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Phase transformation and microstructural changes during the hydriding and aging processes in dual phase Zr alloy

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Synopsis: The present study broadens our understanding of the formation and stability of different hydride phases in dual phase (α/β) Zr alloy.

Abstract

Preventing hydrogen embrittlement and Delayed Hydride Cracking failures requires an understanding of the behaviour of small quantities of hydrogen in zirconium. The Zr-2.5 wt.%Nb alloy was studied in order to elucidate phase transformations and distribution/redistribution of hydrogen. The study focused on understanding the stability of Zr-H system; surface hydride formation and its transformation during ageing was inspected in details, using SEM imaging, EBSD, X-ray diffraction and AFM. During the hydriding process, the *H in solution* $\rightarrow \gamma \rightarrow \delta$ transformation occurred, which resulted in the formation of δ -hydrides on the sample surface. As hydride precipitation occurs, the system enters a metastable state before it reaches a new equilibrium state. The Zr-H system approach to the new equilibrium state was monitored during room temperature ageing over the course of several weeks. The total hydride fraction decreased with ageing time. Along with a $\delta \rightarrow \gamma$ phase transformation, partial hydrogen dissolution occurred followed by diffusion out of the surface X-ray diffracting volume into the depth of the sample.

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1. Introduction

The mechanical properties of metals can be dramatically affected by the presence of hydrogen either in solid solution or as precipitated hydrides. A substantial loss of ductility has been attributed to stress-induced hydride formation at a crack tip [1] or a hydrogen-enhanced localized plasticity [2], [3]. In zirconium alloys precipitated hydrides drastically reduce the ductility, fracture toughness and impact strength at room and at reactor operating temperatures [4], [5]. The hydride type and its microscale morphology are key factors in the degree of embrittlement of zirconium alloy structural components [6].

We focus in this paper on zirconium: under appropriate conditions, the hydrogen/hydride sub-lattice can experience phase transformations similar to that established for a one-component system (Figure 1). These phase transitions (which result in hydride precipitation) occur within the given α -Zr lattice which includes vacancies and (in a typically smaller population) occupied interstitial locations; the distribution of the Zr atoms within the matrix around the hydride precipitates can be considered as remaining essentially unchanged due to the very rapid movement of hydrogen. Hydrogen can occupy interstitial tetrahedral and octahedral sites in the Zr hcp; in the vicinity of a vacancy cluster formed under irradiation, the most favorable insertion site for H is an octahedral site with 2 or 3 vacancies as first nearest neighbors [7]. However, under normal conditions hydrogen in HCP α -Zr tends to solely occupy tetrahedral sites due to the lower absorption/dissolution enthalpy [8].

Figure 1: Phase transformation in a one-component system.

At high temperatures ($T > T_{\text{TSS-D}}$; where TSS-D stands for 'Terminal Solid Solubility for Dissolution') hydrogen atoms randomly occupy interstitial sites in the metal lattice, resembling a 'lattice gas' having a low density of hydrogen atoms in the metal matrix. With a decrease in temperature or an increase in the concentration of hydrogen, long-range interactions between the H interstitials appear and are amplified, leading to a transformation of the lattice gas to a state similar to a lattice liquid having short-range order. Figure 2 shows five possible arrangements of H atoms in the Zr metal matrix for the same local hydrogen concentration. The first two structures (Figures 2a and 2b) correspond to the γ -ZrH phase. The other four variants in Figures 2 c-f have similar density but differ in degree of ordering of the hydrogen atoms on

tetrahedral sites. We might consider a mixture of the structures of the Zr/H system depicted in Figure 2 to form a “lattice liquid”, i.e., in an unordered state.

Figure 2: Possible arrangement of H atoms on tetrahedral sites in metal matrix for $\text{ZrH}_{x=1.0}$. The large green spheres represent Zr atoms, H atoms are represented with small purple spheres.

Further cooling and/or an increase in H concentration provides a long-range ordering of the hydrogen in solid solution similar to that observed during the crystallization of a liquid or gas. One might consider the movement of hydrogen atoms within the unit cell from one tetrahedral site to another as an essence of phase transformation from ‘liquid’ to solid state in Zr-H system (or disordered to ordered). The rearrangement of H atoms from structures depicted in Figures 2 c-f into structures in Figure 2a or 2b results in the formation of the γ -ZrH phase, the presence of which can be determined by EBSD or x-ray diffraction techniques due to the diffraction signal obtained.

