Hydride reorientation in Zr2.5Nb studied by synchrotron X-ray diffraction

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Abstract

The crystallographic texture and stress state of hydride platelets of two different orientations precipitated in Zr2.5Nb pressure tubes were studied by synchrotron X-ray diffraction experiments using an 80 keV photon beam and an area detector in transmission geometry. Circumferential and radial hydrides with platelet normals along the tube radial and circumferential directions, respectively, were precipitated in tube material loaded up to H contents of 130 wt.ppm. This macroscopic hydride orientation was controlled by application of a load along the tube hoop direction during hydride precipitation. The experiments show that both circumferential and radial platelets are composed of δ-hydrides precipitated in α-Zr grains from a wide range of orientations, but with a clear preference for Zr crystals with their c-axes at an angle of ~15–20° from the hoop direction. Some moderate differences between the crystallographic texture of the two hydrides result from application of the load during precipitation. The results are explained in terms of an autocatalytic nucleation process and the Zr2.5Nb microstructure. A careful stress analysis revealed that both hydride types are compressed by the matrix on the plane of the platelet, with the largest stresses always found along the axial direction of the tube. Determination of the stress state of the hydride could be exploited as a diffraction signature of the hydride orientation.

Keywords: Zirconium alloy; Hydride; Stress reorientation; Crystallographic texture; X-ray diffraction (XRD)

1. Introduction

Zr alloys are used for structural components in the nuclear industry because of their corrosion resistance, together with very small neutron absorption. These alloys are susceptible to hydrogen-assisted degradation mechanisms resulting from hydrogen in solution and/or precipitated as hydrides. The protective oxide layer on the surface (responsible for the corrosion resistance of these alloys) found in service usually prevents the ingress of hydrogen into the lattice. However, hydrogen may enter the material during manufacturing and welding processes [1] or during service in nuclear power plants [2]. Hydride precipitates embrittle the Zr matrix, manifested as marked losses in ductility, impact and fracture toughness. The degree of embrittlement is strongly influenced by the morphology and orientation of the precipitates with respect to the direction of the external stress. Plate-shaped precipitates (platelets) of δ-hyrids are particularly detrimental to the toughness of tubing and sheet, as hydride platelets oriented normal to a tensile stress provide an easy crack propagation path. The detrimental effect of radial hydrides was recognized early and accounted for in Zr tube manufacturing [3], so large compressive strains are introduced in the last cold-working stages in order to prevent precipitation of harmful radial hydrides. Nevertheless, reorientation of hydride platelets can occur in service and/or in...
as a result of the dissolution and re-precipitation of hydrides in the presence of stress [4]. Besides this, hydrogen-assisted crack growth is a serious technical issue in components with high levels of internal stress or including sharp flaws when subjected to sustained load. This failure mechanism, known as delayed hydride cracking [1], is particularly relevant to pressure tubes made of Zr–Nb alloys used in CANDU (Canada deuterium uranium) nuclear power plants, so most research effort to understand the phenomenon has been directed to these components [5].

The deep penetration and great sensitivity of diffraction techniques available in modern synchrotron facilities has opened the possibility of studying the minority hydride phase in fine detail, under conditions of temperature and stress equivalent to those experienced in service. In particular, a number of recent studies have exploited the sub-miller-meter spatial resolution of the technique to quantify crystallographic phases and stress state of precipitates across inhomogeneous hydride distributions such as hydride rims [6], blisters [7,8] and crack tip hydrides [9–11]. Such studies rely on quantifying the changes that occur in the area and/or position of selected diffraction peaks at different locations within a specimen, before and after thermo-mechanical treatments performed in situ. Daum et al. [6] and Vicente Alvarez et al. [8] performed quantitative phase analyses (QPA) of the hydrides precipitated through the thickness of Zircaloy-4 cladding and Zr2.5Nb pressure tubes, respectively. These studies covered hydride concentrations from ~50 to 13,000 wt.ppm of H. They found that δ hydrides always represented the major hydride phase, although γ or ε hydrides could appear at specific locations or over certain hydride contents. The QPA is based on comparing the integrated intensities of selected diffraction peaks corresponding to the α-Zr matrix and the hydride phases, assuming that no changes in crystallographic texture occurred across the specimen. In contrast, Kerr et al. [10,11] and Steuwer et al. [9] studied hydride distributions around stress concentrators, namely cracks at notches in loaded CT specimens of Zr2.5Nb and Zircaloy-4, respectively. In Refs [9,10], the work concentrated on the analysis of the spatial distribution of elastic strain that appears around the notch upon the application of a load. The strains observed in the metal and the hydrides were interpreted in terms of different regimes of load sharing between the phases. In a later work, Kerr et al. [15] investigated hydride precipitation at the crack tip in situ, confirming that precipitation of hydrides at the crack tip effectively relaxes the strain field of the matrix.

In this work, special attention is paid to an aspect of hydride precipitation not considered in previous work, namely the dependence of stress state and crystallographic texture of the hydride phase on the morphology and orientation of the precipitates. Hydride reorientation is usually observed at specific locations in specimens containing an inhomogeneous distribution of hydrides. This is particularly clear for the hydrides precipitated around crack tips, where the platelets align concentrically around the crack [11], so differing in orientation from the far-field hydrides. Moreover, it has been proposed [12,13] that the process of hydride reorientation involves precipitation on Zr crystals with orientations different from those producing the original hydrides. Therefore, large differences should be observed between the crystallographic texture of the original and reoriented hydrides, yet no experimental information has been reported so far. Such texture changes due to reorientation would greatly complicate the analysis of phases and stresses on inhomogeneous hydride distributions such as crack tips or blisters. Along this line, Colas et al. [14] recently performed synchrotron X-ray diffraction (XRD) experiments on hydrides precipitated under tension in Zircaloy-4 cladding, seeking a diffraction signature of hydride reorientation, and reported clear differences in peak width between the normally oriented and the reoriented hydrides. In another work, Santisteban et al. [15] found that hydrides in Zircaloy-4 are under a state of biaxial compression on the plane of the platelet [16]. So, proper interpretation of hydride strain distributions around cracks must include the effect of hydride morphology on the actual stress state of the hydride.

