

Hydrogen concentration and hydrides in Zircaloy-4 during cyclic thermomechanical loading

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Abstract

Hydride formation in zircaloy-4 under cyclic thermomechanical loading has been investigated using characterized notched beam samples in four-point beam testing, and microstructurally-representative crystal plasticity modelling of the beam tests which incorporates an atomistically-informed thermodynamically-equilibrium model for hydrogen concentration. The model provided the locations within the microstructure of high hydrogen content, above that required for saturation, hence predicting the anticipated locations of hydride observations in the experiments. The strain rate sensitivity of this alloy over the temperature range considered led to considerable intragranular slip and corresponding stress redistribution, and cyclic strain ratcheting leading to high hydrostatic stresses and in turn hydrogen concentrations, which explains the locations of experimentally observed hydride formation. The interstitial hydrogen interaction energy as well as the intragranular geometrically necessary dislocation density were shown to be important in controlling the spatial distributions of observed hydrides.

1. Introduction

Zircaloy-4, with primary hexagonal close-packed (HCP) phase, is primarily used as fuel cladding tubes in pressurized water reactors (PWR) due to its low thermal neutron absorption, reasonable strength and corrosion resistance at high temperatures. However, hot coolant water reacts with the zirconium alloy during operation, releasing hydrogen that enters the zircaloy metal lattice and forms hydrides (ZrH_x) when the hydrogen solid solubility is exceeded [1,2], which is strongly dependent on temperature. The macro-hydride is considered to be a brittle phase, which can reduce the fracture toughness and lead to embrittlement of the pressure tube. It is known that the hydrogen diffuses favourably into high tensile stress regions, such as at service-induced flaws or manufacturing weak spots (e.g. welding points) and a degradation process called delayed hydride cracking (DHC) can potentially initiate from the pre-crack [3–5]. DHC is a stable, time-dependent crack growth mechanism where hydrides repetitively dissolve and re-precipitate within the zircaloy tubes during thermo-mechanical cyclic loading. Understanding the mechanisms underpinning this phenomenon would allow improved material design and safety control for water-cooled nuclear power engineering.

Macroscopic approaches have been adopted in the past to attempt to quantify DHC based on elastic moduli and component geometry, leading to empirical industry standard solutions [6]. However, zircaloy microstructure is known to play a key role in the distribution of hydrogen and subsequent hydride formation at the grain scale. While direct measurement of the hydrogen profile is not accessible, experimental characterisation techniques such as electron backscatter diffraction (EBSD) and X-ray diffraction (XRD) have been applied to study the hydride distributions instead. δ hydride, a face-centred cubic (FCC) phase, is the most commonly observed in zircaloy and it

prefers to nucleate at grain boundaries at low cooling rate [7,8]. The crystallographic orientation relationship between δ hydride and the Zr matrix is observed to be $\{0001\}_a || \{111\}_\delta$ and $\langle 11\bar{2}0 \rangle_a || \langle 110 \rangle_\delta$ [6,9]. Using EBSD, the habit plane of intergranular and some intra-granular hydride packets is found to be along the $\{10\bar{1}7\}$ plane of the adjacent matrix and the morphology of intergranular hydrides can vary according to the misorientation between habit plane and grain boundary [10]. Twinning within the δ hydride has been found to accommodate the misfit strain between matrix and hydride [10]. Prismatic slip has been suggested to be a necessary source for hydrides to precipitate at grain boundaries, especially for those with c-axis misorientation angles $<40^\circ$ or $>80^\circ$ [10]. Fine-grained zircaloy-4 leads to more inter-granular hydrides with ‘stringer’ shape, whereas thicker hydrides are found on matrix basal planes at grain boundaries under low cooling rate (<3 K/min) [11]. However, at similar cooling rate, ‘blocky- α ’ grains with larger grain size are observed to develop more intragranular hydrides, which has been related to decrease in grain boundary area per unit volume and higher second-phase-particle (SPP) content [12]. During thermo-mechanical cycling, the microstructural effect on hydrogen/hydride content and hydride nucleation sites remains unclear.

A variety of models have been developed to study the hydrogen profile within zircaloy. The fuel performance code BISON uses the effects of mass and temperature gradients for simulating the hydrogen distribution at the macroscopic scale [13]. By incorporating hydrostatic-stress-induced hydrogen flux, the effect of stress raisers resulting from component geometry can be simulated under thermo-mechanical loading [14,15]. These models attempt to address the combined effects of temperature, stress and oxidation on hydrogen transportation within components. At a very different scale, atomistic simulation using accelerated kinetic Monte Carlo methods capture the anisotropic hydrogen diffusion along HCP c - and a -axes where the former is slightly higher than the latter [16]. Ab initio simulations show the preferential location of interstitial hydrogen atoms occupying tetrahedral sites of HCP zirconium [17,18]. The atomistic scale simulations provide valuable information, which may potentially be scaled up to microstructural (mesoscale) simulations, thus explicitly accounting for the polycrystalline orientations and grain morphology. At the mesoscale, crystal plasticity finite element (CPFE) modelling methods allow the explicit inclusion of hydrides embedded within the microstructure to study the effect of orientation relationship on the strain localisation at the phase boundaries and crack propagation paths [19]. However, here the intragranular hydrides were implicitly included. Anisotropic elastic mismatch from grain crystallographic orientation combinations results in constraint effects and hence local heterogeneous stress distributions at the grain scale. This in turn may influence hydrogen uptake known to be favoured by high hydrostatic stress. Grain-level stress and stress-assisted hydrogen diffusion may be addressed using CPFEM, which recognizes the HCP crystallographic anisotropy, grain morphology and interactions from lattice misfit [20]. This method has been applied to zircaloy to compare with 3D stress fields measured by XRD; strong grain interactions were observed near grain boundaries [21,22]. Crystal plasticity coupled with extended finite element methods (XFEM) has been utilized to understand short crack propagation paths and growth rates in zircaloy-4 [23] where the crack growth rate was determined by local stored energy density [24] and the crack path found to be crystallographic and on those slip systems with highest activation near the crack tip. Recently, hydrogen diffusion incorporated within crystal plasticity modelling has explicitly accounted for the role of microstructure, showing good consistency between hydrogen concentration sites at the grain boundaries and the experimentally-observed intergranular hydrides of zircaloy-2 for thermal cycles [4]. In a further recent study, the strain rate sensitivity of zircaloy even at low temperatures of 20°C has been shown to be important and leads

to considerable redistribution of stress (hence influencing hydrogen, and potentially hydride distribution) resulting from grain-level creep [25,26].

In this paper, we use a combined experimental and crystal plasticity modelling methodology to investigate hydrogen and hydride distributions within polycrystal zircaloy-4 subjected to combined thermo-mechanical cyclic loading. An atomistic-scale elastic dipole tensor is incorporated into the dislocation density-based rate-dependent crystal plasticity model to capture steady-state anisotropic hydrogen distributions resulting from the preferential zirconium lattice interstitial hydrogen sites. The strain rate and temperature dependent slip response is fully captured such that grain-scale creep, stress redistribution and geometrically-necessary dislocation (GND) effects on hydrogen distribution are fully recognised. Two differing notched blocky alpha zircaloy-4 samples, subjected to thermomechanical loading, were modelled with fully representative microstructures. Quantitative assessment and comparison of the characterized experimental hydride distributions is then presented.

2. Experimental setup for notched sample Zircaloy-4

Four-point bend testing on pre-hydrided zircaloy-4 samples was utilised to investigate the hydride distribution under thermo-mechanical cycling. The characterized form of the hydrides considered is the ‘macro’-hydride packet, which contains multiple individual microscopic hydride platelets [27].

2.1 Specimen preparation for as-received and blocky materials

The as-received material was hot-rolled recrystallised Zircaloy-4 plates of 10.0 mm thickness with average grain size $l_G \sim 10 \mu\text{m}$. This was increased using a heat treatment technique to yield large-grained ‘blocky- α ’ grains [28]. The samples were heat treated at 800 °C below the α to β transus temperature for 336 h in an argon atmosphere, followed by air cooling [28], which resulted in grain sizes within 300 to 600 μm .

Cuboidal specimens of Zircaloy-4 were cut using electro-discharge machining to dimensions of 42.0 mm $\times$ 10.0 mm $\times$ 6.0 mm. Samples were then ground to introduce ‘V’ notches with geometries of 1 mm depth, 45° flank angle and a root radius of 50 μm . Microstructures were characterised using scanning electron microscopy (SEM) and EBSD to quantify the average grain size and orientation respectively. EBSD and SEM data were produced at 20 kV and 5 kV respectively using Zeiss Sigma and Auriga field emission gun SEM. Sample preparation for SEM imaging involved progressive grinding using SiC papers (800, 1200, 2400 and 4000 grit), and then mechanical polishing using an oxide polishing suspension (OPS) to remove any deformation introduced during the grinding steps. EBSD sample preparation also involved grinding and polishing as for the SEM specimens but in-addition electropolishing was required using a mixture of 10 % perchloric acid and 90% methanol at 20 Volts and 1 A.cm⁻² for 60 s at a temperature of ~ -42 °C, which potentially introduced hydrides of <5 ppm into the microstructure [29].

2.2 Hydrogen charging and measurement

Test samples were electro-chemically hydrogen charged to 100-150 ppm using a diluted sulphuric acid solution (2 % H₂SO₄) at 65 °C $\pm$ 5 followed by thermal diffusion heat treatment at a temperature of ~ 400 °C for 4 hours [30]. Samples were then allowed to furnace cool at 3 °C/min

to form stable macroscopic hydride features [11]. Further details of the hydrogen charging technique can be found in Weekes et al. [29]. Finally, the EMGA-930 inert gas fusion (IGF) element analyser was used to measure the hydrogen concentration after electrolysis and hydride thermal diffusion. The method involved cutting four 0.15-0.30 g specimens of Zircaloy-4 from hydride-embedded material followed by grinding to remove contamination. Specimens were then weighed to ± 0.001 g after thorough rinsing in acetone and then placed in a nickel crucible and inserted in the furnace electrode assembly before starting analysis as outlined in ASTM E1447 standard [31].

2.3 Thermo-mechanical four-point bending test producing hydride formation near notch tip

Four-point bending with the V notched samples was set up to induce hydride dissolution-reprecipitation during thermo-mechanical cycling at temperatures ranging between 293 and 623 K. EBSD was conducted on one surface of the specimen to extract grain geometry and crystallographic orientation near the notch root prior to loading. The loading span (distance between the upper rollers) was half the support span (distance between the lower rollers, $L = 40$ mm). The loading setup and the thermo-mechanical load history are shown in Figure 1 (a) and (b), respectively. The stress intensity factor K used for characterising the load at the notch tip with the given notch geometry, is given by Tada et al. [32],

$$K = \sigma_{\text{nom}} \sqrt{\pi a} f\left(\frac{a}{W}\right) \quad (1)$$

where, a is the notch depth (1 mm) and W the depth of the sample (10 mm). The nominal bending stress σ_{nom} and the geometric factor $f(a/W)$ are given by [32],

$$\sigma_{\text{nom}} = \frac{3}{4} \frac{FL}{bW^2} \quad (2)$$

$$f\left(\frac{a}{W}\right) = 1.122 - \frac{1.4a}{W} + \frac{7.33a^2}{W^2} - \frac{13.08a^3}{W^3} + \frac{14.0a^4}{W^4} \quad (3)$$

where b is the thickness of the sample (6 mm) and F is the applied force (2 kN), shown in Figure 1 (a).

