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Graphic Abstract

H-rich Zr-H alloy system with massive δ -hydrides:
slow cooling from
(α -Zr + δ -hydride) phase region

sluggish transformation
limited by migration of
H atoms from δ
crystal lattice

Observations of temperature stability of γ -zirconium hydride by high-resolution neutron powder diffraction

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Abstract: The phase evolution in a zirconium–50 deuterium (Zr–50D, at.%) alloy system during thermal cycling has been investigated using *in situ* high-resolution neutron powder diffraction. The results showed that the peritectoid reaction $\alpha\text{-Zr} + \delta\text{-ZrD} \rightarrow \gamma\text{-ZrD}$ previously suggested to occur at high temperatures does not take place in the system. Slow cooling, from high temperatures (≥ 520 K) to room temperature at a rate of 5 K min^{-1} , promoted the γ -hydride formation rather than fast cooling as reported earlier. In contrast to the observation that the δ -hydride present in the system remained at temperatures up to 740 K, the produced γ phase transformed to δ -hydride in the temperature range of 370 K to 559 K, with the transformation completing at approximately 559 K. It is confirmed that the formation of the γ -

hydride was reproducible with slow cooling, and a diffusion-controlled sluggish δ - to γ -hydride transformation is suggested to be responsible for the favorable development of γ -hydride during slow cooling.

Keywords: Metal hydrides; Phase transitions; Neutron diffraction; Zirconium hydride; Zirconium; Nuclear materials

1. Introduction

The formation of embrittling zirconium hydrides has been recognized as one of the most important reasons for the ductility degradation and failure in zirconium alloys, which are extensively used in the nuclear industry as structural and fuel cladding materials. The presence of hydrides in the zirconium alloy matrix has been shown to induce a crack initiation and propagation process called delayed hydride cracking (DHC) [1], significantly reducing the useable lifetime of the component. The hydride formation is facilitated essentially due to the strong affinity of zirconium and its alloy with hydrogen and the low solubility of hydrogen in the hexagonal α -Zr phase (less than 10 wt. ppm at room temperature [2]).

Current knowledge suggests that there are four phases of hydrides (ζ , γ , δ and ϵ) in the Zr-H system. Normally, the δ - and ϵ -hydrides are reported as stable phases, while the other two are metastable. The crystal structures and common compositions of these different hydride phases as reported in the literature [3-6] are summarized in Figure 1. A brief review of the crystallography of the δ -, γ - and ϵ -hydrides has been provided by Steuwer et al. [7]. The ζ -hydride (Zr_2H) is a more recently identified metastable phase with a trigonal structure ($P3m1$) that is fully coherent with the hexagonal α -Zr [8]. The difference between the reported stable δ -hydride and metastable γ -hydride is the degree of ordering of the hydrogen atoms at tetrahedral sites [7]. The δ phase is reported to have a disordered face-centred cubic structure ($Fm\bar{3}m$) with the hydrogen atoms randomly occupying part of the eight available