It is the aim of this work to assess the effects of the phenomenon of hydride reorientation on the crystallographic texture and the stress state of the hydrides precipitated on Zr2.5Nb pressure tube material. For this, synchrotron XRD experiments were performed on tensile specimens machined from pressure tubes pre-loaded with different hydrogen contents, using the same experimental arrangement as in Refs [18,19]. Specimens were thermally cycled between room temperature and 400 °C under applied loads, in order to dissolve and re-precipitate the hydrides while recording the Debye rings in situ using a fast charge coupled device (CCD) detector.

2. Samples

Two sets of dog-bone tensile specimens pre-charged with different hydrogen contents were produced from commercial and experimental Zr2.5Nb pressure tubes. The normal fabrication route of CANDU pressure tubes performed for AECL (Atomic Energy of Canada, Ltd) starts from Zr2.5Nb billets forged at ~800 °C, followed by extrusion, air cooling, cold drawing to ~20–30% strain and autoclaving at 400 °C for 24 h. Specimens E1 and E2 correspond to the normal manufacturing process, and were machined from a tube produced for the CANDU power plant at Embalse, Argentina. Specimens L1 and L2 correspond to an alternative manufacturing route for pressure tubes being developed at CNEA (Comisión Nacional de Energía Atómica), Argentina, which replaces the cold drawing stage by a pilger-type cold rolling stage [16]. The microstructure of both types of pressure tubes is the same (Fig. 1), and consists of lamellar α-grains with a hexagonal close packed crystal structure containing between 0.6 and 1 wt.% Nb, surrounded by a grain boundary network of Nb stabilized β-Zr with a body centered cubic crystal structure containing
~18–20 wt.% Nb. On average, the λ lamellae are ~10 μm long along the axial direction, ~1 μm wide along the hoop direction and ~0.5 μm thick across the radial direction. During thermal treatments, there is partial decomposition of the metastable β-Zr phase into the α-Zr (hexagonal) phase and a Nb-rich β-phase.

Cuboid specimens machined from the tubes were charged with hydrogen in two stages. Initially, a hydride surface layer was deposited by cathodic charge, followed by annealing under a N₂ atmosphere for 24 h at 400 °C, to diffuse the hydrogen into the bulk. The samples were polished to remove the oxide and any remaining hydride layer. Different H contents were introduced into the material by changing the time of cathodic charge. The hydrogen concentrations explored in this study are in the range 40–130 wt.ppm, as determined with a chromatograph LECO RH-404 with an error of ±5 wt.ppm. Dog-bone tensile samples 2 mm thick were machined from these pieces with the tensile direction along the hoop direction of the tube, with the dimensions indicated in Fig. 3a. In order to reorient the hydrides during the in situ experiments, the tensile probes were inserted in a loading frame, and heating and cooling cycles under stress were applied using a lamp furnace. Table 1 summarizes the manufacturing conditions, H content and applied loads for the different samples. Fig. 2 presents a series of images showing the distribution of hydrides in the hoop–radial plane before (left) and after (right) the thermo-mechanical treatments, which confirms that reorientation has occurred during the tests. Before testing, all samples contained almost exclusively circumferential (hoop) hydrides, i.e. platelet hydrides with the plate normal along the tube radial direction. For L2, the specimen with the highest hydrogen content (130 wt.ppm), hydrides were considerably longer along the hoop direction (20–40 μm) than for the other three specimens (10–15 μm). After the tests, a considerable fraction of radial hydrides had been formed in all samples, yet a fraction of circumferential hydrides was still observed. To produce the images, the tensile specimens were cut after the test, polished and etched, and observed under the optical microscope following the procedures described in Ref. [17].

Table 1
Intensity and d-spacing of the original material and after precipitation under hoop stress for precipitates formed in α grains with the most important orientations; a 225 MPa load along the hoop direction was applied during precipitation in order to achieve hydride reorientation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Processing schedule</th>
<th>H (wt.ppm)</th>
<th>Experimental condition</th>
<th>Intensity δ(111)</th>
<th>d-spacing (Å) δ(111)</th>
<th>Δd(111) = Δd/d (με) δ(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>Cold drawn</td>
<td>55 ± 3</td>
<td>As-received</td>
<td>7 ± 1</td>
<td>2.7473(5) 2.7393(5)</td>
<td>2800 ± 400</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>After reorientation</td>
<td>13 ± 2</td>
<td>2.7468(5) 2.7396(5)</td>
<td>2600 ± 400</td>
</tr>
<tr>
<td>E2</td>
<td>67 ± 5</td>
<td></td>
<td>As-received</td>
<td>7.8 ± 2</td>
<td>2.7466(3) 2.7392(3)</td>
<td>2700 ± 200</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>After reorientation</td>
<td>21 ± 3</td>
<td>2.751(3) 2.7400(3)</td>
<td>4000 ± 200</td>
</tr>
<tr>
<td>L1</td>
<td>Cold rolled</td>
<td>44 ± 3</td>
<td>As-received</td>
<td>2 ± 0.5</td>
<td>2.740(8) 2.745(8)</td>
<td>2400 ± 300</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>After reorientation</td>
<td>3 ± 0.2</td>
<td>2.7476(9) 2.7408(9)</td>
<td>2500 ± 300</td>
</tr>
<tr>
<td>L2</td>
<td>130 ± 5</td>
<td></td>
<td>As-received</td>
<td>15 ± 2</td>
<td>2.7417(3) 2.7403(3)</td>
<td>500 ± 200</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>After reorientation</td>
<td>34 ± 2</td>
<td>2.7512(3) 2.7427(5)</td>
<td>3100 ± 200</td>
</tr>
</tbody>
</table>