The loading applied in subsequent modelling is shown in Figure 1 (c) for the first cycle. Three cycles were applied in the model loading with 15 hours per cycle. In Figure 1 (c), t_A , t_B , t_C and t_{HE1} are the times at the start of the stress hold, the end of first temperature hold, the end of second temperature hold and the end of stress hold for the first cycle, respectively.

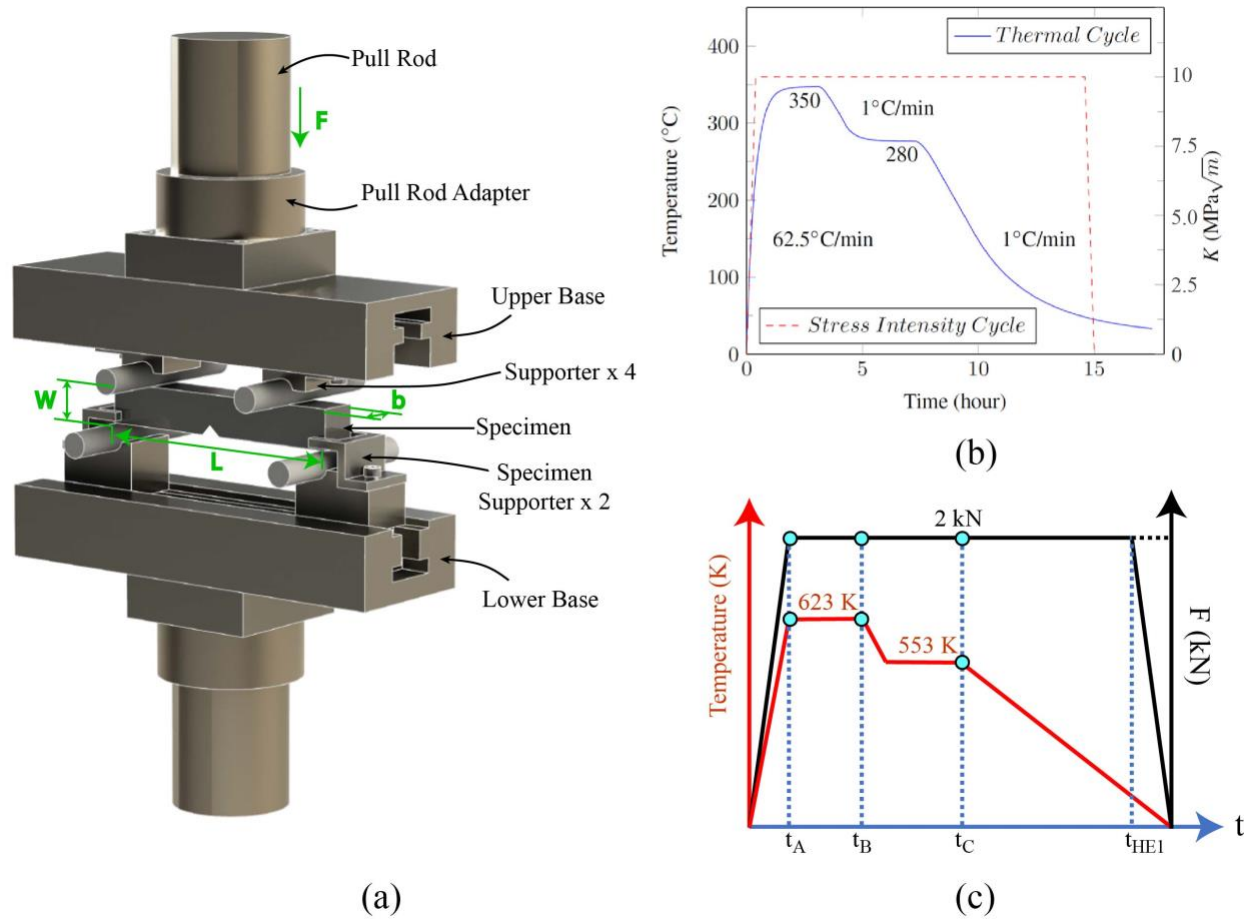


Figure 1 shows (a) the experimental setup for 4-point bend testing of V-notch sample within a furnace and (b) the schematic thermo-mechanical loading history which is simplified in (c) for modelling. t_A , t_B , t_C and t_{HE1} are the times at the start of the stress hold, the end of first temperature hold, the end of second temperature hold and the end of stress hold for one cycle, respectively. For the first cycle, $t_A = 336$ s, $t_B = 11136$ s, $t_C = 26136$ s and $t_{HE1} = 53664$ s. t_{HE1} is at the end of stress hold in the first cycle.

Figure 2 shows typical engineering hydrogen solubility curves [33], and on cooling, the initiation and termination of hydride precipitation. The specimens in this work were mechanically loaded from room temperature and then subjected to a three-hour hold at a temperature above the terminal solid solubility for dissolution (TSSD) of 100-150 ppm H (623 K) [34], as shown in Figure 1(c). This hold allows sufficient time for all the precipitated hydrides in the microstructure to dissolve into the Zircaloy-4 bulk material. The temperature was then decreased from 623 K to 553 K at a rate of 1 K/min, and held for 3 hours at 553K. Hydrogen redistributes via a stress driven diffusion process towards the notches, and precipitates as new hydrides as the terminal solid solubility for precipitation (TSSP) is achieved. The samples were thermo-coupled to monitor the temperature throughout the cycles. Three consecutive thermo-mechanical cycles were performed to allow hydrogen and hydrides to diffuse and reorient around the notch geometries. Here, a much lower TSSP=30 ppm is observed at t_{HE1} for the first cycle.

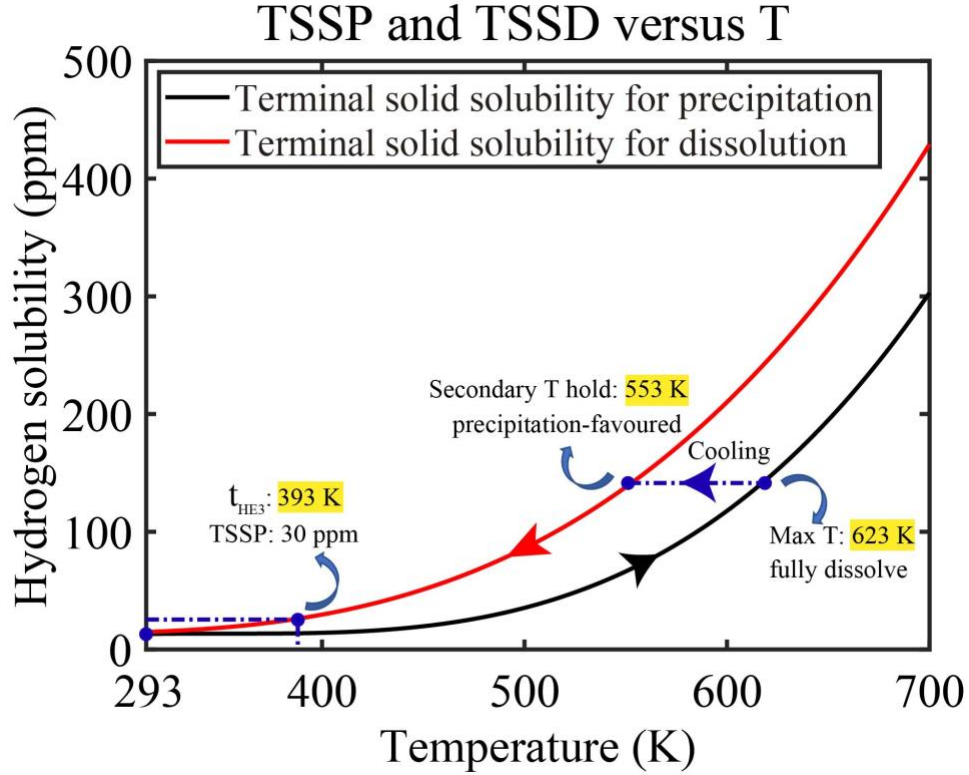


Figure 2 shows the TSSP and TSSD curves during the thermal cycle [33]. Hydrogen is fully dissolved into the sample at 623 K over about 3 hours, reaching the hydrogen solubility at TSSD state. Then it is slowly cooled down to 553 K for favorable hydrogen precipitation for 3 hours, followed by further precipitation during subsequent cooling. TSSP=30 ppm at t_{HE3} for the third cycle.

2.4 Hydride characterisation and quantification

After thermo-mechanical testing, samples were ground and mechanically polished. Optical and secondary electron (SE) images were then taken and analysed using the image software, ImageJ. Micrographs were transformed into a binary format after filtering and background subtraction using a grayscale threshold limit.

3. Micromechanical theory incorporating atomistic-based hydrogen concentrations

A strain-rate and temperature sensitive crystal slip rule is adopted to allow grain-level creep and stress redistribution to be captured such that hydrostatic stresses are accurate within the polycrystal model and the steady-state hydrogen distribution may be calculated during the thermomechanical loading.

3.1 Crystal plasticity method

To capture the plastic deformation near the notch, a finite strain method is utilised with multiplicative decomposition of deformation gradient $\mathbf{F}$

$$\mathbf{F} = \mathbf{F}^e \mathbf{F}^p \mathbf{F}^\theta \quad (4)$$

where $\mathbf{F}^e$, $\mathbf{F}^p$, $\mathbf{F}^\theta$ are the elastic, plastic and thermal deformation gradients. The latter $\mathbf{F}^\theta$ is defined as

$$\dot{\mathbf{F}}^\theta = \dot{T} \boldsymbol{\alpha} \mathbf{F}^\theta \quad (5)$$

where T is the temperature in Kelvin and $\boldsymbol{\alpha}$ is a diagonal tensor in the reference crystallographic coordinate system describing the anisotropic thermal expansion of Zircaloy-4, where $\alpha_a = 1.01 \times 10^{-5}/\text{K}$ and $\alpha_c = 5.25 \times 10^{-6}/\text{K}$ are the thermal expansion coefficients along the a and c crystal directions respectively [21]. The plastic velocity gradient $\mathbf{L}^p$ is determined from the contributions from all active slip systems, and given by

$$\mathbf{L}^p = \dot{\mathbf{F}}^p (\mathbf{F}^p)^{-1} = \sum_{\kappa} \dot{\gamma}^{\kappa} \mathbf{s}^{\kappa} \otimes \mathbf{n}^{\kappa} \quad (6)$$

where, $\dot{\gamma}^{\kappa}$ is the rate of slip system shear, and $\mathbf{s}^{\kappa}$ and $\mathbf{n}^{\kappa}$ are the slip direction and normal of system κ . The rate-sensitive slip rate is deduced from the Orowan equation, which considers planar slip occurring through dislocation glide, pinning and thermally-activated release

$$\dot{\gamma}^{\kappa} = \rho_m (b^{\kappa})^2 v_d \exp\left(-\frac{\Delta F}{kT}\right) \sinh\left(\frac{(\tau^{\kappa} - \tau_c^{\kappa}) \Delta V}{kT}\right) \quad (7)$$

The shear strain rate $\dot{\gamma}^{\kappa}$ is only activated when resolved shear stress τ^{κ} exceeds the critical resolved shear stress (CRSS) τ_c^{κ} , that is, $|\tau^{\kappa}| \geq \tau_c^{\kappa}$. Otherwise, $\dot{\gamma}^{\kappa}$ remains inactivated. Here, ρ_m is the mobile dislocation density, b^{κ} the magnitude of Burgers vector, v_d the Debye frequency, k the Boltzmann constant. Temperature here ranges from 293K to 623K consistent with the thermal tensile test and tracks the temperature during the thermo-mechanical loading in four-point bending. The intrinsic slip strain rate sensitivity is defined by the activation energy ΔF and associated activation volume ΔV .