The type of hydrides formed in Zr alloys and their morphology are determined by purity of the Zr, thermal history, hydrogen concentration, the magnitude of the external load, and cooling rate [9], [6], [10]. According to most of the published literature [11], [12], [9], [13], [14], [15], [16], [17], there exists at least four different hydride phases at ambient temperature under atmospheric pressure. These are the newly observed trigonal ζ -hydride ($P3m1$, $\zeta\text{-ZrH}_x$ where $0.25 \leq x \leq 0.5$, $a=3.242 \text{ \AA}$, $c=10.33292 \text{ \AA}$), the face centered tetragonal γ -hydride with structure type ZrH ($P4_2/n$, $\text{ZrH}_{x=1.0}$, $a=4.592 \text{ \AA}$, $c=4.970 \text{ \AA}$, $c/a > 1$), the face centered cubic δ -hydride with CaF_2 structure type ($Fm\bar{3}m$, $\text{ZrH}_{x=1.4-1.7}$, $a=4.7783 \text{ \AA}$), and the face centered tetragonal ϵ -hydride with ThH_2 structure ($I4/mmm$, $\text{ZrH}_{x=1.75-2}$, $a=4.9689 \text{ \AA}$, $c=4.4479 \text{ \AA}$, $c/a < 1$). A brief review of the crystallography of the δ -, γ - and ϵ -hydrides has been provided by Steuwer et al. [13]. The ζ -hydride is a recently identified and rarely reported metastable phase that is fully coherent with the hexagonal α -Zr and is suggested to be a transitional phase between α -Zr and δ or γ hydrides [16]. However, this new phase was not observed in the current research and will not be discussed further.

Figure 3: Schematic crystal structures of (a) γ -, (b) δ - and (c) ϵ - hydrides. The large green spheres represent Zr atoms, H atoms are represented with small purple spheres.

The crystal structures of the most commonly reported hydride phases are illustrated in Figure 3. All eight possible tetrahedral sites in the unit cell of the ϵ -hydride are completely filled with hydrogen atoms, while they are partly filled in the δ - hydride [1]. The γ -hydride phase has the lowest density of hydrogen atoms in the Zr lattice. Increasing the hydrogen density in the α -Zr matrix results in a reduction of the hydride sub-lattice along the c-axis and dilation along the a-axis (Figure 3). The hydride phases essentially differ in (i) the local density of hydrogen atoms in Zr matrix and (ii) the degree of ordering of the hydrogen atoms on tetrahedral sites [13], what in turn affects the composition.

Although many studies have been carried out on different hydride phases, there is still controversy regarding the stability, crystal structure, formation mechanisms, and the temperatures associated with transformation between phases [13], [18], [19], [20], [21], [22], [23], [24], [25]. Cann et al. [20] performed analysis of the effects of matrix-hydride misfit strains on hydride solubility and showed that the γ phase is expected to nucleate first upon cooling from a state where hydrogen was fully in solution, due to its lower elastic strain energy. For a given concentration of hydrogen, the lower elastic accommodation energy required for γ -hydride compared with δ -hydride provides a higher number density of γ -precipitates [26]. After nucleation, the hydrides grow, thus reducing the hydrogen concentration in solid solution. However, if only γ -hydride forms and grows, the total strain generated is greater than that for δ -hydride. Hence, if there is sufficient concentration of hydrogen in solution, the formation of the δ -hydride with a higher density of H atoms is expected. The δ -phase enables a larger amount of H to be removed from solution and to accommodate them in the matrix as precipitates, hence providing a reduction of the total matrix-hydride misfit strain per H atom. That is, if there is sufficient hydrogen removed from the matrix, the δ -hydride is energetically more favorable than γ -phase, although during initial nucleation the γ -phase is preferred. Once the precipitated hydrides have grown to a critical size, plastic relaxation reduces the difference in the strain energies associated with hydride formation. Elastoplastic deformation results also suggest that the delta phase is favored, due to the slightly lower accommodation energy [27], [20]. Therefore, we assume that if there is a sufficient influx of hydrogen to the initial nucleation sites, the hydride phase with higher degree of ordering and higher concentration of H atoms (i.e., δ -phase) will be preferable.

This article reports a study of changes in Zr alloy caused by the hydride precipitation on the surface of a sample. The focus of this paper is on phase transformations occurring in the surface layer of a dual-phase (α/β) Zr alloy during electrolytic hydriding followed by ageing. The hydrided sample is identified as an open system due to hydrogen transfer across the system boundary. After hydriding, this open system does not exist in the equilibrium state. As a result, hydrogen diffusion is expected, coupled with phase transformations, hydride dissolution and re-precipitation.

The paper is organized as follows. We first investigate phase changes occurring in a sample during electrolytic hydriding, i.e., the process of hydrogen-in-solution – γ -hydride – δ -hydride transformation is considered. Then, phase changes occurring in the as-hydrided sample with time are examined. A separate section is dedicated to examining the microstructure of the formed hydrides. Finally, the movement of the Zr-H system out of an equilibrium state and transition into a new equilibrium state is discussed.

