

MULTISCALE MODELLING OF DELAYED HYDRIDE CRACKING

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A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE DEGREE OF
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at Imperial College London. This dissertation has not been submitted in whole or in part for another degree at this university or any other institution.

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Abstract

A mechanistic model of delayed hydride cracking (DHC) is crucial to the nuclear industry as a predictive tool for understanding the structural failure of zirconium alloy components that are used to clad fuel pins in water-cooled reactors. Such a model of DHC failure must be both physically accurate and computationally efficient so that it can inform and guide nuclear safety assessments. However, this endeavour has so far proved to be an unsurmountable challenge because of the seemingly intractable multiscale complexity of the DHC phenomenon, which is a manifestation of hydrogen embrittlement that involves the interplay and repetition of three constituent processes: atomic scale diffusion, microscale precipitation and continuum scale fracture. This investigation aims to blueprint a novel multiscale modelling strategy to simulate the early stages of DHC initiation: stress-driven hydrogen diffusion-controlled precipitation of hydrides near loaded flaws in polycrystalline zirconium.

Following a careful review of the experimental observations in the literature as well as the standard modelling techniques that are commonplace in nuclear fuel performance codes in the first part of this dissertation, the second and third parts introduce a hybrid multiscale modelling strategy that integrates concepts across a spectrum of length and time scales into one self-consistent framework whilst accounting for the complicated nuances of the zirconium-hydrogen system. In particular, this strategy dissects the DHC mechanism into three interconnected modules: (i) stress analysis, which performs defect micromechanics in hexagonal close-packed zirconium through the application of the mathematical theory of planar elasticity to anisotropic continua; (ii) stress-diffusion analysis, which bridges the classical long-range elastochemical transport with the quantum structure of the hydrogen interstitialcy in the trigonal environment of the tetrahedral site; and (iii) diffusion-precipitation analysis, which translates empirical findings into an optimised algorithm that emulates the thermodynamically favourable spatial assembly of the microscopic hydride needles into macroscopic hydride colonies at prospective nucleation sites. Each module explores several unique mechanistic modelling considerations, including a

multipolar expansion of the forces exerted by hydrogen interstitials, a distributed dislocation representation of the hydride platelets, and a stoichiometric hydrogen mass conservation criterion that dictates the lifecycle of hydrides.

The investigation proceeds to amalgamate the stress, stress-diffusion and diffusion-precipitation analyses into a unified theory of the mesoscale mechanics that underpin the early stages of DHC failure and a comprehensive simulation of the flaw-tip hydrogen profiles and hydride microstructures. The multiscale theory and simulation are realised within a bespoke software which incorporates computer vision to generate mesoscale micrographs that depict the geometries, morphologies and contours of key metallographic entities: cracks and notches, grains, intergranular and intra-granular nucleation sites as well as regions of hydrogen enhancement and complex networks of hydride features. Computer vision mediates the balance between simulation accuracy and simulation efficiency, which is completely novel in the context of DHC research as a paradigm at the intersection of computational science and computer science. Preliminary tests show that the simulation environment of the hybrid model is significantly more accurate and efficient in comparison with the traditional finite element and phase field methodologies. Due to this unprecedented simulation accuracy-efficiency balance, realistic flaw-tip hydrogen profiles and hydride microstructures can be simulated within seconds, which naturally facilitates statistical averaging over ensembles. Such statistical capabilities are highly relevant to nuclear safety assessments and, therefore, a systematic breakdown of the model formulation is presented in the style of a code specification manual so that the bespoke software can be readily adapted within an industrial setting.

As the main contribution to DHC research, the proposed multiscale model comprises a state-of-the-art microstructural solver whose unrivalled versatility is demonstrated by showcasing a series of simulated micrographs that are parametrised by flaw acuity, grain size, texture, alloy composition, and histories of thermomechanical cycles. Direct comparisons with experimental micrographs indicate good quantitative agreement and provide some justification to the known qualitative trends. Furthermore, the overall hybrid methodology is proven to scale linearly with the number of hydrides, which is computationally advantageous in its own right because it allows the bespoke software to be extended without compromising its speed. Several possible extensions are outlined which would improve the phenomenological accuracy of the multiscale model whilst retaining its efficiency. In its current form, however, this hybrid multiscale model of the early stages of DHC goes far beyond existing methodologies in terms of simulation scope.

Outline

Usage Guide

In light of the unique linguistic challenges that emerge during the dissemination of such a multidisciplinary endeavour, it is important to emphasise again that this investigation blends together ideas from mathematical physics, computational materials science and nuclear engineering. However, the writing style aims for self-consistency by adhering to the perspective of a mathematical physicist and hence it naturally caters to this audience; the writing contains some instances of slightly adjusted definitions to the terminology that is standard to computational materials science and nuclear engineering. Many of noteworthy deviations to these definitions are listed into the glossary whereas the text alludes to others.

Upon introspection of this nuanced writing style that could present difficulties to the anticipated readers in nuclear engineering community for whom this work would perhaps be most relevant, each chapter is written in a more or less of standalone format with a self-contained chapter introduction. Accordingly, it is sufficient to begin with Part I and then go directly to Part III whilst treating the intermediate Part II as a technical appendix. But it must be clarified that Part II contains the breakthrough mathematical details that enable the desires of Part I to be realised in Part III.

Certain sections in Part II are expressed in a highly pedagogical manner in order to ensure that the mathematical concepts, notations and conventions are clearly established. Mathematical derivations are also provided herein in rigorous detail because they constitute the original insight that underpins this investigation. Acknowledging that Part II is essential to this work but that it may somewhat be beyond the typical interests of the broader DHC research community, these intermediate chapters can nonetheless provide a smooth transition from Part I to Part III for the purpose of completeness. The mathematical literacy required for delving into Part II involves a core understanding of the following topics: linear algebra, index notation, tensor operations, integral transformations, complex analysis, group theory, partial derivatives, singular integral equations, differential operators, conformal mapping, series expansions, and limit calculus.

This investigation is structured into three parts, each of which is further subdivided into three chapters as follows:

- Part I: Delayed Hydride Cracking. This expositional part dissects the failure mechanism and outlines the modelling blueprint:
 - ▶ **Chapter 1. Introduction.** This opening chapter provides the background and context in terms of nuclear safety economics.
 - ▶ **Chapter 2: Literature Review.** This reference chapter organises experimental findings about the zirconium-hydrogen system.
 - ▶ **Chapter 3. Modelling Strategy.** This computational methodology chapter proposes a hybrid multiscale modelling framework.
- Part II: Mechanistic Modelling. This detailed part rigorously formalises the constituent modules that underpin the hybrid multiscale model:
 - ▶ **Chapter 4. Stress Analysis.** This handbook chapter contains unique derivations of the elastic fields around defects in hexagonal zirconium.
 - ▶ **Chapter 5. Stress-Diffusion Analysis** This setup chapter extends the thermodynamical theory of the elastochemical transport of hydrogen interstitials in anisotropic polycrystalline zirconium.
 - ▶ **Chapter 6. Diffusion-Precipitation Analysis** This technical chapter provides new algorithmic insight into the accurate and efficient treatment of hydride nucleation and growth.
- Part III: Multiscale Theory and Simulation. This framework part unifies the three modular analyses in a self-consistent mesoscale model:
 - ▶ **Chapter 7. Model Formulation.** This bespoke software development chapter delves into the code specification that realises and tests the hybrid multiscale model.
 - ▶ **Chapter 8. Simulated Micrographs.** This results chapter showcases the main output of the hybrid multiscale model: flaw-tip hydrogen profiles and hydride microstructures that can be directly comparable to experimental images.
 - ▶ **Chapter 9. Conclusions.** This final chapter summarises this investigation and suggests avenues of future work.

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Preface

This dissertation describes the work undertaken between October 2014 and October 2017 at Imperial College London under the supervision of Dr Daniel S. Balint (Mechanics of Materials Research Division, Department of Mechanical Engineering), Dr Mark R. Wenman (Centre for Nuclear Engineering, Department of Materials) and Prof. Adrian P. Sutton FRS (Condensed Matter Theory Group, Department of Physics). This research has been supported by the Engineering and Physical Sciences Research Council (EPSRC) through a studentship within the Centre for Doctoral Training in Theory and Simulation of Materials under the grant EP/G036888/1 and an industrial collaboration with Rolls-Royce plc.

Declaration

This dissertation is entirely the result of my own work except where explicitly stated otherwise. Effort has been made to ensure that all references and collaborations are properly acknowledged. No part of this thesis has been submitted to this institution or any other institution for the award of another degree.

Awards

This research project was awarded several accolades, most notably: (i) the Materials Design Advanced Graduate Research Prize; (ii) the Winton Capital Poster Prize at the Physics Postgraduate Research Symposium for the “work on understanding hydride crack formation in relation to the degradation of nuclear fuel pins”; and (iii) the Sutton Prize for the best overall “performance in the Theory and Simulation of Materials course”.

Publications

The work presented in this dissertation draws upon the following peer-reviewed journal publications, conference proceedings and assessed internal

reports:

- [1] M. Patel, S. El Chamaa, M.R. Wenman and C.M. Davies (2018)
 “Multiscale Stress-Diffusion Analysis of Notch-Tip Hydrogen Profiles in Zircaloy-4”
 Proceedings of the ASME 2018 Pressure Vessels and Piping Conference: Materials and Fabrication **6B** V06BT06A013
- [2] S. El Chamaa, M. Patel, C.M. Davies, M.R. Wenman (2018)
 “The Effect of Grain Boundaries and Second-Phase Particles on Hydride Precipitation in Zirconium Alloys”
 Cambridge University Press: Materials Research Advances **3** 1749–1754
- [3] M. Patel, S. Waheed, M.R. Wenman, A.P. Sutton and D.S. Balint (2017)
 “Discrete Dislocation Plasticity Modeling of Hydrides in Zirconium under Thermal Cycling”
 Cambridge University Press: Materials Research Society Advances **2** 3353–3358
- [4] M. Patel and M.A. Stopher (2017)
 “Hydrogen Effects in Non-Ferrous Alloys: Discussion”
 Philosophical Transactions of the Royal Society A **375** 20170030
- [5] E. Luke Simpson and M. Patel (2017)
 “Hydrogen in Steels: Discussion”
 Philosophical Transactions of the Royal Society A **375** 20170027
- [6] R. Nazarov, J.S. Majevalia, M. Patel, M.R. Wenman, D.S. Balint, J. Neugebauer and A.P. Sutton (2016)
 “First-Principles Calculation of the Elastic Dipole Tensor: Application to Hydrogen in α -Zirconium”
 Physical Review B **94** 241112(R)
- [7] M. Patel (2014)
 “Mathematics of Diffusion in Fractured Continua”
 MSc Thesis Imperial College London

There are three more publications in the preparation and submission stages; these are mentioned towards the end of the thesis.