The temperature dependence of CRSSs and of anisotropic elastic stiffnesses are fully incorporated. Based on the Taylor hardening model [35], CRSS increases with the total dislocation density, including statistical stored (SSD) and GND s.

$$\tau_c^{\kappa} = \tau_{c,0}^{\kappa}(T) + G(T) b^{\kappa} \sqrt{\rho_{SSD} + \rho_{GND}} \quad (8)$$

where $\tau_{c,0}^{\kappa}$ is the initial CRSS before straining and G is the shear modulus. The GND densities are considered to accommodate the crystal lattice curvatures which leads to a localised strain hardening effect at the grain scale. Following [36,37], the density of GNDs is computed by relating the curl of the plastic deformation gradient to the Nye tensor to give

$$\sum_{\kappa=1}^n (\mathbf{b}^{\kappa} \otimes \mathbf{s}^{\kappa} \rho_{GND,s}^{\kappa} + \mathbf{b}^{\kappa} \otimes \mathbf{n}^{\kappa} \rho_{GND,en}^{\kappa} + \mathbf{b}^{\kappa} \otimes \mathbf{m}^{\kappa} \rho_{GND,et}^{\kappa}) = \text{curl}(\mathbf{F}^p) \quad (9)$$

where, $\mathbf{m}^{\kappa} = \mathbf{s}^{\kappa} \times \mathbf{n}^{\kappa}$. $\rho_{GND,s}^{\kappa}$, $\rho_{GND,en}^{\kappa}$ and $\rho_{GND,et}^{\kappa}$ are the GND components, and $\mathbf{s}^{\kappa}$, $\mathbf{n}^{\kappa}$ and $\mathbf{m}^{\kappa}$, the slip system orthogonal unit vectors, accounting for all edge and screw type dislocations within each slip system in an HCP crystal. A constrained L2 minimisation scheme is used to compute the GNDs for all slip systems.

For zircaloy-4, the crystal-scale strain rate sensitivity is significant for accurately describing the creep strain accumulation at the notch tip. The crystal-level strain rate sensitivity for zircaloy-4 has been calibrated and validated through comparison with crystal-scale strain measurement using DIC and EBSD [26]. The temperature dependencies of the CRSS and elastic modulus are calibrated based on the thermo-mechanical tests along different texture axes [26]. These crystallographic material properties are incorporated in the CP model to describe the anticipated significant creep strain accumulation at the notch tip during the stress hold period at high temperature. The material properties of zircaloy-4 are summarised in Appendix B.

3.2 Steady-state hydrogen concentration using atomistic elastic dipole tensor

The atomistic-scale elastic dipole tensor is incorporated into the dislocation density-based rate-dependent crystal plasticity formulation to capture steady-state anisotropic hydrogen distributions resulting from the preferential zirconium lattice interstitial hydrogen sites. Since the rate of load-up and temperature change ($\sim 1 \text{ Kmin}^{-1}$) are relatively low in the experiments, the steady-state hydrogen concentrations are anticipated to be achieved well within each time increment of 1 min such that the transient process of hydrogen diffusion occurs relatively quickly and can be neglected. This is certainly also satisfied during the load and temperature hold periods. As opposed to modelling hydrogen interstitials as spherical misfits [14,15] explicitly, the elastic dipole tensor is used to capture the long-range stresses generated by the point defect of each hydrogen atom, occupying the tetrahedral interstitial site in a zirconium crystal shown in Figure 3(a). Based on Neumann's principle, the anisotropy of hydrogen concentration in a crystal is conveyed by the rotational symmetries of the elastic dipole tensor, which is fully detailed and computed using density functional theory (DFT) in [38].

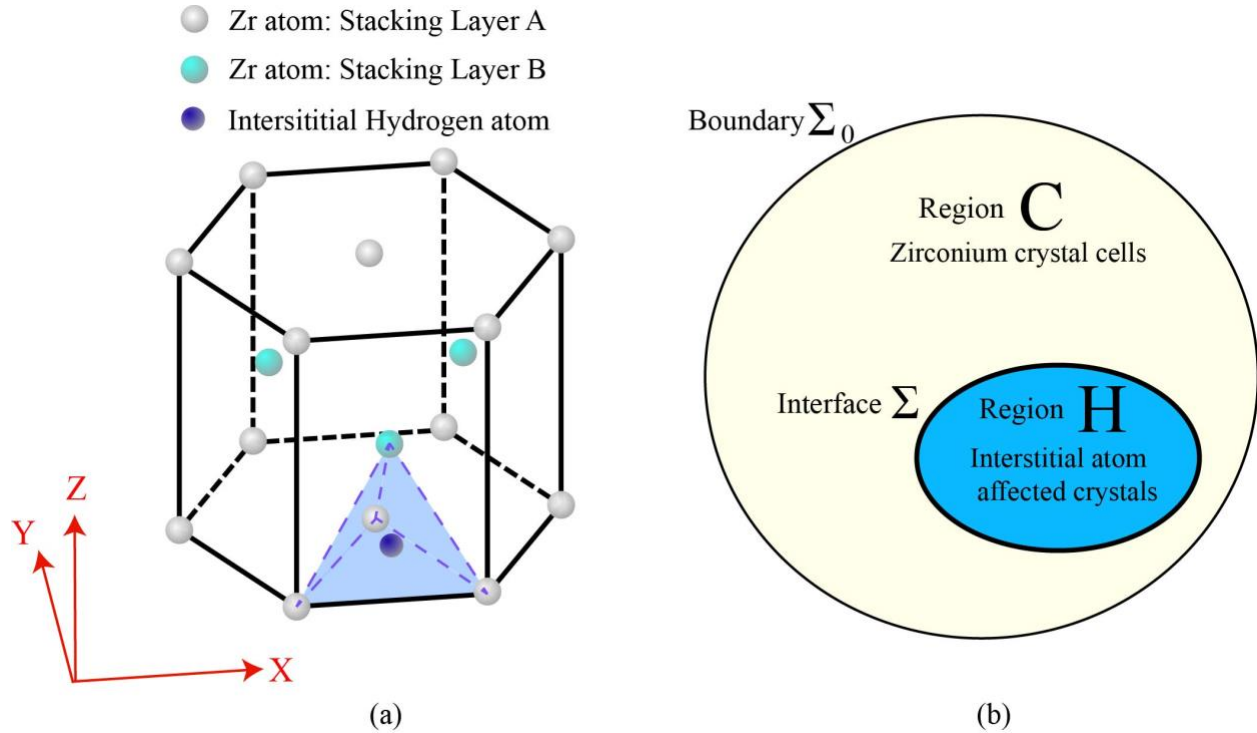


Figure 3 (a) Interstitial hydrogen atom position within the zirconium crystal structure; (b) schematic diagram of interaction energy between hydrogen interstitial and other supercells [38,39].

The interaction energy with the embedded hydrogen interstitial atom is calculated based on the theory proposed by Eshelby [39]. With respect to Figure 3 (b), suppose that in the supercell body of zirconium crystals whose surface is Σ_0 , we have one system of internal stress σ_{ij}^H induced by an interstitial atom whose sources lie within the interface Σ , where the hydrogen interstitials are embedded in the zirconium crystal cells. Another system σ_{ij}^C has sources that lie outside Σ , where the zirconium lattice remains undistorted. Thus, we may write the total energy when they coexist in the form $E_H + E_C + E_{\text{int}}(H,C)$ [39], where the interaction energy $E_{\text{int}}(H,C)$ is defined as

$$E_{\text{int}}(H, C) = E_1 + E_2 = \frac{1}{2} \int_V \sigma^H : (\epsilon^e)^C dV + \frac{1}{2} \int_V \sigma^C : (\epsilon^e)^H dV \quad (10)$$

where $(\epsilon^e)^H$ and $(\epsilon^e)^C$ represent the lattice distortion and stretch generated by stresses of a hydrogen interstitial and the crystal, respectively. Here, E_1 and E_2 represent the interaction energy induced by the internal stress of the interstitial atom and the outside stress from the surrounding zirconium lattice, respectively. Any plastic strain caused by dislocation slip does not change the lattice structure such that only elastic strain need be considered to stretch the crystal lattice to allow a hydrogen interstitial atom to diffuse inside. In addition, the second term of the interaction energy E_2 , is ignored in previous investigations [40]. The first interaction energy term E_1 in Eq. (10) has been approximated to the following form [12,38]

$$E_1 = -\boldsymbol{\rho} : (\epsilon^e)^C \quad (11)$$

where $\boldsymbol{\rho}$ is the elastic dipole tensor of the hydrogen interstitial atom. From previous investigations and experimental comparisons, the DFT calculation using λ -method provides the most accurate calculation of the dipole tensor [38] which was calculated to be

$$\boldsymbol{\rho} = \begin{bmatrix} 1.74 \pm 0.12 & 0 & 0 \\ 0 & 1.74 \pm 0.12 & 0 \\ 0 & 0 & 2.36 \pm 0.18 \end{bmatrix} \text{eV} \quad (12)$$

The second term of the interaction energy is given as [39,41],

$$E_2 = -\sigma^C : \frac{\partial \boldsymbol{\rho}}{\partial \mathbf{K}} = -\sigma^C : (\mathbf{S} : \boldsymbol{\rho}) \quad (13)$$

where, $\mathbf{K}$ and $\mathbf{S}$ are the elastic modulus and compliance tensors of Zircaloy-4. Thus, the total interaction energy may be expressed as

$$E_{\text{int}}(H, C) = E_1 + E_2 = -[\boldsymbol{\rho} : (\epsilon^e)^C + \sigma^C : (\mathbf{S} : \boldsymbol{\rho})] \quad (14)$$

The hydrogen concentration c is assumed to be less than the solubility limit at 623 K for 150 ppm. By applying Henry's law, the entropic diffusion of solute species is controlled by its chemical diffusion potential μ ,

$$\mu(T, c) = f(T) + kT \ln(\varphi c) \quad (15)$$

where, $f(T)$ is the reference potential of zirconium solvent and φ is the activity coefficient of a hydrogen interstitial within the zirconium lattice. The competing effects of the entropy and the interaction energy on hydrogen diffusion is treated by a linear combination of two potentials in Eq.