2. Experimental

2.1. Samples

The composition of the base material is 2.5 wt.%Nb, ~1200ppm O, ~950ppm Fe, ~110ppm C and balance Zr. Details on base material can be found in [28]. Sample preparation started with metallographic grinding, rough and then fine polishing [29]. Since local stress can impact hydriding, any machining induced mechanical stress was minimized by applying electropolishing as the final stage. Electro-polishing of zirconium alloy samples was performed using A3 electrolyte (20% perchloric acid (HClO_4) and 80% methanol ($\text{C}_2\text{H}_5\text{OH}$)) at -24°C and 20V. After electropolishing the specimens are removed from the electrolyte with the current on and quickly immersed and vigorously agitated in an ethanol wash bath. After a few seconds, the specimen was rinsed with DI water. Electropolishing reduces surface stresses and also resulted in an improved surface finish. This made it possible to collect EBSD maps from the same sample before and after the hydriding procedure with no additional surface preparation. All samples were examined as-prepared then as-hydrided.

Electrolytic hydriding of the samples was carried out according to the procedure described in [30]. In this process samples were cleaned and immersed to 0.2M solution of sulfuric acid and hydrided at 70 °C. To provide relatively fast and relatively slow hydrogen ingress into the Zr alloy, hydriding was realized at two different current densities: 1.0 kA/m² and 0.2 kA/m² current density used for 'fast' and 'slow' hydriding, respectively. In total, 10 samples were hydrided (see Table 1). All of these samples were examined as-hydrided. The surface layer containing the hydride remained intact during subsequent ageing, since no additional sample preparation was carried out. Each sample has a plate shape with 15x5x2 mm³ dimensions. The sequence of actions performed within the frame of the experiment is shown in Fig.4.

Table 1. Samples produced for the study of hydride phase transformation.

	hydriding		
	total time, h	rate*	characteristics**
Sample #1	6	fast	continuous
Sample #2	12	fast	continuous
Sample #3	18	fast	continuous
Sample #4	24	fast	continuous
Sample #5	96	fast	continuous
Sample #6	24	fast	with interruptions for monitoring
Sample #7	96	fast	with interruptions for monitoring
Sample #8	24	slow	continuous
Sample #9	96	slow	continuous
Sample #10	96	slow	with interruption for monitoring

* **fast** rate hydriding is at 1.0 kA/m² current density;
slow rate hydriding is at 0.2 kA/m² current density.

** **continuous** hydriding: EBSD and/or X-ray monitoring of the hydride phase was performed after completion of the hydriding phase;

with interruption for monitoring: the hydriding process was put on hold several times: the sample was pulled out the solution, rinsed and an EBSD map was collected. After that, the sample was immersed back into solution and hydriding was continued.

Figure 4: Flowchart of experiment conducted for different samples.

The total hydriding time was chosen such that the hydride layer formed did not uniformly cover the surface; some α -Zr grains were retained uncovered with hydride phase (Figure 5). The structure obtained provides an opportunity to monitor the phase transformations occurring in the surface layer during subsequent material ageing. After hydriding, the material was aged in vacuum at ambient temperature.

Figure 5: The phase map of (a) as-received and (b) as-hydrided sample (3 days hydriding at 1.0 kA/m² current density).

2.2. Instrumentation

Conventional lab X-Ray diffraction experiments were performed on a Rigaku diffractometer with Cu K α radiation ($\lambda = 1.541871$ Å) and scanned in 2-90° range in 2θ . The x-ray diffraction patterns were measured for as-hydrided and aged samples.

Microstructures of hydrided (as-hydrided and aged) and non-hydrided reference samples were characterised using a FEI FEG-Nova NanoSem scanning electron microscope at an accelerating voltage of 20 kV. A Bruker EBSD camera and EDS detector was used. The data collection and post processing of data is done with the ESPRIT 2.0 software by Bruker; EBSD step size was 40 nm.

Surface topography determination and microstructure characterisation of as-hydrided samples by Atomic Force Microscopy was carried out on Veeco NanoScope IV MultiMode AFM.

3. Results

3.1. Sample Hydriding. Hydrogen in Solution $\rightarrow$ Gamma Hydride $\rightarrow$ Delta Hydride Transformation

The study of hydride phase formation was started with electrolytic hydriding with a current density of 1kA/m² as recommended in [31]. The sample was removed and measured using EBSD at various times during the hydriding process; as depicted in Figure 5, both δ - and γ -phases hydrides are observed on the surface after hydriding. The hydride fraction increases with hydriding time: after 4 days hydriding, the sample surface is covered predominantly with δ -ZrH phase. That is, EBSD Kikuchi patterns indexed with EBSD system show the presence of hcp α -Zr and fcc δ -hydrides, with negligible amount of fct γ -hydride (Figure 5b).

