Hydrogen enhanced localized plasticity in zirconium as observed by digital image correlation

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\textbf{ABSTRACT}

Hydrogen embrittlement in zirconium alloys is a highly relevant research topic, important for ensuring the integrity of nuclear fuel clads. While the presence of hydrides in zirconium-based clad is a well-known risk factor due to their brittleness, the effect of the presence of hydrogen in solid solution is unclear.

According to the Hydrogen Enhanced Localized Plasticity (HELP) model, hydrogen in solid solution may affect the mechanical performance of a metal by increasing dislocation mobility due to the shielding effect that hydrogen has on the interaction of dislocations with other types of defects. In the presented work, the presence of HELP has been assessed in Zircaloy-4 samples, under conditions relevant to the storage of spent nuclear fuel.

Elevated temperature tensile tests were performed on samples containing localized areas of higher hydrogen concentration, as quantified by neutron radiography. Digital Image Correlation (DIC) analysis was performed on the specimen surfaces for quantitative characterization of strain heterogeneity during deformation to identify the regions where the plastic strain localization occurs.

These regions could be correlated to elevated amounts of hydrogen in solid solution, that is, in the location immediately adjacent to dissolving hydrides, or in the areas of the samples with local hydrogen concentration close to the expected terminal solid solubility limit (TSS) in the test conditions.

The results confirm the presence of localized softening caused by solid solution hydrogen, indicating that the HELP mechanism needs to be taken into account when modeling the mechanical response of zirconium-based nuclear fuel clads at elevated temperatures.

\section{1. Introduction}

In the area of interest for spent nuclear fuel storage, hydrogen can be found both in solid solution or in the form of hydrides [1]. In conditions below terminal solid solubility, the leading embrittlement mechanism is through cleavage across brittle hydrides (e.g. [2,3]); however, in conditions of high temperature and low hydrogen concentration, hydrogen is stable in solid solution inside the metal lattice. In such conditions, it is speculated that hydrogen enhances dislocation mobility, leading to increased ductility of the material.

This increased ductility has been extensively described for steels (e.g., [4–6]), however, it is unclear whether a similar mechanism is active in Zr alloys under conditions faced by spent nuclear fuel.

The hydrogen-induced softening effect is difficult to observe in zirconium alloys as it is often compensated by the more prominent effect of hardening due to hydrides. However, it cannot be discounted that the conditions necessary to activate the softening mechanism might be active locally within the clad e.g. in the vicinity of large hydrogen accumulations (especially in claddings containing a liner [7,8]).

The mechanical properties of zirconium alloys in the presence of a uniform distribution of low amounts of hydrogen have been recently published by Fagnoni et al. [9]. The results highlighted the presence of softening effects in the region where the majority of hydrogen is expected to be in solid solution. The effect of hydrogen in solid solution appears to be minor compared to the effect of hydrides, but significant, with the most pronounced softening effect recorded at 300 °C for...
Zircaloy-4 samples enriched with 100 wt ppm of hydrogen.

To study the effect that discrete sources of hydrogen have on the strain localization in zirconium, differentially enriched samples were subjected to tensile tests at elevated temperature. The distribution of the strain field during tensile testing was measured by digital image correlation (DIC) analysis. DIC is a non-contact, optical measurement technique that is becoming increasingly popular for measuring the deformation response of materials [10–12].

In this work, DIC analysis was conducted at elevated temperatures during tensile tests to identify the effect of hydrogen distribution on plastic strain localization. The measured strain fields were compared to the hydrogen distribution within the samples as spatially quantified prior to the test by non-destructive neutron imaging [7,8,13,14].

DIC showed substantial strain concentration in areas adjacent to highly charged ones, and generalized strain localization in the presence of hydrogen amounts close to the solid solubility limit, confirming the presence of a hydrogen induced softening mechanism in zirconium.

2. Methods

For the project, a 2.5 mm thick Zircaloy-4 recrystallized sheet was supplied by Framatome.

Samples used for mechanical tests were produced from allocated samples by water-jet cutting. The dog-bone gauge was 18 mm long and 7 mm wide, with a connecting radius of 6 mm. The machining process allowed for tolerances of ±0.02 mm.

The Zircaloy-4 composition, according to the ASTM B351/B351M-13 (2018) standard is: tin 1.20–1.70 wt.%, iron 0.18–0.24 wt.%, chromium 0.07–0.13 wt.%, and other impurities in concentrations <0.05 wt.%. The microstructure of the base material had an average grain size of 5
µm and preferential 0001 orientation along the normal direction, with some tilt towards the transverse direction, as confirmed by EBSD measurements [15].