(14) and (15) and the equilibrium hydrogen concentration profile is defined when the chemical diffusion potential vanishes, such that [40]

$$c(T) = c_0 \exp \left[-\frac{E_{\text{int}}(H, C)}{kT} \right] \quad (16)$$

where c_0 is the uniform background concentration set as 130 ppm consistent with the initial hydrogen content of 100-150 ppm and saturation hydrogen content at 623 K. From Eq. (16), the hydrogen concentration at individual material points is a function of local mechanical responses and the temperature. For the thermo-mechanical loading of the samples considered in this work, the overall (average) hydrogen content in the sample is likely to be constant and we assume that the hydrogen emission from (and reception to) the sample is negligible. Based on this, a numerical method is introduced to assure a constant overall hydrogen content within the entire sample, which is presented in detail in Appendix A with the result that

$$\int_V \alpha c(T) dV = c_{\text{ini}} V \quad (17)$$

where α is a scaling parameter, c_{ini} is the initial average hydrogen concentration and V is the volume of the specimen. In this way, the spatial distributions of hydrogen concentration may be captured, recognising that the overall (average) hydrogen content within the sample remains constant.

The elastic dipole tensor changes with the crystallographic orientation of each grain in the macroscopic coordinate system such that the new global elastic dipole tensor $\boldsymbol{\rho}'$ is defined as,

$$\boldsymbol{\rho}' = \mathbf{R} \cdot \boldsymbol{\rho} \cdot \mathbf{R}^T \quad (18)$$

where, $\mathbf{R}$ is the rotation matrix defined from the Bunge Euler angle framework [42].

4. Hydrogen distribution analyses

Two polycrystal notched zircaloy-4 samples, with differing microstructures near the notches, are investigated when subjected to the cyclic thermomechanical loading introduced above. Results obtained from representative polycrystal modelling of the two characterized microstructures and tested in experiments are presented, assessing in particular the predicted hydrogen distributions which result from the differing microstructures and their relationship to experimental hydride observations. Cyclic effects on stress states and resulting hydrogen concentration distributions are also addressed.

4.1 Model set-up

The four-point bend testing geometry is shown in Figure 4(a) along with the region of interest (ROI) near the sample notches. In order to reduce the size of the required FE geometrical models, and recognizing that only the free surface region is significant with respect to the experimental observations, a smaller sub-model of 500 μm in thickness (z-direction) has been developed and is shown in Figure 4(b). Multiple sub-models have been investigated with larger sample thicknesses and shown to give very close surface mechanical and hydrogen responses thus justifying the use of the sub-model.

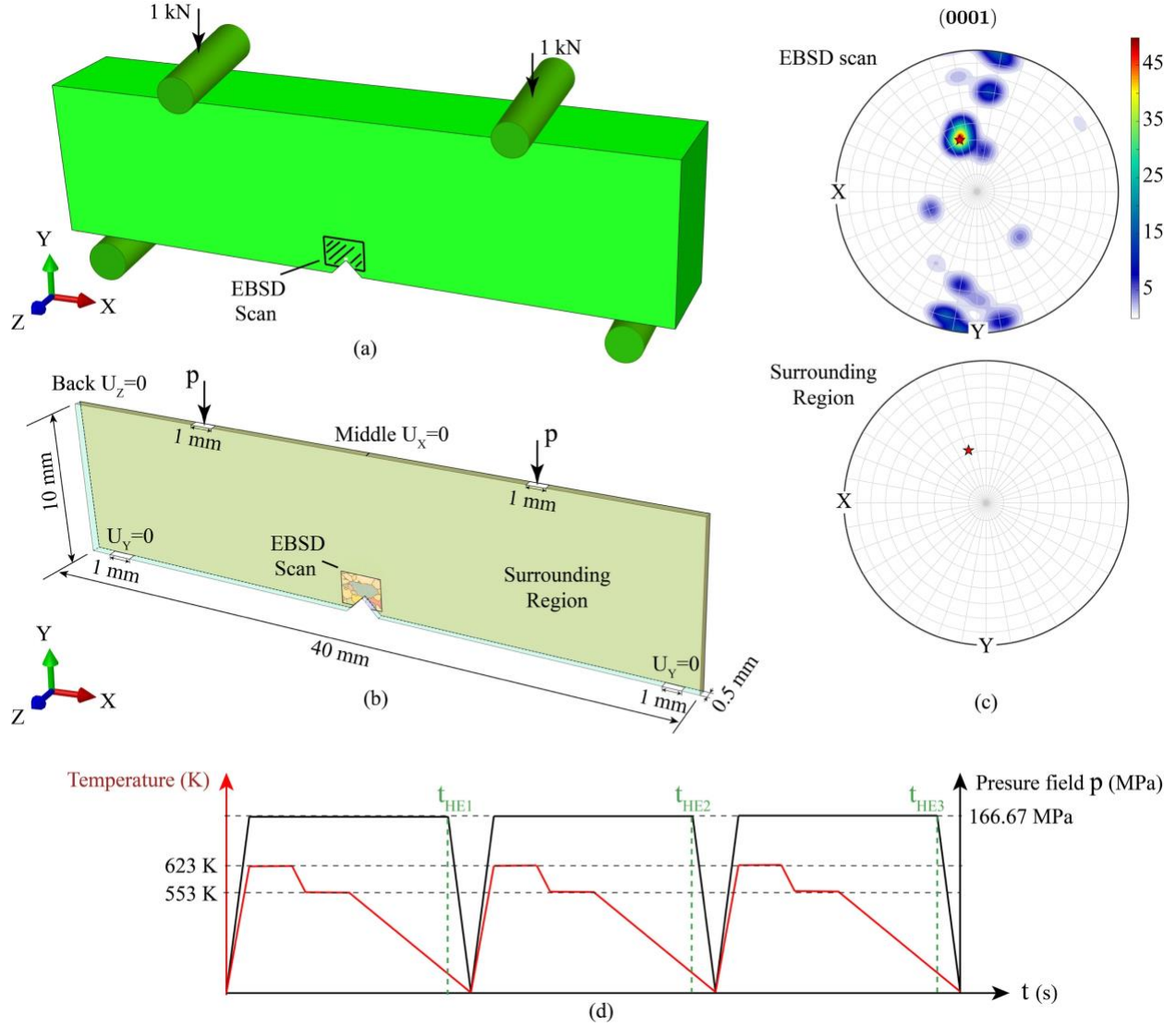


Figure 4 Model set-up for CPFEM framework. (a) full representation of experimental sample geometry under four-point bending with EBSD-scanned region of interest; (b) sub-model incorporating explicit experimental microstructures at the notch (sample A used as an example, U_y is fixed at the bottom contact area [white]. U_z of the back surface is fixed in the surrounding region. U_x is fixed at the middle top line of the sample. Pressure field is applied on the top contact area [white]); (c) inverse (0001) pole figure for sample and that orientation chosen for the model sample outside of the notch region; (d) the thermo-mechanical cycles applied showing loading history times t_{HE1} , t_{HE2} and t_{HE3} at the end of the stress holds for each cycle.

The model representation of the experimental sample includes the explicit inclusion of the EBSD-characterised microstructure local to the sample notches, shown schematically in Figure 4(b), reflecting grain morphology and crystallographic orientation for the two samples investigated. Outside of this region of interest (ROI), the beam material is modelled by a single crystal orientation which was chosen to be that of the strongest pole for the texture as a whole shown in Figure 4(c). In Figure 4(b), the boundary and loading conditions were chosen to reflect as closely

as possible the experimental conditions. Both the ROI and surrounding region are modelled using the crystal plasticity method introduced in Section 3. To ensure the accurate description of local hydrogen concentrations when compared with experimental results, 20- μm average element size is used in the ROI and the resulting full 3D sub-model has $\sim 120,000$ elements (122,367 for sample A and 119,544 for sample B) employing quadratic hexahedral element type (C3D20RT). The number of elements utilized through the thickness of the model was investigated to show that satisfactory independence of free-surface stresses was obtained with a minimum of three elements. However, four elements through-thickness were employed to generate the results presented. Figure 4(d) shows the full three consecutive thermo-mechanical cycles modelled and representative of the experiments where t_{HE1} , t_{HE2} and t_{HE3} are the times in the loading history corresponding to the end of the stress hold for each cycle.

Two blocky alpha V-notch samples (A and B) were tested under thermomechanical four-point bend testing as outlined above. The initial crystal morphologies and orientations within the ROI near the notch were obtained from EBSD scan data, and polycrystal representations constructed using an in-house python code, and imported in to ABAQUS finite element software and are shown in Figure 5 for samples A and B.

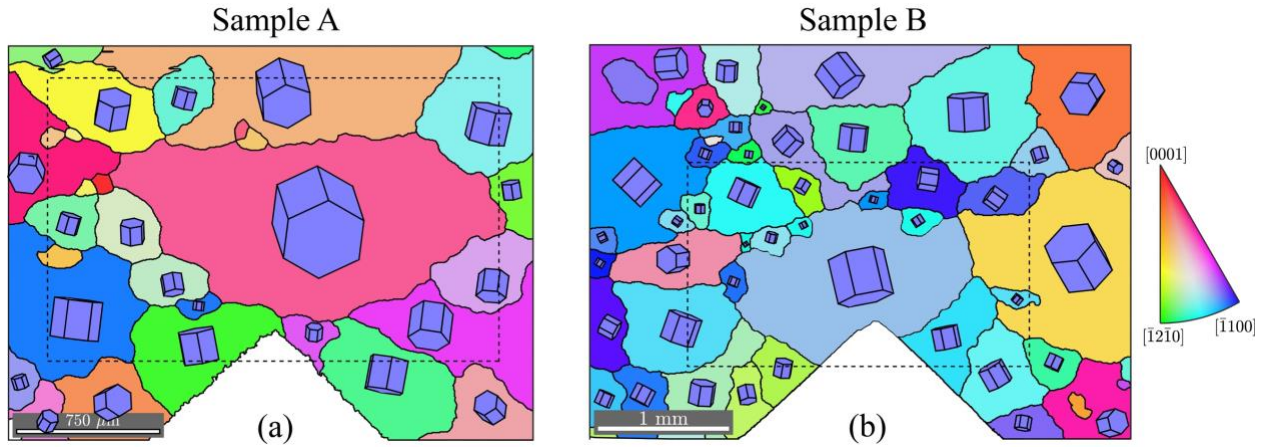


Figure 5 presents ROI grain morphology and orientation reconstructions in ABAQUS from EBSD measured IPFZ map (MTEX processing) for (a) sample A and (b) sample B. Dashed line rectangles indicate the regions for which experimental hydride observations were made.