The intensity of the Kikuchi bands or EBSD pattern quality decreases upon hydriding which resulted in increased number of unindexed points. In general, the EBSD pattern quality is dependent upon many factors: beam conditions, geometrical set-up, material phases, acquisition time, and parameters used for the Hough transform [32]. For consistency, the aforementioned factors were kept constant during the series of measurements. Another factor affecting the pattern quality is the quality of the tested surface. Gradual surface degradation by acidic agents occurs during the hydriding procedure. However, relatively

low temperature and short hydriding time allow us to neglect the surface degradation effect. Finally, the pattern quality is influenced by phase transformations and strains generated in the tested material.

There are a number of contributions to this. First there is significant volume expansion associated with the hydride phase transformation [33], which has the potential to induce dislocations around the hydrides [10], [34]. Second, this expansion will generate a tensile stress in the Zr-matrix around the hydrides; some of the H atoms in solution will migrate to this tensile stress field, thus potentially forming a “lattice liquid” (an unordered set of structures shown in Figure 2) but not resulting in a uniform phase. The combination of these effects causes deterioration of the EBSD signal. Therefore, pattern quality in general and hit rate in particular can serve as a qualitative descriptor of changes associated with hydride phase formation/transformation.

Figure 6: Changes in phase fraction with hydriding time. Current density of 1.0 kA/m² used.

The plot in Figure 6 quantifies the change in phase fraction based on EBSD data recorded from samples being hydrided to different times. 99% of points on the surface were correctly indexed in the as-received unhydrided sample. In hydrided samples, the hit rate decreases with increasing hydriding time due to matrix distortion and increased density of interfaces. Both δ - and γ -hydride phases grow at the expense of α -Zr, as observed during the first 24 hours of hydriding. Further hydriding provides a consistent increase in δ -ZrH and further decrease in amount of α -Zr phases. It remains unclear from Figure 5b and Figure 6, what phase of hydride initially precipitates on the surface. Three options are possible, looking at the 6- and 12-hour data in particular: it might be that initially δ -phase formed, then it transforms into γ -phase. Another option is γ -hydride precipitation occurs with subsequent transformation into δ -phase. A further option is that both δ - and γ -hydrides are precipitating simultaneously. In order to trace the transformation of the dissolved hydrogen (in solid solution) into the hydride phase, a lower rate of hydriding was therefore selected for a subsequent experiment.

Figure 7: (a) SEM image of the sample surface prepared for hydriding. EBSD data of (b) the same area and that after (c) 1 day and (d) 4 days of hydriding at 0.2 kA/m² current density. Region of interests marked by black square is linked with Figure 14 and discussed in section 3.3. (e) Changes in phase fractions observed during the 'slow' hydriding.

Figure 7 compares EBSD patterns obtained from the same location on the surface of a sample before hydriding and after 1 and 4 days of 'slow' hydriding (0.2 kA/m² current density). The reduced current and resultant slower rate of hydriding enables us to observe the initial hydride precipitation more clearly, it is seen to be predominantly γ -phase. The rate of nucleation is relatively high whereas precipitate growth is slow. In comparison to Figure 5b, no pronounced grain structure is observed in the hydride phase (at this length scale) in Figure 7b. The addition of further hydrogen to the system appears to stimulate the $\gamma \rightarrow \delta$ transformation in the hydride phase. After 4 days of slow hydriding, 30% of indexed points corresponds to the δ -ZrH and 45% of them belong to the α -Zr phase; the amount of the γ -phase decreases from 22% to 13% (Figure 6e).

3.2. Sample ageing. Delta Hydride → Gamma Hydride → Hydrogen in Solution Transformation

The previous section reported an out-of-equilibrium state of Zr-H system during the sample hydriding process. The current section considers the changes in the Zr-H system after cessation of hydrogen inflow (after hydriding has been stopped; total hydriding time was 24 hours at 1kA/m² for this sample). As described above, hydrided samples were stored in vacuum at room temperature. Periodically, samples were monitored to detect/trace changes in matrix and hydride phases associated with hydrogen diffusion into the bulk material.

Figure 8 demonstrates changes in the Zr-H system occurring during the first month of ageing. Initially, a few δ -hydride grains formed on the surface; the γ -phase nuclei are detected mainly in the β -Zr phase and at the α/β phases boundaries (Figure 8a). Two days later (Figure 8b), (i) the hydrogen concentration increases within some α -Zr grains which resulted in an appearance of locations in the α -matrix which have become γ -phase (as an example, see α -grain marked with white arrow in Figure 8); (ii) the hydride boundary between α -grains is expanded (see grain boundary marked with black arrow); (iii) the size of δ -hydride precipitates decreases (see δ -grain marked with doubled green arrow). All these changes become more pronounced with time. After 4 weeks of ageing, only a few grains remain free from hydride precipitates; remnants of the initial δ -grains can barely be seen and have been replaced with an irregular mixture of γ/δ -ZrH phases (Figure 8c).

