Dislocation modelling of the plastic relaxation and thermal ratchetting induced by zirconium hydride precipitation

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A B S T R A C T

The precipitation of hydrides in zirconium alloys is accompanied by a significant and anisotropic volumetric expansion. Previous literature quantified the misfit both theoretically and experimentally, but these values differ greatly; the experimental values are consistently lower. One possibility is that the experimental measurements include the effect of dislocations generated by the hydride, which relax the transformation stresses. To test this hypothesis, it is important to determine the stress field of a hydride and its associated dislocations, combined. A simple planar dislocation model was developed of the hydride—dislocation ensemble in α-Zr. By capturing details of the dislocation structures given in the literature, it is shown in this study that including the interfacial dislocations largely reconciles the predicted and experimental values. Discrete dislocation plasticity is then used to model the diffuse plastic relaxation associated with hydride formation. The effects of plastic relaxation on the equilibrium hydrogen profile, hence the implications for subsequent hydride precipitation, are discussed. In particular, precipitation–dissolution cycles were simulated to calculate the magnitude of the residual hydrostatic tension, which is argued to be the primary cause of the “memory effect” for the re-precipitation of both γ and δ hydrides.

1. Introduction

Hydrogen is undesirable but always present inside the zirconium cladding of water-cooled fission reactors. When a region of the cladding becomes supersaturated in H, a hydride forms. Hydrides are detrimental for the fracture resistance of Zr-alloys, a fact that has led to a flourishing literature, both experimental and computational, on the precipitation of hydrides (see reviews (Bair et al., 2015; Motta et al., 2019)). In this work, the hydrides described are individual micro-hydride needles or platelets, of the order of 1 μm in length, that are the building blocks of the macroscopic hydrides observed optically as the origin of delayed hydride cracking (DHC) (Chung et al., 2002; Puls, 2012). The two hydride phases that are found under operating conditions are the fct γ phase and the fcc δ phase (McBae and Coleman, 2017). Since H in an atomic ratio of the order of 1:1 must be added to the Zr lattice upon precipitation, the phase transformation is accompanied by a volumetric expansion of 12.3% for γ and 17.2% for δ hydrides (Carpenter, 1973). The consequences of the volumetric misfit necessarily must be at the heart of any successful modelling of hydride reorientation and DHC. The volumetric misfit is anisotropic, and it causes different strains along the three main directions of the Zr lattice. The theoretical, stress-free transformation strains were determined by Carpenter (1973). The transformation strains were also experimentally measured by Barrow et al. using nano-beam electron diffraction (Barrow et al., 2013a). The numerical
Table 1
Transformation strain for \( \gamma \) and \( \delta \) hydrides in Zr. The theoretical values, \( \varepsilon_{\text{theo}} \), were calculated by Carpenter (1973), while the experimental values, \( \varepsilon_{\text{exp}} \), are the interfacial strains measured by nano-beam electron diffraction (Barrow et al., 2013a). The largest difference between the two is along the \( \langle 11 \overline{2} 0 \rangle \) direction.

<table>
<thead>
<tr>
<th>Direction</th>
<th>( \varepsilon_{\text{theo}} )</th>
<th>( \varepsilon_{\text{exp}} )</th>
<th>( \varepsilon_{\text{theo}} )</th>
<th>( \varepsilon_{\text{exp}} )</th>
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<tbody>
<tr>
<td>( \langle 11 \overline{2} 0 \rangle )</td>
<td>0.55</td>
<td>0.6</td>
<td>4.60</td>
<td>3.1</td>
</tr>
<tr>
<td>( \langle 1100 \rangle )</td>
<td>5.64</td>
<td>0.5</td>
<td>4.60</td>
<td>0.5</td>
</tr>
<tr>
<td>( \langle 0001 \rangle )</td>
<td>5.70</td>
<td>4.1</td>
<td>7.20</td>
<td>5.5</td>
</tr>
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</table>

Values are presented in Table 1. It is important to note that the experimental values were measured on hydrides that had already undergone plastic relaxation (Blackmur et al., 2016). Different theoretical values of 0.05%, 7.16% and 5.72% for the transformation strains of \( \gamma \) along \( \langle 11 \overline{2} 0 \rangle \), \( \langle 1100 \rangle \) and \( \langle 0001 \rangle \) were provided by Louchez et al. (2017) using ab initio calculations. To be consistent with previous work relevant for this study (Tummala et al., 2018; Barrow et al., 2013a; Bair et al., 2017), we adopt the values by Carpenter.

Two direct consequences of the volumetric misfit in this work are:

- the hydride stress field may attract H, thereby affecting both its subsequent growth and the nucleation of neighbouring hydrides;
- there is ample evidence that the misfit induce plasticity both inside the hydride (Bai et al., 1992; Wang et al., 2014; Vicente Alvarez et al., 2016) and in the surrounding matrix (Carpenter et al., 1973; Bailey, 1963; Long et al., 2019; Zhao et al., 2008; Hanlon et al., 2018).

Very small hydrides are considered to be coherent, because of the characteristic contrast that they show in the transmission electron microscope (TEM) (Bailey, 1963; Zhao et al., 2008). Since the misfit with the Zr matrix is significant, of the order of 5%, plastic relaxation with the generation of interfacial dislocations is to be expected. Looking at the body of the literature, it appears that this plastic relaxation can be one of two types. In some cases, so-called “butterfly” dislocations are observed, generally referring to the work by Carpenter et al. (1973). Similar findings can be found, however, both before and after that study, usually in the case of \( \gamma \) hydrides. Images of such hydrides decorated by “butterfly” dislocations, from 4 different studies, are collected in Table 2 together with relevant information on the sample preparation, the hydride size and the dislocation spacing.

Table 2
“Butterfly” dislocations observed in four different studies. For each image it is indicated the reference from which it was reproduced, the alloy type, the cooling rate, the total H content, the approximate hydride size, the range of spacing \( s \) of the dislocations (close/far from the hydride). In all the cases a \( \gamma \) hydride in the basal plane is being imaged, except for the last one, where this is not specified.

<table>
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<tr>
<th></th>
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<tbody>
<tr>
<td>Pure Zr</td>
<td>Zircaloy-2</td>
<td>Pure Zr</td>
<td>Zircaloy-4</td>
<td>Slow cooling</td>
</tr>
<tr>
<td>Quenched</td>
<td>Quenched</td>
<td>Slow cooling</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[H] = 10 ppm</td>
<td>[H] = 17 ppm</td>
<td>[H] = 30 ppm</td>
<td>[H] = 200 ppm</td>
<td></td>
</tr>
<tr>
<td>–</td>
<td>2 ( \mu ) ( \times ) 500 nm</td>
<td>1.2 ( \mu ) ( \times ) 100 nm</td>
<td>1.7 ( \mu ) ( \times ) 400 nm</td>
<td></td>
</tr>
<tr>
<td>–</td>
<td>( s \approx 20/80 ) nm</td>
<td>( s \approx 20/130 ) nm</td>
<td>( s \approx 25/125 ) nm</td>
<td></td>
</tr>
</tbody>
</table>

It has been suggested that the “butterfly” dislocations are an artefact of the sample preparation (Hanlon et al., 2019). However, in-situ observations of precipitating \( \gamma \) hydrides by Long et al. (2019) provide a strong argument against this claim. It is worth noting...
that the understanding of the plasticity inside and around micro-hydrides is further complicated by the fact that both of the usual sample preparation techniques, namely focused ion beam milling and electropolishing, produce artefacts. The first may induce the escape of dislocations to the surface, whereas both can introduce spurious hydrides (Tunes et al., 2017; Hanlon et al., 2019). Zr micro-hydrides are often studied using phase field modelling (PFM) (Shi and Xiao, 2015; Xiao et al., 2015; Bair et al., 2017; Han et al., 2019). These works generally use the theoretical values to calculate the contribution to the energy of the system due to the misfit of fully coherent hydrides. Including the effects of the plastic relaxation appears to be necessary if one is not interested in the nano-hydrides but rather in those that are not fully coherent and where some plasticity took place around the hydride. Only a recent contribution considers a mixed interface that is coherent in the basal planes and semi-coherent in the prismatic planes (Heo et al., 2019).

When hydrided Zr-alloys undergo thermal dissolution and precipitation cycling, it has been observed that the hydrides tend to re-precipitate in the same location as they were previously located. This is referred to, in this context, as thermal ratchetting (Cameron and Duncan, 1977; Eadie et al., 1993; Barrow et al., 2013b; Patel et al., 2017). It is suggested that the dislocations associated with the plastic relaxation are the cause of this “memory effect” (Carpenter et al., 1973; Carpenter, 1978; Hanlon et al., 2018).