1 tetrahedral (0.25, 0.25, 0.25) sites (*see* Fig. 1). This is the most commonly observed hydride
 2 phase which is often reported to form after slow cooling (e.g., furnace cooling [9, 10]) and
 3 have a typical non-stoichiometric composition of $\sim\text{ZrH}_{1.66}$ [6]. The γ -hydride ($\text{ZrH}_{1.0}$) has
 4 been identified to be a tetragonal ($P4_2/n$) phase with the ordered arrangements of hydrogen
 5 atoms at the tetrahedral interstitial sites. This phase is mostly observed in the samples after
 6 rapid quenching [11, 12], but some other investigations judged that the γ -hydride can also
 7 appear in the slow cooling regimes dependent on the alloy compositions and hydrogen
 8 contents of the samples [13-15]. Here, it is worth mentioning the oddness, from a
 9 thermodynamical point of view, as to why an *ordered* structure of γ -hydride would form
 10 during rapid quenching which would essentially freeze the highly mobile H atoms in their
 11 random positions while slow cooling favours δ -hydride. Additionally, there is another
 12 orthorhombic structure ($Cccm$) reported for the γ phase based on neutron diffraction
 13 measurements of deuterided zirconium samples [16]. However, no full pattern Rietveld
 14 refinement of γ -hydride has been reported to the best of our knowledge to discriminate the
 15 exact crystal structure of this phase. Furthermore, Mishra and Bashkin et al. [17, 18] argued
 16 that the γ -hydride is actually an equilibrium phase produced via a peritectoid $\alpha + \delta \rightarrow \gamma$
 17 reaction at high temperatures, although this argument is possibly in violation of the Gibbs
 18 phase rule for the binary system. Root and co-workers [19-21] indicate by neutron diffraction
 19 that a reversible $\delta \rightleftharpoons \gamma$ phase transformation occurred in a Zr-2.5Nb (wt.%) alloy at ~ 453 K.
 20 They suggested that γ -hydride is stable at room temperature as implied by the observation of
 21 continuous formation of γ -hydride during room-temperature aging. Some first-principles
 22 simulations also concluded that γ -hydride is the most stable phase, while δ -hydride is
 23 thermodynamically less stable than the other hydride phases [22, 23].

24 To summarize, despite decades of research, the formation, stability and exact structure of
 25 hydride phases (especially the γ phase) are still not completely resolved. Further

investigations are essential to improve the understanding of these issues, not only due to the technical importance of the hydride-induced embrittlement in zirconium alloys, but also to the fundamental interests in the phase transformation behaviors of stable and metastable hydrides. Towards that end, this study presents *in situ* high-resolution neutron diffraction measurements performed on the deuterided zirconium powders during thermal cycling. The data clearly revealed that the previously reported [17, 18] peritectoid $\alpha + \delta \rightarrow \gamma$ reaction does not occur in the material system investigated. The formation of γ -hydride in the system was found to be promoted by slow cooling rather than rapid cooling. A plausible explanation qualitatively consistent with the diffraction data was proposed to understand this behavior. The δ -hydride was shown to be stable at temperatures up to 740 K while the γ -hydride gradually transformed to δ -hydride during heating. In parallel with the present work, a synchrotron X-ray diffraction study during *in situ* hydrogen loading by Maimaitiyili et al. [24] confirms the hydride formation process outlined here.

Fig. 1. Crystallographic structures and common formulae of four different hydrides (ζ , γ , δ and ϵ) found in the Zr–H system [22]. The larger green and smaller grey spheres represent the Zr and H atoms, respectively. The δ -hydride shown in the phase diagram (after Ref. [4]) is a non-stoichiometric phase which was reported to have a typical H/Zr ratio of ~ 1.66 and a

disordered face-centred cubic structure with the hydrogen atoms partially occupying the eight available tetrahedral sites at random. The γ -hydride ($\text{ZrH}_{1.0}$) was identified to have a tetragonal structure with the ordered arrangements of hydrogen atoms at the tetrahedral interstitial sites.

2. Experimental

Commercial-grade zirconium powders (99.2% purity) were charged with gaseous deuterium using a high pressure furnace. A temperature of 573 K and pressure of 1.9 bar were applied for a period of 10 h which resulted in a final atomic ratio of Zr to D of approximately 50:50 (uncertainty within 3%). The selection of this composition for the present study is to check the existence of a peritectoid reaction $\alpha\text{-Zr} + \delta\text{-ZrD} \rightarrow \gamma\text{-ZrD}$, which was proposed previously to occur at 50 at.% hydrogen and at high temperatures (~ 528 K [17], or 559 K [18]). The prepared deuterated zirconium samples are preferred for the neutron diffraction studies compared with the counterparts with hydrogen charging because of the higher coherent scattering amplitude of deuterium [25]. Additionally, it is commonly accepted that the H-D replacement only marginally affects the diffusion rates and mobility of D in the bulk zirconium sample [26].