Figure 8: EBSD phase map of hot-rolled Zr-2.5 wt% Nb material subjected to 24 hours hydriding at 1 kA/m² current density. As-hydrated surface (a) and the same region of interest 2 days later (b) and 4 weeks after hydriding (c). White arrow points on/shows α -Zr grain which is initially free from ZrH but gradually fills up with γ -ZrH upon ageing. Black arrow points on α/β phases boundary towards which hydrogen atoms migrate with further hydride phase formation. The δ -grain location is indicated with a double green arrow. (d) Changes in phase fraction during ageing.

Therefore, we can see that partial dissolution of the initial precipitates and the formation of new hydride phase can be observed on the sample surface. The hydrogen atoms do not remain localized in the initially precipitated hydride phase sites but instead diffuse within the base material. Hydrogen migration and hydride transformation during the ageing manifests the out-of-equilibrium nature of the as-hydrated system.

The as-hydrated surface and the surface after 1 year of ageing is depicted in Figures 9a and 9b respectively, showing how the initially hydrided surface has lost hydrogen with time. Both α -Zr and β -Zr phase recovery can be observed in the aged sample. After 1 year, the traces of hydrides which initially precipitated on the surface can be seen to have now moved deep into the bulk material (Figure 9c). From the comparison of Figures 9b, 9c, and 9d, negligible differences in phase distribution are observed between sample surface and cross section areas after 1 year.

Figure 9: EBSD map of hot-rolled Zr-2.5 wt% Nb material subjected to 96 hours (4 days) hydriding at 1 kA/m² current density. (a) As-hydrated surface; sample surface (b) and cross section (c) after 1 year aging in vacuum at RT. (d) Changes in phase fraction associated with sample hydriding and further ageing.

The plot in Figure 9d quantifies the phase distribution obtained from EBSD data during the ageing. After a few months, the number of unindexed points increases and total hydride fraction increases at the expense of zirconium. Measurements of the sample aged 1 year show (i) improved hit rate of measurements; (ii) almost completely recovered β-Zr fraction; (iii) increased fraction of zirconium and decreased hydride fraction. These observations indicate an arrest (or at least slowing) in the change of phase transformation in this Zr-H system. It can be concluded that after 1 year of ageing, this Zr-H system has reached (or nearly reached) an equilibrium state. Hydrogen has moved out from the β-phase and adjacent areas (α/β phases boundary) on the surface (Figure 9b) and relocated to similar sites in the bulk

(Figure 9c). Minimal surface degradation occurred during the ageing. The one year old surface and as-prepared cross section area show similar phase distributions and hit rates.

Electron backscatter diffraction was used to rapidly characterize the phase distribution over a large surface area in a ~ 300 nm thick layer. In addition to EBSD, x-ray diffraction measurements were performed to investigate changes occurring in the 2×5 mm² surface area having ~ 5 μ m thickness. The phase fractions changes, Δf was estimated as the difference in peak integral intensity measured during the ageing and that in as-hydrated sample; Δf values were normalized by as-hydrated state of the sample ($\Delta f = (I^{hkl}(\text{measured})/I^{hkl}(\text{as-hydrated}))_0 - 1$).

Figure 10: The changes in phase fractions, Δf obtained using x-ray diffraction as compared to the initially as-hydrated surface. Sample was hydrided 1 day at 1.0 kA/m² current density, then aged in vacuum at RT. The vertical dotted line indicates data obtained from the same sample prior to hydriding.

Figure 10 shows phase transformation occurring in the top layer of the sample during the ageing. The XRD measurements of as-received material before the hydriding are marked with the dotted vertical line. Sample hydriding results in a reduction in both α - and β -Zr phase fractions (by $\sim 50\%$ and $\sim 75\%$ respectively) due to their replacement with hydride. In addition it may be seen that the diffracted signal from the matrix is distorted around the precipitate, by strain and by any “lattice liquid” effect of increased H in the surrounding matrix. A tendency for β -Zr recovery (i.e., due to reverse transformation of hydride phase) is observed during aging, prior to such recovery occurring in α -Zr; recovery of α -Zr is not observed in this X-ray data although it was observed in the longer term EBSD tests. The first week of ageing finished with the β -phase fraction increasing by 15%, then the rate of recovery slows down. After 71 days of ageing, the β -phase was restored to around 60% of that measured in the sample before hydriding. The phase transformation and changes in hydrogen/hydride distribution is particularly pronounced during the first 1.5 months of aging. During that period of time, there is an increase in γ -ZrH fraction accompanied by a reduction in δ -ZrH; the total intensity of the signal scattered by hydride phase decreases with time. Therefore, along with hydride phase transformation, a significant partial hydrogen dissolution followed by diffusion out of diffracting volume into the depth of the sample occurred.