The modelling tool that is used in this study is Discrete Dislocation Plasticity (DDP), which is a planar version of 3D Discrete Dislocation Dynamics (DDD). The plastic relaxation induced by a misfitting hydride was studied using DDD by Tummala et al. (2018). The main finding of the study was that a thermodynamic driving force for the precipitation of stacked hydrides was found. The simulations produced a plastic relaxation similar to what was described by Carpenter et al. (1973). Thermal ratchetting was modelled using DDP by Patel et al. (2017). The study involved the γ phase only, and the misfit stress was treated in a simplified way—representing it by an artificial edge dislocation dipole with a large Burgers vector to represent the hydride strain. A mechanistic basis for the “memory effect” was also proposed, namely the creation of a tensile field in response to the compression of the hydride, which was confirmed in the current investigation.

In this work, we investigate the effect of the dislocations generated by the volumetric expansion of Zr hydrides. In the first part, two different dislocation structures are considered: either ordered arrays of dislocations (cf. Table 2), or those produced by the slip activity predicted by DDP (cf. Fig. 1), to justify the mismatch between theoretical and experimental values of the transformation strains. In the second part, precipitation–dissolution cycles were modelled to investigate whether there is a mechanistic origin for the “memory effect” in Zr-alloys.

2. Methods

This study is concerned with the plastic relaxation around Zr hydrides. What triggers this relaxation is the stress of the hydride–matrix interface. Below, we describe a model of the precipitate based on the concept of stress generators and stress annihilators, after Ref. Sutton and Balluffi (2006). In a 2D model there are two independent parameters, namely the values of the misfit in two orthogonal directions, which determine the nature and intensity of the interfacial stress. These two values are used to generate two discrete distributions of edge dislocations that together simulate the hydride stress. The dislocations in this context are only stress generators, and are not the crystallographic dislocations found in Zr. The hydride is described by its length \( L_{\text{hyd}} \) and thickness \( t_{\text{hyd}} \).

The hydrides modelled here are needle-shaped. The 2D section might be either that of a needle, having one size significantly larger than the other two, or of a penny-shaped platelet having one size significantly smaller than the other two. It was proposed that the γ phase adopts the former shape and the δ phase the latter (Motta et al., 2019). Since the images of both phases, taken from multiple sections in various orientations, consistently show needle-shaped objects, we follow the view of Ref. Bair et al. (2017), where it is proposed that the δ phase grows from a γ precursor, keeping its shape at least in a metastable state. That the δ phase nucleates from a γ precursor in a needle-like shape was also proposed on experimental grounds (Barrow et al., 2013a).
If the plane of interest is taken to be the $x$-$y$ plane, the two aforementioned sets of $N_x$ and $N_y$ fictitious dislocations, or stress generators, share a common line direction along $z$ and have the Burgers vector along $x$ and $y$ respectively. The dislocations, arranged in two overlapping elliptic rings, are evenly spaced in the direction of their Burgers vector, i.e. one distribution is evenly spaced in $x$, the other in $y$. The $\sigma_{xx}$ component of the hydride stress is given by:

$$\sigma_{xx} = \frac{\mu}{2\pi(1-\nu)} \left( b_x \sum_{p=1}^{N_x} \text{sign}_p (y-y_p) \left( \frac{3(x-x_p)^2 - (y-y_p)^2}{(x-x_p)^2 + (y-y_p)^2} \right) \right) + \left( b_y \sum_{q=1}^{N_y} \text{sign}_q (x-x_q) \left( \frac{(x-x_q)^2 - (y-y_q)^2}{(x-x_q)^2 + (y-y_q)^2} \right) \right),$$

where $\mu$ and $\nu$ are the shear modulus and Poisson’s ratio, and where $\text{sign}_p$ and $\text{sign}_q$ take the value of $+1$ or $-1$ so that the extra half-plane of the $p^{th}$ and of the $q^{th}$ dislocation is on the same side as the hydride. The Burgers vectors of the two distributions, which can in general be different, are positive and follow from the global misfit of the hydride, i.e. according to $N_x b_x = L_{hyd} \varepsilon_x$ and $N_y b_y = L_{hyd} \varepsilon_y$. The theoretical values proposed by Carpenter (1973) are used, consistent with previous modelling works on micro-hydrides, which primarily used phase field methods. The $\sigma_{yy}$ and $\sigma_{xy}$ components are derived in the same way starting from the textbook expressions for an edge dislocation. By utilising the stress field of an edge dislocation in a homogeneous material, we are assuming that the hydride has the same elastic properties as the Zr matrix. This is an approximation that is considered to be acceptable since the elastic properties of the two are similar. For instance, the Young’s modulus of the $\delta$ hydride was measured to be about 5% lower than for Zr (Chan et al., 2016), but calculated using first principle simulations to be about 25% higher (Zhu et al., 2010). In the case of the $\gamma$ phase, it was predicted to be about 13% higher (Zhu et al., 2010). However, the advantages gained by using the equal modulus approximation are twofold, and especially important as far as the DDP implementation is concerned. First, the calculation of the stress field of the hydride is faster. Second, the same expressions can be used for the dislocations generated by plastic relaxation. Implementing the hydride as a harder or softer inclusion is possible, but it adds significantly to the computational overhead (O’Day and Curtin, 2004) without—in this case—much improvement in accuracy.

Fig. 2 shows how discrete dislocations can represent the stress due to the hydride. The $\sigma_{xx}$ component of a $\delta$ hydride is taken as an example. For the sake of exposition, a small value of $N_x = N_y = 20$ was selected to highlight how the discrete dislocations collectively build up the misfit stress. It is worth noting that the fields become smooth and not ascribable to individual dislocations anymore at a distance from the interface of the order of their spacing. The plots of the stress components of a $\gamma$ and of a $\delta$ hydride are presented in Appendix A. In the DDP simulations below, the stress caused by the hydride is calculated using two discrete distributions of 100 dislocations each. This number was chosen to compromise between computational time and smoothness of the interfacial stress. The Burgers vector of the dislocations associated with the largest misfit that is modelled, i.e. 5.6%, is of about 1.6 Å, which is half as large as that of the prism edge dislocations. This ensures that there are no spuriously high local stresses.

In Fig. 2, dislocations are used to generate the stress state of the hydrides. Similar arrays of dislocations can also be used to model the “ordered” plastic relaxation. By this, we mean that interfacial dislocations can be placed in an ordered fashion to reduce the stress of the hydride. In this case, they are crystallographic and discrete by nature (as opposed to the previous case, where they were a discrete approximation of a continuous misfit). Several studies showed that $\gamma$ hydrides are able to relax the misfit stresses by generating dislocations (e.g. Table 2 from Refs. Carpenter et al. (1973), Bailey (1963), Long et al. (2019) and Zhao et al. (2008)). These dislocations are very similar across the various studies and experimental conditions. They stretch from tip to tip of the hydride, and they are of the order of 5 to 10 for hydrides that are needle-shaped, in the basal plane, and whose dimensions are approximately 1 μm along the (1120) direction and hundreds of nm in thickness. It has been proposed that they are responsible for relaxing the transformation stresses in the matrix (Carpenter et al., 1973; Bailey, 1963; Long et al., 2019; Zhao et al., 2008). We observe that this view is supported by the fact that there seems to be no further dislocation activity beyond these “butterfly” dislocations. If,
conversely, these dislocations are not generated, the plastic relaxation is somewhat more disordered, with dislocation tangles such as in Fig. 1.

Barrow et al. (2013a) found by nano-beam electron diffraction that the misfit of γ hydrides is about 0.5% in both the principal basal plane directions. In their Fig. 3, Barrow et al. (2013a) showed one of the hydrides (whose phase composition was not specified), around which the presence of (a)-type dislocations was reported. It can be appreciated that even if this hydride is significantly longer than the ones in Table 2, the dislocations are very ordered straight lines stretching from the (not visible) tips of the hydride. We assume that the experimental measurements by Barrow et al. (2013a) correspond to the superposition of the stress of the interface and of the “butterfly” dislocations, i.e. to the relaxed configuration, as also noted by Blackmur et al. (2016). This array of interfacial dislocations balances the volumetric misfit. This may be attained partially, i.e. a misfit matching the experimental values of Table 1 remains; or wholly, i.e. the hydride is entirely deprived of its long-ranged stress.

Evidence of “butterfly dislocations” with that particular morphology was found, to our knowledge, only for the γ phase. Theoretical and experimental values differ significantly also for the δ hydride (Table 1), and therefore it is possible to find a configuration of interfacial dislocations that allows the relaxed stress field to match the measured one.