In situ temperature-dependent neutron diffraction experiments were carried out using the high-resolution powder diffractometer Echidna [27] at the OPAL research reactor of the Australian Nuclear Science and Technology Organisation. The deuterated powder was loaded into an 8 mm diameter vanadium can which was then sealed with copper gasket. The can was placed inside a cryofurnace for temperature cycling between room temperature (290 K) and 763 K. The thermal cycle profile used is shown in Fig. 2. Neutron wavelengths (λ) of 2.4395 and 1.6215 Å were used for the data collection in the 2θ range of 5 – 165° with 2θ step-size of 0.05° at specific soaking temperatures. Note that during thermal cycling, heat treatments

using two different cooling rates of 30 K min^{-1} and 5 K min^{-1} were conducted to determine the effect of cooling rate on the formation of $\gamma\text{-ZrD}$ phase. Additionally, high-resolution synchrotron X-ray diffraction measurements were performed on the as-deuterided powders at room temperature at the beamline ID31 of the European Radiation Synchrotron Facility in Grenoble, France. An X-ray beam of wavelength $\lambda = 0.306589(92) \text{ \AA}$ (energy 40.44 keV) was used for the experiments with the powder samples packed in glass capillaries. The collected neutron and X-ray diffraction data were analyzed using the Rietveld refinement program TOPAS (Version 4.2) [28]. The peak profile was modelled using a pseudo-Voigt peak shape function and the background of the diffraction pattern was fitted by a linear interpolation between selected background data points. The zero point error, scale factor, lattice parameters and isotropic atomic displacement parameters were refined. For the site occupancy of the D atom in the deuteride phases (δ , ϵ and γ) potentially formed in the sample, this parameter was refined for the δ - and ϵ -deuteride phases but was fixed to be 1.0 for the stoichiometric γ -deuteride ($\text{ZrD}_{1.0}$) phase as evidenced in previous works [4, 5]. For simplicity the stoichiometry of hydride phases were not specified in most cases hereinafter unless necessary. The D atoms occupy the special positions in the unit cells of the deuteride phases in the reported structural models [5] and their atomic positions were constrained to the corresponding special values.

Fig. 2. Thermal profile used in the neutron diffraction experiments. The figure numbers were included to show which diffraction data were presented in this work at a specific temperature.

3. Results and discussion

The initial as-deuterided sample was investigated using high-resolution synchrotron X-ray and neutron diffraction at room temperature. The cubic ($Fm\bar{3}m$) δ -ZrD and tetragonal ($I4/mmm$) ϵ -ZrD phases as well as the hexagonal ($P6_3/mmc$) α -Zr phase were identified in the initial sample based on the measured diffraction data (Fig. 3, black data points), while the tetragonal γ -ZrD phase was not detected. A combined Rietveld refinement using the X-ray and neutron diffraction data was performed with the structural models of the phases observed and the results of the fit are shown in Figure 3. The inset in Fig. 3a shows a detailed fit of the X-ray diffraction pattern at a higher 2θ region (19 – 31°). The phase quantification from the combined refinement indicated that the δ -ZrD phase is a minor phase in the initial sample with a fraction of $11.5(4)$ wt.%, and the majority are the α -Zr ($46.5(2)$ wt.%) and ϵ -ZrD ($42.0(2)$ wt.%) phases. The lattice parameters for the observed phases from the combined refinement are (i) α -Zr: $a = 3.23503(1)$ Å, $c = 5.15215(1)$ Å; (ii) ϵ -ZrD: $a = 3.51213(19)$ Å, $c = 4.45543(11)$ Å; and (iii) δ -ZrD: $a = 4.78051(5)$ Å, in line with the reported literature values [5]. Additionally, the refinement showed a fully occupied D site (i.e., occupancy of 1.0) in the