* Only a 65 MPa load was applied for sample L1.
3. Testing

XRD experiments were conducted at the beamline 1-ID of the Advanced Photon Source at Argonne National Laboratory [18] using the same experimental arrangement as in Refs. [14,15]. The beamline was used in the Debye–Scherrer transmission geometry, with a monochromatic beam of 0.15 Å wavelength (80 keV) and size 300 × 300 μm²; in conjunction with a high-speed CCD area detector composed of 2048 × 2048 pixels with 200 × 200 μm² size located at 1948 mm from the sample. This geometry allows a number of full diffraction rings to be recorded within a very short time (~1 s), providing information that is averaged over the full thickness of the sample. Fig. 3a shows a schematic representation of the experimental arrangement. The detector displays a typical image captured during the experiments. Tensile specimens were placed on the MTS loading frame and heated up by a lamp furnace, while images of the Debye rings were recorded at intervals of 1 s. The temperature was sensed by a thermocouple placed near the center of the gauged length of the sample. Heating and cooling rates of 20 °C s⁻¹ were applied, and a maximum temperature of 400 °C was reached during the test and held at this value for ~5 min. For the H contents analyzed in this work, this temperature is high enough to completely dissolve the pre-existing hydrides. For each specimen, the first heating and cooling cycle was performed without force, but on subsequent cycles stress was applied at low temperature (~90 °C) and maintained during the heating and cooling cycles. A stress value of 225 MPa was applied to all samples except for L1, with 65 MPa.

The intensity variations observed around the rings in Fig. 3a, represented by the azimuthal angle φ, are due to the crystallographic texture of the material. The signal...
recorded at the azimuth $\phi$ comes from those grains with their plane normal contained almost in the hoop–axial plane, at an angle $\phi$ from the hoop direction. The crystallographic texture and stress state of both the $\alpha$-Zr and hydride phases were determined by careful quantification and analysis of the azimuthal variations observed in the intensity and radius of the rings, respectively. To quantify such variations, the images were transformed into a set of 20 diffractograms, analyzed as conventional $\theta$–$2\theta$ scans, as the two examples show in Fig. 3b. The analysis procedure has been extensively described elsewhere [8], so only the main steps are outlined and specific details in relation to the texture analysis indicated. The raw CCD image is corrected by dark current, flat-field and spatial distortion corrections, in order to obtain intensities that depend only on the sample and the diffraction geometry. The Debye rings was divided into 72 azimuths, so each diffractogram in Fig. 3b corresponds to an angular section with a $5^\circ$ width, as indicated in Fig. 3a. The diffractograms are expressed in terms of $d$-spacing to aid the indexation of diffraction peaks. The $d$-spacing calibration was done after measuring a Ceria powder standard sample. For all diffractograms, the position, integrated intensity (area) and width of all diffraction peaks were determined by least-squares refinement using a Pseudo-Voigt profile. In some cases, and due to the superposition of peaks, simultaneous fitting of up to five peaks was necessary. To do so, homemade software written in MATLAB language was developed. The background was fitted assuming a linear shape, the parameters that define this line were obtained, together with the peak parameters from the least squares method.

4. XRD results

Fig. 3b shows two diffractograms for the L2 material in the as-received condition for two different azimuths ($\phi$). Four main phases are identified, the $\alpha$, $\beta$ and $\omega$ phases of Zr and the $\delta$-hydride. The peaks of the $\beta$ phase are superimposed on those of the $\omega$ phase. Here, the study concentrates on the analysis of the hexagonal $\alpha$-Zr and face centered cubic $\delta$-hydride phases. Small peaks from the $\gamma$-hydride phase were also observed in the diffractograms recorded for the other samples (L1, E1, E2). The large differences observed in the intensity of the same diffraction peak measured at the two azimuthal angles reveal the strong texture present in all phases. Peaks from the (111) and the (220) reflections of the $\delta$-hydride phase are seen clearly in both diffractograms. The $\alpha$-Zr texture is manifested in the figure mainly through a very intense $\alpha(0002)$ peak for $\phi = 0^\circ$, which becomes almost negligible for $\phi = 70^\circ$. The full azimuthal dependence of the intensity in the hoop–axial plane for the $\alpha(0002)$ and $\delta(111)$ reflections of the L2 specimen is shown in Fig. 4, both in the as-received material and after reorientation has occurred. The plots display several intensity maxima of different heights located at precise azimuth angles. The values at $\phi = 0^\circ$, $180^\circ$ in the figure nearly correspond to $\alpha$-Zr/hydride grains with their (0002)/(111) plane normal pointing along the tube hoop direction (Fig. 3), while the values $\phi = -90^\circ$, $90^\circ$ give the tube axial direction, so the plots must be invariant under the $\phi \rightarrow \phi + 180^\circ$ transformation. Moreover, owing to the orthorhombic sample symmetry, the results must be identical under reflections on $\phi = 0^\circ$ and $90^\circ$, reducing the meaningful section of the plots to the $[0^\circ, 90^\circ]$ interval, indicated by two vertical dotted lines. The fact that the experimental data comply with the symmetry requirements provides additional confidence to the data analysis procedure. In the full range plots, arrows of the same size and color1 indicate

1 For interpretation of color in Figs. 1–10, the reader is referred to the web version of this article.
symmetry-equivalent diffracting conditions of particular interest to the present work, i.e. produced by grains with equivalent orientations. For the \( \alpha \)\((0002)\) reflection, a single maximum is observed at \( \phi = 0^\circ \), while two distinctive maxima are observed for the \( \delta \)\((111)\) reflection, at \( \phi = 0^\circ \) and \( \phi = 70^\circ \). These hydride peak intensities are identified as \( p_{\text{Hoop}} \) (green arrow) and \( p_{\text{Tilted}} \) (blue arrow) contributions, respectively (p for precipitate). Also identified in the figure is \( p_{\text{Axial}} \) (pink arrow), which corresponds to the \( \delta \)\((111)\) intensity registered in the vicinity of \( \phi = 90^\circ \). A thorough analysis of the texture of both phases is presented in next section.

