whereas it was complete in the HTP1 experiments. Therefore both the Zr_3Fe structure in [9] and $\text{Zr}_3\text{FeD}_{6.7}$ structure in [1] were used to refine the deuterated $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}$ pattern. The data residual R_w after the refinement was 8.0%.

Figure 4 Rietveld refinement for undeuterated (top) and deuterated (bottom) $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}$ (red: $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}$; blue: $\text{Zr}_3\text{FeD}_{6.7}$). Blue crosses: experimental data; red line: calculated profile; black line: calculated background, including peaks from the stainless-steel pressure cell; lower black line: difference between experimental data and model.

Table 2. Structure parameters of undeuterated $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}$ from neutron diffraction.

a (Å)	3.2690(4)	b (Å)	10.818(2)	c (Å)	8.739(1)
	Coordinates			Occupancy	U_{iso} (Å ²)
Fe1	0	0.7372(3)	0.25000	0.705(9)	0.019(5)
Zr1	0	0.4307(5)	0.25000	1.000	0.009(2)
Zr2	0	0.1362(2)	0.0579(4)	1.000	0.018(2)
Ni1	0	0.7372(3)	0.25000	0.296(7)	0.004(1)
					Multiplicity
					4
					4
					8
					4

Table 3. Structure parameters of $\text{Zr}_3\text{FeD}_{6.7}$ phase (weight fraction 0.451) in deuterated $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}$, from neutron diffraction.

a (Å)	3.552(1)	b (Å)	10.856(3)	c (Å)	9.521(3)
	Coordinates			Occupancy	U_{iso} (Å ²)
Zr1	0	0.424(1)	0.250	1.000	0.011(6)
Zr2	0	0.134(1)	0.049(2)	1.000	0.009(4)
Fe1	0	0.720(1)	0.250	0.705	0.02(1)
Ni1	0	0.720(1)	0.250	0.296	0.02(3)
D1	0	0.226(1)	0.250	0.77(6)	0.01(1)
D2	0	0.402(1)	0.636(1)	1.000	0.020(5)
D3	0	0.330(1)	0.059(1)	0.90(5)	0.009(8)
D4	0	0.965(1)	0.125(1)	0.90(5)	0.006(8)

MD

Two kinds of AMD calculations were performed to investigate the effect of Ni substitution. The first type of calculation simulated heating from 0 K to 300 K, 500 K, 700 K, 1000 K and 1200 K, with 4 steps per kelvin and 3 fs per step. After each heating calculation, the obtained structure was relaxed for 10000 steps, with 1 fs per step.

The mean-square displacements (MSDs) of all the atoms in Zr_3FeH_7 and $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}\text{H}_7$ were compared. The MSD should increase linearly with time if the diffusion is correctly modelled by a random walk and so obeys Fick's law. The adopted Zr_3Fe hydride structure was from [1], and the $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}\text{H}_7$ structure used was from the neutron powder diffraction results in Table 3.

The MSDs of Zr and Fe during heating of Zr_3FeH_7 and $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}\text{H}_7$ from 0 K to 1200 K are shown in Figures S 13 and S 14. The relaxation phase is shown for the heavy atoms in Figures S 15 and S 16 for Zr_3FeH_7 and Figures S 17, S 18 and S 19 for $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}\text{H}_7$. As expected for these relatively heavy atoms, the implied diffusion rates are low, since the MSDs do not noticeably increase with time, and the MSD for Zr is lower than that of Fe/Ni. The MSDs are consistently higher in Zr_3FeH_7 .

Figure 5 shows the MSD of H during heating of Zr_3FeH_7 and $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}\text{H}_7$. The values are much higher than for the heavy atoms at the same temperatures. Above about 700 K, the MSD of H in Zr_3FeH_7 was significantly higher than in $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}\text{H}_7$, indicating slower diffusion in the Ni-substituted hydride.

Figure 5 MSD of H in Zr_3FeH_7 and $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}\text{H}_7$ during heating from 0 K to 1200 K (left), expanded at right

Figure 6 compares the time evolution of the MSDs of H in Zr_3FeH_7 and $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}\text{H}_7$ at different temperatures during relaxation at constant temperature. The MSDs are comparable at low temperatures but H diffusion is significantly faster in Zr_3FeH_7 at 1000 K.