1 ϵ phase, suggesting that the observed ϵ -deuteride is a stoichiometric phase ($\text{ZrD}_{2.0}$). This
 2 result confirms the previous reports that the ϵ phase is a hydrogen-rich phase which tends to
 3 form in the Zr–H system at very high hydrogen concentrations [5, 15, 29]. For the δ phase in
 4 the as-deuterided sample, the D site occupancy was determined to be 0.65, corresponding to a
 5 composition of $\delta\text{-ZrD}_{1.3}$. Here, the errors of the determined D site occupancies for the ϵ and δ
 6 phases are very small ($\leq 1\%$) and have negligible effect on the reported hydride
 7 stoichiometries. Furthermore, although the D atoms cannot be distinguished by X-rays, it is
 8 confirmed that the combined refinement with X-ray and neutron data as performed here does
 9 not affect the accuracy of the reported occupancy factors through the comparison of the
 10 results of D site occupancies from the combined refinement and the individual analysis only
 11 using the neutron data. The result of the δ -hydride stoichiometry, however, is not consistent
 12 with the earlier findings from the X-ray powder diffraction analysis of the zirconium hydrides
 13 with the known compositions, showing a typical δ phase composition of $\sim\text{ZrH}_{1.66}$ [6]. The
 14 different δ phase compositions observed might be attributed to the discrepancy in the phase
 15 constitutions and hydrogen concentrations of the samples used in the different experiments,
 16 which affects the hydrogen partition between the phases, and the site occupancy within them.

Fig. 3. Combined Rietveld refinement with (a) synchrotron X-ray and (b) neutron diffraction data measured from as-deuterated zirconium sample at room temperature. The inset in (a) shows an enlarged section of the diffraction pattern at a higher 2θ region of $19\text{--}31^\circ$. The phase fractions determined from the combined refinement were also included in (a).

In situ temperature-dependent neutron diffraction measurements were carried out during the heat treatments on the deuterided samples to investigate the phase evolutions and clarify the formation conditions of γ -hydride. The main results from the measurements are presented below. Figure 4 depicts some typical diffraction patterns recorded at various soaking temperatures in the initial heating process. Compared with the diffraction pattern measured from the as-deuterided sample at 290 K (Fig. 4c), no significant changes were observed in the patterns collected at temperatures of 559 K (Fig. 4a) and 450 K (Fig. 4b). The phases present in the sample at these high temperatures remain to be δ -ZrD, ϵ -ZrD and α -Zr. The γ phase was not observed during the initial heating process. It should be pointed out that, as shown in Fig. 2, the sample was held at 559 K for 15 h, and the data in Fig. 4a was collected from the last hour at this temperature. Based on this direct evidence from *in situ* observations, we can state that the previously reported phase transformation of α -Zr + δ -ZrD $\rightarrow$ γ -ZrD at 559 K [17, 18] does not occur in our system during the heating process. Our result supports the viewpoint

that the γ phase is not an equilibrium phase produced by a peritectoid reaction [3]. Moreover, Root and Small et al. [19-21] reported a slow δ -ZrD $\rightarrow$ γ -ZrD phase transformation in a Zr–2.5Nb alloy which initiated at ~ 453 K during cooling. The present result at 450 K shown in Fig. 4b, however, is recorded during the heating process. Without consistent heat treatment experiments, it is difficult to discern only based on the result in Fig. 4b whether or not the $\delta \rightarrow \gamma$ transformation exists in the present system.

Fig. 4. Selected neutron diffraction patterns collected in the initial heating process at soaking temperatures of (a) 559 K and (b) 450 K. The pattern (c) was measured from the as-deuterided sample at room temperature (290 K) and was included for comparison. The major reflections of the observed phases are indexed in the patterns. Diffraction data were normalized for the equivalent collection time.