Conferences

The work presented in this dissertation has been disseminated at the following conferences, workshops and meetings:

- [1] M. Patel, M. R. Wenman, D.S. Balint and A. P. Sutton (2017)
“Multiscale Modelling of Delayed Hydride Cracking”
Rolls-Royce University Technology Centre Annual Review
Rolls-Royce plc, Derby
- [2] M. Patel, D. S. Balint, M. R. Wenman and A. P. Sutton (2017)
“Multiscale Modelling of Delayed Hydride Cracking”
International Conference on Materials Modelling 2017 (ICMM 2017)
Rome, Italy
- [3] M. Patel, D. S. Balint, M. R. Wenman and A. P. Sutton (2017)
“Multiscale Modelling of Delayed Hydride Cracking”
Materials Research Society Spring Exhibit 2017
Phoenix, Arizona, USA
- [4] M. Patel, D. S. Balint, M. R. Wenman and A. P. Sutton (2016)
“Multiscale Modelling of Delayed Hydride Cracking: Hydrogen and Hydrides”
The Nuclear Materials Conference 2016 (NuMat 2016)
Montpellier, France
- [5] M. Patel, D. S. Balint, M. R. Wenman and A. P. Sutton (2016)
“Multiscale Modelling of Delayed Hydride Cracking”
Rolls-Royce Nuclear University Technology Centre Annual Review
Rolls-Royce plc, Derby
- [6] M. Patel, D. S. Balint, M. R. Wenman and A. P. Sutton (2016)
“Multiscale Modelling of Delayed Hydride Cracking: Diffusion - Precipitation - Fracture Framework”
International Workshop on Mechanistic Behaviour of HCP Alloys
Pembroke College, University of Oxford
- [7] M. Patel, D. S. Balint, M. R. Wenman and A. P. Sutton (2015)
“Multiscale Modelling of Delayed Hydride Cracking: Diffusion - Precipitation - Fracture Framework”
Hydrogen Embrittlement in Steels (HEmS) Early Career Group
St. Anne’s College, University of Oxford
- [8] M. Patel, D. S. Balint, M. R. Wenman and A. P. Sutton (2015)
“Multiscale Modelling of Delayed Hydride Cracking”
University Nuclear Technology Forum 2015 (UNTF 2015)
Open University, Milton Keynes

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Nomenclature

A variety of mathematical structures and operations are used in this work and so it is useful to employ distinguishable notation for consistency.

Notation	Definition
Structure	
A, a, α	Scalar
$\mathbf{A}, \mathbf{a}, \boldsymbol{\alpha}$	Vector
$[A], [a], [\alpha]$	Tensor
$\mathfrak{A}, \mathfrak{a}$	Matrix
$\mathfrak{A}, \mathfrak{a}$	Mapping or transformation
$\hat{A}, \hat{a}, \hat{\alpha}$	Operator
$\mathbb{A}$	Set or domain or interval
$\mathcal{A}, \mathcal{a}$	Graph or network
$\mathscr{A}$	Group or ring or field
$\mathscr{A}$	Vector space
$\mathbf{A}$	Computational object
Maps	
$A(m)$	Function
$A(\cdot; m)$	Parametrisation
$A[m]$	Functional

List of Symbols

The following is an ordered list of the most commonly-encountered symbols throughout the text and any local exceptions to this usage are indicated explicitly.

Symbol	Definition	Page
Latin		
A	The Airy function.....	104
$a, \mathbf{a}$	The hexagonal unit cell lattice parameter along the basal plane.....	30
$b, \mathbf{b}$	The Burgers vector of a dislocation....	127
$C, [C]$	The elastic stiffness tensor.....	30
$c, \mathbf{c}$	The hexagonal unit cell lattice parameter along the basal pole <i>or</i> the conserved or non-conserved thermodynamic field variable.....	29
E	The quantum mechanical total energy	66
F	The thermodynamic free energy <i>or</i> the universal quantum mechanical electron functional.....	66
$G, [G]$	The elastostatic Green tensor.....	108
$h, \mathbf{h}$	The Cartesian vector in a hexagonal crystal.....	104
H	The quantum mechanical Hamiltonian operator.....	66
i	The imaginary unit.....	104
l	The physical length of a microstructural feature.....	24
J	The concentration flux vector.....	88
$k, \mathbf{k}$	The reciprocal space vector.....	104
K	The stress intensity factor.....	58
N	The discrete count number.....	194
O	The quantum mechanical operator....	66
p	The hydrogen pick-up fraction.....	40
P	The pressure.....	12
$S, [S]$	The elastic compliance tensor.....	30
T	The temperature.....	12
t	The time variable in the stress-diffusion analysis.....	168

$u, \mathbf{u}$	The displacement vector field	104
U	The elastic strain energy	194
W	The elastic stress-strain work	104
$x, \mathbf{x}$	The position vector	104
Y	The Young's modulus	30
z	The complex variable	104

Greek

$\varepsilon, [\varepsilon]$	The strain tensor field	104
κ	The stoichiometric coefficient	194
μ	The shear modulus	30
ν	The Poisson ratio	30
τ	The time variable in the diffusion-precipitation analysis	218
$\sigma, [\sigma]$	The stress tensor field	104
Σ	The total system stress	4

Chemical Elements

Ba	Barium	4
Be	Beryllium	4
D	Deuterium	24
Fe	Iron	4
H	Hydrogen	4
Kr	Krypton	4
Mg	Magnesium	4
Ni	Nickel	4
Nb	Niobium	4
O	Oxygen	4
Pl	Polonium	4
Sn	Tin	4
T	Tritium	24
Th	Thorium	4
U	Uranium	4

Zr	Zirconium	4
Physical Constants		
q_e	The electron charge	66
k_B	The Boltzmann constant	168

List of Abbreviations

The following is a list of commonly-used abbreviations, acronyms, initialisms and short-hands which are introduced for convenience, especially to clarify the physical meanings of symbols in equations through their subscripts and superscripts; any local deviation is stated explicitly.

Abbreviation	Definition	Page
Phenomenology		
CHC	Corrosion Hydrogen Cracking	24
BCS	Bilby-Cottrell-Swinden	104
DB	Dugdale-Barenblatt	104
DHC	Delayed Hydride Cracking	4
HED	Hydrogen-Enhanced Decohesion	24
HELP	Hydrogen-Enhanced Localised Plasticity	24
HID	Hydrogen-Induced Decohesion	24
HIPT	Hydrogen-Induced Phase Transformation	24
Experimental Methods		
SEM	Scanning Electron Microscopy	24
TEM	Transmission Electron Microscopy	24
Modelling Methods		
DFT	Density Functional Theory	71
FEM	Finite Element Method	88
PFM	Phase Field Method	80
MD	Molecular Dynamics	4
EP	Empirical Potentials	4
TB	Tight Binding	4

LDA	Local Density Approximation	71
CZ	Cohesive Zone	88
PZ	Process Zone	88
PAW	Projector Augmented Wave	71
GGA	Generalised Gradient Approximation	71
DD	Dislocation Dynamics	298
DDD	Discrete Dislocation Dynamics	298
DDP	Discrete Dislocation Plasticity	4
CP	Constitutive Plasticity	4
CPFE	Constitutive Plasticity	4
XFEM	Extended Finite Element Method	298
DEM	Discrete Element Method	4
CG	Course Grain	4
QMC	Quantum Monte Carlo	4
KMC	Kinetic Monte Carlo	4
Material Properties		
BCC	Body-Centred Cubic	24
FCC	Face-Centred Cubic	24
HCP	Hexagonal Close-Packed	4
FCT	Face-Centred Tetragonal	24
Homo	Homogeneous	104
Hetero	Heterogeneous	104
AC	Anisotropic Continuum	104
IC	Isotropic Continuum	104
TIC	Transversely Isotropic Continuum	104
Defects		
p	Point Interstitial	104
d, ed	Edge Dislocation	127
g, gb	Grain Boundary	134
spp	Second-Phase Particle	24
md	Mixed Dislocation	127

Nomenclature

sc	Slit Crack	139
sd	Screw Dislocation	127
vd	Volterra Dislocation	127
vn	V-Notch	139

Conventions

The following system of conventions are employed and all mathematical expressions adhere to these definitions unless stated otherwise.

Dimensionless Units

This investigation spans multiple scales of length and time that differ by orders of magnitude. Therefore, it is convenient to present a useful list of typical scales which can be consulted as comparative references, approximation gauges or validation benchmarks; the range of values for these scales is given in standard units. Additional explanations of the following parameters are given in the text.

Scale	Parameter	Symbol	Value
Length			
Electronic	atomic radius	$\ell[\text{atomic}]$	10^{-10} m
	crystal	$\ell[\text{lattice}]$	10^{-10} m
Atomistic		$\ell[\text{electronic}]$	10^{-9} m
Microstructural		$\ell[\text{microstructure}]$	10^{-8} – 10^{-5} m
	grain size	$\ell[\text{grain}]$	10^{-5} – 10^{-6} m
	needle	$\ell[\text{microprecipitate}]$	10^{-6} m
	colony	$\ell[\text{macroprecipitate}]$	10^{-5} – 10^{-4} m
Continuum			10^{-4} m–
	flaw	$\ell[\text{flaw}]$	10^{-5} – 10^{-4} m
	component	$\ell[\text{component}]$	10^{-3} m

Time

Atomistic	transport	$\tau[\text{diffusion}]$	10^3 s
Microstructural	nucleation/growth	$\tau[\text{microprecipitate}]$	10^3 s

Conventions

Continuum	autocatalysis	$\tau[\text{macroprecipitate}]$	10^5 s
	thermomechanical	$\tau[\text{cycle}]$	$10^3\text{--}10^5 \text{ s}$
	test period	$\tau[\text{test}]$	10^7 s

Index Notation

The Einstein convention of repeated index summation is employed throughout unless otherwise stated; the physical significance of indices adheres to the list that is tabulated below.

Index	Variant	Usage
Latin		
Beginning letters	$a, b, c, d, \dots$	labelling of extensive and intensive thermodynamic variables <i>or</i> labelling conserved phase field variables
	a', b', c', d'	labelling non-conserved phase field variables
	$A, B, C, D, \dots$	
Middle letters	$i, j, k, l, \dots$	labelling of vector components of spatial coordinates
	$\tilde{i}, \tilde{j}, \tilde{k}, \tilde{l}, \dots$	labelling of vector components of spatial coordinates of the stimulus in the Green function formalism
	$\bar{i}, \bar{j}, \bar{k}, \bar{l}, \dots$	labelling of vector components of spatial coordinates in the coordinate system of stress raisers
	$I, J, K, L, \dots$	labelling of components of symmetric (3×3) matrices and 3-dimensional vectors in Voigt engineering notation
Later letters	$r, s, \dots$	labelling of components of thermodynamic solutions
Greek		
Beginning letters	$\alpha, \beta, \gamma, \delta, \dots$	labelling of dislocations
Middle letters	$\mu, \nu, \rho, \dots$	labelling of nearest neighbouring atoms
Later letters	$\varsigma, \tau, \dots$	labelling of elastostatic multipolar contribution

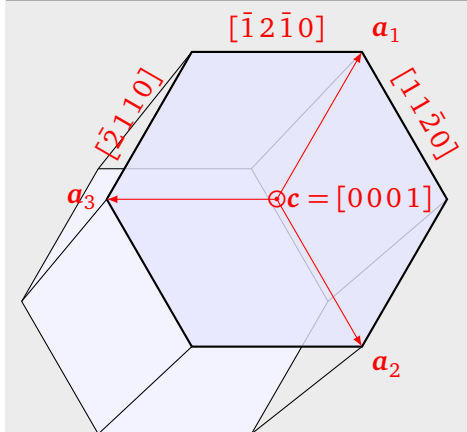
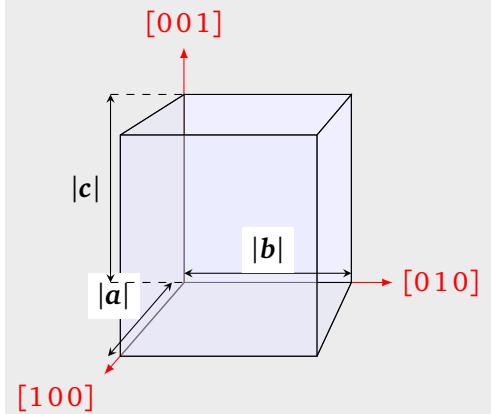
Crystallographic Notation

In an ideal or perfect crystal system, the atomic arrangement is in the form of a lattice that is infinite in spatial extent. Therefore, the atomic environment is the same when viewed from any lattice site. The lattice sites are given by the points of intersection of three sets of evenly-spaced parallel planes; these planes partition the crystal into primitive unit cells which are identical elementary parallelepipeds whose vertices are the lattice sites. Suppose that the set of basis vectors $\{\mathbf{a}, \mathbf{b}, \mathbf{c}\}$ defines the non-parallel edges of the unit cell as depicted. Then crystallographic vectors may be expressed using Miller notation:

$[h k \ell]$	denotes the vector $h\mathbf{a} + k\mathbf{b} + \ell\mathbf{c}$
$\langle h k \ell \rangle$	denotes the family of vectors that are identical by crystallographic symmetry to $[h k \ell]$
$(h k \ell)$	denotes a plane with the normal $[h k \ell]$
$\{h k \ell\}$	denotes the family of planes that are identical by crystallographic symmetry to $(h k \ell)$

For hexagonal crystal systems, the standard three-index Miller notation does not make apparent all vectors and planes that are identical by crystallographic symmetry. For example, the families $\{100\}$ and $\{\bar{1}10\}$ constitute equivalent planes. In order to clarify hexagonal crystallographic symmetries, the extended four-index Miller Bravais notation is employed in which there are three axes $\{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\}$ that are orientated $\frac{2}{3}\pi$ rad with respect to each other on the hexagonal plane, alongside a fourth axis $\mathbf{c}$ normal to the hexagonal plane. The crystallographic vectors can accordingly be expressed in Miller-Bravais notation:

$[h k \ell m]$	denotes the vector $h\mathbf{a}_1 + k\mathbf{a}_2 + \ell\mathbf{a}_3 + m\mathbf{c}$ where the indices $\{h, k, \ell\}$ satisfy $h + k + \ell = 0$ due to the redundancy in the three non-orthogonal axes formulation on the hexagonal plane.
$\langle h k \ell m \rangle$	denotes the family of vectors identical by crystallographic symmetry to $[h k \ell m]$
$(h k \ell m)$	denotes a plane with the normal $[h k \ell m]$
$\{h k \ell m\}$	denotes a family of planes identical by crystallographic symmetry to $[h k \ell m]$



Engineering Notation

The vectorisation of equations involving symmetric rank-4 tensors and rank-2 tensors is given using Voigt or engineering notation, which provides a convenient means of relabelling tensor indices; for a 3-dimensional tensor T , this takes the form

$$ij \longrightarrow I = \begin{cases} i & \text{if } i = j \\ 9 - (i + j) & \text{if } i \neq j \end{cases},$$

which is explicitly tabulated below.

Tensor Indices		Voigt Index
11	$\longrightarrow$	1
22	$\longrightarrow$	2
33	$\longrightarrow$	3
23, 32	$\longrightarrow$	4
13, 31	$\longrightarrow$	5
12, 21	$\longrightarrow$	6

In order to demonstrate the relevant use of Voigt notation, consider Hooke's law in the framework of linear elasticity, which proposes the general most linear relationship between the symmetric 3-dimensional rank-2 stress tensor $[\sigma]$ and strain tensor $[\varepsilon]$ as given by the tensor equation:

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl} \quad \text{with } i, j, \dots = 1, 2, 3,$$

where $\sigma_{ij} = \sigma_{(ij)}$ and $\varepsilon_{ij} = \varepsilon_{(ij)}$, and the rank-4 tensor $[C]$ is the stiffness matrix. This tensor equation can be expressed in Voigt notation:

$$[\sigma] = [T] : [\varepsilon]$$

where the equivalent Voigt vectors for the rank-2 tensors are given by

$$[\sigma] = \begin{bmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{33} \\ \sigma_{23} \\ \sigma_{13} \\ \sigma_{12} \end{bmatrix} \quad \text{and} \quad [\varepsilon] = \begin{bmatrix} \varepsilon_{11} \\ \varepsilon_{22} \\ \varepsilon_{33} \\ 2\varepsilon_{23} \\ 2\varepsilon_{13} \\ 2\varepsilon_{12} \end{bmatrix}$$

and the equivalent Voigt matrix for the rank-4 tensor is given by

$$[C] = \begin{bmatrix} C_{1111} & C_{1122} & C_{1133} & C_{1123} & C_{1113} & C_{1112} \\ C_{1122} & C_{2222} & C_{2233} & C_{2223} & C_{2213} & C_{2212} \\ C_{1133} & C_{2233} & C_{3333} & C_{3323} & C_{3313} & C_{3312} \\ C_{1123} & C_{2223} & C_{3323} & C_{2323} & C_{1113} & C_{1112} \\ C_{1113} & C_{2213} & C_{3313} & C_{1113} & C_{1313} & C_{1112} \\ C_{1112} & C_{2212} & C_{3312} & C_{1112} & C_{1112} & C_{1212} \end{bmatrix}$$

Glossary

The work in this dissertation draws upon concepts from various academic disciplines. In order to facilitate comprehension, a collection of technical terminology alongside their definitions, description and usage is given for clarity.

Term [◇] [Discipline] *Field*

▷ Definition

Amalgam [Computer Science] *Software Development*

▷ A high-level description of the prospective interfaces between constituent modules in a multi-modular program.

Algorithmic Workflow [Computer Science] *Software Development*

▷ A schematic representation of a set of algorithms through a flowchart that conveys the manipulation of computational data structures.

Anisotropic Homogeneous Medium [Materials Science] *Characterisation*

▷ A continuum that represents a monocrystalline or polycrystalline specimen in which the constituent anisotropic crystallites are perfectly aligned.

Basal Pole [Materials Science] *Crystallography*

▷ The principal axis of six-fold symmetry of a hexagonal close-packed crystallographic unit cell.

Code Specification [Computer Science] *Software Development*

▷ A standalone document that provides a detailed breakdown of the relationship between the aspects of computational science and computer science, which is the preface to any sizeable code development.

Computer Vision [Computer Science] *Digital Imaging*

▷ Algorithmic automation of tasks that involve acquiring and processing any spatial cues in simulated images.

Conformal Symmetry [Mathematics] *Group Theory*

▷ The symmetry transformation that preserves the angular relationships when a multi-dimensional field is rescaled.

Density Functional Theory [Materials Science] *Computational Materials Science*

▷ A first-principles electronic structure method used to solve the many-electron Schrodinger equation exactly.

Discrete Dislocation Plasticity [Materials Science] *Computational Materials Science*

▷ A multiscale microstructural method used to simulate the evolution of the dislocation microstructure.

Finite Element Methodology [Materials Science] *Computational Materials Science*

▷ A continuum scale method used to solve partial differential equations that pertain to topological properties and behaviour.

Hybrid Model [Materials Science] *Computational Materials Science*

▷ A multiscale modelling strategy in which sub-models at distinct length and time scales are unified into one self-consistent framework.

Hydrogen Embrittlement [Engineering] *Failure Mechanics*

▷ In the context of delayed hydride cracking, this is the effect of repeated thermomechanical cycles over which the hydrided microstructure of zirconium alloys become denser.

Isotropic Heterogeneous Medium [Materials Science] *Crystallography*

▷ A continuum that represents a polycrystalline specimen in which the constituent isotropic crystallites are misaligned.

Line Segment Intersection [Computer Science] *Computational Geometry*

▷ A family of algorithms that can determine whether there is some spatial overlap of two straight line segments.

Macro-Hydride Colony [Engineering] *Failure Mechanics*

▷ In the context of delayed hydride cracking, this is used to describe a macroscopic zirconium hydride precipitate feature which is understood to be a composite assembly of micro-hydride needles.

Micro-Hydride Needle [Engineering] *Failure Mechanics*

▷ In the context of delayed hydride cracking, this is used to describe microscopic zirconium hydride precipitate feature which are observed as individual platelets with a lenticular morphology.

Phase Field Methodology [Materials Science] *Computational Materials Science*

▷ A microstructural modelling method based on the construction and optimisation of a thermodynamic free energy.

Point-in-a-Polygon [Computer Science] *Computational Geometry*

▷ A family of algorithms that can determine whether a spatial coordinate is contained within the bounds of a closed cyclic network of straight line segments.

Polygon-Line Segment Intersection [Computer Science] *Computational Geometry*

- A family of algorithms that can determine whether there is spatial overlap between an individual line segment and a closed cyclic network of line segments.

Program Architecture [Computer Science] *Software Development*

- A breakdown of the software in terms of the constituent functions, classes, modules and libraries.

Thermal Ratchetting [Engineering] *Failure Mechanics*

- In the context of delayed hydride cracking, this is the effect of repeated thermomechanical cycles over which the hydrided microstructure of zirconium alloys become denser.

Part I

Delayed Hydride Cracking

1

Introduction

Chapter Overview

The central problem of this investigation is delayed hydride cracking (DHC), a failure mechanism that affects zirconium (Zr) alloy components used in nuclear fuel pin technology. Zirconium alloys are ubiquitous in the nuclear industry because the material properties of Zr are desirable for structural applications in water-cooled reactors. However, the reactor operating conditions of high temperature, high pressure and high irradiation can compromise the structural integrity of the components, leading to potential DHC failures. Therefore, it is imperative to safeguard against DHC failure in order to preserve the operation lifetime of Zr components, and hence increase fuel pin longevity. In order to then address the issue of nuclear safety economics, it is crucial to develop a framework for predicting DHC initiation, which is an inter-disciplinary endeavour at the intersection of mathematical physics, computational materials science and nuclear engineering.

In line with current nuclear safety assessments of Zr components, such a predictive framework would correspond to theoretical and computational models that simulate DHC failure criteria at sensible length and time scales. Predictive models of DHC should be capable of not only replicating actual cases of component failure but also exploring criteria beyond the practical limitations of experimental studies; these predictive capabilities should ideally provide novel insight into the optimal design of Zr alloys. Developing predictive models of DHC failure requires a fundamental mechanistic understanding of Zr metallurgy. In general, a deeper understanding is essential for simulating physical phenomena both accurately and efficiently, which, in turn, improves the predictive capabilities of materials modelling. This paradigm of formulating an accurate and efficient mechanistic model of DHC serves as the impetus of this investigation.

The cause of DHC is attributed most simply to the fact that Zr is a hydride-forming metal that has an affinity for hydrogen (H) pick-up. In the terminology of structural engineering and failure mechanics, DHC is a manifestation of hydrogen embrittlement or, more specifically, hydride embrittlement of Zr components. Since the earliest reported cases of DHC over half a

century ago, devising a non-conservative failure criteria has proven to be difficult [Puls (2012), Coleman (2003), McRae, Coleman, and Leitch (2010), Efsing and Pettersson (2000), and Syasin, Boyko, and Markin (1989)]. The difficulty stems from the very nature of DHC itself because it is a complex multiscale phenomenon that constitutes the coupling and repetition of three main sub-processes:

- ▶ Diffusion: the atomic scale process by which mobile particles of a solute species migrate over time from one region to another within a host solvent; here it is the diffusion of H atoms in the Zr matrix.
- ▶ Precipitation: the microscale process by which small islands of a daughter phase nucleate and grow at localised sites within a parent phase; here it is the precipitation of brittle hydride features in the Zr microstructure.
- ▶ Fracture: the continuum scale process by which a material separates or breaks under the action of stress by the propagation of flaws; here it is the fracture of H-enhanced and hydride-rich zones in the Zr component.

These constituent sub-processes are traditionally modelled as isolated phenomena at their distinct length and time scale. But the DHC mechanism is complicated by the manner in which these sub-processes are intertwined so as to form a cycle of three principal sub-mechanisms:

- ▶ Stress-driven diffusion: the atomic-to-continuum mechanism by which the migration of mobile particles is influenced by elastic fields in the host material; here it is the enhancement of H in the tensile regions ahead of flaws in the Zr component.
- ▶ Diffusion-controlled precipitation: the atomic-to-microscale mechanism by which the nucleation and growth of daughter phase islands is mediated by the migration of solute particles to localised sites within the parent phase; here it is formation of hydride features due to the accumulation of H at heterogeneous precipitation sites in the Zr microstructure.
- ▶ Precipitation-induced fracture: the micro-to-continuum scale mechanism by which the failure criteria is met, in part, by the evolution of a precipitate-rich microstructure within the material; here it is propagation of flaws in the hydrided microstructure of the Zr component.