4.2 Numerical results compared with experimental hydride map

During in-service application, zircaloy cladding tube undergoes multiple thermomechanical cycles in operation. In this section, the results of both cyclic experiments and characterization together with crystal plasticity model results are assessed, in particular addressing experimental observation of hydride distributions along with model hydrogen profiles, and cyclic thermomechanical loading effects on hydride nucleation.

Figure 6 shows the numerical results, including the hydrostatic stress, effective plastic strain and hydrogen distribution profile, compared with the hydride nucleation map for Sample A for the experimental ROI in Figure 5(a). The numerical results are shown at t_{HE3} in Figure 4(d), the end of third stress hold, which explicitly shows the historic stress-assisted hydrogen distribution at maximum stress level after secondary creep accumulation. In Figure 6 (a), the hydrostatic stress σ_H distribution shows higher tensile magnitudes near the grain boundaries and its highest point is

near the grain boundary that is directly ahead of the notch tip. This results from the large amount of plasticity occurring at the notch tip in Figure 6 (b), where incompressibility dominates for metallic HCP materials and lattice triaxial stretching (hydrostatic strain) is small [43]. This means that the local plasticity accumulation leads to lower or even compressive hydrostatic stress shown in Figure 6 (a) close to the notch tip. Note that a purely elastic analysis leads to a concentrated hydrostatic stress at the notch tip [40].

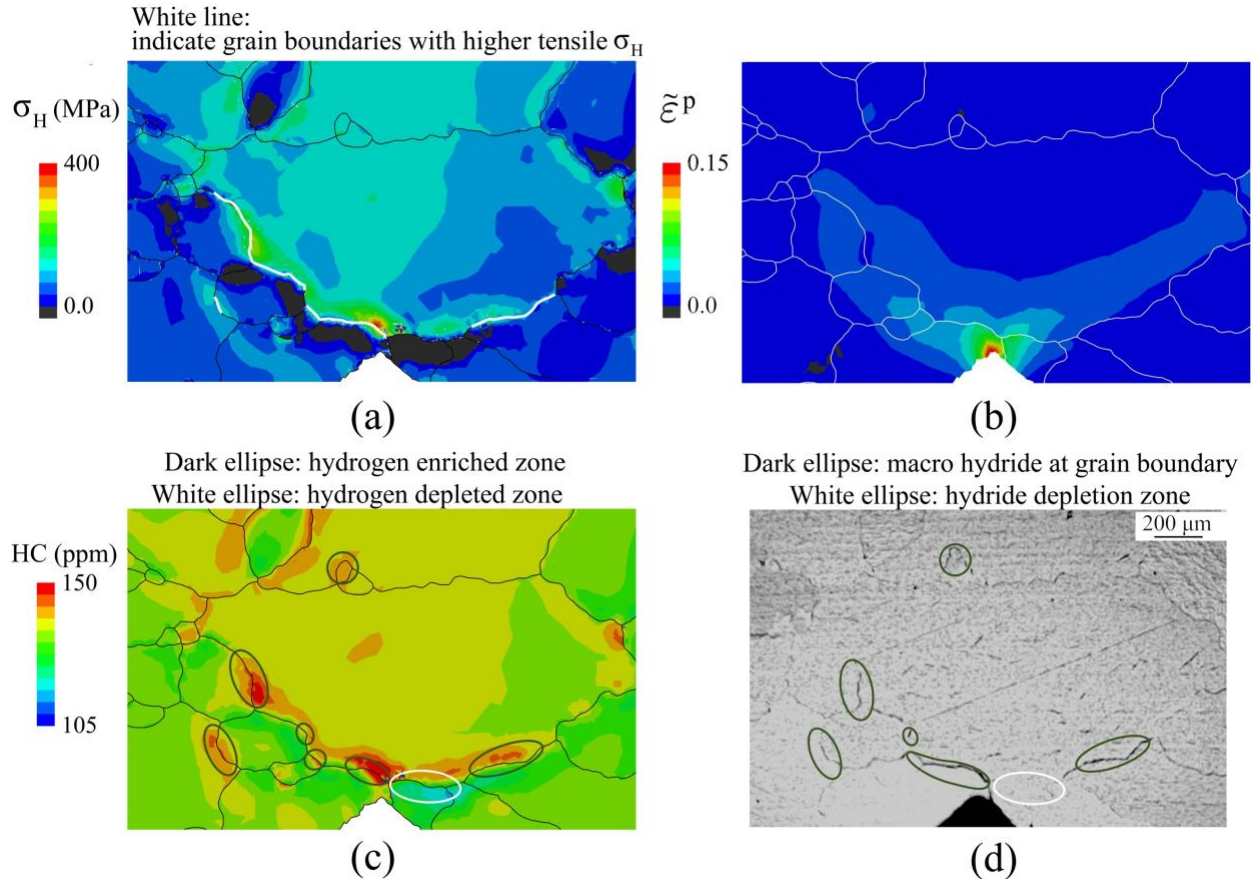


Figure 6 shows model results for (a) positive hydrostatic stress σ_H map, (b) the accumulated plastic strain, (c) hydrogen concentration (HC) distribution at time t_{HE3} in loading history, compared with (d) Sample A experimental hydride distribution showing mostly intergranular nucleation at the grain boundary for after three thermomechanical cycles.

Figure 6 (c) shows that the hydrogen concentrates at the grain boundaries where high tensile hydrostatic stress occurs, which is consistent with former observations [4] that the triaxial tensile stress (positive hydrostatic stress) drives the hydrogen atom diffusion and redistribution into the zirconium lattice. It is noted that the HC computed from crystal plasticity is significantly higher than the macroscale TSSP (30 ppm) at the end of the stress hold (Figure 2) and this leads to the prediction of hydride precipitation at these locally enhanced hydrogen concentration areas. Figure 6(d) shows the experimental observation of hydride distribution where hydrides prefer to form on the grain boundaries of the sample, as reported in other studies [10,44]. Specific grain boundaries are favoured for inter-granular hydride nucleation whereas a hydride depletion zone (white ellipse)

is observed at to the right of the grain boundary that is near the notch tip. The computed hydrogen distribution shows enriched hydrogen at all the hydrided grain boundaries, which is 4 to 5 times higher than the TSSP at t_{HE3} . Relatively lower hydrogen content (3 to 4 times TSSP) is found at the hydride depletion grain boundary, caused by the triaxial compressive hydrostatic stress there shown in Figure 6 (a). The consistency between model predicted hydrogen distribution and experimental hydride observations supports the model capability of capturing the stress-assisted hydrogen distribution during thermo-mechanical load cycles. In Figure 6(a), white lines are drawn along grain boundaries where higher positive (tensile) hydrostatic stress (> 100 MPa) occurs and these are the locations where hydrides are more favoured to form (Figure 6(d)) since the positive high hydrostatic stress stretches the local lattice, allowing interstitial hydrogen atoms to diffuse to these grain boundary regions. Here, it is argued that the high steady-state hydrogen content is reasonable, since in a recent atom probe tomography (APT) study remarkable high hydrogen content has been experimentally observed near a hydride, which are potentially needed for the neighboring hydride to nucleate [45]. It should also be noted that the hydride precipitation is not considered in the model, which would potentially change the local stress, strain responses and hydrogen content.

Figure 7 shows the comparison between model predicted hydrogen concentration and experimentally observed hydrides in Zircaloy-4 sample B near the notch tip for the experimental ROI in Figure 5(b). This sample was subjected to exactly the same loading (thermal and mechanical) as for Sample A. Grain boundaries, demonstrated to be energy-favourable sites for hydride formation in sample A, are further removed from the notch tip in sample B, because of the very large blocky α grain located directly ahead of the notch in this sample. Though the local plasticity at the notch root redistributes stress and reduces triaxiality in Figure 7 (a) and (b) and hence repels hydrogen very locally, reasonably high concentrations of hydrogen remain in this grain, as shown in Figure 7 (c), which is higher than the global TSSP, at 30 ppm at t_{HE3} (Figure 2), for potential hydride nucleation.

Experimental observation indicates that multiple intra-granular hydrides are detected within the large grain at the notch, as shown in Figure 7 (d). The intra-granular hydrides observed are thinner than the macro-hydrides detected at the grain boundaries. They are assumed to nucleate at microstructural defects such as dislocation entangled clusters, and second phase particles (SPPs) that are too small to be explicitly incorporated within the crystal plasticity modelling. Interestingly in Figure 7 (d), the region in sub-figure (i) shows a scattered distribution of hydrides with shorter lengths compared to those observed at grain boundaries, whereas sub-figure (ii) shows a region with a relatively denser hydride distribution that are longer than those in region i. It has been reported that a higher hydrogen content leads to denser and longer hydrides in Zircaloy [45,46], and thus this phenomenon is captured by the computational model, which shows lower hydrogen concentration in region (i) compared to region (ii) in Figure 7 (c). It is consistent with the hydrostatic stress σ_H distribution Figure 7 (a) where a much lower tensile σ_H is detected near region i than region ii.