3.3. Hydride microstructure

Scanning electron microscopy observations were performed to examine the microstructural changes associated with hydride precipitation. An SEM image of the as-prepared sample and that after 1 day hydriding at 1.0 kA/m² current density is shown in Figure 11a and Figure 11b, respectively. New structures appeared on the surface in Figure 11b are δ -ZrH precipitates, as confirmed by EBSD (Figure 11c). The

orientation relationship between observed hydrides and the matrix agrees with the most commonly reported, i.e., $\{111\}_{\delta} // (0001)_{\alpha}$ (Figure 12).

Hydrides are barely discernible using conventional SEM imaging due to low contrast between phases. An alternative method for an investigation of the ZrH microstructure is an atomic force microscopy (AFM) which enables visualization of the hydrided surface topography. As shown in Figure 13a, AFM readily distinguishes the hydride phase from the zirconium matrix. Since, as noted, the δ -phase expands the zirconium lattice locally by $\sim 17\%$ at room temperature [35], the precipitates protrude above the surface (up to ~ 50 nm) and have well-defined edges.

According to Figure 13, the hydride formation starts within or in the vicinity of β -Zr phase at grain boundaries and grows preferentially into the α -phase thus connecting opposite sides of the α -grain. An early stage of an initial 'string' structure formation is clearly seen in Figure 13 (a5). The hydride there has not yet finished bridging to the other side of the grain, probably due to the cessation of hydriding. The string structures depicted in Figure 13 (a5 and a4) have a characteristic delta-shaped profile (Figure 13b). Figure 13 (a1-a3) shows another common geometry for observed hydrides. A narrow stem/rod there is decorated with spreading out wings, away from this stem/rod. The hydride formed in this way has a wide flattened profile protruding above the surface (Figure 13c). In summary, two different hydride microstructures were observed on the same surface plane. One of them is narrow string, having a clear delta-shaped profile. The other hydride microstructure has a flat surface and irregular shape. According to Figure 12, these two hydride microstructures were obtained from differently oriented α -grains, therefore from different cross sections relative to the parent matrix orientation. It remains unclear if the differences in microstructures are caused by being due to different cross sections or if these two hydride groups actually have a different morphology.

γ -hydride grains were observed on the sample surface after 4 days of slow hydriding (current density of 0.2 kA/m^2). As an example, two adjoined hydride grains were recognized in the EBSD phase map in the region of interests marked with a square in Figure 7d: one grain is fcc δ -ZrH, the other is fct γ -ZrH. According to the topography image of that region in Figure 14a, both phases have a similar microstructure. These are similar irregular shaped precipitates with flattened profile protruding above the surface.

The height of the δ -grain is greater than γ -grain in Figure 14b, due to higher volume misfit (17% for δ -ZrH versus 12% for the gamma phase) [33]. An important feature in Figure 14 is apparent deformation of the matrix in vicinity of the hydride. An observed pile-up suggests that α -Zr undergoes plastic deformation; the irregular (non-symmetric) shape of the pile-ups around the precipitate is presumably caused by anisotropy in the mechanical properties of the matrix.

Figure 11: Micrographs (SEM) of the sample before (a) and after (b) 1 day hydriding at current density of 1.0 kA/m^2 . (c) EBSD phase map of the region of interest in the sample after hydriding. Precipitated hydrides are marked by circles and numbered.

Figure 12: Pole figures illustrating $\{111\}\delta//\{0001\}\alpha$ relationship plotted for selected δ -grains from Figure 7.

Figure 13: (a) AFM topography images of the region of interest (the same as in Figures 8a, 11bc) in the hydrided sample. Hydride phase locations are marked by circles and numbered a2-a6 in accordance to Figure 11c. Cross-sections taken along the straight lines in shown in red for grains #4 and #5 (b) and grain #2 (c). For clarity the height in grain #5 in (b) is shifted by 10 nm.

4. Figure 14: (a) AFM topography image of adjoined δ - and γ -hydride grains on the region of interest marked by black square in Figure 7d. The scan area is $5 \times 5 \mu\text{m}^2$. (b) Cross-sections taken along the straight lines in (a). **Discussion**

In this work a combination of atomic force and electron microscopy, and X-ray diffraction have been used to study changes occurring in hot-rolled Zr-2.5wt.%Nb material during hydriding and subsequent ageing.