In its most simplest form, DHC can then be decomposed into three stages: (i) the stress-driven diffusion of H to tensile regions ahead of any volumetric flaws such as loaded cracks or notches; (ii) the diffusion-controlled precipitation of brittle hydride features in the H-enhanced zones in the vicinity of existing flaws; and (iii) the precipitation-induced fracture in the H-enhanced

and hydride-rich zones which leads to the propagation of the aforementioned flaws. But even in this simplistic and high-level description of DHC, it is difficult to formulate accurate and efficient models of DHC because of the inherent multiscale complexity of the constituent sub-mechanisms. The respective notions of accuracy and efficiency appear to be somewhat contradictory in materials modelling. That is, there is a trade-off between accuracy and efficiency, which can be understood intuitively by considering how a finer (or coarser) simulation would typically require the computation of a more (or less) detailed physical description at a given length and time scale. Increasing physical detail is often compensated by simulation run-time. For this reason, multiscale modelling has proven to be a formidable task for even the individual stages, let alone the overall DHC phenomenon [Puls (2012), Coleman (2003), Tonks et al. (2017), Bair, Zaeem, and Tonks (2015), and Jernkvist and Massih (2014)].

Furthermore, the multiscale complexity of the DHC is exacerbated by the underlying polycrystalline nature of the commercial Zr alloy material. As Zr possesses a hexagonal close-packed (HCP) crystal structure, the polycrystallinity adds directionality and non-uniformity to the length and time scales pertaining to the sub-processes. This scale-dependent directionality and non-uniformity are more generally categorised under the effects of material anisotropy and heterogeneity. For example, the atomic scale diffusion of H in Zr is anisotropic as the time scales for diffusive steps are faster along specific crystallographic directions, and the microscale precipitation of hydrides in Zr is heterogeneous as the nucleation sites are not uniformly distributed.

Moreover, the three-stage description of DHC is, as stated, far too simplistic because the principal sub-mechanisms themselves constitute an assortment of smaller scale phenomena. Again, as an example, the diffusion-controlled precipitation of hydrides leads to the formation of networks of macroscopic hydride features that are composite assemblies of microscopic hydride features. Therefore, quantifying the complexity of DHC requires a careful analysis of the multiscale sub-mechanisms that take place within the anisotropic and heterogeneous Zr alloy components. This is undeniably a considerable challenge that has persisted to this date [Puls (2012) and Tonks et al. (2017)].

It is now clear why it is difficult to convey the multiscale richness of DHC using a single mono-disciplinary technique that is traditionally confined to the separate academic fields of Physics, Chemistry, Materials Science and Engineering, be it theoretical, computational or experimental. In this respect, DHC is a quintessential example of inter-disciplinary research. Since the initial nuclear reactor designs, the problem of DHC has both inspired

a tremendously diverse volume of literature as well as advanced methodologies in disparate-appearing research areas: electronic structure theory in quantum mechanics; lattice defect modelling in crystallography; experimental micrography in microstructural characterisation; and thermomechanical analysis in structural failure testing. The overarching aim of DHC research is then to extract and unify the important findings from the respective mono-disciplinary studies into one self-consistent multiscale framework.

In embracing the theme of inter-disciplinarity, this investigation seeks to conceptualise a multiscale model of DHC, that is, a theoretical and computational methodology for simulating the DHC sub-mechanisms as observed in experiments. More specifically, this work focuses on formulating a parametric model that is able to study the cross-scale intricacies of, and the interplay between, the sub-processes of diffusion and precipitation. The main deviations from existing modelling strategies involve addressing the accuracy-efficiency balance and incorporating of the effects of anisotropy and heterogeneity. The motivation is to develop a multiscale model of DHC that can ultimately be validated by industry standards such that it can be employed in nuclear safety assessments of Zr components.

Prior to any further elucidation of the eponymous terms that entitle this work, namely multiscale modelling and DHC, consider first a hierarchical exposition into the broader context of the problem. This exposition is a top-down narrative beginning with nuclear energy and culminating in the problem of modelling DHC in Zr alloys. The present work is indeed interdisciplinary; it brings together concepts from three research areas: mathematical physics, computational materials science and nuclear engineering. Hence, the purpose of this exposition is three-fold to mirror the blend of these three themes. The first section provides a short background on nuclear energy and its future, which will serve as the motivation for this work as well as providing a theoretical foreground. The second section outlines nuclear reactor technology, which will contextualise the importance of Zr alloys in nuclear industry. The third section focuses on the philosophy of computational modelling of materials, which will greatly enrich later discussions on developing a multiscale simulation methodology for the DHC mechanism.

Chapter Outline

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1.1 Nuclear Energy

The broad context of this research is nuclear power and, more generally, global energy production. As summarised in **FIG. 1.1**, continued progression in the quality of life in human civilisation requires an energy source panacea that is reliable, abundant and sustainable. The first requirement of reliability enforces the need to have steady supply of electricity that meets demands and consumption of the growing population. The second requirement of abundancy serves as a stark reminder to current global dependence on combustible fossil fuels and their dwindling supplies in the decades to come. The third requirement of sustainability is arguably the most important in the pathway towards decarbonisation, which is crucial considering the excessive and irreversible environmental damage caused by human activity since the Industrial Revolution [Mackay (2009)].

In terms of these three requirements, nuclear power is regarded as a prototype candidate for such an energy panacea: a mere 1 kg sample of fissile uranium fuel could produce 100 TJ worth of useful clean (low-carbon) electricity, which corresponds to the lifetime energy consumption of dozens of individuals, and the Earth has enough natural mineable uranium that could satiate ten billion inhabitants for the next millennium. Despite this impressive capacity, nuclear power constitutes less than 5 % of the world total primary energy supply. It is naive to aggrandise reliability, abundancy and sustainability as the sole deciders based on scientific discourse and technological innovation when energy sectors are critically shaped by political initiatives, financial constraints, social narratives and geohistorical circumstances, which have snookered nuclear energy.

Rebranding as atomic energy has not absolved the nuclear industry of its ingrained notoriety due to the cultural association with nuclear weapons as well as nuclear accidents such as Three Mile Island (1979), Chernobyl (1986) and Fukushima (2011), whose media coverage has distorted public perception and disrupted ecological movements [Allison (2016)]. Clinical evidence from nuclear medicine has not dispelled radiotoxic emission phobia due to the nuclear holocaust mythos surrounding warfare fallout, operational meltdowns and waste mutants. In such gamed controversies that characterise nuclear safety economics, any perceived hazard is a chess piece that could either advance towards nuclear security based on accepted research or retreat from nuclear ideals due to lay misunderstandings about its risk; and DHC failure is one such political pawn because it was implicated as the culprit behind early radiation leaks in the infamous Chernobyl reactors. Therefore, assessing the present risk of DHC failure requires a careful understanding of modern reactor technology.

FIG. 1.1

The panacea for global energy production
An infographic conveying the main facts about energy usage through the challenges faced by humanity.

Energy Source Panacea

Reliability



8 billion people

Estimated world population in 2020



80 kWh per person

Daily energy consumption in average living standards

Abundance



85% Fossil Fuels

Current dependence on non-renewables: coal, gas, oil



30 Years Remaining

Time left before fossil fuel resources are depleted

Sustainability



3°C Global Warming

Expected rise in mean planet surface temperature



Halved Biodiversity

Risk of mass extinction event due to climate change

Nuclear Futures



1 YJ Clean Energy

Uranium reserves sufficient for the next 1000 years

TAB. 1.1

Modern commercial reactor designs

The problem of DHC concerns Zr alloys which only affects the water-cooled reactor designs. The prototype reactors are currently only in research development phase and are not commercialised.

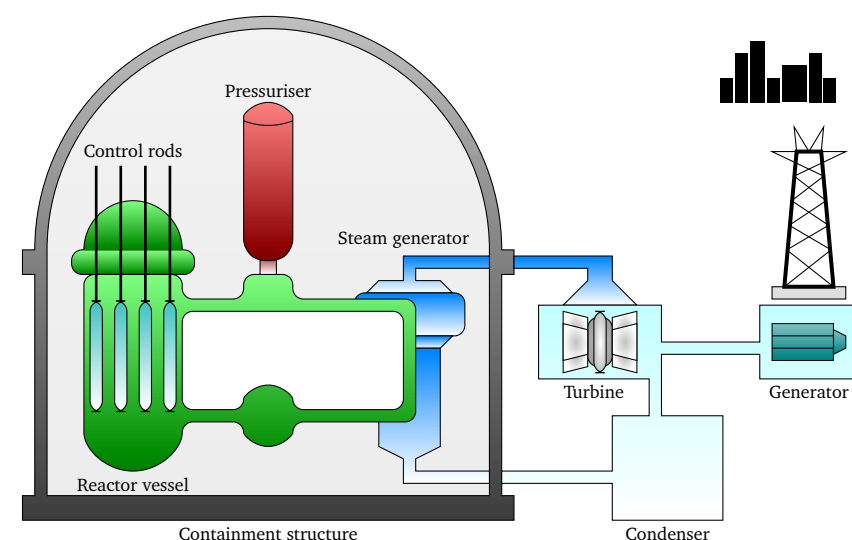
Acronym	Definition
WATER-COOLED REACTORS	
BWR	Boiling water reactor
CANDU	Canadian deuterium uranium
LWR	Light water reactor
P(H)WR	Pressurised (heavy) water reactor
RBMK	Reaktor Bolshoy Moshchnosti Kanalnyy
GAS-COOLED REACTORS	
AGR	Advanced gas-cooled reactor
GCR	Gas-cooled reactor
PROTOTYPE REACTORS	
HTGR	High temperature gas reactor
GCBR	Gas-cooled breeder reactor
LMFBR	Liquid metal fast breeder reactor
MSBR	Molten salt breeder reactor

1.2 Fission Reactor Technology

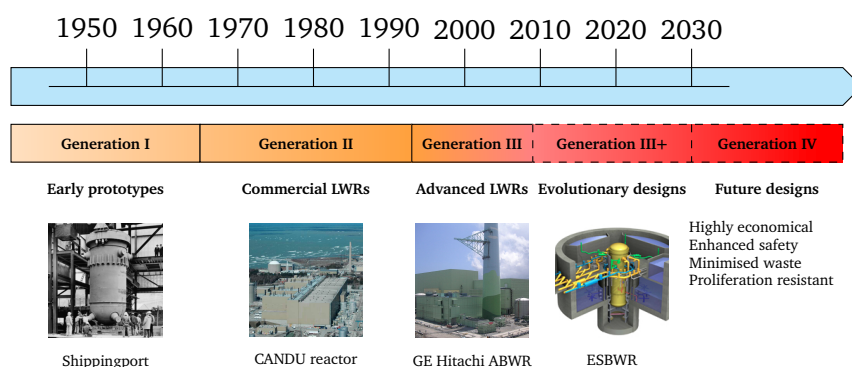
The purpose of a nuclear reactors is to harness energy from a sustained but controlled chain reaction of induced fission events in the fuel. Nuclear reactors have both civil applications within nuclear power plants that generate electricity as well as naval military applications within nuclear submarines that marine propulsion. In both cases, the kinetic energy released from fission is used to heat water into steam in order to power a turbine. As listed in [TAB. 1.1](#), there are currently a variety of reactor designs in operation. The simplest of these is the boiling water reactor (BWR), which is very similar to conventional fossil fuel plants. The BWR design can be extended into the pressurised water reactor (PWR) design depicted in [FIG. 1.2](#) so that the steam that passes through the turbine need not be part of the same cooling loop that extracts heat from the reactor. This allows for a greater flexibility in the choice of coolant and also the neutron moderator.