For each direction i, the spacing si of the dislocations follows from the hydride phase, to which a different theoretical (εthexp.) and experimental (εexp.) misfit are associated, and the Burgers vector of the dislocations. A discrete array of crystallographic dislocations, or stress annihilators, introduces a misfit of the opposite sign to the one introduced by the interface. The spacing in the direction i, where i could be (1120), (1100) or (0001), is given by

\[ s_i = \frac{b}{\epsilon_{\text{theo}} - \epsilon_{\text{exp}}} \]  

(2)

In the case of γ hydrides in the basal plane, only an array of dislocations with Burgers vector along (1 1 0 0) is needed. If the needle is oriented along one of the three (1 1 2 0) directions, the combined action of two (a)-type dislocations, one for each of the other two prism slip planes, gives a net Burgers vector in the correct direction and of magnitude \( \sqrt{3} \cdot 3.232 = 5.598 \) Å. It is possible to repeat the analysis for the (1 1 2 0) – (0 0 0 1) plane. (a)-type dislocations are able to accommodate the misfit along x, namely the (1 1 2 0) direction, hence nothing changes in this respect. To accommodate the misfit along y, dislocations that have a (c)-component are required. The slip system with the lowest critical resolved shear stress that has this characteristic is the first-order pyramidal (c + a) slip (Gong et al., 2015). In order to cast the stress of (c + a)-type dislocations in the (1 1 2 0) – (0 0 0 1) plane, we make use of the same strategy that is used in DDP to deal with pyramidal slip (Zheng, 2017). In this reference frame, two of the possible first-order pyramidal Burgers vectors have components \( \sqrt{3} a x \pm \frac{1}{2} a y + cz \). By superimposing the two, we obtain a dislocation whose effective Burgers vector is contained in the x – z plane and has magnitude \( \sqrt{2} a^2 + c^2 = 5.859 \) Å in Zr. The angle between the x axis and the angle of the trace of this effective slip system coming from the simultaneous activation of the two first-order pyramidal systems, takes the value of \( \theta_{\text{pyr}} = \arctan \left( \frac{2c}{\sqrt{3}a} \right) = 1.073 \sim 61.5^\circ \). The two possible slip systems defined in such a way are at an angle of \( \theta_{\text{pyr}} \) and \( \pi - \theta_{\text{pyr}} \) from the x axis. It is then possible to place two dislocations from each of the two pyramidal slip systems on top of one another so that their x components cancel out, but a net (c) component remains.

We stress the fact that a direct correspondence between this simple model and reality cannot be drawn: the 2D analysis has some inherent limitations. The dislocations in Table 2 are coplanar with the hydride and they bend around it. However, each pair of edge dislocations in our simple model could be thought of as two segments of a loop that is closed by two screw segments, one above and one below the edge segments, which are the counterpart in the model of the “butterfly dislocations”. Moreover, this analysis does not include the fact that in the thin TEM foils, the constraint of the matrix is lower than in the ideal case considered by Carpenter et al. (1973).

2.1. The DDP model

To build a DDP model of the Zr hydrides, we use a similar approach as in the case of Nb second phase particles (SPPs). The details of the DDP framework are explained in Reali et al. (2021b,a); here we offer only a brief overview. Point sources and obstacles are randomly scattered across the simulation box with densities \( \rho_{\text{src}} \) and \( \rho_{\text{obs}} \). Edge dislocation dipoles are nucleated if the resolved shear stress \( \tau \) acting on the sources exceeds \( \tau_{\text{src}} \) for a time \( t \geq t_{\text{src}} = 1.0 \) ns. The dislocations are pinned upon encountering obstacles, and released only if \( \tau \geq \tau_{\text{obs}} \). As is often the case in DDP (Brinckmann and van der Giessen, 2004; Balint et al., 2006; Tarleton et al., 2015), we set \( \tau_{\text{obs}} = 3 \cdot \tau_{\text{src}} \). The obstacles do not have an elastic field. The motion of the dislocations is driven by \( \tau \) under a drag-controlled regime. Their velocity is calculated according to

\[ v = \begin{cases} \frac{br}{B[1 + \left| \mathbf{b} \cdot \hat{\mathbf{t}} \right|]} & v < v_{\text{cut}} \\ \frac{v_{\text{cut}}}{v_{\text{cut}}} & v \geq v_{\text{cut}} \end{cases} \]  

(3)

where \( B \) is the drag coefficient, \( \hat{\mathbf{t}} \) is the time step, \( v_{\text{cut}} \) is the cutoff velocity and \( \mathbf{b} \) is the direction of the resolved shear stress in the direction of the slip plane. \( B \) was set to \( 5 \cdot 10^{-5} \) Pa s (Reali et al., 2021b), to be an intermediate value between what was used in Tarleton et al. (2015) and Tummala et al. (2018). Eq. (3), based on backward Euler integration, was proposed by Chakravarthy and Curtin (2011) to lessen the issue of numerical oscillations of dislocations under high stress gradients (such as in pile-ups). This enables one to increase the cutoff velocity from the typical 20 m/s (van der Giessen and Needleman, 1995; Chakravarthy and Curtin, 2011) to e.g. 200 m/s as we used here.
The precipitation of a hydride at the centre of a simulation box of dimensions \( w_{\text{box}} \times h_{\text{box}} \) was modelled. The aspect ratio of the hydride was held constant at 10:1. The final length and thickness were 1.5 \( \mu \text{m} \) and 150 nm respectively. These dimensions approximately match the hydrides imaged in Table 2. Table 3 lists the numerical values of the parameters of the model.

The interface is characterised by a seamless transition between the two phases, owing to the fact that two of the four \{111\} slip systems of the hydride are aligned with two of the prism slip systems of the alpha-Zr matrix, say those whose Burgers vectors are \( \frac{3}{2}[1210] \) and \( \frac{1}{2}[2110] \) (Reali et al., 2021b). There are no horizontal slip planes aligned with the [1120], which is also parallel to the long axis of the hydride. With this, we are considering that the hydride follows the fcc/hcp orientation relationship that is predominant among those reported in the literature (Hanlon et al., 2018; Bradbrook et al., 1972):

\[
\{111\}_{\text{hyd}}//\{0001\}_{\text{Zr}}
\]

\[
[1\overline{1}0]_{\text{hyd}}//[11\overline{2}0]_{\text{Zr}};
\]

and we further assume that the \{111\} planes are those where slip occurs in the hydride. Although there are no interfacial obstacles between the two phases, the stress field of the hydride is such that the dislocations glide towards the interface and remain in its proximity. Unless stated otherwise, the 2D section is the basal plane, the \( z \) axis is parallel to the \( \langle 0001 \rangle \) direction, the \( x \) axis is parallel to the \( \langle 1120 \rangle \) direction and the \( y \) axis is parallel to the \( \langle 110 \rangle \) direction.

There are three factors that were deemed important when devising the DDP simulations: (1) the availability of dislocations around the hydride, embodied by the dislocation Frank–Read source density \( \rho_{\text{src}} \); (2) the kinetics of the hydride precipitation, compared to the timescale of dislocation motion; (3) whether the hydride precipitates in pure Zr or in a Zr-alloy.

Regarding (1), three different values of source density \( \rho_{\text{src}} \) were chosen: 50, 100 and 150 \( \mu \text{m}^{-2} \). The resulting dislocation density was compared with the available experimental data. Since the stress resulting from the hydride is very localised, to an area of the order of 1 \( \mu \text{m}^2 \), the plastic relaxation is expected to be highly dependent on the local environment. With these three values of \( \rho_{\text{src}} \) we study hydrides growing in regions that may have a substantially different availability of Frank–Read sources. As \( \rho_{\text{src}} \) increases, the spacing of the slip planes \( \Delta S_P \) is correspondingly decreased (100 \text{h}, 50 \text{h} and 30 \text{h} respectively). \( \rho_{\text{obs}} \) was held constant at 300 \( \mu \text{m}^{-2} \).

(2) To explore the effect of the timescale of the precipitation, three growth modes were devised. In the first mode (M1), the hydride was assumed to have grown instantaneously, and only after this are dislocations allowed to nucleate. In a second mode (M2), the hydride grows in 500 ps, so that the microstructure continuously responds to the changing stress field. In a third mode (M3), the hydride is grown in a “quasi-static” fashion. Its length is linearly increased by \( L_{\text{hyd}}/10 \) in steps of 50 ps, followed by an equilibration step of 50 ps. This time scale was selected so as to allow the occurrence of the equilibrium configuration of dislocations after each incremental growth. In fact, dislocations travel at a speed of the order of 10–100 \text{m/s} in the simulations. Since the maximum distance they need to cover is of the order of 1 \( \mu \text{m} \), the estimated equilibration time is of the order of 10–100 ps.

(3) The plastic relaxation depends on the critical resolved shear stress required to activate the Frank–Read sources in the matrix surrounding the hydride. A nucleation stress \( \tau_{\text{src}} = 100 \text{MPa} \) was chosen to model the case of pure Zr having an oxygen concentration of the order of 1200 ppm (see Fig. 8 in Ref. Gong et al. (2015)). \( \tau_{\text{src}} = 153 \text{MPa} \) was chosen instead to model the case of Zircaloy-4 (Zry-4) (Wilson et al., 2019).