Fig. 1 represent schematically the experimental procedure adopted. To manifest the hydrogen enhanced localized plasticity (HELP) effect, the samples were charged with hydrogen. Diffusion of high purity hydrogen following high vacuum conditions was employed, following a similar procedure to the one described in [16].

For optimal hydrogen charging, samples were first polished using 2000 grit silica abrasive paper. Post-polishing, they were cleaned in acetone and then treated to a 3-minute ultrasonic bath in ethanol to ensure thorough cleanliness. After air-drying, the samples were accurately weighed on a precision balance.

To obtain the desired hydrogen gradient within the samples, half of the sample was coated prior to hydrogenation with heat resistant silicon paint to prevent hydrogen absorption into the metal in the coated area.

In the hydrogenation phase, samples were placed in a high-vacuum environment (10^-7 mbar) at room temperature for 12 hours. The system underwent three cycles of hydrogen flushing at 100 mbar, with high-vacuum restoration after each. The temperature was subsequently raised to 400 °C and held for 24 hours. The hydrogenation level was controlled through the formula

\[ C_r = K \frac{p_f - p_i}{m_r} \]

where \( C_r \) is the target hydrogen concentration, \( m_r \) represents the sample weight, \( p_i \) and \( p_f \) are the starting and final hydrogen pressures, and \( K \) is an experimental constant assumed to be equal to 660.

The sample was subsequently de-coated by mechanically grinding both faces of the samples with 600 grit paper prior to assessing the resulting hydrogen distribution within the sample by neutron imaging.

Transmission contrast neutron images of the samples were acquired at the BOA cold neutron beamline [17] of the Swiss spallation neutron source [18] at the Paul Scherrer Institut (Switzerland). The imaging detector consisted of a 100 µm thick (LiF/ZnS(Ag)) scintillator screen and an optical Andor iKon-L CCD camera (2048 × 2048 pixels) equipped with a Zeiss MAKRO-PLANAR 2/100 mm ZF.2 objective lens. The magnification of the lens was such to achieve a field of view of 96 × 96 mm², thus, an effective pixel size of 47 µm. In order to have optimal image resolution, the samples were attached to the scintillator screen, from the head and the tail of the dog-bone, with aluminum tape.

The hydrogen concentration within the sample was estimated adapting the calibration obtained by Gong et al. [7] to 2.5 mm plate material, obtaining hydrogen sensitivity of 2.1 ± 0.1 cm⁻¹/wt ppm H.

Mechanical tests were performed using a 10 kN MTS universal tensile machine equipped with an environmental chamber and contact extensometer. The samples were subjected to tensile test in the transversal (rolling) direction. The tensile tests were conducted with displacement control, imposing crosshead movement of 0.5 mm/min until fracture. The temperature during the tests was set to 350 °C. Testing conditions
were reached after 10 °C/min heating, and a hold time of 30 minutes for the hydrogen-free samples, and 180 minutes for the hydrated samples. The temperature was monitored using a thermocouple sded to the specimen. After sample rupture, the necking position and fracture surface were measured with an optical microscope.

The total hydrogen distribution and solid solution fraction expected within the sample at the beginning of the tensile test can be calculated from the initial conditions assessed by neutron radiography, applying concentration-gradient diffusion during heating-up and dwell time at test temperature. Simulations were performed using an in-house developed finite volume solver. The dissolution and precipitation of hydrides were simulated with the hydride nucleation-growth-dissolution (HNGD) model [19]. Since the temperature gradient within the sample was absent, the only driving force for hydrogen flux \( J_h \) is the hydrogen concentration gradient in solid solution \( \nabla c_{SS} \):

\[
J_h = D \nabla c_{SS},
\]

where the diffusion coefficient \( D \) is given by [20]:

\[
D = 7.9 \times 10^{-7} \exp\left(-\frac{4.49 \times 10^4}{RT}\right) \text{[m}^2\text{s}^{-1}].
\]

where \( R \) [Jmol\(^{-1}\)K\(^{-1}\)] in Eq. (2) is the gas constant, and \( T \) [K] is temperature. The HNGD model requires specifying the terminal solid solubility for dissolution (TSSD) and precipitation (TSSP). In this work, the correlations derived by Kammenzind et al. are used [21]:

\[
\text{TSSD} = 66000 \exp\left(-\frac{32177}{RT}\right) \text{[wt ppm H]},
\]

\[
\text{TSSP} = 31000 \exp\left(-\frac{25264}{RT}\right) \text{[wt ppm H]}.
\]