Comparing the curves obtained in the as-received and after-reorientation conditions, it is observed that the intensity of the \( \alpha \)(0002) curves registered for both cases are almost identical. The same is observed for the other \( \alpha \)-Zr reflections, not shown here. This result is to be expected, as the crystallographic texture of \( \alpha \)-Zr is only negligibly affected by precipitation of the minority hydride phase with a volume fraction of only \( \sim 1\% \). In contrast, the \( \delta \)\((111)\) peaks present a noticeable variation between the as-received and after-reorientation conditions. There is a clear increment in the intensities \( p_{\text{Hoop}} \) and \( p_{\text{Tilted}} \), accompanied by a slight decrease in \( p_{\text{Axial}} \). The same qualitative behavior was observed for the other specimens, as listed in Table 1, which summarizes the results obtained for all samples tested. Fig. 5 provides a graphical representation of the results listed in the table, which clearly visualizes the increase in \( p_{\text{Hoop}} \) and \( p_{\text{Tilted}} \) and the decrease in \( p_{\text{Axial}} \) due to the application of stress along the hoop direction during precipitation. The \( \delta \)\((111)\) intensity for \( p_{\text{Hoop}} \) and \( p_{\text{Tilted}} \) hydrides formed under stress is almost twice the intensity of equivalent hydrides in the as-received condition. The reduction in \( p_{\text{Axial}} \) is clear only for the larger H contents (E2 and L2 specimens). The hydride peaks along the axial direction for E1 and L1 specimens (low H content) are very hard to separate from the background, so the results are not reported in the table.
5. Stress state of hydride precipitates

The presence of stress in a crystalline material changes the distance between atomic planes. So the stress state of the hydride precipitates can be inferred from the analysis of small distortions of the Debye rings. For non-hydrostatic stress fields, the elastic strain tensor manifests through slight variations in radius around the ring circumference. Yet only a limited number of azimuths are available for stress analysis in the present case due to the strong texture and low volume fraction of the hydride phase. As inferred from Fig. 4, only the $p_{\text{Hoop}}$ and $p_{\text{Tilted}}$ contributions (at $\phi = 0^\circ$ and $70^\circ$ respectively) offer $\delta(111)$ peaks with statistically sound data to define the peak position within the uncertainty demanded by stress analysis ($\Delta d/d \approx 10^{-4}$). The $d_{111}$ interplanar distances registered at these angles in the as-received and after-reorientation conditions are listed in Table 1. For all specimens, the $\delta(111)$ $d$-spacing measured along the hoop direction of the tube is markedly different from that measured along the “tilted” direction, i.e.

![Diagram](image)

Fig. 6. Evolution of $d$-spacing of the $\delta(111)$ peak of hydrides with the (a) $p_{\text{Hoop}}$ and (b) $p_{\text{Tilted}}$ orientations, for the E2 and L2 samples as a function of temperature during the thermo-mechanical cycles: 1, heating at 0 MPa; 2, cooling at 0 MPa; 3, loading; 4, heating at 225 MPa; 5, cooling at 225 MPa; 6, unloading. The value of the room temperature unstressed $d$-spacing ($d_0$) reported in Refs. [7,15] is indicated in the figure.
at ~20° from the tube axial direction. This difference in d-spacing can be quantified in terms of an elastic strain amplitude \( \Delta \varepsilon_{111} = (d_{111 \text{ Hoop}} - d_{111 \text{ Tilted}})/d_{111 \text{ Hoop}} \) also listed in the table. This elastic strain amplitude gives direct evidence of the stress field experienced by the hydride precipitate due to the mechanical constraints imposed by the Zr matrix to the local volume increase, as the hydride phase occupies a larger volume than the Zr atoms it replaces. For samples E2 and L2, both the d-spacing and \( \Delta \varepsilon_{111} \) values vary significantly after reorientation, hence revealing a change in the actual constraints imposed by the matrix on the precipitates. Further insight into such changes is provided in Fig. 6, which shows the evolution of the \( \delta(111) \) d-spacing through the experiment as a function of the specimen temperature. Fig. 6a shows the results for the \( \rho_{\text{Hoop}} \) component, i.e., for \( \delta(111) \) planes with their normal parallel to the applied load, while Fig. 6b displays the evolution for \( \rho_{\text{Tilted}} \) corresponding to \( \delta(111) \) planes with their normal inclined at 70° from the applied load. The thermo-mechanical treatment performed in situ to the specimen is easy to follow in the right plot of Fig. 6a (L2 specimen). As described earlier, the test consisted in: (1) a first heating stage up to 400 °C in order to dissolve all hydrides, a 5-min hold time at 400 °C (not shown in the plot), followed by (2) a cooling stage down to 90 °C to re-precipitate the hydrides, which occurs at a lower temperature than dissolution. At this temperature, (3) a load is applied to the specimen, which stretches the lattice along the hoop direction and so increases the \( \delta(111) \) d-spacing for the \( \rho_{\text{Hoop}} \) planes. Following this, (4) a second heating stage dissolves the hydrides; and (5) on the final cooling stage hoop hydrides re-precipitate under the applied load. After cooling, (6) the specimen is unloaded. More details about the complete thermo-mechanical process are presented in a companion paper dealing with the dependence of dissolution and precipitation temperatures on applied stress [19]. To aid visualization, in all graphs red symbols correspond to heating stages and blue symbols to cooling stages, and arrows indicate the direction of temperature variation. Also, the first thermal cycle is plotted with solid squares, while the final thermal cycle uses hollow symbols. For each specimen and azimuthal contribution, the values listed in Table 1 correspond to the first and last point of the complete thermo-mechanical cycle. The dependence of the hydride \( \delta(111) \) d-spacing on temperature is complex, and departs largely from the simple thermal expansion displayed by most solid materials. Different behaviors are observed along the two directions, \( \rho_{\text{Hoop}} \) and \( \rho_{\text{Tilted}} \), yet a clear similarity exists for identical directions in E2 and L2. Along \( \rho_{\text{Tilted}} \), Fig. 6b shows that both the absolute values and the overall d-spacing dependence are very similar in both specimens; and there is only a 400 µε change between the start and end of the tests. However, the d-spacing values along the direction of the load display a wider and more complex behavior. The actual dependence of d-spacing along a given direction is the result of the interplay between the unconstrained thermal expansion of the hydride phase, the response of the material to the applied load, and the constraints imposed by the metal matrix to hydride growth along that direction. In a later section, a simple model is proposed for the hydride stress state, which can explain the changes observed in d-spacing along the two directions after reorientation has occurred.