### 2.2. Precipitation–dissolution cycles

In another set of simulations, we investigated the thermal ratchetting mechanism by repeatedly precipitating and dissolving the hydride for 10 cycles over a total time of 2 \( \mu \text{s} \). This was simulated by cycling the length and thickness of the hydride from zero to \( L_{\text{hyd}} \) and \( t_{\text{hyd}} \) respectively, while keeping the fixed aspect ratio of 10:1. The growth and dissolution are both linear and there are

| Table 3 | Numerical parameters for the DDP simulations, unless stated otherwise. Sources and obstacles strengths follow a Gaussian distribution whose standard deviation is 10% of the mean value. Different values were used for some of the parameters; details are provided in the relevant sections. |
|---|---|---|---|---|
| Material | \( \mu \) \([\text{GPa}]\) | \( b \) \([\text{\AA}]\) | \( \nu \) \([\text{\sim}]\) | \( B \) \([\text{Pa s}]\) |
| | 33 | 3.23 | 0.34 | \( 5 \times 10^{-3} \) |
| Sources/Obstacles | \( \rho_{\text{src}} \) \([\mu \text{m}^{-2}]\) | \( \tau_{\text{src}} \) \([\text{MPa}]\) | \( \rho_{\text{obs}} \) \([\mu \text{m}^{-2}]\) | \( \tau_{\text{src}} \) \([\text{MPa}]\) |
| & 50/[100]150 | 100/[153] | 150/[300] | 3 \cdot \tau_{\text{src}} |
| Computational | \( \delta t \) \([\text{ps}]\) | \( \tau_{\text{cut}} \) \([\text{\mu s}]\) | \( \tau_{\text{cut}} \) \([\text{m/s}]\) | \( \Delta P \) \([\text{N}]\) |
| & 10 | 1/2 | 200 | 30/[50]100 |
| Geometry | \( w_{\text{box}} \) \([\mu \text{m}]\) | \( h_{\text{box}} \) \([\mu \text{m}]\) | \( L_{\text{hyd}} \) \([\mu \text{m}]\) | \( t_{\text{hyd}} \) \([\mu \text{m}]\) |
| & 3 | 1.5 | 1.5 | 0.15 |
| Diffusion | \( \rho_{\text{diff}} \) \([\text{eV}]\) | \( \rho_{\text{diff}} \) \([\text{eV}]\) | \( T \) \([\text{C}]\) |
| & 1.74 | 2.36 | 25/250 |
hold periods after each of them. All four steps have an identical duration, a fourth of that of the cycle. Three cases were considered: a δ hydride in Zry-4, a γ hydride in Zry-4 and a γ hydride in Zr. Initially, the obstacle density was treated as a variable. However, after observing that its influence on the results was marginal, it was instead assigned a constant value of 150 μm⁻².

In order to quantify the increased likelihood of precipitation in the location of a pre-existing hydride, the value of the residual hydrostatic stress, \((σ_{xx} + σ_{yy})_{res}\), was calculated as the spatial average over 10,295 equally spaced points inside the region where the hydride was located. Here and throughout this work we refer to the two-dimensional quantity \((σ_{xx} + σ_{yy})\) as the hydrostatic stress. As the 2D edge dislocation fields assume plane strain conditions, the 3D conventional hydrostatic stress is given by \((1 + ν)(σ_{xx} + σ_{yy})/3\).

The results were then further averaged over the 20 simulations. With the simple cycling of the dimensions of the hydride, it is assumed that the tensile field forms upon heating and subsequent hold at high \(T\), when the hydride fully dissolves. This hydrostatic stress drives the H accumulation that becomes more pronounced as \(T\) decreases, to the point that a new precipitation event occurs. The \(T\) at which the H profile was calculated, i.e. the \(T\) reached by the parent phase before precipitation, was set to 250 °C, on the basis of the terminal solid solubility upon precipitation (TSSP) of a Zr-alloy with a H content of approximately 50 ppm (Ref. McMinn et al. (2000, Figure 8)).

In evaluating the hydride stress, we considered the transformation strain only, and not the thermal stress arising from different thermal expansion coefficients. A hydrided region undergoing a thermal cycle of 300 K would experience a thermal mismatch of about 0.6%: considering a volumetric expansion coefficient of δ hydrides of \(42 \cdot 10^{-6} \text{ K}^{-1}\) (Cimbiz et al., 2018) and an isotropic average for Zr of \(22 \cdot 10^{-6} \text{ K}^{-1}\) (Skinner and Johnston, 1953). This is much less than the transformation strain of the hydride phases (12.3% for γ 17.2% for δ) and can be neglected. Although the thermal ratchetting necessarily involves a changing temperature, this is not directly captured by the current DDP formulation. Zr exhibits plastic relaxation by creep at the operating temperature, hence \(τ_{str}\) is likely to decrease as \(T\) increases. The mobility law should exhibit a \(T\) dependence as well. Finally, this work deals with hydrides growing in a single α-Zr grain. The grain boundary may play an important role in arresting the growth of the hydride. These final notes constitute interesting avenues for further research.

2.3. The equilibrium hydrogen concentration

H diffuses against the gradient of its chemical potential in Zr, which depends on the H concentration \(c^H\) on the temperature \(T\) and on the lattice stress \(σ_{ij}\) (or strain, \(ε_{ij}\)). If the system reaches equilibrium, the concentration profile can be described using the elastic dipole tensor \(ρ_{ij}\), which for this specific system was taken from Ref. Nazarov et al. (2016), which was calculated using density functional theory. The value of \(ρ_{ij}\) in any of the directions contained in the basal plane, \(ρ_{(0001)} = 1.74 \text{ eV}\), is lower than the value in the direction normal to the basal plane, \(ρ_{(0001)} = 2.36 \text{ eV}\). If the plane of interest \(x - y\) is the basal plane, then \(ρ_{xx} = ρ_{yy}\) and, under plane strain conditions,

\[
c^H = c^H_0 \exp \left( \frac{ρ_{(0001)}(1 + ν)(σ_{xx} + σ_{yy})}{3Kk_BT} \right),
\]

(4)

where \(c^H_0\) is the H concentration in the absence of stress, \(K\) is the bulk modulus and \(k_B\) is Boltzmann’s constant. If the plane of interest is normal to the basal plane, for instance if \(x\) is along \((1120)\) and \(y\) is along \((0001)\),

\[
c^H = c^H_0 \exp \left( \frac{ρ_{(0001)}ε_{xx} + ρ_{(0001)}ε_{yy}}{k_BT} \right).
\]

(5)

In other words, the lattice stress perturbs the concentration \(c^H_0\) of the unstressed crystal. The anisotropy of the hcp Zr lattice influences both the elastic dipole tensor and the stress field of the dislocations, which in turn are responsible for the stresses. We take into account the former factor but not the latter. Moreover, Eqs. (4) and (5) hold for a dilute solution, e.g. of H in Zr. In the case of the hydrides, the H concentration is set by the stoichiometry and is far from being dilute, being of the order of 10⁴ wpmp.

One notable feature of the hydride stress is that if the two orthogonal values of the misfit are identical, the hydrostatic stress can be neglected. Although the thermal ratchetting necessarily involves a changing temperature, this is not directly captured by the current DDP formulation. Zr exhibits plastic relaxation by creep at the operating temperature, hence \(τ_{str}\) is likely to decrease as \(T\) increases. The mobility law should exhibit a \(T\) dependence as well. Finally, this work deals with hydrides growing in a single α-Zr grain. The grain boundary may play an important role in arresting the growth of the hydride. These final notes constitute interesting avenues for further research.

3. Results

3.1. The plastic relaxation resulting from ordered misfit dislocations

We begin analysing how the misfit stress (e.g. Eq. (1) for \(σ_{xx}\)) can be altered by placing arrays of dislocations at the interface of the hydride (spaced according to Eq. (2)). This produces a model consistent with hydrides observed after plastic relaxation, but it cannot shed light on how these interfacial dislocations are generated.

\[\text{L. Reali et al.}
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Considering the case of a γ hydride in the basal plane, for which \( \xi_{\text{shear}} - \xi_{xz} = 5.1\% \), Eq. (2) gives \( s_{(100)} \sim 11 \text{ nm} \). This is reasonably close, albeit somewhat lower, than the value of about 20 nm that can be estimated for the dislocations in the proximity of the interface (Table 2). Moreover, as the hydride thickness in (1100) is of the order of 100 to 500 nm, the number of dislocations that are to be expected is of the order of 10–50, which is comparable to what is experimentally observed, albeit slightly higher. The findings from the DDP simulations (Section 3.2) suggest that the residual misfit may be of the order of 2% instead, increasing the expected spacing to about 16 nm.