Figure 6 MSD of H atom in Zr_3FeH_7 (left) and $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}\text{H}_7$ (right) during relaxation at (bottom to top) 300 K, 500 K, 700 K, 1000 K and 1200 K

Figure 7 confirms that the MSD of H increased linearly with time at the highest temperatures. The same linear behaviour was observed at all temperatures down to 300 K.

Figure 7 Comparison of MSD of H in Zr_3FeH_7 and $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}\text{H}_7$

Using the Einstein equation

$$\text{MSD}(t) = 6Dt \quad (1)$$

for a random walk in 3 dimensions, the diffusion coefficient D for migration of H was calculated for Zr_3FeH_7 and $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}\text{H}_7$. The obtained values are shown on an Arrhenius plot in Figure 8. Since the data points do not lie on a straight line, an activation energy cannot be obtained straightforwardly. A likely reason is that the supercell ($3 \times 1 \times 1$, approximately $900 \text{ \AA}^3$, 132 atoms) was not large enough. A similar problem was encountered in the MD study of zirconium hydride by Yanilkin [18], who observed significant differences between the D values for deuterium calculated with supercells of volume $900 \text{ \AA}^3$ and $3000 \text{ \AA}^3$ of more than 1 order of magnitude as the temperature decreased to about half the melting point. The values of D at 500 K and 300 K in Figure 7 were therefore discarded. The highest-temperature D values indicate an activation energy for H diffusion of about 0.73 eV in Zr_3FeH_7 and about 0.85 eV in $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}\text{H}_7$.

Figure 8 Diffusion coefficients of H in Zr_3FeH_7 and $Zr_3Fe_{0.7}Ni_{0.3}H_7$ based on MD and Eqn (1).

NEB

NEB calculations were performed in which one H atom migrated in the unhydrided structures of Zr_3Fe and $Zr_3Fe_{0.7}Ni_{0.3}$, i.e. in the dilute limit. The hydrogen migration path was determined by consideration of the interstitial sites occupied by D in the deuterated structures shown in Figure 9. Since the two structures were similar, identical migration paths were chosen within them covering all four types of occupied interstitial sites, indicated in the figures by the red arrows.

The images (corresponding to the states through which the system passes) in the NEB calculation were made by adding the D coordinates from the deuterated structures to the POSCARs (VASP files defining lattice geometry and atomic coordinates) of unhydrided Zr_3Fe and $Zr_3Fe_{0.7}Ni_{0.3}$.

Figure 9 Hydrogen migration path in $\text{Zr}_3\text{FeH}_{6.7}$ (left) and $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}$ (right). Green balls: Zr; bronze and bronze/white: Fe in Zr_3Fe and Fe/Ni in $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}$; small balls numbered 1 – 4: the four interstitial sites occupied by hydrogen.

The NEB calculation results are presented in Figure 10 and indicate that H encounters a higher energy barrier in empty $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}$ (0.55 eV for the jump from site 0 to site 1 in Fig. 9) compared to 0.45 eV for the same jump in empty Zr_3Fe . As found for the filled structures examined with MD, this is consistent with the experimentally observed slower H diffusion in $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}$. The results obtained from MD and NEB calculations are not directly comparable because the lattice is relaxed in the MD calculation but not in the NEB calculation.

Figure 10 NEB calculations of the energy barriers encountered in the H migration paths of one hydrogen atom in Zr_3Fe and $Zr_3Fe_{0.7}Ni_{0.3}$.

Summary and conclusions

The intermetallic Zr_3Fe and alloys with partial substitution of Ni for Fe having nominal compositions $Zr_3Fe_{0.7}Ni_{0.3}$ and $Zr_3Fe_{0.5}Ni_{0.5}$ were synthesized by Ar arc melting. SEM/EDX analysis showed that the synthesized alloys were close to the desired composition and were homogeneous phases within the resolution of the EDX analysis.

Powder diffraction (laboratory XRD and neutron) confirmed that the Zr_3Fe had the expected *Cmcm* structure. $Zr_3Fe_{0.7}Ni_{0.3}$ retained the *Cmcm* structure, but at the crystallite scale probed by high-resolution neutron diffraction, “ $Zr_3Fe_{0.5}Ni_{0.5}$ ” was not single-phase. Since the hydrogen absorption properties of $Zr_3Fe_{0.7}Ni_{0.3}$ turned out to be superior, the study focused on $Zr_3Fe_{0.7}Ni_{0.3}$, with Zr_3Fe as a benchmark.