6. Matrix and precipitate textures

In order to rationalize the changes in hydride diffraction intensity after reorientation listed in Table 1, the crystallographic texture of the \( \alpha \)-Zr and \( \delta \)-hydride phases was studied. The orientation distribution function (ODF) for the four specimens was determined in the as-received and after-reorientation conditions. The procedure used to determine the ODF was similar to that presented in Ref. [8]. This involves the transformation of the \( \phi \) intensity variations along all Debye rings into incomplete pole figures, and the use of the novel MTEX library [20] to determine the ODF from those pole figures. For a given sample orientation, the \( \phi \) curve of each Debye ring transforms into a line within the corresponding pole figure. For the \( \alpha \)-Zr texture, a total of eight independent diffraction peaks, \((10\overline{1}0), (10\overline{1}1), (11\overline{2}0), (11\overline{2}2), (20\overline{2}0), (20\overline{2}2), (22\overline{1}0), (22\overline{1}1)\), were used for determination of the ODF; while for \( \delta \) hydrides only the \((11\overline{1})\) and \((22\overline{0})\) peaks could be used. It must be mentioned that, in the study of similar pressure tubes performed in Ref. [8], Debye rings with the X-ray beam incident along the three principal directions of the tube were recorded, which provided accurate descriptions of the ODF for both phases. As only a single sample orientation could be explored during the present experiments, there will be an impact on the accuracy of the resulting ODF.

Fig. 7 presents the texture for the \( \alpha \)-Zr phase of the as-received L2 sample, obtained from the incomplete experimental pole figures. Fig. 7b shows the \( \varphi_2 = 0 \) section of the experimental ODF, where the most important texture components reported in the literature [21,22] have been identified. Such components correspond to ideal crystal orientations with the c-axis of the hexagon along the hoop, radial and axial directions, respectively, as shown schematically in Fig. 7a. The main texture component is \( m_{\text{Hoop}} \) \((\varphi_1 = 0, 180°, \varphi = 90°, \varphi_2 = 0)\), which also has the \((10\overline{1}0)\) axis aligned to the tube axial direction. The second ideal component is \( m_{\text{Radial}} \) \((\varphi_1 = 0, 180°, \varphi = 0, \varphi_2 = 0)\), corresponding to a 90° rotation of \( m_{\text{Hoop}} \) around the axial axis. In practice, there is also an important population of crystals with orientations between \( m_{\text{Hoop}} \) and \( m_{\text{Radial}} \), that decreases gradually between \( \varphi = 90° \) and 0°. So an additional component, \( m_{\text{Tilted}} \) tilted by 15° from \( m_{\text{Hoop}} \), has also been included in the figure and will be discussed in the next section. The last component reported in the literature, \( m_{\text{Axial}} \) with \((\varphi_1 = 90°, 270°, \varphi = 0, \varphi_2 = 0)\), which corresponds to crystals with c-axes along the axial direction, is not directly visible in this representation of the experimental ODF. Fig. 7c shows selected pole figures for the \( \alpha \)-Zr phase calculated from the experimental ODF.
The locations of the poles expected for the four texture components referred above have been identified by symbols of different colors. The pole figures are nearly identical to those measured on Zr2.5Nb pressure tubes using other techniques [21,22], and do not vary substantially among the different samples or precipitation condition. The good accuracy in the determination of the pressure tube ODF with a single CCD image was possible thanks to the marked crystallographic texture of the $\alpha$ phase, together with a good choice of the sample orientation respect to the incident beam.

Fig. 8a presents the (111) and (220) pole figures for the hydride phase, calculated from the experimental ODF refined by MTEX after fitting the hydride peak intensities recorded for the L2 specimen at the start of the test. The results are representative of all samples and conditions investigated in this study. The present results are compared with the pole figures presented in Ref. [8], which were determined from three diffraction peaks (instead of two) and three sample orientations (instead of one). Despite the use of a reduced number of diffraction peaks and a single sample orientation, there is some similarity between the present results and those previously reported. The structures of the pole figures are relatively close, although some
differences regarding the intensity and precise shape of the structures become evident. First, the maximum observed at the center of the (110) pole figure in (b) is absent in (a) and, instead, it is split between two poles at the sides. Secondly, the horizontal structures observed in the (111) pole figure in (b) appears as a cross structure in (a). These differences can be directly ascribed to the use of a single sample orientation in the present experiment. Nevertheless, some interesting features emerge from the present results. In Fig. 4b, the pole figures show that the (111) poles lying close to the axial direction are stronger than those close to the hoop direction. Moreover, the (111) poles close to the hoop direction seem to be peaked along the radial–hoop line, at an angle between 10° and 30° from the hoop direction.