This superposition of ordered arrays of discrete dislocations is possible for both the γ and δ phases and for the three possible 2D sections. As an example, Fig. 3 shows this in the case of the δ hydride viewed on the (1100) plane. The equivalent for the γ hydride on the basal plane is displayed in the bottom part of Fig. 8.

### 3.2. The plastic relaxation predicted by DDP

Both γ and δ hydrides can induce plasticity in the surrounding matrix (see Fig. 1). In the absence of “butterfly” dislocations, the dislocation structures around γ hydrides are somewhat more disordered. The plastic relaxation around both phases was studied using DDP. At first, let us focus on the γ phase. There are typical features emerging from the simulations. First, dislocations of the two prism slip systems that are associated with the two \( \langle a \rangle \) directions that are not along the hydride growth direction, are invariably found at the interface. Second, the majority of the dislocations at the interface have a Burgers vector orientation that depends on the quadrant of the hydride nearest to where they are found. In particular, with reference to Fig. 4, at the top-left portion of the interface the dominant Burgers vector is \( \xi[1210] \), at the bottom-left portion it is \( \xi[2110] \), at the (not shown) top-right portion it is \( \xi[2110] \) and at the (not shown) bottom-right portion it is \( \xi[1210] \). This results from the fact that the hydride exerts different resolved shear stresses on the three prism systems, and that the dislocations tend to shield the stress field created by the hydride. They do this most effectively by gliding to the hydride–matrix interface so that their missing half-plane points towards the hydride. The dislocations that are found at the interface are the same as those that are placed in Section 3.1 to change the interfacial misfit. In this case, though, they are not ordered and their presence depends upon the availability of active sources on slip planes. Hence, their shielding is less effective, i.e. more dislocations are required to obtain a similar result. Another difference is that each of the misfit dislocations for γ hydrides in Section 3.1 is given by the superposition of two dislocations from two different prism slip systems, whereas in the DDP simulations only one slip system tends to dominate in each quadrant of the hydride. In the case where dislocations were placed, there are two perfectly symmetric distributions. In the DDP case, the distribution of dislocations remains still, on average, balanced. It is a balance now of the four quadrants, in each of which one type of dislocation dominates.

In summary, there are three recurrent features in the dislocations that decorate the hydride, which are also highlighted in Fig. 4:

1. In each of the four quadrants of the hydride, the presence of one particular type of dislocation is predominant;
2. Near the hydride tips, short pile-ups shield the high, localised stress;
3. Less often, two dislocations near one another combine exactly to equal one of the ordered dislocations of Section 3.1.

We focus now on the impact on the plastic relaxation of the three factors that the DDP model was used to investigate, namely the availability of dislocation sources \( \rho_{\text{src}} \), the effect of different hydride growth modes and the properties of the matrix phase (through \( \tau_{\text{src}} \)). The effect of growing the hydride instantaneously, linearly in time or in a step-wise fashion proved to be small (see Appendix B). Therefore, we focus on the results obtained using the step-wise growth, which are summarised in Table 4.

As shown in Fig. 5, the number of dislocations \( N_{\text{disl}} \) plateaus after each time \( t_{\text{hyd}} \) is increased, hence the dislocation structure can be considered to be in equilibrium. If \( t_{\text{hyd}} \propto t \), then \( N_{\text{disl}} \propto t^2 \). This quadratic trend was found by calculating the average of \( N_{\text{disl}} \) after each incremental increase in hydride length (black dots in Fig. 5), and then fitting the curve \( N_{\text{disl}} = A_t t^2 \). This curve fits the data very well, with a coefficient of determination \( R^2 \) of 99.9%, 99.9% and 99.8% for the three values of \( \rho_{\text{src}} \) respectively.
Fig. 4. Close-up view of half of a $\gamma$ hydride to show a typical dislocation structure after the precipitation. The numbers refer to the features explained in Section 3.2. Although the horizontal slip planes are shown inside the hydride, they are not part of the model. There are no dislocation sources there and dislocations cannot enter the hydride from horizontal Zr planes.

Fig. 5. The length of the hydride is increased linearly in 10 steps. The hydride stress generates dislocations, whose number increases quadratically. Increasing the source density, as expected, affects the curvature of the parabola leading to a faster increase in $N_{\text{disl}}$. Black dots mark the average value over the 20 simulations, and they are fitted by the function $N_{\text{disl}} = A L^2$ (broken black lines).

Since $L_{\text{hyd}} \propto t$, we find that $N_{\text{disl}} = A_L L_{\text{hyd}}^2$. $A_L$ is of the order of 100 $\mu$m$^{-2}$, meaning that a hydride of length 1 $\mu$m generates approximately 100 dislocations (that is, approximately 50 complete loops). There is no noticeable change in behaviour as $N_{\text{disl}}$ increases: one simple curve fits the whole range of $L_{\text{hyd}}$. If the frequency distribution of the length of the hydrides were to be experimentally determined, the data in the current work may be used to estimate the increase in dislocation density of the alloy as a result of the precipitation of the hydrides.

The dislocation density after the complete growth of the $\gamma$ hydride was found to be, on average, $0.30 \cdot 10^{14}$, $0.44 \cdot 10^{14}$ and $0.55 \cdot 10^{14}$ m$^{-2}$ for $\rho_{\text{src}} = 50$, 100 and 150 $\mu$m$^{-2}$ respectively. This quantity is not the total dislocation density of the material, but only the increase in dislocation density following the hydride precipitation. Precisely the increase in $\rho_{\text{disl}}$ after $\gamma$ hydride precipitation has been measured experimentally to be of the order of $0.3 \cdot 10^{14}$ m$^{-2}$ (Shiman et al., 2019), which is in excellent agreement with our findings for $\rho_{\text{src}} = 50$ $\mu$m$^{-2}$. However, only an order of magnitude comparison is possible in that the experimental value is a global one, i.e. it depends on the number of hydrides per unit area of the analysed microstructure, whereas we measure the dislocation density in the matrix surrounding a single hydride. The total dislocation density in hydrided Zr-alloys is of the order of $10^{14}$ m$^{-2}$ (Vicente Alvarez et al., 2016; Tummala et al., 2018). Thus, the process of hydride precipitation may contribute a noticeable fraction of the dislocation density in otherwise undeformed Zr-alloys.

As it has been proposed that the elastic stress induced by one hydride may trigger the nucleation of a neighbouring one (Patel et al., 2021), it is important to quantify how much this stress can be affected by the plastic relaxation. When calculated on the basal plane, the two circular regions at the tips of a $\gamma$ hydride are of interest with respect to positive hydrostatic stress. An average value inside these regions, which depends on the radius $R$ of the circle, is denoted by $(\sigma_x + \sigma_y)R$. If interest is in the localised H accumulation at the hydride tips, taking $R = R_1 = 50$ nm, then $(\sigma_x + \sigma_y)R_1 = 1360$ MPa for the given hydride geometry. If the circle
is comparable with the hydride size, i.e. \( R = R_1 = 500 \, \text{nm} \), then \( \langle \sigma_{xx} + \sigma_{yy} \rangle_R_2 = 247 \, \text{MPa} \). Depending on the choice of the material and \( \rho_{src} \), we find that, after the plastic relaxation, the hydrostatic stress value for \( R_1 \) is reduced by at least half for the highest source density, whereas for \( R_2 \) it decreases by up to a factor of 6 (Table 4). Fig. 6 summarises the effect of \( \rho_{src} \) on \( \rho_{disl} \) and \( \langle \sigma_{xx} + \sigma_{yy} \rangle_R_1 \); \( \rho_{disl} \) linearly increases for increasing \( \rho_{src} \), as expected, and is about twice as large in pure Zr than it is in Zry-4; \( \langle \sigma_{xx} + \sigma_{yy} \rangle_R_1 \), on the other hand, linearly decreases for increasing \( \rho_{src} \), and is substantially higher in Zry-4 than in pure Zr.

Similar simulations were performed for the \( \delta \) phase in Zircaloy-4 (\( \rho_{src} = 50 \, \text{µm}^{-2} \)). In this case it was again observed that the ordered arrays of misfit dislocations and DDP produce stress fields that are in qualitative agreement. To compare the two, the average stresses were computed inside the hydride. The elastic stress of the hydride (using the theoretical transformation strains) is constant: \( \sigma_{xx} = -418 \, \text{MPa} \), \( \sigma_{yy} = -418 \, \text{MPa} \) and \( \sigma_{xy} = 0 \, \text{MPa} \). After the plastic relaxation, and averaging over the 20 DDP simulations, \( \sigma_{xx} \) decreased in magnitude to \( -2774 \, \text{MPa} \), \( \sigma_{yy} \) decreased in magnitude to \( -264 \, \text{MPa} \) and \( \sigma_{xy} \) remained close to zero at 4 MPa. From this, an estimation based on DDP is that \( \varepsilon_{(1120)} \sim 3.1\% \) and \( \varepsilon_{(1100)} \sim 2.7\% \), which would produce \( \sigma_{xx} = -2811 \, \text{MPa} \), \( \sigma_{yy} = -260 \, \text{MPa} \) and \( \sigma_{xy} = 0 \, \text{MPa} \). Fig. 7 shows the stress of the dislocations involved in the plastic relaxation only, that is, excluding the stress of the hydride. The DDP results are compared with the stresses based on the experiments by Barrow et al. (2013a). As in the rest of this study, the stresses were not taken directly from the experiments, since the values are unavailable, but were rather calculated from the reported lattice misfit.