Figure 5a compares the neutron diffraction patterns measured from the samples after cooling from high temperatures to room temperature at different cooling rates. The diffraction data were collected at $\lambda = 2.4395$ Å for a high angular resolution to facilitate hydride phase identification. When the sample was first cooled to room temperature from 559 K at a rate of 30 K min^{-1} , only the α , δ and ϵ phases were observed whereas the expected formation of γ

phase under this fast cooling condition was not found. In the subsequent experiment, the sample was heated up to a higher temperature of 763 K to investigate whether a higher temperature would facilitate the phase change and the formation of γ phase. After slowly cooling to room temperature from 763 K at 5 K min^{-1} , in addition to the α and δ phases which showed some strong reflections, the γ phase was clearly detected in the sample. The production method of γ phase discovered here appears to be opposite to what has been reported in literature, i.e., slow cooling promotes the γ phase formation, not fast cooling. It should be clarified that, although at the starting high temperatures the sample composes of α , δ and ϵ phases in the fast cooling experiment, while in the subsequent slow cooling experiment the sample consists of only α and δ phases, this conclusion is not affected by the difference in the phase constitution. This is because at the starting high temperature (559 K) in the fast cooling experiment the sample actually contains two phase regions of $(\alpha + \delta)$ and $(\delta + \epsilon)$ based on the Zr–H binary phase diagram [5], and the coexistence of the two phase regions in this material would not affect the phase transformation behavior of each region during fast cooling. This observation gives weight to an argument that in the present material the γ phase forms by a diffusion-controlled transformation, rather than a displacive or martensitic type transformation which was generally reported in dilute Zr–H alloys [13]. Additionally, after slow cooling the ϵ -ZrD phase was found to disappear completely (Fig. 5a), suggesting that ϵ is thermodynamically unstable and readily decomposes during slow cooling. The metastable ζ -Zr₂H phase, which was reported to form under both fast and slow cooling conditions [8, 30], was not observed in the present experiment.

Figure 5b shows the Rietveld refinement of the sample after slow cooling to room temperature using the neutron diffraction data collected at $\lambda = 1.6215 \text{ \AA}$ for a high Q-range. A good fit ($R_{\text{wp}} = 6.0\%$) was obtained with the three-phase structural models of $P6_3/mmc$ (α -Zr), $P4_2/n$ (γ -ZrD) and $Fm\bar{3}m$ (δ -ZrD). The refined lattice parameters for the tetragonal γ phase

are $a = 4.5833(5) \text{ \AA}$ and $c = 4.9449(13) \text{ \AA}$. Apart from the tetragonal $P4_2/n$ structure, another orthorhombic $Cccm$ structure [16] was reported for γ -ZrD. We attempted to model the measured diffraction pattern with the $Cccm$ space group for γ -ZrD and found this model does not fit well ($R_{wp} = 7.8\%$), showing noticeable misfits of some reflections. This confirms the tetragonal $P4_2/n$ structure for the γ phase.

Fig. 5. (a) Neutron diffraction patterns collected at $\lambda = 2.4395 \text{ \AA}$, showing the phase constitution in the deuterided samples after cooling from high temperatures to room temperature at different cooling rates of 30 and 5 K min^{-1} . (b) Rietveld refinement of the neutron diffraction pattern measured at $\lambda = 1.6215 \text{ \AA}$ from the sample cooled to room temperature at a slow rate of 5 K min^{-1} .

After the production of γ -ZrD with slow cooling, the sample was incrementally heated up from 290 to 740 K to investigate the hydride phase evolutions during heating. Figure 6 shows the measured diffraction patterns at various soaking temperatures. Each pattern was collected for a soaking period of 2 h at specific temperatures. The δ phase was present throughout the heating process, as evidenced by the observation of their strong reflections including the 111 peak at 2θ of approximately 34.3° and 220 at approximately 57.5° (Fig. 6a). To track the evolution of γ phase, the enlarged sections of the patterns near the δ -/ γ -111 reflections are shown in Fig. 6b. The intensities of γ -111 reflections were found to decrease gradually with increasing the soaking temperature to 530 K and vanish with further soaking at 559 K, indicating that γ -ZrD disappeared completely at this temperature. On the other hand, the intensities of δ -111 reflections appeared to increase with increasing the soaking temperature. Furthermore, it is noteworthy that the ϵ -ZrD phase which was present in the initial heating stage (Fig. 4) and decomposed after slow cooling (Fig. 5a) has not returned in this heating process. To follow the phase evolutions during this process, quantitative phase analysis was performed by the Rietveld method using the collected neutron data and the result is shown in Figure 7. It reveals that, before the high-temperature treatments, δ -ZrD was the predominant phase in the system at 290 K with a fraction of 50.0(6) wt.%, and the contents of the remaining α -Zr and γ -ZrD phases were 29.4(3) wt.% and 20.6(7) wt.%, respectively. The relative fraction of δ phase increased significantly as compared with the as-deuterided state, presumably attributed to the decomposition of ϵ phase during slow cooling. With increasing soaking temperature, the δ phase content first gradually increased in the range of 290 K to 450 K and then rapidly rose with further elevating temperature to 559 K. In contrast, the γ phase content displays an inverse variation trend with increasing temperature, i.e., first slowly decreasing with increasing temperature from 290 to 450 K and then quickly diminishing to