The test was monitored with a Canon EOS 200D camera through a small opening into the test chamber. To perform DIC analysis at elevated temperatures, heat resistant black and white vinyl-based paints were used to generate speckle patterns on the specimen surfaces. The specimen surfaces were covered with black paint as a background, and white paint was applied to generate white speckle distributions. The applied speckle pattern had a strong optical contrast and could withstand high temperature environments up to 500 °C. The diameter of the resulting speckles, as viewed by the DIC camera, were \(~30–50\) μm. The images for DIC analysis were acquired using a Canon EOS 200D camera at the standard image resolution 2048 pixels x 2048 pixels.

Fig. 4. Linear neutron transmission profiles and corresponding estimated hydrogen concentration obtained along the length of the gauge. The measurements are referenced to 0 mm at the center of the specimen. The neutron transmission profiles of the reference samples, low-H samples (possessing low hydrogen gradient), and high-H samples (possessing sharp hydrogen gradient) are reported in the sub-figures a), b), and c) respectively.
A view of the setup, with the environment chamber open, is shown in Fig. 1–vii. Fig. 2 shows an example of the image acquired during the imaging process, and the corresponding pattern. Pictures were taken at 5 s intervals during tensile deformation, corresponding to a picture every 83 µm of movement of the crosshead.

The images acquired in situ during tensile tests were subjected to DIC.

Fig. 5. Strain maps along the direction of the tensile deformation ($\epsilon_{xx}$) obtained by DIC at 3.5% global strain of the tensile specimens. Hydrogen distribution maps from Fig. 3 are provided again in the small windows for convenient reference. A strong localization of strain is observed in the samples containing a high hydrogen gradient (high-H). The samples charged with lower amounts of hydrogen (low-H) present strain localization at the micro-level. Strain distribution in the reference material is comparatively uniform. The line-scans along the vertical mid-section of the tensile samples (average between the 2 homologus) is presented at the bottom of the image.

Fig. 6. Samples after tensile test at 350 °C. The position of the necking appears in the hydrogen-poor side in the high-H samples possessing large hydrogen gradient, and in the hydrogen-rich side in the samples low-H possessing hydrogen concentration closer to solid solubility. The necking position is central in the reference samples.
analysis using VIC 2D 6 software (Correlated Solutions, Inc.) to obtain strain maps at different stages of deformation. In post-processing of the images, a 31 pixels × 31 pixels (corresponding to 465 um × 465 um) subset size and a 3 pixels (corresponding to 45 µm) step size were chosen. The size and distribution of the speckles in the speckle pattern were taken into consideration when choosing the dimensions of the subset to ensure that each subset had sufficient speckle distribution. During the strain computation, a 5 × 5 decay filter was selected as the minimum filter length required by the software to smooth the strain fields. The image processing was carried out until it reached approximately 5 % global strain whereupon paint delamination started on the specimen surfaces and the speckle pattern quality degraded. The images for DIC analysis were processed by using the image taken at the undeformed state as reference and processing all the images at the deformed state relative to the reference image by using Zero-mean normalized sum of squared differences (ZNSSD) as a correlation criteria. The global strains were estimated from the average value of strains computed by DIC on the gauge section of the specimens.

To assess the presence of localization of plasticity in presence of non-uniform hydrogen concentration, three categories of samples were employed in the presented study:

1. **Reference samples** (in the subsequent text referred as “reference”), consist of dog-bones obtained directly from the material in the as-received state. The hydrogen concentration in the base material was certified to be lower than 9 wt ppm H;
2. **Highly hydrogen enriched samples** (in the subsequent text referred as “high-H”), where a strong hydrogen gradient was created within the sample, leading to half of the sample being hydrogen-poor (<9 wt ppm H), and the other half having hydrogen well above TSSP at the test temperature (>240 wt ppm H at 350 °C [1]);
3. **Slightly enriched samples** (in the subsequent text referred as “low-H”), where half the sample was enriched to a hydrogen concentration between TSSD and TSSP at the test temperature (between 120 wt ppm H and 240 wt ppm H at 350 °C [1]), while maintaining the other half as hydrogen-free as possible.

Two samples per category were tested with the described
methodology. Results and considerations are discussed in the following sections.