The ordered (Section 3.1) and DDP (Section 3.2) ways of relaxing the hydride stress are very different in nature. The two cases are schematically compared in Fig. 8 for the \( \sigma_{yy} \) component of a \( \gamma \) hydride. In the ordered case, a value of \( N_{disl} \) of the order of 20 is enough to nearly completely offset the stress of the hydride. In the DDP case, \( N_{disl} \) is of the order of 200 and the shielding is only approximately 50% of the hydride stress. In both cases the dislocations tend to generate a stress field that is equal and opposite to the interfacial stress. The total stress, which is what one has to consider both when analysing the conditions for hydride fracture and for calculating the interstitial concentration profile, is much lower than in the purely elastic case. By comparing the

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**Table 4**

Summary of the numerical results from the simulations on the \( \gamma \) hydride as a function of the input parameter \( \rho_{src} \) for Zr and Zry-4. Every entry is the mean over 20 simulations \( \pm \) one standard deviation.

<table>
<thead>
<tr>
<th>( \rho_{src} ) [( \mu \text{m}^{-2} )]</th>
<th>50</th>
<th>100</th>
<th>150</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho_{disl} ) [( \times 10^{14} ) m(^{-2} )]</td>
<td>0.30 ± 0.04</td>
<td>0.44 ± 0.05</td>
<td>0.55 ± 0.06</td>
<td>Zr</td>
</tr>
<tr>
<td>( \mathcal{A}_1 ) [( \mu \text{m}^{-2} )]</td>
<td>63</td>
<td>99</td>
<td>132</td>
<td>Zr</td>
</tr>
<tr>
<td>( \frac{\langle \sigma_{xx} + \sigma_{yy} \rangle_{K_1} }}{\langle \sigma_{xx} + \sigma_{yy} \rangle_{K_1} }} ) [( \mu \text{m}^{-2} )]</td>
<td>880 ± 210</td>
<td>680 ± 220</td>
<td>570 ± 230</td>
<td>Zr</td>
</tr>
<tr>
<td>( \frac{\langle \sigma_{xx} + \sigma_{yy} \rangle_{K_1} }}{\langle \sigma_{xx} + \sigma_{yy} \rangle_{K_1} }} ) [( \mu \text{m}^{-2} )]</td>
<td>1080 ± 200</td>
<td>950 ± 160</td>
<td>790 ± 150</td>
<td>Zr</td>
</tr>
<tr>
<td>( \frac{\langle \sigma_{xx} + \sigma_{yy} \rangle_{K_1} }}{\langle \sigma_{xx} + \sigma_{yy} \rangle_{K_1} }} ) [( \mu \text{m}^{-2} )]</td>
<td>1.34 ± 0.09</td>
<td>1.25 ± 0.09</td>
<td>1.21 ± 0.09</td>
<td>Zr</td>
</tr>
<tr>
<td>( \frac{\langle \sigma_{xx} + \sigma_{yy} \rangle_{K_1} }}{\langle \sigma_{xx} + \sigma_{yy} \rangle_{K_1} }} ) [( \mu \text{m}^{-2} )]</td>
<td>1.43 ± 0.09</td>
<td>1.37 ± 0.07</td>
<td>1.30 ± 0.06</td>
<td>Zry-4</td>
</tr>
<tr>
<td>( \frac{\langle \sigma_{xx} + \sigma_{yy} \rangle_{K_1} }}{\langle \sigma_{xx} + \sigma_{yy} \rangle_{K_1} }} ) [( \mu \text{m}^{-2} )]</td>
<td>140 ± 40</td>
<td>80 ± 30</td>
<td>40 ± 30</td>
<td>Zr</td>
</tr>
<tr>
<td>( \frac{\langle \sigma_{xx} + \sigma_{yy} \rangle_{K_1} }}{\langle \sigma_{xx} + \sigma_{yy} \rangle_{K_1} }} ) [( \mu \text{m}^{-2} )]</td>
<td>210 ± 30</td>
<td>160 ± 40</td>
<td>100 ± 30</td>
<td>Zry-4</td>
</tr>
<tr>
<td>( \frac{\langle \sigma_{xx} + \sigma_{yy} \rangle_{K_1} }}{\langle \sigma_{xx} + \sigma_{yy} \rangle_{K_1} }} ) [( \mu \text{m}^{-2} )]</td>
<td>1.05 ± 0.01</td>
<td>1.03 ± 0.01</td>
<td>1.01 ± 0.01</td>
<td>Zr</td>
</tr>
<tr>
<td>( \frac{\langle \sigma_{xx} + \sigma_{yy} \rangle_{K_1} }}{\langle \sigma_{xx} + \sigma_{yy} \rangle_{K_1} }} ) [( \mu \text{m}^{-2} )]</td>
<td>1.07 ± 0.01</td>
<td>1.05 ± 0.01</td>
<td>1.03 ± 0.01</td>
<td>Zry-4</td>
</tr>
</tbody>
</table>
Fig. 7. (a) The $\sigma_{xx}$ and (b) the $\sigma_{yy}$ stresses generated by the misfit dislocations of a $\delta$ hydride, organised in order to fit the experiments of Ref. Barrow et al. (2013a), are compared to the stresses averaged over 20 DDP simulations (Zry-4, $\rho_{src} = 50 \mu m^{-2}$) in (c) and (d). The horizontal axis is along $\langle 11\overline{2}0 \rangle$, the vertical axis is along $\langle 1\overline{1}00 \rangle$. The four fields are plotted in (e), for a quantitative comparison, on a line crossing the hydride along its major axis (the label exp. in the legend of (e) means that the stresses were calculated on the basis of experimental misfit from Ref. Barrow et al. (2013a)). Axes in $\mu m$.

Fig. 8. The stress in the material after the $\gamma$ hydride precipitation is the sum of the hydride stress and that of dislocations that the hydride causes to nucleate. In the top row, the plastic relaxation is modelled by DDP (average over 20 simulations with $\rho_{src} = 100 \mu m^{-2}$). In the bottom row, it is modelled by an ordered array of misfit dislocations. In both cases the hydride stress is shielded, although the ordered array is more effective. The colour bar is the same in all the images except for the DDP inset, where the extrema are halved to show that the stress is approximately half of that in the ordered array case beneath it.

stresses of arrays associated with different misfits and the DDP results, we estimate that after the plastic relaxation for the $\gamma$ phase $\varepsilon_{(1100)} \sim 1.5$–$2\%$, higher than the experimental value of $0.5\%$ (Barrow et al., 2013a). For the $\delta$ phase, the remaining compression inside the hydride is compatible with a misfit after plastic relaxation of $\varepsilon_{(11\overline{2}0)} \sim 3.1\%$, in good agreement with the experiments, and of $\varepsilon_{(1100)} \sim 2.7\%$, higher than the measured value of $0.5\%$ (Barrow et al., 2013a).
If the hydride is precipitated and dissolved multiple times (the hydride length is in red), dislocations are nucleated and annihilated accordingly. This leads to the oscillating trend of the dislocation density \( \rho_{\text{disl}} \). Both the mean value and the amplitude of the oscillations are much larger for the \( \delta \) phase than for the \( \gamma \) phase. In the case of the \( \gamma \) phase, they are about twice as large if the hydride grows in pure Zr as opposed to Zry-4. The mean value tends to saturate (\( \gamma \)), or to only show a weak increase (\( \delta \)) after about five cycles. Colour-coded bands corresponding to \( \pm 1 \) standard deviation are added to the mean values calculated on 20 simulations.

After the hydride dissolution, there remains a residual hydrostatic tension caused by the dislocations generated during the precipitation. \( (\sigma_{xx} + \sigma_{yy})_{\text{res}} \) is its spatial average over the area of the dissolved hydride, further averaged over 20 simulations. This quantity increases during the first 10 cycles by approximately 45% in each of the three cases. The values for the \( \delta \) hydride are more than twice as large as those for the \( \gamma \) hydride, which in turn are about 70% higher if the \( \gamma \) hydride precipitates in pure Zr as opposed to Zry-4. The corresponding contour plots of \( (\sigma_{xx} + \sigma_{yy}) \) are included for the 1st and 10th cycles.