To estimate the diffusion length for hydrogen in α -Zr, a simple approximation $d = (Dt)^{1/2}$ is used, where D is the diffusion coefficient of H in Zr and t is time. The bulk diffusion is consistent with classical diffusion solutions where the diffusion coefficient normally obeys a relation close to an exponential Arrhenius relation:

$$D = D_0 \times \exp(-Q/RT), \quad (1)$$

here D_0 is diffusion constant, Q is an activation energy of diffusion in J mol^{-1} , $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ and T is the temperature in K. The diffusion distance for 25°C temperature calculated based on the D_0 and Q values reported by Kammenzind et al. [36], Kearns [37], Greger [38], and Austin [39] and shown in Table 2. We expect tritium to diffuse more slowly than hydrogen due to its higher mass, so the use of the tritium data for low temperature diffusion calculations means that the distances so determined would be expected to be a lower bound.

Table 2. Literature parameters for the H diffusion in zirconium.

	Material	$D_0(\times 10^{-3}), \text{cm}$	$Q (\times 10^3), \text{kJ mol}^{-1}$	$D^* (\times 10^{-10}), \text{cm}$
Kammerzind [36]	hydrogen in Zircaloy- 4	0.80	33.28	11.72
Kearns [37]	hydrogen in zirconium, Zircaloy-2 and Zircaloy-4	5.84	43.05	1.66
Greger [38]	tritium in Zircaloy-2	1.04	42.10	0.43
Austin [39]	tritium in Zircaloy-2	0.21	35.56	1.23

* calculated using Eq.(1) for 25°C

The result of diffusion distance calculations shown in Figure 15 gives an indication of how far from the initial precipitation area (or sample surface) hydrogen is able to diffuse. The data serve to illustrate that hydrogen atoms diffuse significant distances through the zirconium matrix even at room temperature. During one year ageing at room temperature, the diffusion distance is calculated in the range of 0.3-1.9 mm. Kearns reported (i) no effect observed of grain size or cold work on the diffusion coefficient; (ii) small differences found depending on sample orientation; (iii) the ratio of the single crystal diffusion coefficients parallel and perpendicular to the “c” axis of the hexagonal structure, $D_{||}/D_{\perp}$ is greater than one, but not more than two. These observations mean that texture, prior cold work or grain size will not make significant changes in the diffusion distances estimation, at least in terms of this semi-quantitative analysis.

Figure 15: Diffusion distance at room temperature as a function of time calculated based on the diffusion coefficient determined by Kammerzind et al. [36], Kearns [37], Greger et al. [38], Austin et al. [39], showing distances relevant to (a) sample dimensions and (b) α -Zr grain size.

No measurable differences have been reported for the diffusion coefficients of α -Zr and single phase Zircaloy-2 and Zircaloy-4 [37]. However, the diffusivity of hydrogen in the β -Zr is much higher (about 50 times) than in the α -phase [40]. For the dual phase (α/β) alloy considered in current paper, the possibility exists of short-circuit diffusion paths which in turn increases the calculated distances. Therefore, it is evident that during one year of ageing, hydrogen is capable to migrate hundred microns in bulk of the sample as shown Figure 9c.

Hydrogen diffuses moderate distances through the zirconium matrix not only during the ageing but during hydriding too. For that reason, when analyzing the Zr-H system upon hydriding, in addition to the

hydrogen uptake and hydride nucleation and growth, the redistribution of hydrogen by diffusion needs to be considered. All these 4 competing processes will occur with different rates, the resultant defining the distribution, phase(es) and morphology of the precipitates which ultimately determines system stability. The hydrogen uptake rate was the only parameter which was controlled during the hydriding, via the two different values of current density used which provided relatively fast (1.0 kA/m²) and slow (0.2 kA/m²) hydrogen ingress into the base material.

The H in solution $\rightarrow \gamma$ -ZrH transformation is detected in the early stage of the slow hydriding (Figure 7b). At this time the rate of the hydrogen uptake slightly exceeds the diffusion rate into the bulk. As a result, the hydrogen concentration in the very top layer of the sample increases and soon surpasses the TSS-Precipitation occurs, which results in γ -phase formation. Further hydriding continues to increase the local concentration of the hydrogen in the top layer which promotes not only the formation of new γ -nuclei but partial $\gamma \rightarrow \delta$ transformation (since, as noted above it is energetically favourable for δ to form over γ when more H is present). The fraction of converted (δ) hydride increases with hydriding time (Figure 7c). Apparently, a faster rate of hydriding promotes the process $H \rightarrow \gamma \rightarrow \delta$ which makes detection of the sequence of transformation steps very challenging. The widely reported precipitation of δ -phase is commonly the final stage of the complex sequence of transformations occurring in the Zr-H system. From these results we conclude that the δ -phase formation occurs via a series of sequential steps. First, H lattice gas transforms into a locally more dense H lattice 'liquid'. Some fraction of this 'liquid' is ordered thus forming the γ -ZrH phase. Subsequently some fraction of the vacant tetrahedral interstitial sites in the as-formed γ -hydrides are filled with hydrogen atoms, which result in the $\gamma \rightarrow \delta$ hydride transformation. That is, based on our observations even though δ -ZrH phase is the end-result, the γ -hydride is expected to form first; subsequent uptake of H atoms results in the formation of δ -ZrH.