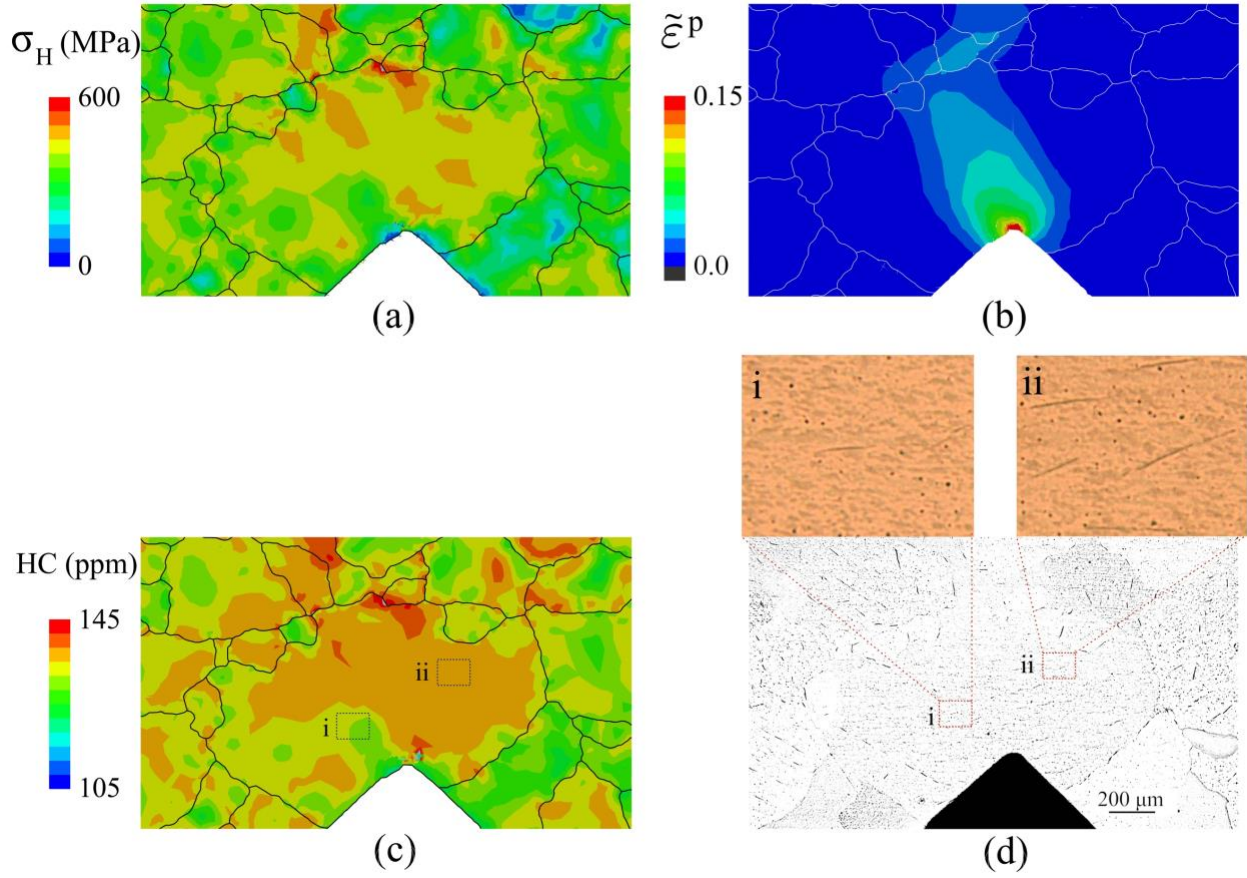


Figure 7 shows the model results for (a) positive hydrostatic stress σ_H map, (b) and (c) HC distribution from crystal plasticity at time t_{HE3} in loading cycles (Figure 4(d)), compared with (d) experimental hydride distribution for Sample B after three cycles. Regions i and ii in (c) and (d) are chosen for comparison between low and high hydrogen content with respect to observed hydride formation.

The primary focus here is on the observations of inter-granular hydride nucleation sites, which are usually shown to be preferential in experiments [2,10,33]. The stress state effects generated by the notch encourage hydrogen redistribution and hence the likelihood of hydride formation. Experimental observations are in good agreement for these locations, particularly at grain boundaries. However, intragranular hydrides are known to nucleate, and SPPs or twins are thought to be energetically favourable for this [28,40]. However, the SPPs are at a length scale below that of the crystal plasticity modelling methodology and hence cannot be captured explicitly; lower scale modelling (such as discrete dislocation plasticity) along with appropriate characterization techniques including transmission electron microscopy (TEM) or APT would therefore be useful [44].

4.3 Cyclic stress redistribution effects on hydrogen content

Under conditions of cyclic thermomechanical loading for which considerable non-zero mean stress is applied, stress redistribution through cyclic plasticity and creep (see later) are likely to be non-negligible. The role of the cyclic plasticity in particular is considered here for Sample A. The effect of thermomechanical cycles on the local accumulated effective plastic strain $\tilde{\epsilon}^p$, hydrostatic stress

σ_H and hydrogen content are presented in Figure 8; three particular paths have been chosen within the microstructure, which traverse three grain boundaries, two of which see high hydrogen content (and correspond to experimentally observed sites of hydride formation) and one with low hydrogen content (for which hydride nucleation was not observed in experiment). The microstructure and path locations are shown in Figure 8 (a).

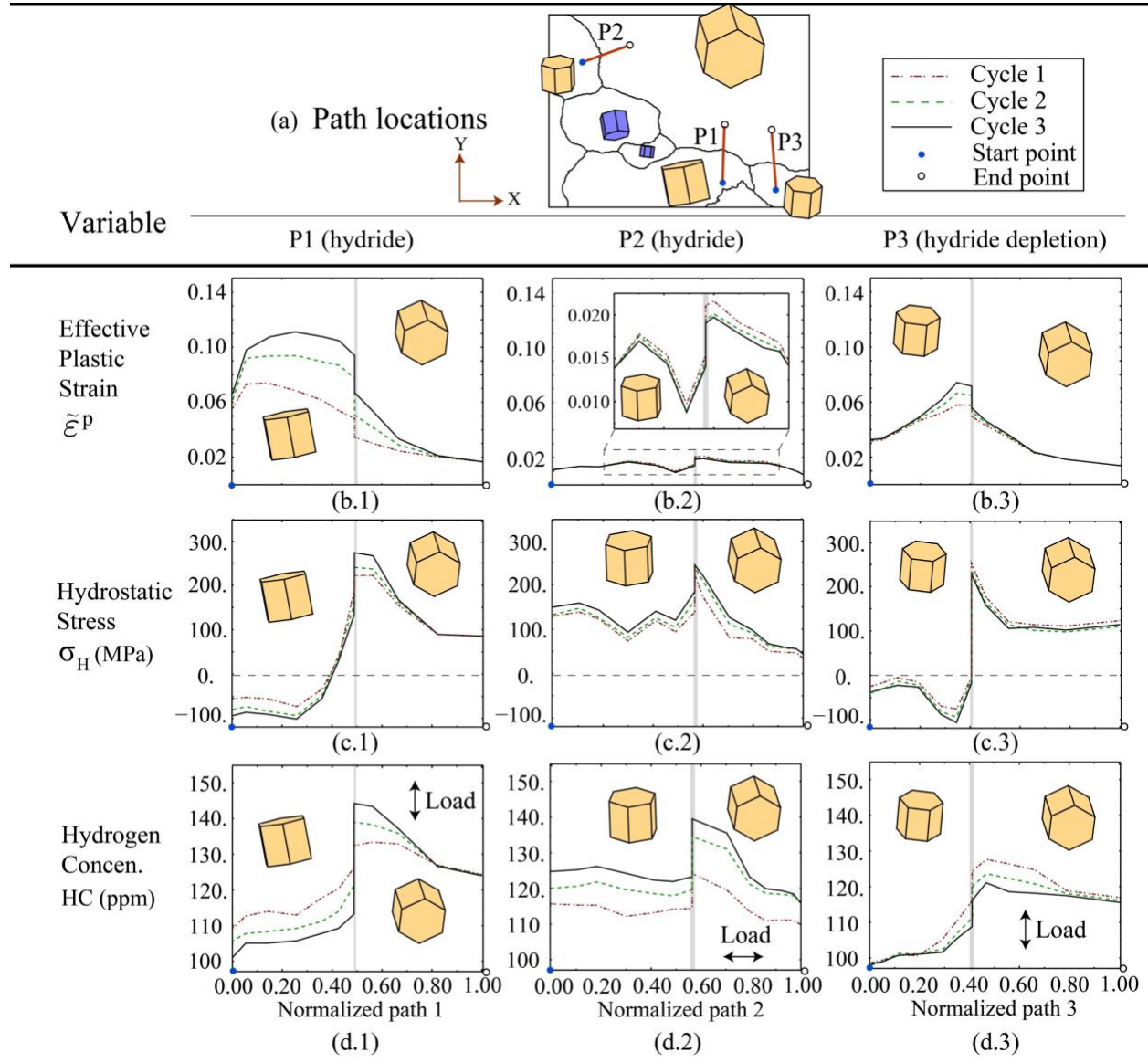


Figure 8 shows model predicted microstructural results along three paths (P1, P2 and P3) shown in (a) across grain boundaries with experimentally observed inter-granular hydrides (P1 and P2) and hydride depletion (P3), for (b) effective plastic strain $\tilde{\epsilon}^P$, (c) hydrostatic stress σ_H and (d) HC at t_{HE1} , t_{HE2} and t_{HE3} for each cycle in Figure 4 (d). For the paths, the starting point is indicated by the blue points.

The results are shown at cycle times of t_{HE1} , t_{HE2} and t_{HE3} that correspond to the end of the stress hold for each cycle in Figure 4 (d). Along path P1 where horizontal inter-granular hydride is

observed, the cyclic plastic strain increases with cycles in Figure 8 (b.1), resulting from high creep strain accumulation during the stress hold period within each cycle. This leads to redistribution of stress such that negative hydrostatic stress develops in the region of high accumulated plasticity (bottom grain in path 1) in Figure 8 (b.2), whereas the positive hydrostatic stress increases in the relatively low plasticity region (top grain in path 1) with cycles. Since the hydrogen prefers to transport from triaxial compression to triaxial tensile regions, the hydrogen content, shown in Figure 8 (b.3), moves from the bottom to the top grain and the hydrogen content mismatch between these neighbouring grains increases with the number of thermomechanical cycles. This means that the creep strain ratcheting behaviour during each cycle is significant in order to capture the hydrogen transport during consecutive thermo-mechanical cycles.

Along path P2 near the vertical hydride nucleation (shown in Figure 6 (d)), the effective plastic strain in Figure 8 (b.2) is much smaller than that in P1 near the notch tip (Figure 8 (b.1)), but increases with cycles. The hydrostatic stresses are positive along path P2 and increase with thermomechanical cycles, leading to the cyclic hydrogen content increase in both grains along this path. For Path P3 where hydride nucleation is not observed, the cyclic plasticity (Figure 8 (b.3)) redistributes stress and correspondingly reduces hydrostatic stress (Figure 8 (c.3)) at this grain boundary, and the hydrogen content cyclically decreases.

5 Creep, interstitial interaction energy and GND density effects on hydrogen redistribution

5.1 Strain rate sensitivity and creep

The hydrogen content and distribution within the microstructure depends very much on the hydrostatic stresses developed and these, in turn, depend upon the stress redistribution. Part of the latter results from (rate-independent) cyclic plastic stress redistributions due to cyclic plastic strain ratcheting, but Zircaloy-4 along with other Zr alloys, has quite strong strain rate sensitivity (SRS), even at low (e.g. 20 °C) temperatures [25,26]. This results in quite considerable creep strain developing, thus influencing local stress redistribution. This effect is investigated here and is made possible by the slip rule in Eq. (7) in which the SRS is implicitly controlled by the individual slip system properties ΔF and ΔV . Hence the microstructural distributions of hydrogen content are studied for two cases in which the fully-quantified rate sensitivity of Zircaloy-4 was included (as it has been in all previous calculations) with an activation volume $\Delta V = 20.93 b^3$, and for the case of very low rate sensitivity (and hence no creep) with $\Delta V = 1000 b^3$ in order to establish the importance (or otherwise) of the creep response of Zircaloy-4 in hydrogen content.

The results of these calculations are shown in Figure 9 at time t_{HE3} in Figure 4 (d). In the strain rate sensitive case ($\Delta V = 20.93 b^3$), the stress redistribution during the creep leads to higher hydrostatic stress concentration at the grain boundary shown in Figure 9 (a), whereas the stress barely redistributes in the strain rate-insensitive case, leading to lower hydrostatic stresses at the grain boundary in Figure 9 (b). The differing stress redistributions, which take place during the stress hold period, result in the quite different hydrogen maps. In the strain rate insensitive case ($\Delta V = 1000 b^3$), the hydrogen content is much lower as shown in Figure 9 (d) compared with the strain rate sensitive Zircaloy-4 (Figure 9 (c)).