7. Texture modelling

Understanding the origin of the hydride texture is necessary for proper interpretation of the changes observed in the intensity/area (Fig. 4) and position (Fig. 6) of hydride peaks after reorientation. In particular, the poles appearing in the hydride pole figures of Fig. 8 and 4 need to be linked to the ideal texture components of the α-matrix identified in Fig. 7. In doing so, one is able to assess the stress state of the actual Zr grains where different hydrides are formed. The precise crystal relation between hydrides and matrix depends on the type of hydrides (trans-granular or intergranular) and their morphology. The orientation relationship most widely reported in the literature for δ hydride precipitates for Zr2.5Nb pressure tubes is one that conserves close packed planes and directions, namely, α(0001)//δ(111) and α[1120]/δ[110] [23]. This relation was previously applied to model the hydride texture found in Zr alloys [8,15]. This relation allows direct interpretation of the results presented in Fig. 4b. Because of the α(0001)//δ(111) relation between matrix and precipitates, two of the ideal orientations introduced in the previous section, mHoop and mAxial, can be directly referred as being the precursors for the pHoop and pAxial contributions identified in the plot of Fig. 4. It must be noticed that the contribution (pAxial) from hydrides precipitated in Zr grains belonging to the mAxial component clearly emerges from the experiment, despite the fact that this α-Zr texture component is hardly seen in Fig. 7. This suggests that, in the as-received condition, (no applied load) hydrides have a much larger probability of precipitating in grains belonging to the mAxial component, in agreement with previous observations [8]. Identification of the origin of the largest hydride component, pTilted at ϕ = 70° of Fig. 4, is not intuitive and requires a more subtle analysis. For this, a synthetic model of the Zr matrix ODF composed of the three ideal texture components (mHoop, mRadial, mAxial), plus the fourth component, mTilted, was produced, which represents the large population of Zr crystals with orientations between mHoop and mRadial (Fig. 7a). Using the above-mentioned hydride/matrix orientation relationship, the orientation for hydrides formed within Zr grains belonging to each texture component was evaluated. Fig. 9a shows the predicted δ(111) poles resulting from the four α orientations as circles of different colors, superimposed on the experimental pole figure of Fig. 8a. The great number of circles of the same color is due to the multiplicity of ⟨111⟩ directions of the cubic crystal compared with the ⟨0001⟩ direction of the hexagonal crystal. Qualitatively, the main features of the experimental pole figures are well described by these four ideal orientations. In particular, the most intense poles, observed near the axial direction, result mainly from the mTilted component with some minor contribution from the mHoop component. Fig. 9b shows calculated azimuthal intensity profiles for the different texture components, equivalent to the experimental profiles presented in Fig. 4. In the calculation, equal probability was assumed for the two transformation variants and equal weights for all texture components; i.e. the actual weight of each component corresponding to the different populations within the α-Zr
ODF is not included in the plot. The calculation represents each α texture component as an 8° wide distribution of crystal orientations centered in the ideal orientation with a probability distribution given by a von Mises–Fisher-type distribution [20]. The values for the mTilted contribution in Fig. 9b are low because the hydride pole lies off the axial–hoop circle, so one sees only the tail of the distribution. The figure clearly demonstrates that the intensity at ϕ = 70° (pTilted in Table 1) results from contributions from hydrides precipitated in Zr grains from both mTilted and mHoop components. Table 1 indicates that, for all specimens investigated, the intensity for pTilted is almost double that for pHoop, while Fig. 9b indicates that the contribution of mHoop to pTilted is roughly half of the intensity observed at pHoop, exactly opposite to the experimental finding. This confirms that the main contribution to pHoop comes from hydrides precipitated in Zr grains from the mTilted component, i.e. with orientations lying between the hoop and radial directions. So, hydrides precipitated in Zr grains from the mTilted component represent the main contribution to the δ hydride ODF, even when the α-Zr ODF is dominated by the mHoop texture component.

8. Discussion

8.1. Hydride precipitation probabilities

The texture analysis revealed that hydride precipitation (for both radial and circumferential) occurs in α-grains with a variety of orientations, mHoop, mAxial, mTilted, etc., yet the probability for hydride precipitation does depend on the Zr grain orientation. This is in direct contradiction to earlier proposals that circumferential hydrides result exclusively from precipitation in α-Zr grains from the mRadial component, while radial hydrides come from grains from the mHoop component [12,13]. The average size of α-Zr grains along the hoop direction is ~1 μm, so each circumferential (hoop) hydride in Fig. 2 (left) is a collection of hydrides precipitated on several α-grains. The present results indicate that these α-grains could actually belong to any texture component. The present finding is reasonable, as the ~40 μm-long hydrides of the L2 specimen would require nearly ~40 α-grains from the mRadial texture component adjacent to each other; a situation that seems, in principle, very unlikely.

As listed in Table 1, in the “as-received” condition specimens E2 and L2 present a significant number of hydrides precipitated in α-grains from the mAxial orientation, despite the fact that this texture component is more than two orders of magnitude smaller than the mHoop component (Fig. 4a). This indicates that the probability of hydride precipitation is much higher in mAxial grains than in other texture components. It is usually accepted [2] that precipitation is more favorable on α-grains with their c-axis stretched by external or internal stresses, as this helps to accommodate the large mismatch (7.2%) between the two phases along the α(0002)/β(111) direction [23]. Indeed, in a previous work on similar pressure tubes [8], it was found that the c-axes of the mAxial grains are stretched by ~1000 με when compared with the mHoop and mRadial grains. Application of an external load along the hoop direction stretches the c-axes along this direction and should favor hydride precipitation on the mHoop and mTilted components over mAxial. Indeed, an increase in the pHoop and pTilted and a decrease in the pAxial components are clearly observed in the experiments (Table 1 and Fig. 5). However, the decrease registered for the pAxial component cannot fully account for the increase observed in the pHoop and pTilted components. So part of this increment must come from a corresponding decrease in hydrides formed in α-grains from the mRadial component. Unfortunately, the mRadial component was not accessible during the experiment, as can be appreciated in the calculations presented in Fig. 9.

Comparison of Fig. 9b with the pHoop and pTilted values listed in Table 1 reveal a clear difference in the hydride precipitation probability between α-grains from the mHoop and mTilted texture components. In order to roughly estimate these probabilities, Fig. 10 compares the measured δ(111) peak areas of Fig. 4b with calculations that vary the hydride precipitation probability of the two main texture components of the α-Zr texture; mHoop and mTilted. The analysis is intended to compare the precipitation probabilities between the available α-Zr orientations, but not its absolute value. For this reason, these relative probabilities will be...
expressed in terms of a standard value “p0”. This value was taken to make the area of the δ(111) peak coincide with the experimental results for φ = 0 (m_Hoop orientation) when the same probability is assigned to all α-Zr grain orientations (isotropic case).

The solid symbols in the top and bottom figures represent the experimental results for the as-received and after-reorientation conditions for the L2 specimen, respectively. The calculations apply the α–δ orientation relationship to the experimental α-Zr ODF, but assign a different hydride precipitation probability to the different grain orientations: all α-grain orientations in three groups were separated: (i) within a 5° cone around m_Hoop; (ii) within a 5° cone around m_Tilted; and (iii) the rest. The blue solid lines in Fig. 10 correspond to an isotropic precipitation probability (same probability for all orientations); clearly not capable of reproducing the experimental profiles. For the as-received hydrides, the calculation presented as a dashed red line shows good agreement with the experiment and predicts the correct intensity ratio between p_Hoop and p_Tilted. In this case, the precipitation probability for m_Tilted was eight times “p0”, while for m_Hoop and the others orientation the probability was just “p0”. For the after-reorientation condition, the effects of stress on precipitation probability were introduced by increasing the weight of both m_Hoop from 8 to 14.6 and m_Tilted from 1 to 2.5 while reducing the weight of the other orientations. This analysis clearly shows that: (i) hydride precipitation is not the same for all orientations; (ii) hydride precipitation for orientations near m_Tilted is roughly an order of magnitude higher than orientation close to m_Hoop; and (iii) hydride precipitation for both orientations becomes more probable upon the application of a load along the hoop direction.