zero with further temperature elevation to 559 K (Fig. 7). The α -Zr phase fractions were almost unchanged during heating. These observations clearly indicate that the γ phase actually transforms to the δ phase during heating supporting the previous report by Sidhu et al. [5], and the kinetics of this transformation is enhanced at high temperatures above 450 K. The measurements also provide direct experimental evidence to support that δ -ZrD is stable up to 740 K (under the present experimental conditions), while γ -ZrD gradually transforms to δ -ZrD in the temperature range between 370 K and 559 K. Moreover, with the occurrence of this $\gamma \rightarrow \delta$ transformation, there is an overall trend of slightly decreasing D site occupancy in δ -ZrD with increasing temperature (Fig. 7). We believe that this change is resulted from the difference in stoichiometric compositions between δ and γ phases.

Fig. 6. Neutron diffraction patterns showing the evolution of γ -ZrD phase during the heating process. Note that γ -ZrD disappeared completely at 559 K while δ -ZrD phase was present at high temperatures up to 740 K.

Fig. 7. Phase fractions of α -Zr, δ -ZrD and γ -ZrD and the D site occupancy in δ -ZrD as a function of soaking temperature determined by the Rietveld refinement analysis of neutron diffraction data. The dash line indicates the observed temperature (450 K) above which the rate of γ - to δ -hydride phase transformation increases during heating.

Following the thermal treatment experiment with the observation of $\gamma \rightarrow \delta$ transformation, we repeated the slow cooling measurements three times to clarify whether or not the γ -ZrD is reproducible during slow cooling. For this purpose, as shown in Fig. 2, the sample was first cooled step-wise from 740 to 520 K with the diffraction patterns recorded at each temperature step to understand the starting high temperatures at which the γ phase was not present during cooling. The continuous slow cooling experiments in the last stage of *in situ* observations were then conducted at a rate of 5 K min^{-1} with different starting temperatures of 520, 540 and 580 K. The neutron diffraction measurements revealed that only δ -ZrD and α -Zr were present at these starting high temperatures. All the slow cooling experiments led to a consistent observation that γ -ZrD reappeared after slow cooling to 290 K, as demonstrated in a representative refinement in Figure 8 of the sample cooled from 520 K, verifying that γ -ZrD is reproducible with slow cooling in the present system. Table 1 summarizes the Rietveld

phase quantification results for the sample after slow cooling to 290 K from four different starting temperatures. Interestingly, the quantitative comparison of the phase contents showed that the phase constitutions in the sample at 290 K after various slow cooling treatments are very similar. Because the deuterided sample was measured in a sealed environment, no significant loss of deuterium was expected during measurements. It is thus reasonable to deduce that a certain fraction of δ -ZrD present at high temperatures reversibly transforms to γ -ZrD during slow cooling, resulting in the reproduction of the γ phase and the similar phase constitutions in the sample after slow cooling to 290 K (Fig. 8 and Table 1). This conclusion for the occurrence of the $\delta \rightarrow \gamma$ transformation is consistent with the observations of Root and Small et al. [20, 21].