It worth emphasizing that β -Zr is a more favorable site for hydride precipitation than α -Zr (Figures 7c, 8a). Upon hydriding, the β -phase quickly becomes saturated by the hydrogen due to the small volume fraction; we note that even at room temperature β -Zr has a higher solubility for H than α -Zr [41]. When H concentration exceeds the TSS-P, the formation of a fct γ -ZrH sublattice occurs at an α - β interface, and then it grows into the β -Zr phase. If local hydrogen inflow exceeds the cumulative diffusion of hydrogen into bulk and removal by conversion into γ -phase, the active formation of hydrides in the α -phase occurs. Thus it seems that the β -Zr is the preferred location for introduction of hydrogen into the material during the hydriding process. The β -phase potentially acts as a primary sink for hydrogen collection, and subsequent distribution and hydride phase formation.

While hydride precipitation occurs, the system is locally for a time out of its state of equilibrium. Transformations occurring in the sample in the beginning of ageing start to move the top layer of the hydride sample towards a local steady state. It should be recalled that during the first month of ageing, no further hydrogen uptake occurred yet new hydrides were formed. It is likely that in the as-hydrided samples, hydrides form at locations preferred by the electrolytic procedure. In addition some amount of hydrogen remains in solution in the top layer of the sample. Moreover, it is possible that H atoms clustered around precipitates form an unordered "lattice liquid", i.e., a mixture of the structures depicted in Figure 2. During the ageing, these hydrogen atoms migrate gradually towards alternative precipitation sites resulting in further hydride formation. This redistribution and reprecipitation takes time and results in the delayed rise of hydride fraction observed in the aged samples in Figure 8d. Hydrogen migration into the bulk occurs alongside the formation of new hydrides on the surface (Figures 7, 8). An increased time for hydrogen redistribution allows greater distances for diffusion, hence long-term ageing provides conditions for hydride homogenization in the base material and the Zr-H system approaches an equilibrium state.

5. Conclusions

In current paper, the surface hydride formation and its transformation during ageing was inspected in detail. The Zr-H system was studied using SEM coupled with EBSD, X-ray diffraction and AFM. Hydrogen uptake and diffusion in zirconium coupled with phase transformations, hydride dissolution and re-precipitation occurred in a sample during the hydriding process followed by room temperature ageing. The following conclusions can be drawn:

1. Hydrogen in solution $\rightarrow \gamma\text{-ZrH} \rightarrow \delta\text{-ZrH}$ transformations were observed in the sample during the hydriding process. As expected, the as-hydrided sample is not at equilibrium.
2. Sample hydriding causes a reduction in zirconium fraction due to replacement with hydride and we believe an unordered "lattice liquid" occurs.
3. Reverse conversions ($\delta\text{-ZrH} \rightarrow \gamma\text{-ZrH} \rightarrow \text{H in solution}$) was observed upon prolonged ageing as redistributed into the material. Partial dissolution of initially precipitated hydride grains and formation of new precipitates was detected on the surface.
4. During ageing, the Zr-H system goes through a local steady state on the sample and reaches a new equilibrium state.
5. $\beta\text{-Zr}$ phase has higher susceptibility to hydrogen pick-up and hydride sublattice structures formation than that in $\alpha\text{-Zr}$.
6. AFM in combination with EBSD is a powerful tool for hydride microstructure observation.
7. In dual phase Zr alloys, the surface hydride precipitates in $\alpha\text{-Zr}$ were always attached to the $\beta\text{-Zr}$ phase; this is due to the higher solubility of H in $\beta\text{-Zr}$ which means that the $\beta\text{-Zr}$ acts as a H source.
8. Only one orientation relationship was observed between $\alpha\text{-matrix}$ and $\delta\text{-ZrH}$ precipitates: $\{111\}_{\delta} // (0001)_{\alpha}$.
9. Using atomic force microscopy, no differences in microstructure were detected between $\delta\text{-}$ and $\gamma\text{-}$ hydrides precipitated on the sample surface.

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7. References

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