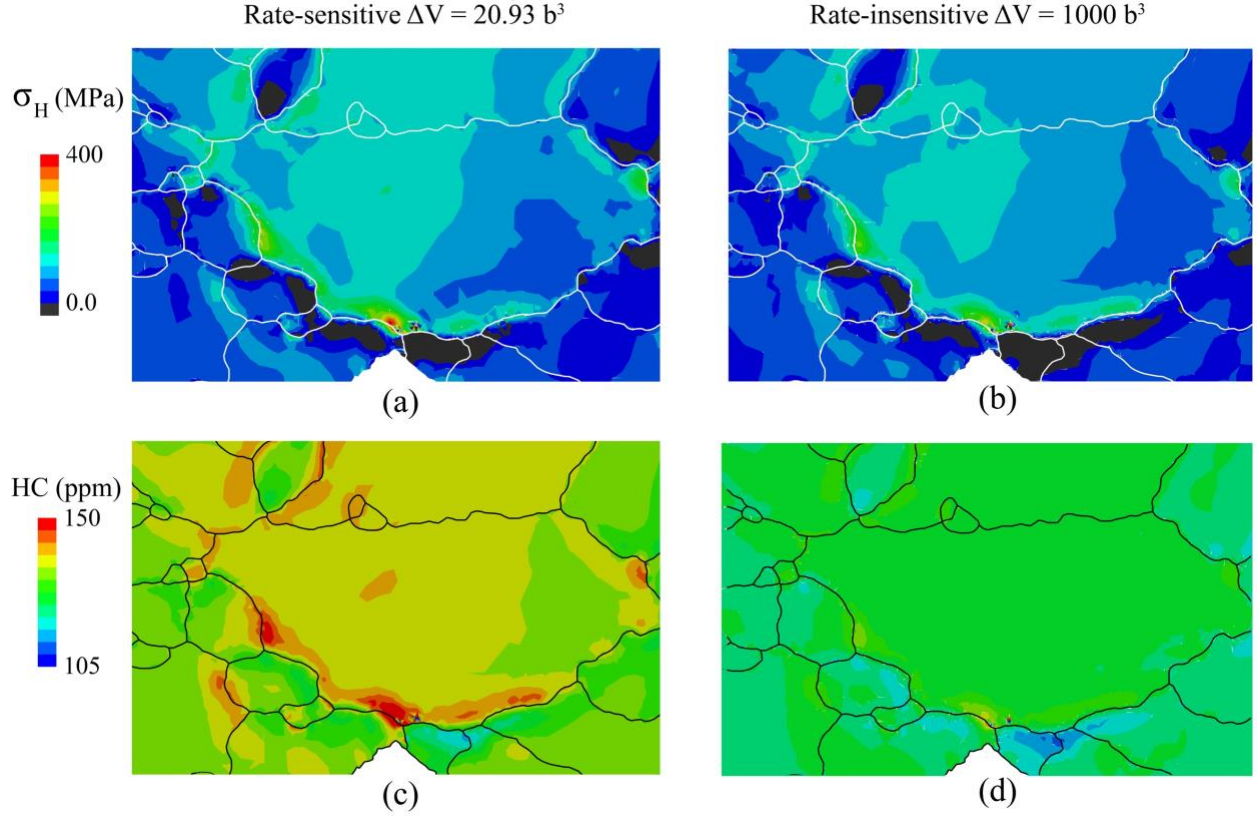


Figure 9 shows the effect of rate sensitivity compared with a rate-insensitive material on the local distributions of (a,b) hydrostatic stress σ_H and (c,d) HC. The activation volumes ΔV of rate sensitive and rate insensitive materials are $20.93 b^3$ and $1000 b^3$, respectively, while keeping other material properties the same. The results are shown at time t_{HE3} .

A noteworthy feature is that the hydrostatic stresses that result from the rate-sensitive (true) response do not appear to be markedly higher than those for the simulated rate-insensitive (i.e. no creep) material. The differences are modest, but the hydrogen concentration, determined by the atomistically-informed approach described in Section 3.2 and Eq. (16), involves a highly non-linear (that is, exponential) dependence of hydrogen content on stress. As a consequence, relatively small variations in type III (intra-granular) stresses can develop strong changes to hydrogen content and in turn the preferred locations and initiation time for hydride nucleation. An important consequence of this is for long stress hold periods, relevant to nuclear fuel dry storage conditions for Zircaloy-4, during which long term creep may progressively lead to modest redistributions of hydrostatic stress but which, as demonstrated above, may lead to quite precipitous and early onset of hydriding. In addition, the SRS of Zircaloy-4, controlling its creep properties, is crucial to understanding the fundamental mechanisms during in-service performance and for the determination of hydride nucleation and crack propagation associated with delayed hydride cracking.

5.2 Hydrogen interstitial interaction energy and GND density

The hydrogen interstitial interaction energy and dipole tensor were introduced in Section 3.2 in relation to quantifying the steady state hydrogen distributions developing within the Zircaloy-4 microstructures. In addition, the crystal slip rule is dislocation based and incorporates the density

of GNDs related through the Nye tensor and lattice curvatures to the plastic strain gradients established. Both the interaction energy and the GND density influence hydrogen content, the former directly from Eq. (16) and the latter from its influence on the slip strength hardening in Eq. (8). Hence, we investigate the role of these quantities on hydrogen content at the notch tip in Sample A and key results are shown in Figure 10. The results in Figure 10 (a)-(c) are at time t_{HE3} in Figure 4 (d), and Figure 10 (d)-(f) are for the unloaded state. Figure 10 (a) shows the hydrogen content resulting from the inclusion of both of the H interstitial interactional energy terms E_1 and E_2 (Eq. (14)) and allowing the influence of GND density evolution resulting from lattice curvature. Here, considerably higher hydrogen content at grain boundaries (as discussed earlier) develops near the notch root, and in good overall agreement with experimental intergranular observations of hydride nucleation sites (Figure 6 (d)). Recently, Chamaa et al. [40] utilised the first interaction energy term E_1 only to account for the internal stress field induced by the interstitial hydrogen to predict the hydrogen distribution around the notch tip. The full energy term (E_1+E_2), however, accounts for the stress field coming from outside the hydrogen interstitial cell (E_2). Here, E_2 is mainly caused by the microstructural heterogeneity including multiple grains with different crystallographic orientations and the stress field induced by both geometric effects and the grain interactions from lattice mismatch. When only considering the interaction energy E_1 accounting for the stress field from the interstitial atoms in Figure 10 (b), much lower hydrogen content is observed at the grain boundaries of interest and at which hydrides are found to nucleate, indicating that E_2 representing the stress field from grain interaction due to lattice mismatch is important to capture the hydrogen distributions accurately.

The distribution of hydrogen content obtained from the model when the density of GNDs is disabled is shown in Figure 10 (c) and results in considerably lower concentrations at the key grain boundary locations where hydrides are observed. Figure 10 (d) shows that the plastic strain at t_{HE3} is large at the notch root but is quite localized thereby indicating very strong plastic strain gradients and in turn lattice curvatures and high GND densities. This means that the local elastic strains accommodating the lattice curvatures are correspondingly high, which leads to high predicted GND density distributions near the notch root area, and also along grain boundary regions emanating from the root area, shown in Figure 10 (e). The resulting GND density contributes to local CRSS increase during hardening in grains, which changes the hydrogen profile simultaneously. It is interesting to note that the GND density distribution is consistent with the experimentally-determined inner-grain misorientation angle distribution in Figure 10 (f).

In conclusion, the above results reinforce the importance of both the interactional energies and the GND densities in influencing the hydrostatic stresses, which in turn drive the hydrogen content and distribution within the microstructure. These results indicate that they are essential in capturing experimental observations of hydride nucleation.

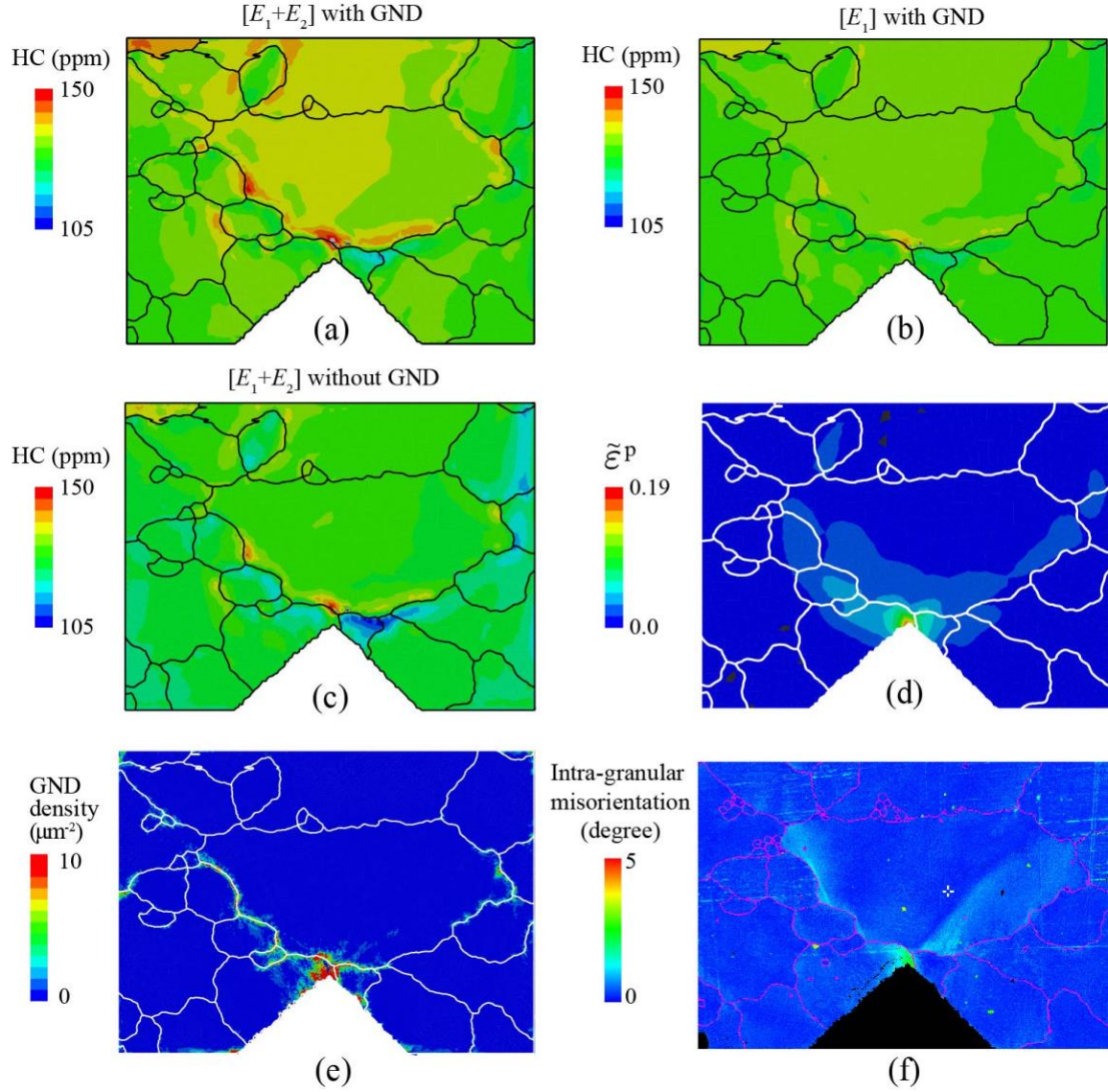


Figure 10 shows the hydrogen distribution calculation with (a) the total $[E_1+E_2]$ interaction energy incorporated with GND density, (b) the E_1 interaction incorporated with GND density and (c) the total $[E_1+E_2]$ interaction energy incorporated without GND density. (d) is the effective plastic strain distribution, (e) the GND density distribution and (f) the intra-granular misorientation angle distribution. (a)-(c) are at time t_{HE3} and (d)-(f) show the unloaded state.