Over the generations of nuclear reactor designs, different variants of PWRs have been developed. The design of a PWR plant requires a variety of functional materials, including metals, ceramics, polymers and composites. But the overall layout of a PWR plant has the following key components: (i) the nuclear fuel which is usually in the form of small sintered uranium dioxide (UO₂) pellets stacked into assemblies of fuel pins; (ii) the neutron moderator which governs the thermal neutron economy; (iii) the neutron control rods which control the rate of fission reactions; (iv) the liquid coolant which extracts heat from the fuel; (v) the pressuriser which prevents the coolant from boiling; and (vi) the steam generator which exchanges heat from the primary loop into the water in the secondary loop. In addition, there is a hierarchy of containment barriers that prevent the release of radiotoxicity into the environment. In this depth of defence strategy, the second barrier is the cladding as it protects the fuel pellets from the strong flow of potentially corrosive water and impedes the diffusion of radionuclides into the coolant.

The main components of the BWR and PWR variants are summarised in [TAB. 1.2](#), which shows the prominence of Zr alloys in the nuclear industry. The Zr alloy components encase the UO₂ pellets. The main differences lie in the choices of coolant and moderator. For example, in the Canadian Deuterium Uranium (CANDU) reactor design, uncompressed heavy water composed of the H isotope deuterium (D) is used as a coolant and a moderator. It is the contact between the Zr alloys and the water that instigates the DHC sub-mechanisms. Hence DHC is a major safety concern that affects the Zr alloy components used in over 500 built reactors. It is, therefore, necessary to review in more detail the suitability of Zr in nuclear fuel pin technology.



(a)



(b)

FIG. 1.2

Nuclear reactor designs

(a) A schematic of a PWR nuclear reactor design. The fission reactions take place within the reactor vessel, which contains the nuclear fuel pins, moderators and the coolants. The exothermic energy output of these nuclear reactions is used to heat water into steam, which then turns a turbine that is connected to an electricity generator. The power output of a nuclear power plant can be adjusted to meet demand by load following. Certain strategies for load following can introduce large thermomechanical stresses in the reactor vessel, exacerbating the conditions for DHC initiation. (b) Generations of nuclear reactor designs. The timeline shows the evolution of nuclear reactor technology from the earliest prototypes to modern commercial designs and future proposals. The problem of DHC has persisted for over a half century since the earliest nuclear reactors.

Adapted from [Wikimedia \(2018\)](#).

TAB. 1.2

Functional materials for nuclear reactor designs

The problem of DHC affects every water-cooled reactor design as it involves contact between the Zr alloy clad component and the coolant. The last column is an estimate of the number of reactors built, which is a scale of how widespread the risk of DHC in the nuclear industry. The other reactor designs do not suffer from the risk of DHC failure; however there are analogous mechanisms, some of which can be described by the ideas conceived in the present work.

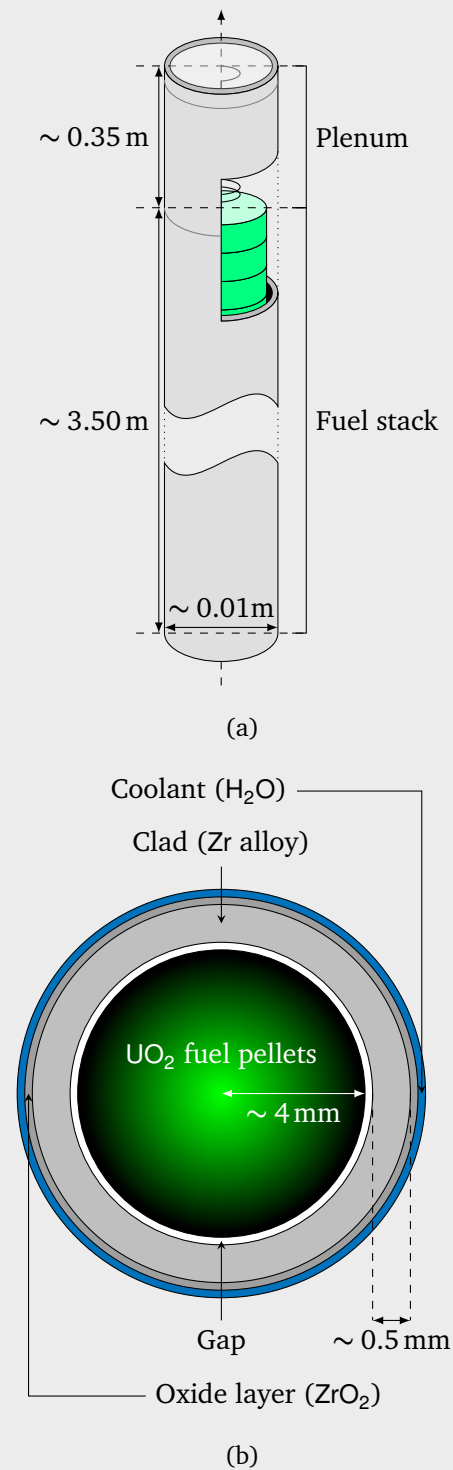
Adapted from [Burr \(2014\)](#).

Reactor	Fuel	Coolant	Moderator	Cladding	Number
WATER-COOLED REACTORS					
CANDU	UO ₂	H ₂ O or D ₂ O	D ₂ O	Zr alloy	37
PWR	UO ₂	H ₂ O	H ₂ O	Zr alloy	400
BWR	UO ₂	H ₂ O	H ₂ O	Zr alloy	78
RBMK	UO ₂	H ₂ O	graphite	Zr alloy	21
GAS-COOLED REACTORS					
AGR	UO ₂	CO ₂	graphite	stainless steel	14
MAGNOX	U	CO ₂	graphite	Mg alloy	39
PROTOTYPE REACTORS					
HTGR	UO ₂	He or H ₂ O	-	SiC	-

FIG. 1.3

Nuclear fuel pin

(a) Schematic of a fuel pin. (b) Cross-sectional schematic of a fuel pin. Adapted from Wikimedia



1.2.1 Fuel Pin Assembly

In water-cooled reactors, the nuclear fuel is arranged into bundles of rods, each of which is a stack of UO₂ fuel pellets encased in the cladding. Each pellet is a pressed cylinder with a cross-sectional diameter of ~ 10 mm and an axial length of ~ 20 mm, and there are usually pellets in a stack. There is a small gap between the pellet stack and the clad and so the stack is held in place by a spring in the plenum of the fuel pin. As shown in FIG. 1.3, the fuel pin clad is a hollow cylindrical tube that is composed of a single continuous piece of metal. The typical dimensions of the clad geometry define the (minimum) length scale of the component,

$$\ell[\text{component}] \in [O(10^{-3} \text{ m}), O(1 \text{ m})] \quad (1.1)$$

which is a useful measure for later discussions on multiscale modelling. As shown in FIG. 1.4, each fuel assembly is a 7×7 or 14×14 square lattice whose unit element is a single fuel pin. There may be ~ 150 fuel pin assembly cells in the reactor vessel at any given time, which equates to ~ 1000 clad components per reactor. Therefore the choice of clad material must reflect the duality of safety economics, that is, it must fulfil effectively the burdensome role of preventing a radiological hazard whilst simultaneously adhering to financial overheads during its operation lifetime [Olander (2009)].

Operation Lifecycle. Once-through reactor fuel pin assemblies go through a series of stages during their lifetime. During the pre-service manufacturing stage, the constituent sub-components of the fuel pin are fabricated. The UO₂ fuel pellets are processed from U ores that are mined and enriched. Clad engineering design involves machine cutting, weld joining and work hardening of metals. During the in-service stage, the fuel assemblies are transported and placed in the reactor core, where they are managed until they reach their end-of-life period. Each fuel pin assembly is expected to last up to about ~ 7 years, which defines the in-service component lifetime

$$\tau[\text{component}] \simeq O(10^8 \text{ s}). \quad (1.2)$$

After this time, the spent fuel pin assembly is discharged from the reactor and transferred into interim storage facilities that contain the radiotoxic emissions. A standard post-service stage could begin with underwater storage in spent fuel pools for up to ~ 10 years followed by dry cask storage. Throughout the pre-service, in-service and post-service stages, the cladding houses the radiotoxicity and so the choice of material is crucial [Olander (2009) and Billone, Burtseva, and Liu (2013)].

Clad Material. The historical choice of Zr in BWRs and PWRs was based on its desirable nuclear, chemical and mechanical properties [Rickover (1975)].

Firstly, the cladding surrounds the fission events whose rate depends on thermal neutron economy; so the clad material must have a low (thermal) neutron absorption cross-section. This neutron transparency means that clad nuclei do not interfere with the core neutronics, that is, the exchange of neutrons between fuel pellets, the moderators and control rods. A low value of the macroscopic cross-section for thermal neutrons, Σ_{MCSTN} , is indicative of neutron transparency. The clad material must also exhibit a tolerance to radiation damage from the radioactive fission products. Secondly the cladding is exposed to the coolant and so it must have a high waterside corrosion resistance in the core environment. Thirdly, the cladding must maintain its structural integrity during reactor operating conditions. Typical core temperature and pressure conditions are defined by

$$T_{\text{reactor}} \simeq 573 \text{ K} \quad \text{and} \quad P_{\text{reactor}} \simeq 16 \text{ MPa.} \quad (1.3)$$

The component must also withstand the sharp temperature gradients between the fuel and the coolant. Accordingly the clad material should have a sufficiently high melting point, $T[S \rightarrow L]$, so that its chemomechanical properties are not significantly compromised. The material strength can be described by the ultimate tensile stress, $\sigma_{\text{UTS}}(T_{\text{reactor}})$, which is the maximum applied load before any large irreversible deformation or abrupt breaking.

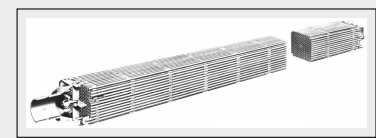
The decision to use Zr as the clad material is attributed to its optimal $\{\Sigma_{\text{MCSTN}}, \sigma_{\text{UTS}}, T[S \rightarrow L]\}$ combination and high corrosion resistance. As listed in **TAB. 1.3**, alternative candidates include aluminium (Al), beryllium (Be), iron (Fe) alloy steel, magnesium (Mg), nickel (Ni) and titanium (Ti), but each of these metals has its own shortcomings. Note also that Be is expensive, toxic and difficult to manufacture whilst Mg is flammable and poor in corrosive environments. So Zr is the obvious choice [Rickover (1975)].

Material	$\Sigma_{\text{MCSTN}}/(\text{cm}^2/\text{cm}^3)$	$\sigma_{\text{UTS}}(T_{\text{reactor}})/\text{MPa}$	$T[S \rightarrow L]/\text{K}$
Zr	0.01	900	2128
Al	0.014	90	933
Be	0.001	180–350	1560
Fe	0.17	1100	1811
Mg	0.005	90	923
Ni	0.31	1000	1728
Ti	0.26	1000	1941

FIG. 1.4**Nuclear fuel assemblies**

(a) PWR fuel assembly. (b) CANDU fuel bundle. Note that individual fuel pins are re-positioned at various stages throughout the lifetime of the entire assembly to optimise fuel performance.

Adapted from [Wikimedia \(2018\)](#).



(a)



(b)

TAB. 1.3**Comparison of metals as potential fuel clad materials**

A low macroscopic neutron cross-sections is highly desired for thermal neutron economy, and so Ni and Ti are particularly unsuitable. A high value for the ultimate tensile stress is crucial for preservation of structural integrity in reactor environment, which rules out Al and Mg due to their low melting points. Overall, Zr has the best spread of properties out of the remaining candidates.