8.2. Hydride reorientation

Application of stress changes precipitation probabilities between different α-Zr texture components, but does not qualitatively modify the ODF of the hydride phase (there are no new poles). However, such differences in precipitation probabilities have a clear impact on the resulting hydride microstructure (Fig. 2). The stress state of the precursor α-Zr grain is not the only factor affecting precipitation probabilities. Perovic et al. [24] showed that the macroscopic hydrides observed in Fig. 2 are in fact composed of stacks of smaller, microscopic hydride plates with habit planes close to the basal plane of the parent α-grains, as depicted in Fig. 11. The microscopic habit plane is dictated by the crystallography of the martensitic transformation, which defines a strain misfit tensor able to partially accommodate the 17% volume expansion. The energies involved in this transformation are so high that it is almost impossible to modify this situation by an external factor. However, the apparent habit plane of the macroscopic hydride plate, either circumferential or radial, is defined by the geometry of the stack. This geometry is determined by an auto-catalytic nucleation process where the stress field of a large hydride plate aids the nucleation of a neighbor hydride. For δ-hydrides, this leads to the formation of stacks of hydrides with a platelet shape. The energies involved in this process are much lower compared with those involved in the martensitic transformation, so the

![Fig. 11. Effect of grain morphology and hydride–hydride interactions on the probability for hydride precipitation in grains belonging to three of the α-Zr texture components identified in Fig. 7. The idealized hydride stacks that compose circumferential (top) and radial (bottom) hydrides are distinguished. Arrangements (a) and (f) are energetically unfavorable.](image-url)
actual orientation of the platelet can be modified by the application of external loads. The formation of a macroscopic hydride platelet requires hydride precipitation in many neighboring \( \alpha \)-grains. Thus, definition of the most favorable hydride arrangement must consider not only elastic hydride–hydride interactions and external loads, but also the grain shape, crystallographic texture and the actual distribution of plastic deformation within the parent material. In practice, all these factors are strongly interconnected and become very hard to isolate. Following Ref. [24], Fig. 11 depicts the hydride stacks that result from precipitation in \( \alpha \)-grains from the three main texture components of the pressure tubes, where it becomes clear that both grain shape and texture play important roles in the process. The lamellar shape of pressure tube \( \alpha \)-grains, which are long along the axial and hoop directions and thin along the radial direction, imposes different obstacles for hydride stacks appearing in different texture components. Thus, microscopic hydrides plates can grow considerably in the \( m_{\text{Radial}} \) component, while those in the \( m_{\text{Hoop}} \) component are quickly stopped by grain boundaries. Yet, the auto-catalytic process favors the nucleation of hydride plates with the same habit plane, but offset one another along the direction normal to that plane (Fig. 11b, d and e). A stack arrangement where microscopic hydride plates are displaced along the \( c \)-axis (Fig. 11a) is repulsive, because the major expansion due to hydride formation occurs along the \( c \)-axis of the matrix. Thus, growth of a macroscopic circumferential hydride in the axial–hoop plane proceeds mainly by precipitation on \( p_{\text{Tilted}} \) and \( p_{\text{Radial}} \) components (Fig. 11b and c), because \( p_{\text{Hoop}} \) stack arrays are energetically unfavorable. The actual driving force for circumferential hydride growth in the as-received material is still unclear. Circumferential hydrides also appear on Zircaloy tubing [5], with microstructures and textures considerably different from those found in the present case. Marshall [25] found very good correlation between hydride orientation and a directional strain parameter, representing the plastic deformation introduced along different directions by the tube manufacturing process. In all cases, the presence of hoop stresses makes radial hydrides more favorable, as it becomes easier from a macroscopic point of view to accommodate the hydride volume expansion perpendicular to the load. That is, the external load adds to the auto-catalytic hydride–hydride interaction, making the \( p_{\text{Hoop}} \) arrangement depicted in Fig. 11d energetically favorable. On a microscopic scale, the load stretches the \( c \)-axis of \( \alpha \)-grains from the \( m_{\text{Hoop}} \) component, while it compresses the \( c \)-axis of those from the \( m_{\text{Radial}} \) component. For all this, when macroscopic radial hydrides grow, precipitation on the \( p_{\text{Hoop}} \) component becomes a better option than precipitation on the \( p_{\text{Radial}} \) component.

### 8.3. Hydride stresses and reorientation

The presence of stress within the hydride precipitates manifested in Table 1 through differences in the \( \delta(111) \) interplanar spacing measured along the hoop and tilted directions, quantified by the strain amplitude \( \Delta \delta(111) \). This magnitude is a robust experimental indication of the presence of stress, because it is independent of “do”, which is always very difficult to define in absolute terms. The values measured for all samples and conditions are compatible with the existence of a state of compressive plane stress on the plane of the hydride platelets, in agreement with previous observations on Zircaloy-4 hydrides [15]. The stress state is represented schematically in Fig. 12. The compressive stress exerted by the matrix results from the volume increase associated with hydride growth, which occurs essentially on the plane of the platelet. Moreover, as indicated by the length of the arrows, the stress exerted by the matrix along a given direction is expected to be proportional to the hydride length, i.e. to the deformation along this direction.