Hydrogen absorption/desorption isotherms were measured and confirmed that Zr_3Fe formed a stable hydride $Zr_3FeH_{6.6}$. $Zr_3Fe_{0.7}Ni_{0.3}$ formed a stable hydride $Zr_3Fe_{0.7}Ni_{0.3}H_{6.88}$; and $Zr_3Fe_{0.5}Ni_{0.5}$ formed a stable hydride with overall composition $Zr_3Fe_{0.5}Ni_{0.5}H_{6.96}$. After heat treatment at 390 °C for 3 – 4 hours, 0.6 H/M, 0.9 H/M and 0.77 H/M hydrogen respectively

was desorbed from the formed stable hydrides, showing that substitution of 30 at.% Ni for Fe destabilized the Zr_3Fe hydride without causing fundamental structural change.

Consistent results were obtained from thermal desorption spectroscopy. The main thermal desorption peak occurred in the range 500–700 °C for $\text{Zr}_3\text{FeH}_{6.6}$, which suggested that disproportionation had occurred, since ZrH_2 dissociates at approximately 650 °C. However, in the $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}\text{H}_{6.88}$ case, the thermal desorption peak occurred in the range 200–400 °C. Thus substituting 30 at.% Ni for Fe in Zr_3Fe not only lowered the desorption temperature, but apparently also avoided disproportionation.

In-situ neutron diffraction under deuterium pressure confirmed the disproportionation of deuterated Zr_3Fe . Disproportionation was likely caused by the high heat of formation of the deuteride leading to a high sample temperature during deuterium absorption. The reaction was not self-limiting because the D_2 pressure was at least several bar, well above the equilibrium pressure in the investigated temperature range. The diffraction data disagreed with the expected $\text{ZrD}_2 + \text{ZrFe}_2$ disproportionation scheme. This disagreement was not pursued, as it is peripheral to the aims of the work. Further neutron diffraction measurements at higher resolution, perhaps combined with high-resolution synchrotron x-ray diffraction, would be required to identify the disproportionation products confidently. In-situ neutron diffraction also confirmed that the deuteride of the 30 at.% Ni substituted alloy had the Zr_3FeD_7 structure, although the absorption was incomplete within the available experiment time, in contrast to the laboratory experiment.

Ab-initio molecular dynamics calculations showed that 30 at.% Ni substitution for Fe lowered the rate of increase with time of the mean-square displacement of H atoms, implying slower diffusion, consistent with the experimentally observed slower kinetics of H uptake. It was concluded that the AMD results at temperatures below about 700 K suffered from inaccuracy

owing to the relatively small size of the supercell (about $900 \text{ \AA}^3$). The activation energy for H migration in the Zr_3FeH_7 intermetallic hydride and the 30 at.% Ni substituted alloy hydride were estimated at about 0.73 and 0.85 eV respectively, ignoring the entropy contribution.

Nudged elastic band calculations for H migrating in otherwise empty Zr_3Fe and $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}$ indicated that H encountered a higher potential energy barrier (0.55 eV) when migrating in the $\text{Zr}_3\text{Fe}_{0.7}\text{Ni}_{0.3}$ lattice compared to Zr_3Fe (0.45 eV), which is also consistent with the experimentally observed slower kinetics of hydrogen absorption in Ni-substituted Zr_3Fe relative to the unmodified intermetallic, and with the observed decrease of the absorption rate as the Ni-substituted alloy filled with deuterium.

In summary, substitution of 30 at.% Ni for Fe in Zr_3Fe leads to significantly improved hydrogen absorption properties, strongly lowering the desorption temperature and avoiding disproportionation.

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Highlights

W. Liu et al.: Experimental and computational modelling study of Ni substitution for Fe in Zr_3Fe and its hydride

- new metal hydride introduced
- desorption temperature lowered by about 300°C compared to parent intermetallic
- new alloy and its hydride are single-phase
- disproportionation noted for Zr_3FeH_7 is avoided
- experiment and computational modelling combined to explain improved properties

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