TAB. 1.4

Commercial zirconium alloy fuel pin cladding for pressurised water reactors

It is worthwhile to highlight that research concerning Zircaloy-4 and Zr-2.5Nb is particularly relevant to the background of the present work. Note that Zircadyne-702 is only commercially pure. Note also that Zircaloy-1 and Zircaloy-3 are no longer used in the nuclear industry.

Clad Material	Alloying Elements
ZIRCALOYS	
Zircaloy-1	Sn
Zircaloy-2	Sn, Fe, Cr, Ni, O
Zircaloy-3	Sn, Fe
Zircaloy-4	Sn, Fe, Cr, O
CANDU	
Zr 2.5-Nb	Nb, O
AREVA	
M5	Fe, Nb, O
M5+	Sn, Fe, Nb, O
WESTINGHOUSE	
ZIRLO	Sn, Fe, Nb, O
PURE	
Zircadyne-702	-

Commercial Development. The business model of the nuclear industry is most simply based on power output of nuclear reactors, which partly depends on the longevity of fuel pin assemblies. Evidently, the safe operation lifetime of fuel pins corresponds to the integrity of the cladding. Now, the aforementioned metallurgical properties of pure Zr suggest that it can perform adequately in the relatively high-temperature, high neutron-flux and high pressure environment of the reactor core; but these strengths can be further capitalised upon to extend component durability. In addition, Zr has excellent resistance to chemical attack from oxidation, but the cladding is still susceptible to a certain degree of waterside corrosion; this is a potential weakness that could be counteracted. The commercial motivation for such improvements of Zr clad performance has led to extensive research on fabrication techniques and alloying additions [Cheadle (1977)].

Prior to any commercial development, sufficiently pure Zr material must be acquired. Naturally occurring Zr contains $\sim 2\%$ hafnium (Hf), an element with an extremely high neutron absorption cross-section that is capable of disrupting the desired neutronics of the reactor. Hence Hf separation is necessary before the Zr material is suitable for the clad design.

During the pre-service stage, the Zr alloy components are fabricated using machining, welding and cold work hardening techniques. Utmost care is taken during the manufacturing process, but these techniques invariably lead to the introduction of flaws and contaminants [Sutherlin (2005)]. These variations can reduce the quality of the final product, engineering tolerances are enforced for the component geometry and material characterisation parameters.

Over the generations of PWR designs, several commercial varieties of Zr base alloys have been widely circulated. The two main categories Zr alloys include the single-phase Zircalloys and the dual-phase Zr-2.5Nb alloys [Kass (1964), Cox, Garzarolli, and Rudling (2004), Nikulina (2003), and Rudling, Strasser, and Garzarolli (2007)]. As listed in TAB. 1.4, the main alloying additions include tin (Sn), Fe, chromium (Cr), Ni, niobium (Nb) and oxygen (O), which, in appropriate concentrations, can change corrosion resistance, enhance phase stability and increase mechanical strength.

In quantifying and extending the lifetime of Zr alloy components, it is important to note that analysis of fabrication tolerances and alloying effects is currently based on empiricism. It is, therefore, essential to complement the experimentation on Zr alloys with sound theoretical principles. This is particularly important in foreseeing how DHC failure varies from component to component. This holistic approach to Zr alloy metallurgy is becoming increasingly important in the context of safety economics.

1.2.2 Industrial Safety Economics

Safety and associated economics are very important themes in the nuclear industry. As identified by the policies outlined by the International Atomic Energy Agency (IAEA),— which classifies safety as a top priority for financial commitments—, basic scientific studies and evaluation form the foundation of nuclear safety [Fischer (1997)]. Large amounts of capital are invested into the research and development of advanced materials for high value reactor components. The primary driver is long-term public and environmental safety because nuclear power plants are extensively lengthy projects; modern reactors are expected to take nearly a century to go from the initial stages of planning and building to the final stages of decommissioning. The day-to-day running costs of reactors are relatively low given that only a small amount of fuel is required per megawatt hour of electricity generated, but the construction and waste disposal costs are very high. In stark contrast to other forms of power generation, this stage-by-stage economical breakdown is somewhat unique to the nuclear industry. Risk management is technologically challenging and financially demanding at every stage, but the nuclear industry has adopted the principles of ALARP (As Low As Reasonably Practical) to justify vast spending on lowering risk. Adding to this any potential setbacks due to government policy changes and volatile energy market fluctuations, lowering the risk corresponds to reduced operating costs, which in turn makes nuclear power a more attractive and viable option [Lumley (2013)].

Risk Management Strategy. The safe operation of a nuclear power plant requires a careful implementation of safety margins that have been defined by risk-informed regulations. These regulations pertain to all aspects of nuclear reactor technology, but the most important safety margins concern the physical barriers to radiotoxic emissions, the fuel pellet matrix and the fuel pin cladding being particular priorities. Knowledge of the safety margins for these barriers assists in evaluating reactor power uprating, improving utilisation of nuclear fuel, preparing for emergency operating procedures and developing accident management programmes [International Atomic Energy Agency (2003)].

Safety Analysis Software. Advanced computer codes are critical tools in modern safety analysis of the performance of fuel pin assemblies. These fuel performance codes can be validated by experimental findings and (prospectively) simulate scenarios of extreme reactor conditions that are impractical to recreate in experiments. One such extreme scenario is the failure of Zr cladding; therefore, a computational model of DHC is very valuable.

1.3 Fuel Performance Simulation

Fuel performance codes are a network of computational programs that simulate the multi-physical behaviour of materials that are used in nuclear fuel pin technology during various reactor operating conditions. As shown in FIG. 1.5, this is somewhat of an overwhelming task because of the sheer complexity of variables, phenomena and scales involved. But the benefits of fuel performance simulation can be revolutionary to safety in the nuclear industry. Nuclear safety has thusfar relied on expensive and time-consuming experimental research, which has only led to incremental improvements in the fuel pin designs since the earliest reactors; this is evidenced by the fact that UO_2 fuel pellets and Zr alloy clad are still used today. The future of nuclear energy requires the development of better fuel and cladding materials, and computational codes provide an inexpensive playground to explore such materials [Olander (1976), Aybar and Ortega (2005), and Tonks et al. (2017)].

The main drawback of existing fuel performance codes is that the analysis relies on empirical materials modelling that is limited by considerable reliance on dated burn-up calculations, which measure the number of fission events but do not predict the material behaviour [Tonks et al. (2017)].

FIG. 1.5

Fuel performance mindmap

A visualisation of the complexity associated with fuel performance analysis for PWR technology. Observe that, despite its own phenomenological complexity, DHC still constitutes only one aspect of the overarching problem of nuclear fuel pin safety. Therefore any models of the DHC mechanism in isolation must still be contextualised within the entire scope of fuel performance analysis. For example the conditions that suppress the risk of DHC failure could potentially augment the risk of other failure mechanisms. Ideally, a fuel performance simulation package should be a self-consistent integration of sub-models of each isolated mechanism.



1.3.1 Mechanistic Materials Modelling

The transition beyond dated burn-up calculations has led to the inception of modern nuclear fuel performance codes such as the BISON, MARMOT, MOOSE and FALCON codes [Tonks et al. (2017)]. These progressive codes employ mechanistic models of materials with the intention to predict fuel behaviour under abnormal reactor conditions. In particular, these mechanistic models adopt a state variable approach in which the current state of material is quantified by a set of physical parameters that span the atomic, electronic, microstructural and continuum scales. This approach has been facilitated, in part, by the recent advances in the field of computational materials science.

Computational Materials Science. The landscape of computational materials science is incredibly broad in terms of the methodologies, techniques and strategies that have been pioneered for modelling materials properties and behaviour. Models span first-principles electronic structure and atomistic solvers that account for quantum mechanical effects to the coarse-grained microstructural and continuum scale solvers that are based on the equations of classical mechanics and thermodynamics [Janssens et al. (2007)].

Four particular solvers have emerged as generic all-purpose methods for modelling various types of materials at specific length and time scales: (i) density functional theory (DFT) for first-principles electronic structure simulations; (ii) empirical potential molecular dynamics (EPMD) for semi-classical atomistic simulations; (iii) phase field (PF) method for mesoscopic and microstructural simulations; and (iv) finite element (FE) method for continuum simulations. The aforementioned fuel performance codes are heavily reliant on DFT, EPMD, PF and FE models [Tonks et al. (2017) and Aybar and Ortega (2005)].

The main drawback of standalone DFT, EPMD, PF and FE solvers is that their functionality is restricted to their respective scales. This is problematic because materials phenomena involve constituent processes that are operative at a multitude of length and time scales, DHC being a quintessential example of this paradigm.

Multiscale Theory and Simulation. The theme of multiscale modelling has attracted a considerable amount of attention in recent times because of the growing need to describe materials phenomena in which there is constant feedback between first-principles and coarse-grained levels of the physical description. Several unification strategies have been proposed to address this theme but there is currently no standardised approach for multiscale modelling [Vvedensky (2004), Curtin (2017), and Spaldin (2017)].

In context of nuclear fuel performance codes, there are two basic strategies for multiscale modelling. The first is the rudimentary approach that involves manually analysing the findings of separate DFT, EPMD, PF and FE simulations in conjunction with experimental studies during the post-processing stage. The second is a bottom-up sequential parametrisation approach that involves incorporating the output of small-scale simulations into large-scale simulations; for example, FE models may be parametrised by PF models that are, in turn, parametrised by DFT and EPMD models [Tonks et al. (2017)]. The main limitations of either approach is the simulations are ultimately limited by what DFT, EPMD, PF and FE can offer, which is not always ideal or even convenient for the problem at hand.

There is a third strategy that will be referred to as the concurrent hybrid modelling approach. The hybrid qualifier here refers to the notion that different modelling methods and techniques can be appropriately combined into a unified framework that provides a multi-level description of the physical system and simulates concurrently the constituent multiscale processes. The previous two strategies are, in some sense, generally applicable but the hybrid modelling strategy involves the conception of a bespoke framework for the sole purpose of simulating certain materials phenomena in isolation. The advantages of a purpose-built bespoke model are numerous: (i) the input and output can be chosen beforehand; (ii) experimental studies and existing computational studies can be used to guide the model formulation; and (iii) methods and techniques can be customised to optimise the accuracy and efficiency of the simulation. Therefore, the present work will focus on the hybrid modelling strategy. The obvious disadvantage is that this approach is uncharted territory for DHC research, but then again this is the novelty of the present work.

1.3.2 Application to Zirconium Alloys

Prior to any hybrid model formulation, it is worth premeditating its novelty in the context of existing models. As stated earlier, DHC is a complex multi-scale manifestation of hydrogen embrittlement in Zr alloys. For this reason, various computational methods have been used to study the Zr-H system at different length and time scales. This includes, amongst DFT, EPMD, PF and FE solvers, more tailored models based on tight-binding (TB) methods and kinetic Monte Carlo (KMC) methods as well as other models based on methods that are more specific to the domain of computational metallurgy, such as dislocation dynamics (DD) and crystal plasticity (CP) methods [Tonks et al. (2017), Burr (2014), Lumley (2013), Majevadia (2014), Nazarov et al. (2016), Zhang, Jiang, and Bai (2017), Bair, Zaeem, and Tonks (2015), and

Guo et al. (2008)]. There has yet to be any substantial application of the newer techniques such quantum Monte Carlo (QMC) methods and discrete element (DE) modelling.

The electronic structure and atomistic solvers are used to study the Zr-H at a more fundamental level [Tonks et al. (2017), Burr (2014), Lumley (2013), Majevadia (2014), and Nazarov et al. (2016)]. The microstructural solvers are used to reproduce the phenomenological observations of microscale diffusion-controlled precipitation as well as quantify the micromechanics of pure Zr specimens [Guo et al. (2008), Dunne and Petrinic (2005), and Patel et al. (2017)]. The continuum solvers are used to perform coupled diffusion-precipitation analysis at the component scale [Puls (2012), Eadie, Metzger, and Léger (1993), Martin (2013), Jernkvist and Massih (2014), Jernkvist (2014), and Patel et al. (2018)]. As it stands, it is currently industry standard to employ cohesive zone (CZ) models to study the fracture in a very conservative engineering approach [Martin (2013)].