Fig. 8. Rietveld refinement of a typical neutron diffraction pattern from the sample after cooling from 520 to 290 K at 5 K min⁻¹, showing that γ -ZrD is reproduced with slow cooling.

Table 1 Phase fractions of α -Zr, δ -ZrD and γ -ZrD in the sample after slowly cooling to 290 K at 5 K min⁻¹ from various elevated temperatures, determined by the Rietveld quantitative phase analysis.

Starting temperatures in slow cooling \ Phase fractions (wt.%)	α -Zr	δ -ZrD	γ -ZrD
763 K	29.4(3)	50.0(6)	20.6(7)
520 K	30.1(6)	51.6(6)	18.3(8)
540 K	30.8(6)	53.5(6)	15.7(7)
580 K	29.9(6)	50.7(8)	19.4(8)

In light of the knowledge of the existence of the $\delta \rightarrow \gamma$ transformation in the present system derived from these *in situ* diffraction measurements, it is considered that the opposite formation conditions of γ -hydride observed in the present and previous works can be rationalized in the following:

(1) In the dilute Zr–H alloy system, the γ -hydride was mostly observed in previous investigations after rapid cooling of the sample from the α -Zr phase field [11, 12]. It has been often suggested the γ -hydride forms in this case by a displacive or martensitic $\alpha \rightarrow \gamma$ transformation which involves the displacive motion of zirconium atoms and the cooperative movement of hydrogen atoms by rapid diffusion [13].

(2) In the present hydrogen-rich Zr–H system with large phase fraction of δ -hydride, it is confirmed the γ -hydride forms through a $\delta \rightarrow \gamma$ transformation during slow cooling. Cassidy and Wayman [31] revealed in a crystallographic study of the $\delta \rightarrow \gamma$ transformation that hydrogen atoms diffuse prior to the transformation, due to the different bulk compositions of δ and γ phases. They suggested that relative to the very rapid diffusion of interstitial hydrogen atoms in the metallic α -Zr phase, the hydrogen diffusivity in the δ -hydride phase is considerably slower [17]. Root et al. [21] also pointed out that the dissociation of hydrogen

atoms from the δ -hydride crystal lattice is the rate-limiting step of the $\delta \rightarrow \gamma$ transformation. This provides evidence that the $\delta \rightarrow \gamma$ transformation is sluggish or diffusion-limited and thus this transformation and the resultant formation of γ -hydride are favored by slow cooling.

Additionally, the $\delta \rightarrow \gamma$ transformation was found to be incomplete after slow cooling (Table 1), probably related to the slow migration process of hydrogen away from the δ -hydride in order to achieve a lower concentration of hydrogen to allow the formation of the γ -hydride phase. Furthermore, it should be mentioned that during slow cooling, the migration of hydrogen atoms from the δ -hydride unit cell occurs simultaneously with a reduction in the solubility of hydrogen in α -Zr. In this case, the released hydrogen atoms from δ -hydride may not react with the surrounding α -Zr but tend to deposit on the surface of existing δ -hydrides [21]. Consequently, the α -Zr phase fractions were nearly unchanged after slow cooling (Table 1).

4. Conclusions

The zirconium hydride phase evolution during thermal cycling and the formation conditions of γ -hydride have been studied by *in situ* high-resolution neutron powder diffraction with the deuterided zirconium samples containing 50 at.% deuterium. It is clarified that the previously proposed peritectoid reaction $\alpha\text{-Zr} + \delta\text{-ZrD} \rightarrow \gamma\text{-ZrD}$ at high temperatures does not occur in this material. The process method for the development of γ -hydride with the present system was confirmed to be opposite to that reported before, i.e., slow cooling appears to always promote the formation of γ phase, rather than fast cooling, which is consistent with disordered and ordered nature of the δ - and γ - phases, respectively. The Rietveld refinements justify the tetragonal $P4_2/n$ structure for the γ phase produced upon slow cooling. Further, the γ -hydride was found to gradually transform to δ -hydride during heating and disappeared completely after soaking at 559 K. In contrast, the δ -hydride was stable at higher temperatures