3. Results

The neutron images of the analyzed samples are provided in Fig. 3, and the corresponding neutron transmission profiles along the spine of the sample, referenced to the midpoint of the gauge, are plotted in Fig. 4.

The total hydrogen concentration within the gauge of the sample as measured by integration for the neutron transmission curves is: 8 wt ppm H and 14 wt ppm H for the reference samples, 126 wt ppm H and 99 wt ppm H for the low-H samples, 123 wt ppm H and 146 wt ppm H for the high-H samples. Both the high-H samples present a well-defined hydrided area of macroscopic size, visible to the naked eye, formed during the hydrogen enrichment process. In all the hydrogen-enriched samples, the majority of the hydrogen is concentrated in the area of the gauge section that was uncoated during hydrogen pickup. Average hydrogen concentrations in the hydrogen-poor half of the gauge (coated during hydrogen pickup) and hydrogen-rich half of the gauge (uncoated during hydrogen pickup) are presented in Table 1. In the high-H samples, the measured hydrogen concentration in the hydrogen-rich area of the sample exceeded TSSP at test temperature (above 240 wt ppm H), whereas in the low-H samples, strain is comparatively more uniformly distributed, however, there are strong fluctuations in the recorded strain in regions of around 30 µm.

The test was conducted until rupture. In all the tested cases, the sample failed in a ductile way after 45–53 % elongation. Fig. 6 presents images of the samples after rupture, with the necking region highlighted. Necking appeared in the hydrogen-poor side of the high-H samples, whereas in the low-H samples, fracturing appeared towards the hydrogen-rich side. The reference samples broke within 0.35 mm from the mid-line. Fracturing appeared after 87 % reduction of the cross-sectional area in the reference samples, and after an 83 % and 82 % reduction of the cross-sectional area in the low-H and high-H samples respectively, as shown in Fig. 7. The hydrogen distribution in the samples was checked after the test once again by neutron imaging. The resulting image is presented in Fig. 8. Stress-strain curves are shown in Fig. 9. The ultimate tensile strength was considerably higher for the samples enriched with hydrogen compared to the reference samples. Both the elongation at rupture and the material toughness, considered one of the

![Fig. 9. Strain-Stress curve obtained during tensile test at 350 °C. The reference material represents the lower ultimate tensile strength (UTS), while the maximum elongation at rupture is reached by the samples containing lower hydrogen gradient (low-H samples).](image)

<table>
<thead>
<tr>
<th>Ref.</th>
<th>εtot (mm/mm)</th>
<th>UTS (MPa)</th>
<th>Toughness (J/m²)</th>
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<td>1</td>
<td>0.49</td>
<td>212.4</td>
<td>89.20</td>
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<tr>
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<tr>
<td>Low-H 1</td>
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<tr>
<td>Low-H 2</td>
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<tr>
<td>Average</td>
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Fig. 10. Toughness, ultimate tensile strength (UTS) and strain at UTS recorded in the tested samples and averaged by category. The hydrogen distribution profiles presented in Fig. 4 were produced applying a Loess smoothing, with span of 0.3. In the reference samples, the fluctuations in the estimated hydrogen concentration amounts to ±20 wt ppm H. As the neutron transmission is expected to be constant in the hydrogen-free sample, this measurement can be considered a good estimate of the measuring error of the technique. Strain mapping obtained by DIC analysis at 3.5 % global strain during tensile tests at 350 °C is provided in Fig. 5. The results indicate a strong localization of the deformation in the hydrogen-poor area of the high-H samples with large dissolving hydrides. In the low-H samples, strain is comparatively more uniformly distributed, however, there are strong fluctuations in the recorded strain in regions of around 30 µm. The reference samples present a uniformly distributed strain along the full length of the gauge.

The test was conducted until rupture. In all the tested cases, the sample failed in a ductile way after 45–53 % elongation. Fig. 6 presents images of the samples after rupture, with the necking region highlighted. Necking appeared in the hydrogen-poor side of the high-H samples, whereas in the low-H samples, fracturing appeared towards the hydrogen-rich side. The reference samples broke within 0.35 mm from the mid-line. Fracturing appeared after 87 % reduction of the cross-sectional area in the reference samples, and after an 83 % and 82 % reduction of the cross-sectional area in the low-H and high-H samples respectively, as shown in Fig. 7. The hydrogen distribution in the samples was checked after the test once again by neutron imaging. The resulting image is presented in Fig. 8. Stress-strain curves are shown in Fig. 9. The ultimate tensile strength was considerably higher for the samples enriched with hydrogen compared to the reference samples. Both the elongation at rupture and the material toughness, considered one of the