5.3 Thermal (in absence of mechanical) loading

In this section, the hydrogen distributions resulting from solely cyclic thermal load are shown in Figure 11, so that comparisons with results for the thermomechanical loading (shown in Figure 6 for Sample A) can be made. Note that the three thermal cycles imposed are identical to those considered above and shown in Figure 4 (d), and results are provided for time t_{HE3} . In the case of solely thermal load, the positive hydrostatic stresses also concentrate at the notch tip, and only within the grains close to the notch tip in Figure 11 (a), whereas negative hydrostatic stresses develop throughout the remainder of the microstructure away from the notch tip as shown in Figure

11 (b). Hence the hydrogen is predicted to have a higher concentration at the notch tip as shown in Figure 11 (c), but the thermal effect is clearly not strong, and results from the crystal anisotropy of the thermal expansivity, which is lower along the HCP crystal c -axis than for the a -axis directions (see Figure 8). Thus, the misorientations at the grain boundaries lead to thermal expansion mismatch between adjacent grains. The thermal strains and hence stresses developed are too small to activate slip and plasticity. The notch geometry plays a (small) role in the elastic strain distribution, which leads to higher hydrostatic stress σ_H and correspondingly higher hydrogen content in the left grain near to the notch tip.

Compared with the results from the thermo-mechanical loading in Figure 6 (a), (b) and (c), it is clear that the creep accumulation and plastic strain localisation at the notch tip during the (bending) stress hold cycles are the main drivers to increase the hydrostatic stress σ_H within the microstructure, especially at the grain boundaries, leading to much higher hydrogen content at these locations compared to that from thermal loading alone. It can be concluded that in-service cladding tube stress resulting from mechanical loading is the predominant factor leading to the inhomogeneous distribution of hydrogen concentration, which then depends upon geometrically-favourable sites, such as at notch tips and, at the microstructural scale, the energy-favourable sites such as grain boundaries, twins or SPPs and irradiation damage sites, which may be preferred sites for hydrides. The role of the thermal cycle is to drive the hydrogen saturation levels and hence hydride dissolution and re-precipitation, but not to influence the hydride locations.

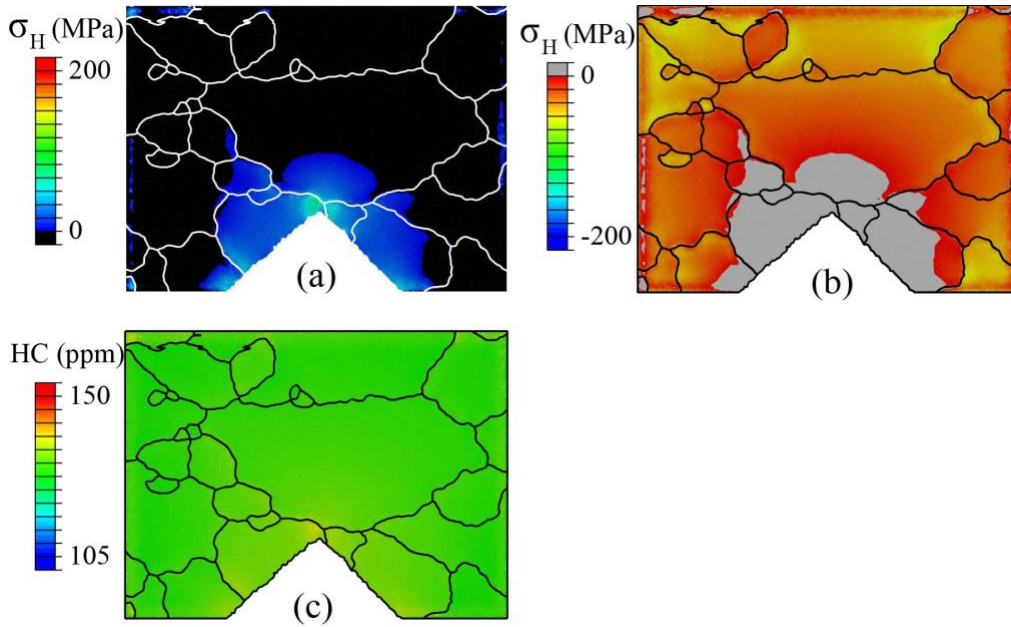


Figure 11 shows model predicted (a) positive hydrostatic stress σ_H , (b) negative hydrostatic stress σ_H , and (c) hydrogen content. The results are shown at the t_{HE3} of the third thermal cycle.

6. Conclusion

The steady state stress-dependent hydrogen concentration model integrated within a dislocation-based, rate-dependent crystal plasticity formulation for Zircaloy-4 alloy has been developed to

simulate thermomechanical loading. Fully-representative model microstructures were shown to identify the locations within two experimentally characterized and tested samples of high hydrogen concentration resulting from cyclic loading. Those locations predicted to have hydrogen content well in excess (4-5 times) of the saturation levels, at the appropriate temperatures, were found to be in reasonably good agreement with experimental observations of hydride formation locations in characterized samples.

The SRS of Zircaloy-4 was shown to lead to creep strain accumulation in grains appropriately orientated for slip, leading to stress redistribution and cyclic strain ratcheting in the microstructure, in turn influencing the locations of high hydrostatic stress and hence hydrogen concentration. The inclusion of the crystal-level creep was found to be crucial in determining the locations of hydride formation. In addition, both the interstitial hydrogen interaction energy (generated by the stress from the surrounding zirconium lattice, influencing hydrogen uptake) and the GND density (influencing intragranular stress) were found to be important factors in controlling the location and onset of hydride formation but thermal behaviour alone was not shown to have a strong influence on hydride locations.

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Appendix A Scaling method

In a heated vacuum chamber, the hydrogen emission from the hydrided zircaloy-4 sample is argued to be negligible. Thus, we assume that hydrogen content over entire sample remains constant, and following Eq. (17),

$$\int_V \alpha c_0 \exp \left[\frac{E_{int}(x, y)}{kT} \right] dx dy dz = c_{ini} V \quad (19)$$

Recall that the interaction energy is a function of the elastic dipole tensor $\mathbf{p}$ and the stress tensor $\mathbf{\sigma}$. The interaction energy may be written as,

$$E_{int}(x, y) = \{\mathbf{p}\}^T [\mathbf{S}] \{\mathbf{\sigma}\} + \{\mathbf{\sigma}\}^T [\mathbf{S}] \{\mathbf{p}\} \quad (20)$$

where $\{\mathbf{p}\}$ and $\{\mathbf{\sigma}\}$ are reshaped from matrices (3×3) into vectors with dimension of 6×1 due to the symmetry of their matrices, using the same notation order in ABAQUS/UMAT. $[\mathbf{S}]$ is the elastic modulus matrix of zircaloy-4 with dimension of 6×6 [37]. So that $E_{int}(x, y)$ is a linear function of local stress $\mathbf{\sigma}(x, y)$. With the approximation (for small x)

$$e^x = 1 + \sum_{n=1}^{\infty} \frac{x^n}{n!} \quad (21)$$

so that $c(T, x, y)$ which contains an exponential term can be approximated by polynomials, so that $c(T, x, y)$ satisfies the quadrature integration in finite element method,

$$\int_V c(T, x, y) dx dy dz \approx \sum_{i=1}^2 \sum_{j=1}^2 H_i H_j \cdot t \cdot c(T, x_{(i,j)}, y_{(i,j)}) \quad (22)$$

where, H_i and H_j are the weight value of Gaussian quadrature points and t is the thickness of the element. Thus, the scaling α is extracted by the volume integration of hydrogen concentration to give

$$\alpha = \frac{c_{ini} V}{\sum_{i=1}^2 \sum_{j=1}^2 H_i H_j \cdot t \cdot c_0 \exp \left[\frac{E_{int}(x_{(i,j)}, y_{(i,j)})}{kT} \right]} \quad (23)$$

That is,

$$\alpha = \frac{c_{ini} V}{\sum_{i=1}^2 \sum_{j=1}^2 H_i H_j \cdot t \cdot c_0 \exp \left\{ \frac{[\{\boldsymbol{\rho}\}^T [\mathbf{S}] \{\boldsymbol{\sigma}\} + \{\boldsymbol{\sigma}\}^T [\mathbf{S}] \{\boldsymbol{\rho}\}](x_{(i,j)}, y_{(i,j)})]}{kT} \right\}} \quad (24)$$

Appendix B Material properties for Zircaloy-4

The slip properties of zircaloy-4 including its strain rate sensitivity have been calibrated in a separate three-point bending test [26]. The thermal expansion coefficients and other material properties have been determined [21]. The summarised material properties for prismatic slip in zircaloy-4 is shown below in Table 1.

Table 1 Elasto-plastic material properties for Zircaloy-4

Parameters		Unit	Prismatic
Elastic	$E_1(T)$	MPa	$-75.5 T + 120441.1$
	$E_3(T)$	MPa	$-32.7 T + 132862.1$
	$G_{13}(T)$	MPa	$-23.3 T + 38836.7$
	$\nu_{12}(T)$		$3.4 \times 10^{-4} T + 0.3002$
	$\nu_{13}(T)$		$-9.1 \times 10^{-5} T + 0.2642$
Plastic	ρ_m	μm^{-2}	0.01
	ν_d	Hz	1.0×10^{11}
	b^κ	μm	3.2×10^{-4}
	k	$\text{J} \cdot \text{K}^{-1}$	1.38×10^{-23}
	ΔV	μm^3	20.93 b^3
	$\tau_{c,0}^\kappa(T)$	MPa	$26.3 \exp(514.7/T)$

	ΔF	J	5.13×10^{-20}
Thermal	α_a	K^{-1}	1.01×10^{-5}
expansion	α_c	K^{-1}	5.25×10^{-6}

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