As shown in FIG. 1.6, the typical system sizes and relative accuracies of each of these methods show the benefits and limitations of each method. Note that accuracy is defined here in terms of the quantum mechanical description of the material. It is evident that these standard modelling methods cannot adequately capture the multiscale complexity of DHC or even

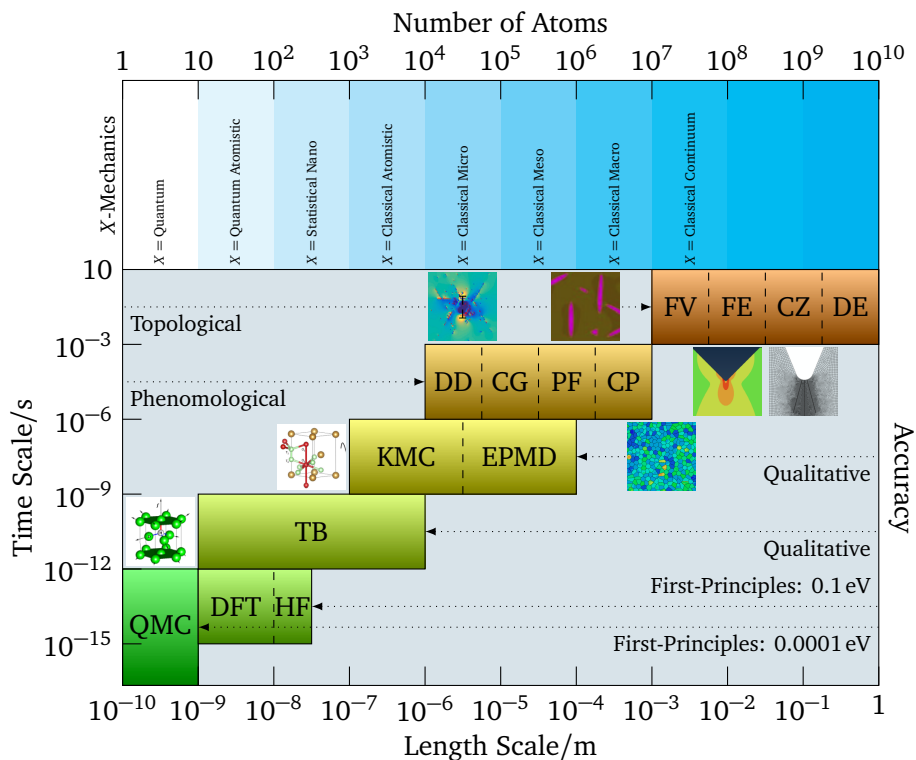


FIG. 1.6

Computational material science

A graphical representation of the methods of computational materials science that particularly relevant to metals. For any given method, there is an increased computational expenditure as the simulated system size increases. The inset images are positioned to show which methods have been applied to the problem of DHC to date.

its sub-mechanisms. It is, therefore, necessary to conceive a bespoke hybrid model in which it is possible to convey the physics of the Zr-H system across a spectrum of length and time scales. In order to do so effectively, it is crucial to first review in depth theoretical, computational and, most importantly, experimental research surrounding the problem of DHC and then carefully dissect its sub-mechanisms to extract the essential physics so that the desired accuracy-efficiency balance can be achieved.

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2

Literature Review

Chapter Overview

The multiscale phenomenon of DHC has been studied for over half a century. Historically, DHC research was prompted by the discovery of leaks from pressure tubes in the earliest operating CANDU reactors [Puls (2012)]. Post-mortem analysis of these Zr alloy components showed the presence of precipitates. These precipitate features were identified to be metallic compounds of the Zr-H phase system, collectively referred to as hydrides. Previous studies on hydride phases in transition metals reported that certain hydrides, comprising a very high H stoichiometric composition, may be more brittle than the parent metal [Beck and Mueller (1960)]. Therefore, it was suggested that the brittle hydrides could have a deleterious effect on the mechanical properties of Zr, that is, a Zr alloy component could be embrittled when a sufficiently high density of hydrides is present. It was postulated that this hydride embrittlement mechanism could be instigated by the reactor environment in which the Zr alloy components are prone to H pick-up [Mueller, Blackledge, and Libowitz (1968), Strasser, Adamson, and Garzarolli (2008), and Puls (2012)].

Further studies confirmed the brittle nature of bulk hydride phases as well as the reduced fracture toughness of Zr alloy specimens containing hydrides [Mueller, Blackledge, and Libowitz (1968), Strasser, Adamson, and Garzarolli (2008), and Puls (2012)]. In particular, the fracture susceptibility was determined to be significantly greater in H-enhanced and hydride-rich zones of the Zr material. Such H-enhanced and hydride-rich zones were localised in the vicinity of potent stress-raisers or large volumetric flaws such as loaded cracks or notches. It was suggested that the long-ranged tensile stress state ahead of such flaws could provide an attractive potential for H migration within the component. Over time the flaw tips would become H-enhanced and hydride-rich zones. The hydride features would grow to critical sizes upon the continued elevation of the H concentration near the flaw. The flaw-tip H profile and hydrided microstructure could then embrittle the region. Subsequently, the fracture initiation threshold could be exceeded due to the thermomechanical conditions in the reactor environ-

ment, and this would allow a secondary flaw to emanate from the original flaw. The secondary flaw would then continue to propagate through the component over repeated cycles of H accumulation and hydride formation in its vicinity [Puls (2012), Coleman (2003), and Schofield (2002)].

In early studies, the hydride embrittlement of Zr alloys was classified as a sub-critical cracking mechanism [Strasser, Adamson, and Garzarolli (2008) and Puls (2012)]. The notion of sub-criticality refers to the (slow) time-dependent processes that govern the cracking, namely, H migration and hydride formation. In later studies, the existence of such an embrittlement mechanism was confirmed by the observation of leaks of radioactive fission products due to failures in several Zr components: (i) CANDU pressure tubes that had fractured following crack initiation in rolled joints; and (ii) BWR fuel pin cladding that had split axially due to the presence of massive hydride blisters [Puls (2012), Schofield (2002), Perryman (1978), Price and Cheadle (1985), Edsinger, Davies, and Adamson (2000), Edsinger (2000), Lysell, Grigoriev, and Efsing (2000), Huang and Mills (1991), Efsing and Pettersson (2000), and Mahmood et al. (2000)].

In modern studies, this embrittlement mechanism has been termed DHC, which has been a major field of study in its own right. Generally, all studies delving into some aspect of DHC have a single unified aim, that is, to identify the quantitative criteria that must be met for DHC flaw initiation. Currently, there exists over six decades of scoping literature on DHC from various academic and industrial communities working on nuclear reactor technology [Puls (2012)]. In the following, a systematic review of the literature is presented.

The breadth of the literature on DHC is attributed to the multiscale complexity of the mechanism. As stated earlier, DHC involves three primary sub-processes: (i) atomistic scale diffusion which corresponds to H migration in the Zr matrix; (ii) microscale precipitation which corresponds to hydride formation in the Zr matrix; and (iii) the continuum scale fracture which corresponds to flaw initiation and propagation in the H-enhanced and hydride-rich zones. These three sub-processes form a cyclic trifecta of sub-mechanisms: (i) stress-driven diffusion that encapsulates how H migration is directed towards the stress-raising flaw; (ii) diffusion-controlled precipitation that encapsulates how the localised accumulation of H governs the evolution of hydride-rich zones; and (iii) precipitation-induced fracture that encapsulates how readily cracking occurs due to the embrittling effect of densely-populated hydride networks.

However it is not straightforward to completely isolate these sub-processes or sub-mechanisms; in reality there is coupling between the traditionally distinct length and time scales associated with diffusion, precipitation and

fracture. In addition, the underlying properties of the Zr alloy component influence these coupled sub-processes. For example, the CANDU pressure tubes, composed of the Zr-2.5%Nb alloy, are more susceptible to DHC initiation than, say, their unirradiated Zircaloy counterparts [Schofield (2002), Huang and Mills (1991), Efsing and Pettersson (2000), and Mahmood et al. (2000)]. Therefore, in order to effectively convey the main findings from DHC research in spite of its multiscale complexity, it is useful to organise this review into four inter-related themes: (i) the metallurgical properties of Zr alloys; (ii) the behaviour of H in Zr alloys; (iii) the formation of zirconium hydride phase features; and (iv) the analysis of failure criteria as a function of the Zr alloy metallurgy and the hydrogen and hydride content in the Zr component as well as the reactor operating conditions.

Collectively these four themes constitute the vast majority of the research on the DHC mechanism. Understandably, this research is mostly experimental because of historical reasons; since the discovery of DHC, it has persisted as a practical engineering problem that has important safety implications for the nuclear industry. Over the six or so decades in which commercial nuclear reactors have remained in operation, experimental test programs have been used to investigate DHC failure, which has produced the extensive body of experimental research. Over much of this period, however, the standard methods for modelling materials had remained in their infancy until the most recent advances in computational power in the last two decades. Although the present investigation concerns the development of a model of DHC, it is sensible to initially restrict the review to the experimental findings. This approach is not only more representative of DHC research but, more to the point, it provides real evidence of the Zr-H system. The strategy here is to build the foundation for identifying the important (or irrelevant) mechanistic details underpinning the DHC phenomenon that would be necessary to include in (or omit from) a computational model that should be both accurate and efficient.

Furthermore, in order to emphasise the multiscale nature of DHC, this thematic review establishes carefully the notions of the various length and time scales encountered in experimental materials science: atomic, electronic, nanoscopic, microscopic, mesoscopic, macroscopic, continuum and component. Exploring these scales is an essential in the foregoing analysis on the methods for modelling materials phenomena and, in particular, those methods that have been applied to DHC to date. In turn, this analysis will be useful in the development of a multiscale model of DHC that unifies these scales into one standalone framework.

Finally, prior to commencing this thematic review, it is worthwhile to mention that DHC falls into a more general class of failure mechanisms

known as hydrogen embrittlement of metals. Common to all of these hydrogen embrittlement mechanisms is the chemistry of the formation of coordinated metal-hydrogen ligand bonds and, more generally, the presence of H in metals. Alongside DHC, there are alternate suggestions for hydrogen embrittlement mechanisms in Zr, such as corrosion hydrogen cracking (CHC), hydrogen enhanced decohesion (HED) and hydrogen enhanced localised plasticity [Barrera et al. (2018)]. There are also failure mechanisms analogous to DHC in other metals, the one with the most similarities being stress hydride cracking (SHC) in the titanium (Ti) alloys that are employed in the aerospace industry [Mueller, Blackledge, and Libowitz (1968), Schofield (2002), Majevadia (2012), Patel and Stopher (2017), and Simpson and Patel (2017)]. It is crucial to acknowledge that the operating environment may instigate structural failure of the component through mechanisms other than hydrogen embrittlement; this is particularly true for Zr alloys that undergo creep, fatigue, corrosion and irradiation in reactor conditions. Although these separate-appearing degradation mechanisms may occur in unison, it is nevertheless important to treat DHC in isolation. Doing so helps identify the specific criteria for DHC initiation, a crucial step in nuclear safety economics of Zr components.