up to 740 K. Detailed phase quantification analysis by Rietveld refinements revealed that the γ -hydride phase transforms to the δ phase during heating. A reversible but incomplete transformation of δ - to γ -hydride is suggested to occur in the present system during slow cooling, resulting in the development of γ phase. This $\delta \rightarrow \gamma$ transformation is considered to be sluggish, due to limits by the migration of hydrogen atoms away from the crystal lattice of δ -hydride in order to attain a lower composition to facilitate the formation of γ phase. This characteristics accounts for the favorable formation of γ -hydride after slow cooling.

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Figure captions

Fig. 1. Crystallographic structures and common formulae of four different hydrides (ζ , γ , δ and ϵ) found in the Zr–H system [22]. The larger green and smaller grey spheres represent the Zr and H atoms, respectively. The δ -hydride shown in the phase diagram (after Ref. [4]) is a non-stoichiometric phase which was reported to have a typical H/Zr ratio of ~ 1.66 and a disordered CaF_2 -prototype structure with the hydrogen atoms partially occupying the eight available tetrahedral sites at random. The γ -hydride ($\text{ZrH}_{1.0}$) was identified to have a tetragonal structure with the ordered arrangements of hydrogen atoms at the tetrahedral interstitial sites.

Fig. 2. Thermal profile used in the neutron diffraction experiments. The figure numbers were included to show which diffraction data were presented in this work at a specific temperature.

Fig. 3. Combined Rietveld refinement with (a) synchrotron X-ray and (b) neutron diffraction data measured from as-deuterated zirconium sample at room temperature. The inset in (a) shows an enlarged section of the diffraction pattern at a higher 2θ region of $19\text{--}31^\circ$. The phase fractions determined from the combined refinement were also included in (a).

Fig. 4. Selected neutron diffraction patterns collected in the initial heating process at soaking temperatures of (a) 559 K and (b) 450 K. The pattern (c) was measured from the as-deuterided sample at room temperature (290 K) and was included for comparison. The major reflections of the observed phases are indexed in the patterns. Diffraction data were normalized for the equivalent collection time.

Fig. 5. (a) Neutron diffraction patterns collected at $\lambda = 2.4395 \text{ \AA}$, showing the phase constitution in the deuterided samples after cooling from high temperatures to room temperature at different cooling rates of 30 and 5 K min^{-1} . (b) Rietveld refinement of the neutron diffraction pattern measured at $\lambda = 1.6215 \text{ \AA}$ from the sample cooled to room temperature at a slow rate of 5 K min^{-1} .

Fig. 6. Neutron diffraction patterns showing the evolution of γ -ZrD phase during the heating process. Note that γ -ZrD disappeared completely at 559 K while δ -ZrD phase was present at high temperatures up to 740 K.

Fig. 7. Phase fractions of α -Zr, δ -ZrD and γ -ZrD and the D site occupancy in δ -ZrD as a function of soaking temperature determined by the Rietveld refinement analysis of neutron diffraction data. The dash line indicates the observed temperature (450 K) above which the rate of γ - to δ -hydride phase transformation increases during heating.

Fig. 8. Rietveld refinement of a typical neutron diffraction pattern from the sample after cooling from 520 to 290 K at 5 K min⁻¹, showing that γ -ZrD is reproduced with slow cooling.

List of Table

Table 1 Phase fractions of α -Zr, δ -ZrD and γ -ZrD in the sample after slowly cooling to 290 K at 5 K min⁻¹ from various elevated temperatures, determined by the Rietveld quantitative phase analysis.

Highlights

- The zirconium hydride phase evolution during thermal cycling was studied.
- Slow cooling was found to promote the γ -hydride formation, not fast quenching.
- We suggest a possible explanation for the observed γ -hydride formation.
- The produced γ -hydride was unstable and transformed to δ -hydride during heating.
- The δ -hydride was stable at high temperatures up to 740 K.