![Table 1. Strain at rupture (εtot), ultimate tensile strength (UTS) and toughness obtained from the stress-strain curves presented in Fig. 9.](image)

![Fig. 10. Toughness, ultimate tensile strength (UTS) and strain at UTS recorded in the tested samples and averaged by category.](image)
most important plasticity parameters, are significantly higher in the samples presenting higher amounts of hydrogen in solid solution (low-H). This can be further understood by examining the data in Table 1, where we see that the average UTS for low-H samples is approximately 9 % higher than the reference average, and their toughness, calculated as area under the stress-strain curve, is about 17.5 % greater than the reference samples. It is worth noting that high-H sample 1 and high-H sample 2 behaved remarkably similarly, despite the presence of strongly differing hydrogen distributions within the samples; this confirms that the deformation and failure mechanism is governed by the hydrogen-poor side (possibly with a contribution of hydrogen in solid solution). Fig. 10 further underscores this point; the UTS of high-H samples is slightly greater than that of the low-H samples, yet their toughness is almost comparable to the reference samples, being just marginally higher.

4. Discussion

The necking position can be correlated with the expected hydrogen distribution profiles to assess the influence of hydrogen in solid solution on the failure mechanism and softening behavior. The calculated hydrogen concentrations during tensile tests, taking into account hydride dissolution and hydrogen diffusion, are presented in Fig. 11. In the low-H samples, possessing a smooth hydrogen gradient, it is noted that fracturing appears close to where hydrogen in solid solution reaches a maximum, in the area directly adjacent dissolving hydrides (Fig. 11a and b). In the high-H samples, possessing a much sharper hydrogen gradient, the hardening effect due to large hydrides which force localization of strains towards the hydrogen-poor area of the sample, where necking and fracturing appears, possibly with a contribution of solid solution hydrogen, (Fig. 11c and d).

In the presence of high hydrogen concentration gradients within the sample, strain appears highly localized in the hydrogen-poor area of the
samples (Fig. 6 high-H). In the presence of smaller hydrogen gradients (Fig. 6 low-H), strain appears highly variable, with micro-regions possessing high deformation adjacent to micro-regions with low deformation. The same behavior is observed both in the hydrogen-rich and hydrogen-poor side of the samples, possessing total hydrogen concentration respectively above and below the expected TSSD at the testing temperature (120 wt ppm H at 350 °C). Therefore, the observed micro-localization of strain cannot be fully attributed to the presence of hydrides in the matrix, and the presence of hydrogen in solid solution must play a central role.

The total amount of hydrogen in solid solution expected during the test was determined from the simulations as 90 wt ppm H and 85 wt ppm H for the low-H samples and 73 wt ppm H and 66 wt ppm H for the high-H samples. Ultimate tensile strength (UTS) and sample toughness are both improved by the addition of hydrogen. However, while the UTS increases with increased hydrogen content, the sample toughness reaches a maximum in the samples containing the highest amounts of hydrogen in solid solution. Also, the elongation at rupture and strain at UTS appear to be larger in the samples possessing TSSD amounts of hydrogen in the system, indicating a correlation between hydrogen in solid solution and increased plasticity.

5. Conclusion

The main findings can be summarized as follows:

- Coating proved to be a successful method to control the hydrogen pickup to produce zirconium samples with a concentration gradient;
- Total elongation at fracture and sample toughness reaches a maximum in the specimens possessing higher amounts of hydrogen in solid solution;
- Digital image correlation analysis highlighted substantial strain localization in the areas directly adjacent to the highly charged ones in differentially charged samples subjected to tensile test at 350 °C;
- Micro-localization of stresses are observed in areas exhibiting hydrogen amounts below the solid solubility limit at the tested temperature;
- All samples failed in a ductile way; no cleavage across the hydride fraction was observed in samples possessing a macroscopic hydride section spanning the full width of the sample.

The results indicate strain localization in regions where elevated amounts of hydrogen in solid solution is expected, that is, in the regions immediately adjacent to dissolving hydrides or in the areas of the samples with local hydrogen concentration close to the expected terminal solid solubility limit in the test conditions. The results imply that hydrogen in solid solution induces material softening in Zircaloy-4 samples, supporting the presence of HELP effect in zirconium alloys in conditions relevant for nuclear fuel cladding application.

**References**