To check this, it is noted that, for all specimens investigated, \( \delta_{\text{Hoop}} > \delta_{\text{Tilted}} \), revealing compression along the tilted direction, which lies just 20° from the axial direction of the tube. In the as-received condition, there are almost exclusively circumferential hydrides, subjected to compressive stresses along the hoop and axial directions. For E1, E2 and L1, hydrides are much shorter along the hoop than along the axial direction (Fig. 2), therefore, \( \sigma_{\text{Axial}} > \sigma_{\text{Hoop}} \) and relatively similar values were found for the strain amplitude (\( \sim \)2600 ± 400 \( \mu \)). For the L2 specimen, hydrides are considerably longer along the hoop direction, so \( \sigma_{\text{Axial}} \approx \sigma_{\text{Hoop}} \), and the strain amplitude between the two directions reduces to \( (500 \pm 200 \mu) \). After reorientation, there are an important number of radial hydrides, which are under compressive stresses along the radial and axial directions. The hydride size along the axial direction remains essentially constant after reorientation, and so the compressive stress along the axial direction is unaltered too. For low H contents (E1 and L1), the size of the hydrides along the radial direction is small, and the compressive stress along this direction would be small too. This means that the stress state for E1 and L1 is close to uniaxial.
compression along the axial direction for both circumferential and radial hydrides, and no change in strain amplitude is observed after reorientation; see Table 1. For higher H contents, E2 and L2, the hydride length along the radial direction results in a non-negligible stress developing along this direction. This new stress is responsible for the increments observed in $d$-spacing along the hoop direction after reorientation.

Estimation of absolute stress values requires knowledge of the room temperature unstressed interplanar distance $d_0$ for the hydride, which would require a specimen composed of 100% hydride phase produced from a pressure tube. In companion experiments reported in previous work, very similar $d_0$ values were found for a hydride blister (80% δ hydride, 20% $\alpha$-Zr) in a similar pressure tube (2.7450 Å) [7], and for 200 wt.ppm H hydrides in Zircaloy-4 plates (2.7448 Å) [15]. The two values are indicated in Fig. 6. Thus, in order to estimate the magnitude of the hoop stresses, $d_0 = 2.7449$ Å was adopted, and it was assumed that the hydrides are in plane stress condition, as discussed earlier (Fig. 12). The stress components along the three principal directions of the tube for all samples and conditions are listed in Table 2, where values of $E = 97$ GPa and $\nu = 0.35$ are adopted for the Young's modulus and Poisson ratio of the hydride precipitates [14]. In the as-received condition, hydrides are under a 200–250 MPa compressive stress along the axial direction, and hoop stresses are low in all samples, with the exception of L2, where a similar stress is found also along the hoop direction. For this specimen, the large stress value estimated along the radial direction after reorientation indicates that a unique plane stress tensor is not capable of modeling the hydride microstructure. This is not unexpected, as Fig. 2 clearly shows that, after reorientation, there is a fair mixture of both circumferential and radial hydrides; and the measured $d$-spacings actually correspond to the average of all them.

8.4. Reorientation signature

The present results suggest that a diffraction-based signature of the reorientation process may be identified. Moderate changes in the texture and in the stress state of the hydrides occur after reorientation, which manifest through small but measurable differences in the intensity and position of diffraction peaks. The largest differences are expected for the $\delta(111)$ peaks measured along directions contained in the hoop–radial plane of the pressure tube, which unfortunately have not been measured during these experiments. A simple recipe to separate radial from circumferential hydrides based on peak intensities is not evident. This is because $\delta(111)$ intensity profiles for radial and circumferential hydrides are expected to be relatively similar, as observed here for the hoop–axial plane (Fig. 4b). However, from the previous discussion, hydride interplanar distances are expected to be compressed for directions contained within the platelet, and stretched for the direction normal to this plane. So it is expected that for circumferential hydrides $d_{\text{Radial}} > d_{\text{Hoop}}$, while for radial hydrides $d_{\text{Radial}} < d_{\text{Hoop}}$.

Unfortunately, in Zr2.5Nb pressure tubes very few hydrides are found with $\delta(111)$ parallel to the radial direction (Fig. 8), so in practice the value of $d_{\text{Radial}}$ is unavailable. Yet the same information can be obtained from the relative change $\varepsilon_R = \Delta d/d$ observed when moving away from the hoop direction, with $\varepsilon_R > 0$ for circumferential hydrides, and $\varepsilon_R < 0$ for radial hydrides. Measurements of circumferential hydrides on a commercial pressure tube [8] agree with these ideas, but additional measurements on controlled specimens should be performed in order to generalize this observation.

9. Conclusions

Synchrotron XRD experiments were performed on samples from commercial and experimental Zr2.5Nb pressure tubes charged with H contents up to 130 wt.ppm. The crystallographic texture and stress state of hydride precipitates of two different morphologies were determined by careful analysis of the Debye rings from the $\alpha$-Zr matrix and the δ-hydride precipitates. Circumferential hydrides were observed after 24 h annealing at 400 °C followed by air cooling, while a majority of radial hydrides was observed when cooling was performed under a load of 225 MPa along the hoop direction of the tube. The main findings of the present studies are as follows.

1. For both circumferential and radial hydrides, precipitation occurs in $\alpha$-grains with a variety of orientations, but with a clear preference for $\alpha$-Zr crystals with their $c$-axes...
at an angle of 15–20° degrees from the hoop direction. This preference was interpreted in terms of the interplay between the α grain morphology and an autocatalytic nucleation process.

2. Application of an external stress modifies this probability for hydride precipitation, favoring precipitation on α-grains with their c-axis stretched by the external stress, while preventing precipitation on grains where the c-axis is compressed. This is reflected in a moderate change in the crystallographic texture of the hydride phase. This change should be accounted for in quantifications of hydride phase volumes by diffraction techniques.

3. Hydride precipitates are under nearly plane compression on the plane of the platelet, with the largest stresses always along the axial direction of the tube, with stresses in the range ~200–350 MPa. The distances between hydride atomic planes are compressed on the plane of the platelet and stretched normal to this plane. This effect should be accounted for in assessments of the stress state of hydrides precipitated near crack tips.

4. Hydride reorientation changes the orientation of the hydride platelet, which could provide a diffraction signature of the hydride orientation. In principle, the hydride orientation could be derived from a comparison of the d-spacing values measured along (or near) the radial and hoop directions of the tube.

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