3.3. Thermal ratchetting

\( \rho_{\text{disl}} \) rapidly increases during the first precipitation cycle, and then further increases especially during the first few cycles. After the first cycle, \( \rho_{\text{disl}} \) is about 70%–80% of the values reached after the 10th cycle. It is evident there is a strong influence of both the type of the hydride phase and of the Zr matrix phase. The precipitation of the \( \delta \) hydride in Zry-4 leads to a dislocation density that is about 7 times larger than that induced by the \( \gamma \) hydride in the same parent phase. If \( \gamma \) precipitates in pure Zr instead, the lower \( \tau_{\text{src}} \) causes a roughly 2.4-fold increase in \( \rho_{\text{disl}} \). Compared to precipitation in Zry-4, it is worth emphasising that the \( \rho_{\text{disl}} \) of the \( \gamma \) hydride in Zr oscillates between 0.2–0.4 \( \times 10^{14} \) m\(^{-2}\), i.e. about a mean value that matches the one measured as the increase in \( \rho_{\text{disl}} \) after the precipitation of \( \gamma \) hydrides in Zr (Shiman et al., 2019).

A residual hydrostatic stress \( (\sigma_{xx} + \sigma_{yy})_{\text{res}} \) of the order of hundreds of MPa, calculated as the average over the dissolved hydride area and over the 20 simulations, remains after each dissolution event. Its value upon each cycle is plotted in Fig. 10 for the three cases considered, of \( \delta \) in Zr, \( \delta \) in Zry-4 and \( \gamma \) in Zr and Zry-4. Similar conclusions as in the case of \( \rho_{\text{disl}} \) can be drawn: the residual hydrostatic stress is on average approximately 3.8 times higher for the \( \delta \) phase than for the \( \gamma \) phase in Zry-4, and approximately 1.7 times higher if the \( \gamma \) phase precipitates in pure Zr as opposed to Zry-4. The saturation of the values is fully achieved for the \( \gamma \) phase after 5 cycles, whereas the \( \delta \) phase shows a continual but declining increase throughout the 10 cycles.
Table 5
Summary of the results at the 10th cycle; mean values ± one standard deviation. \( \rho_{\text{disl}} \) is given after the 10th precipitation (left of the | symbol) and after the 10th dissolution (i.e. the leftover dislocation density, right of the | symbol). The dislocation activity and the related residual stress are more than twice as high for the \( \delta \) phase than for the \( \gamma \) phase. Given the same hydride phase (\( \gamma \)), they are about twice as high if the hydride precipitates in Zr than if it precipitates in Zry-4. Both global and local \( c^H \) are calculated at 250 °C.

<table>
<thead>
<tr>
<th></th>
<th>( \rho_{\text{disl}} \times 10^{14} \text{ m}^{-2} )</th>
<th>( (\sigma_{xx} + \sigma_{yy})_{\text{res}} ) [MPa]</th>
<th>( \frac{c^H}{c^H_0} ) [-]</th>
<th>( \frac{c^H_{\text{max}}}{c^H_0} ) [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \delta ) phase in Zry-4</td>
<td>1.3</td>
<td>0.8</td>
<td>450 ± 80</td>
<td>1.09 ± 0.02</td>
</tr>
<tr>
<td>( \gamma ) phase in Zry-4</td>
<td>0.2</td>
<td>0.1</td>
<td>120 ± 40</td>
<td>1.02 ± 0.01</td>
</tr>
<tr>
<td>( \gamma ) phase in Zr</td>
<td>0.4</td>
<td>0.3</td>
<td>210 ± 40</td>
<td>1.04 ± 0.01</td>
</tr>
</tbody>
</table>

Fig. 11. The equilibrium H concentration was calculated by inserting into Eq. (4) or Eq. (5) the stresses following from the theoretical transformation strains (Carpenter et al., 1973) for the different phases and crystalline orientations (except for inside the hydride, where \( c^H \) is dictated by the stoichiometry).

(a) A schematic of the three different 2D sections; in (b), (d), (f) \( c^H \) for the \( \gamma \) phase; in (c), (e), (g) \( c^H \) for the \( \delta \) phase.

The similar trends in \( \rho_{\text{disl}} \) and \( (\sigma_{xx} + \sigma_{yy})_{\text{res}} \), when comparing the three different cases, show that a sizeable fraction of the dislocations that are generated are effective in promoting the ratchetting effect. The numerical values referring to the last cycle of Fig. 9 and to the last data point of Fig. 10 are presented in Table 5. In Ref. Patel et al. (2017), similar results were obtained for the case of the \( \gamma \) hydride (the only one therein analysed). The reported values of \( \rho_{\text{disl}} \) and of residual stress are lower than what we report here, possibly due to the smaller size of the hydride.

3.4. The hydrogen around the hydrides

The spatial profile of H is given by Eqs. (4) and (5). It is the hydrostatic stress in particular that is important to drive the H diffusion. To begin, we assume that the hydrides are small enough that no significant plasticity has ensued from their precipitation and that the theoretical purely elastic transformation strains can be used. DDP shows that this is the case for only very short and
Fig. A.1. Stress field of a $\gamma$ (a, c, e, g) and $\delta$ hydride (b, d, f, h) in the basal plane. As $\epsilon_{(110)} \gg \epsilon_{(11\bar{2})}$, the $\gamma$ phase shows a tensile hydrostatic stress at its tips. This is not observed in the $\delta$ phase where $\epsilon_{(11\bar{2})} = \epsilon_{(110)}$. The annotated values are inside the hydride and at about 10 nm from the interface.

Fig. 5. This is in agreement with DDD, where plastic relaxation was observed around a $\delta$ hydride of dimensions $375 \times 91 \times 37.5$ nm (Tummala et al., 2018). In Fig. 11, $c^H$ is plotted for a $\gamma$ and a $\delta$ hydride of length 500 nm and thickness 50 nm.

In the specific case that the two orthogonal transformation strains are in the basal plane and equal in magnitude, $\epsilon_{(11\bar{2})} = \epsilon_{(110)}$, i.e. isotropic volume expansion and H diffusion, then there is no H enrichment around the hydride; this is the case for the $\delta$ hydride (Fig. 11(e)). Another interesting example is the $(1\bar{1}00) - (0001)$ section of the $\gamma$ hydride. Also in this case the hydrostatic stress is nearly zero because $\epsilon_{(1\bar{1}00)} \approx \epsilon_{(0001)}$, but the anisotropy of the H diffusion leads to H accumulation in the $(\bar{1}1\bar{2}0)$ direction, and H
depletion in the ⟨0001⟩ direction (Fig. 11(f)). Overall, the similarities in the $c^H$ fields of the two phases, although with very different theoretical transformation strains, may explain why the morphology of the two phases is quite similar. Both present H enrichment at the tips in the ⟨11̄20⟩ direction and depletion in the ⟨0001⟩ direction, which helps to drive the growth of elongated hydrides. They differ significantly in the basal plane, providing grounds for expecting more of a needle shape for $\gamma$ and penny shape for $\delta$, as proposed e.g. by Motta et al. (2019), although, to the authors’ knowledge, clear experimental evidence of the penny shape for $\delta$ is not published in literature.

The H enrichment near the tips of the $\gamma$ hydride can promote the nucleation of “daughter” hydrides in its proximity in the basal plane, which, significantly, is not predicted for the $\delta$ hydride. Conversely, the stacking on different basal planes ought to be expected in both cases, as indeed is experimentally observed (Bradbrook et al., 1972; Perovic et al., 1983; Long et al., 2017). The actual process of growth and secondary nucleation events is more complicated, and also depends on e.g. the availability of nucleation sites at pre-existing features such as dislocation tangles or SPPs or grain boundaries, but this analysis may nonetheless open up avenues for an experimental validation.

We propose here, as already suggested by Patel et al. (2017), that there is a link between the residual hydrostatic tension upon repeated precipitation cycles and the ratchetting effect. Eq. (4) states that a hydrostatic stress of 1 GPa leads to a relative increase in $c^H$ of about 40% at 25 °C and 20% at 250 °C. The residual tension (Fig. 10) is associated with an increase in the average $c^H$ that is noticeable but moderate and below 10%. However, a much larger increase was observed in the local $c^H_{\text{max}}$, which for the $\delta$ phase is more than twice as high as $c^H_{\text{max}}$. Also, this increase is predicted to be 45% larger in the $\delta$ than it is in the $\gamma$ phase, hence showing that the $\delta$ phase should exhibit a stronger ratchetting effect. Also, as the initial hydride seed must be nucleated at the atomic scale, the local H concentration is expected to be more important for assessing the likelihood of a precipitation event. The values for the different hydride and parent phases are reported in Table 5. As also noted by Patel et al. (2017), it should be emphasised that it is not merely the presence of dislocations that may promote the ratchetting effect, but rather their generation in response to a misfitting particle. It is this fact that leads to a strong tensile field to offset the stronger compression inside the hydride that, once the compression vanishes when the hydride dissolves, drives the H accumulation.

4. Conclusions

This study investigated the stress field generated by the volume expansion that accompanies the Zr hydride precipitation in Zr and Zr-alloys. The main findings are summarised below.

1. By organising dislocations (∼20) at the hydride interface in a manner consistent with the observed “butterfly” dislocations around $\gamma$ hydrids, the theoretical stress-free transformation strains are thereby reduced to the experimental values available in the literature.

2. A DDP model of a Zr hydride, including its interfacial stress, was developed. The stress-free transformation strain was used to drive the plastic relaxation around the hydride. The resulting dislocation density was found to depend on the square of the length of the hydride, and its numerical value was very close to the experimental measurements available in the literature.

3. The interfacial stress of the hydride was partially shielded by the dislocations generated by the volume misfit of the hydride in the DDP model. An estimate was obtained for the misfit after the plastic relaxation in the basal plane, which may be used for multi-scale modelling that implicitly includes the plastic relaxation. For $\gamma$, $\varepsilon_{(1120)} = 0.6\%$ and $\varepsilon_{(1000)} = 1.5\%–2\%$. For $\delta$, $\varepsilon_{(1120)} = 3.1\%$ and $\varepsilon_{(1100)} = 2.7\%$.
4. If averaged over a radius of 50 nm, a localised hydrostatic elastic stress of 1.4 GPa is predicted to be present at the tips of the $\gamma$ hydride for the geometry considered. This stress is greatly attenuated by the plastic relaxation. It becomes negligible in the case of the ordered plastic relaxation, and is in the range 0.6–1.0 GPa in the DDP case. This has direct consequences in diminishing the H accumulation around the hydrides, e.g. at room $T$ the H enhancement would decrease from 60% to approximately zero or 30% in the ordered and DDP cases respectively.

5. The model gives qualitatively similar results in the cases of pure Zr and Zircaloy-4, but in the latter case the dislocation density is approximately half as large, and the residual stresses are significantly higher.

6. The DDP simulations predict that $\delta$ hydrides should be more prone to thermal ratchetting than $\gamma$ hydrides, and pure Zr more prone than Zr-alloys. The hydrostatic stress following the plastic relaxation in Zircaloy-4 leads to a H concentration that is 1.55 ($\gamma$) to 2.25 ($\delta$) times higher than it is far from the dissolved hydride. This H is primarily segregated to the region where the hydride was located.

CRediT authorship contribution statement

Luca Reali: Conceptualization, Methodology, Software, Formal analysis, Investigation, Writing – original draft, Visualization.
Daniel S. Balint: Conceptualization, Methodology, Writing – review & editing, Supervision.
Mark R. Wenman: Conceptualization, Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that support the findings of this study are available on request from the corresponding author (L.R.). The data are not publicly available due to them containing information that is commercially sensitive or not in the interest of commercial/national security.

Acknowledgements

This work was supported through a studentship in the Centre for Doctoral Training on Theory and Simulation of Materials at Imperial College London funded by the EPSRC, United Kingdom (EP/L015579/1) and through an industrial collaboration with Rolls-Royce plc. L.R. acknowledges the invaluable support received by Adrian P. Sutton through many useful discussions and comments on this study. Michael Rogers is kindly acknowledged for comments and support.

Appendix A. $\gamma$ And $\delta$ hydrides: stress fields

Fig. A.1 shows the stress field of a hydride of length 500 nm and thickness 100 nm in the basal plane. The first column refers to the $\gamma$ phase, the second column to the $\delta$ phase. The values of the misfit according to Carpenter (1973) are used. The aspect ratio of 5:1, higher than the 10 to 20:1 that is experimentally observed, is selected for clarity. 100 dislocations are used for the discrete elliptic representation of both the horizontal and the vertical misfit.

In the $\gamma$ phase, the high $\sigma_{yy}$ stress that is generated near the hydride tips by the 5.6% misfit along the $y$, or $\langle 1\bar{1}00 \rangle$ direction is not counterbalanced by the weaker field originated by the 0.55% misfit in the $x$, or $\langle 11\bar{2}0 \rangle$ direction. This leads to a hydrostatic stress that is tensile in nature at the tips, and to a diffuse compression field above and below the hydride (Fig. A.1(g)). These stresses have a magnitude of the order of 1 GPa at a distance of about 50 nm from the interface, while the hydrostatic compression inside the hydride is about $-1.3$ GPa. $\sigma_{yy}$ is greater than 3 GPa very close to the tips.

The stresses in the case of the $\delta$ phase are of the same order of magnitude as those of the $\gamma$ phase. An important difference is that $\sigma_{xx}$ was much smaller than $\sigma_{yy}$ outside of the $\gamma$ hydride. On the other hand, $\sigma_{xx}$ and $\sigma_{yy}$ outside of the $\delta$ hydride are exactly equal and opposite. This leads to the vanishing hydrostatic stress outside of the hydride (Fig. A.1(h)). The $\delta$ field is mathematically equivalent to that of a 2D Eshelby ellipsoidal inclusion.

It is interesting to point out that, at this length scale, and more specifically at distances of the order of micrometres from a micrometre-sized hydride, the stress components are of the order of hundreds of MPa. This implies first that it is not unreasonable to expect the onset of plasticity, and second that both the length scale and stress levels are appropriate for DDP.
Table B.1

<table>
<thead>
<tr>
<th>$\rho_{\text{src}}$ [$\mu m^{-2}$]</th>
<th>$Zr$ (t$_{\text{src}}$ = 100 MPa)</th>
<th>Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>$\rho_{\text{ext}}$ [10$^{-7}$m$^{-2}$]</td>
<td>0.24 ± 0.03</td>
<td>0.36 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>0.30 ± 0.04</td>
<td>0.47 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>0.30 ± 0.04</td>
<td>0.44 ± 0.05</td>
</tr>
<tr>
<td>($\sigma_{x} + \sigma_{y}$)$_{x}$</td>
<td>1020 ± 210</td>
<td>690 ± 190</td>
</tr>
<tr>
<td>[MPa]</td>
<td>900 ± 240</td>
<td>650 ± 190</td>
</tr>
<tr>
<td></td>
<td>880 ± 210</td>
<td>680 ± 220</td>
</tr>
<tr>
<td>($c^H x H_{1}P_{x}$)</td>
<td>1.40 ± 0.10</td>
<td>1.26 ± 0.08</td>
</tr>
<tr>
<td>[-]</td>
<td>1.35 ± 0.11</td>
<td>1.24 ± 0.08</td>
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<tr>
<td></td>
<td>1.34 ± 0.09</td>
<td>1.25 ± 0.09</td>
</tr>
<tr>
<td>($\sigma_{x} + \sigma_{y}$)$_{y}$</td>
<td>150 ± 30</td>
<td>70 ± 30</td>
</tr>
<tr>
<td>[MPa]</td>
<td>150 ± 40</td>
<td>70 ± 40</td>
</tr>
<tr>
<td></td>
<td>140 ± 40</td>
<td>80 ± 30</td>
</tr>
<tr>
<td>($c^H x H_{1}P_{y}$)</td>
<td>1.05 ± 0.01</td>
<td>1.02 ± 0.01</td>
</tr>
<tr>
<td>[-]</td>
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<td>1.02 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>1.05 ± 0.01</td>
<td>1.03 ± 0.01</td>
</tr>
</tbody>
</table>

Appendix B. The effect of different growth modes

The time scale at which the precipitation occurs may significantly influence the plastic relaxation. If the growth was quick with respect to the motion of the dislocations, the dislocations would respond only to the larger and farther-reaching stress induced by the fully grown hydride. If, conversely, the growth was slow compared with the typical dislocation flight time, the dislocations could have the time needed to shield the hydride field as it grows. This motivated the choice of the three growth modes (M1, M2, M3) detailed in Section 2.1. 60 simulations were run for each growth mode, in three batches of 20 with different values of $\rho_{\text{src}}$.

Analysing the results from the simulations, we conclude that the growth mode does not have a significant impact on the results. The variations are well within one standard deviation and there is not a pattern emerging from the analysis (see Table B.1).

The output of the simulations, e.g. the hydride tip stresses, can be tracked over time to show that, although the growth mode obviously affects how the final value is reached, it does not strongly affect the final value itself. This is displayed in Fig. B.1. Also, by comparing $\rho_{\text{ext}}$ we reach the same conclusion. The dislocation density after the $\gamma$ hydride was grown linearly (M2) was found to be (0.47 ± 0.06) · 10$^{11}$ and (0.59 ± 0.07) · 10$^{11}$ m$^{-2}$ for $\rho_{\text{src}}$ = 100 and $\rho_{\text{src}}$ = 150 $\mu m^{-2}$ respectively. These results differ by about 7% from those in Table 4, the difference being well within one standard deviation.

References