Chapter Outline

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2.1 Physical Metallurgy of Zirconium Alloys

The first theme of this review concentrates primarily on the multiscale metallurgy of Zr alloys. As previously stated, there are various commercial Zr alloy clad material used in different reactor designs. Each commercial alloy has differing metallurgical properties and, in reality, each component is fundamentally different from another, even if both have been fabricated from the same alloy. During all stages of the manufacturing process, engineering tolerances and safety factors are applied to the component design when control over the material design is not possible or understood [Sutherlin (2005), Cheadle (1977), and Kass (1964)]. Therefore, components invariably differ in terms of their metallographic features because the local atomic environment is different. Even if these atomic scale differences appear to be subtle in engineering design, the sub-processes that govern DHC initiation will invariably be affected. In this respect, DHC may be thought of as an umbrella term for a failure mechanism in Zr alloys that involves hydrogen diffusion and hydride precipitation; however, each Zr alloy component has its own unique manifestation of the DHC phenomenon owing to its distinct metallurgical properties.

The challenge is to quantify the effect of atomic scale differences in engineering design, and then justify the extent to which such material differences are acceptable. Of course, this challenge can be approached from a purely statistical standpoint as an average over many empirical studies. However, in industry, there are also financial restrictions and legal overheads to consider when designing materials. In the nuclear industry, such statistical empiricism is the norm but this is impractical in the long term for many reasons, including the high costs associated with fuel pin engineering and experimental test programs [Strasser, Adamson, and Garzarolli (2008) and Puls (2012)]. Moreover, a statistical approach leads to very conservative estimates for engineering tolerances and safety factors [Martin (2013)].

As understanding of DHC failure in Zr alloys has progressed, there has been greater emphasis on specific fabrication techniques and manufacturing considerations into final Zr alloy clad designs in order to extend their longevity. Therefore, it is important to begin an analysis of DHC by reviewing the nature of Zr alloys. The following discussion is an analysis of the multiscale physics of Zr alloys through the lens of theoretical and experimental metallurgy. This will provide a top-down breakdown of Zr alloy components across the typical length scales and dimensionalities of key metallographic features. This will also help identify the differences between the commercial Zr alloys and subsequently assess how these differences correlate to DHC initiation.

2.1.1 Material Properties

It is essential to first consider a hypothetical specimen of pure Zr across various length scales. Understanding the properties of this Zr specimen will prove insightful in later discussions on the Zr-H system as well as modelling its behaviour.

Electronic Structure. The electronic shell configuration of a single neutral atom Zr is given by

$$\text{Zr} : |1s^2\rangle|2s^2\rangle|2p^6\rangle|3s^2\rangle|3p^6\rangle|3d^{10}\rangle|4s^2\rangle|4p^6\rangle|4d^2\rangle|5s^2\rangle, \quad (2.1)$$

This configuration of Zr bestows it with the characteristic chemistry common to the group IV transition metals in the periodic table of elements. In turn, the quantum chemistry of Zr underpins its crystallography, phase transformations and elastomechanical properties, which are all important to the Zr-H system. For later discussions, it is worth highlighting that this electronic structure complicates the application of DFT methods to the Zr-H system [Burr (2014), Lumley (2013), and Nazarov et al. (2016)].

As a transition metal, Zr has partially filled d bands, which results in very strong metallic bonds [Cahn and Haasen (1996)]. As usual, the partially filled outermost sub-shells of Zr contain the valence electrons: the two $|4d(m_3)\rangle$ electrons and the two $|5s(m_1)\rangle$ electrons are valence electrons. But the two outermost sub-shells of a Zr atom that are completely filled exhibit valence behaviour because these electrons are not as tightly bound to the Zr nuclear as the innermost core electrons; these outer semi-core electrons are two $|4s(m_1)\rangle$ electrons and the six $|4p(m_2)\rangle$ electrons. These valence electrons are responsible for the very strong metallic bonds between Zr atoms and, in turn, its high mechanical strength (resistance to distortions) and high melting point (resistance to separation) as previously stated.

In addition, the partially filled d bands also allow multiple oxidation states and the formation hydrides [Mueller, Blackledge, and Libowitz (1968)]. Understanding the electronic structure of Zr is, therefore, a vital prerequisite in constructing a less conservative DHC failure criterion because it underpins the formation and fracture toughness of Zr-H compounds.

Crystallography. The crystallographic phase of Zr is polymorphous, that is, it depends on the ambient conditions of temperature and pressure. As depicted in the temperature-pressure phase diagram in FIG. 2.1(a), there are several distinct crystal structures. In ambient conditions of standard temperature and pressure, Zr is in its α -Zr phase, which has a hexagonal close-packed (HCP) crystal structure as shown in FIG. 2.1(b) and a {ABABAB...}

stacking of adjacent planes as shown in FIG. 2.1(c). The rotational symmetries of Zr unit cell are those of the space group P63/mmc. For example, the basal plane exhibits a six-fold symmetry around the $\langle c \rangle$ -axis, whereas the prism plane may exhibit only a two-fold symmetry around the $\langle a \rangle$ -axes.

The hexagonal unit cell is defined by two lattice parameters: (i) a denotes the translational offset between adjacent basal planes; and (ii) c denotes the axial distance between the nearest two aligned basal planes. In general, these lattice parameters depend on temperature and pressure, but they define the atomic length scale:

$$a \sim \ell[\text{atomic}] \quad \text{and} \quad c \sim \ell[\text{atomic}] \quad (2.2)$$

One measure of anisotropy in a HCP crystal system is the a/c ratio, which is a geometrical parameter that defines the pyramid-shaped polyhedron formed by the inter-atomic bonds between the four nearest neighbouring metal atoms. The ideal c/a ratio is $\sqrt{8/3} = 1.633$ for which the pyramid-shaped polyhedron is a regular tetrahedron. However, if the a/c ratio is non-ideal, the pyramid-shaped polyhedron is instead an equilateral triangular-based pyramid with less isometries. For α -Zr in ambient conditions, a and c are 3.2331 Å and 5.1491 Å respectively, and so its c/a ratio of 1.593 is a deviation from the ideal value. This deviation is a manifestation of the atomistic scale anisotropy in Zr, that is, the interatomic metallic bonds are different along the various crystallographic directions. The effects of this atomistic scale anisotropy in Zr persists at all length scales because the various materials properties are fundamentally related to these inter-atomic bonds and their distortions.

The crystallography of Zr changes at high temperatures and high pressures. At high temperatures Zr is in its β -Zr phase, which has a body-centred cubic (BCC) crystal structure. At high pressures, Zr is known to form ω -Zr and ω' -Zr phases, which are hexagonal and cubic respectively. But the α -Zr phase is most relevant for the reactor operating temperatures and pressures.

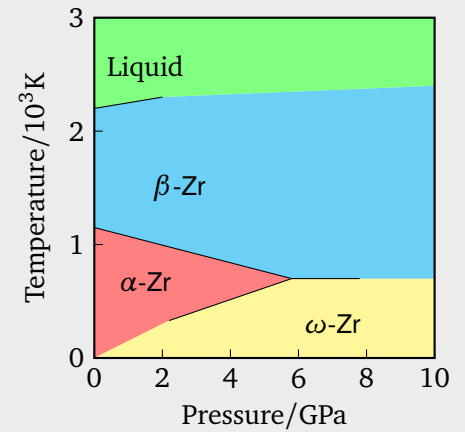
Deformation. The non-ideal c/a ratio of Zr has significant implications on how the regularity of the HCP crystal lattice can be disrupted by deformations caused by an external force. There are two primary deformation mechanisms in hcp crystals, namely, slip and twinning. The activation of either mechanism also depends on the c/a ratio, which in turn changes with temperature and pressure. Hence, at a given temperature, the dominance of either mechanism depends on the strength and direction of the external force resolved along specific crystallographic planes.

Slip systems can be classified by the slip plane and the displacement vector. In hexagonal metals, notable slip systems include basal, prism and pyramidal slip. In Zr, the most common slip systems at low temperatures

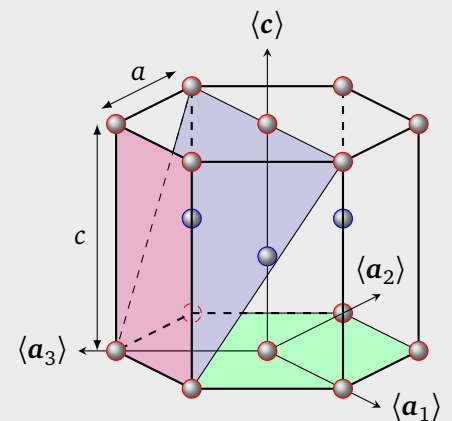
FIG. 2.1

Crystallography of pure zirconium

(a) The temperature-pressure phase diagram. (b) Hexagonal unit cell. (c) Stacking of hcp planes.

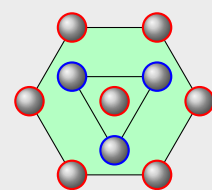


(a)



- Basal plane: (0001)
- Prism plane: (10 $\bar{1}$ 0)
- Pyramidal plane: (10 $\bar{1}$ 1)
- Atom on stacking layer A
- Atom on stacking layer B

(b)



(c)

are the the basal slip $\{0001\} \langle \bar{1}2\bar{1}0 \rangle$ and prismatic slip $\{10\bar{1}0\} \langle \bar{1}2\bar{1}0 \rangle$, which occur more easily than pyramidal slip. At higher temperatures, however, first-order $\langle \alpha \rangle$ pyramidal slip $\{10\bar{1}1\} \langle 12\bar{1}0 \rangle$ and second-order $\langle \alpha + c \rangle$ pyramidal slip $\{11\bar{2}2\} \langle 11\bar{2}3 \rangle$ become more operational. The distinguishability of each of these slip systems in Zr is an important consequence of its anisotropic crystallography.

Twin modes are often an alternative deformation mechanism when the activation of a slip system is unfavourable. But, twinning may dominate over slip in hexagonal metals in which the number of slip systems is limited. The activation of twin modes is particularly important to the study of cracks in Zr due to the von Mises yield criterion [Akhtar (1973), Heheman (1972), and Ibrahim and Cheadle (1985)]. This also has implications on the continuum scale mechanical properties of HCP α -Zr and the need for five independent elastic stiffness constants within the framework of linear (Hookean) elasticity; this is discussed in due course.

Polycrystallinity. The anisotropic crystallography of Zr underpins the collective behaviour of the numerous hcp crystallites that constitute the component-scale Zr specimen. The microstructure of commercial specimens of Zr can be distinguished, in part, by the average grain size

$$l_g \sim \begin{cases} 10 \times \ell[\text{microscopic}] & \text{for fine grain} \\ 10^2 \times \ell[\text{microscopic}] & \text{for coarse grain} \\ 10^3 \times \ell[\text{microscopic}] & \text{for blocky-}\alpha \end{cases} \quad (2.3)$$

Note, however, there is usually a distribution of grain sizes and so $\ell[\text{grain}]$ is not always a suitable measure of the average grain size. For example, blocky- α specimens can be composed of a bimodal distribution of some very large grains and lots of smaller grains [Tong (2016)]. For hereon in, intra-granular, inter-granular and trans-granular are adjectives that respectively refer to metallographic features being within a grain, between two grains and across multiple grains.

Texture. A standard convention for quantifying the texture of commercial Zr clad material is to use the Kearns parameters, $\{f_l, f_n, f_t\}$ which are depicted in FIG. 2.2 and are defined as follows. Suppose that component is overlayed with a cylindrical polar coordinate system $\{x_l, x_n, x_t\}$ where the x_l -axis is the longitudinal (or axial) direction along the length of the cylinder, x_n is the normal (or radial) direction on the plane whose normal is the x_l -direction, and x_t is the transverse (or circumferential) direction around the circular cross-section. Then the Kearns parameters f_l, f_n and f_t denote the fraction of grains whose basal poles are orientated along the longitudinal, normal

and transverse directions of the component.

Due to the crystallite anisotropy, the texture of Zr plays a very important role in various aspects of the DHC mechanism. For example, the texture of a Zr alloy can affect the mechanical performance, corrosion properties, H diffusion and hydride precipitation. Accordingly there has been considerable industrial research focused on the fabrication of Zr alloys with favourable texture that may inhibit the unfavourable radial orientation of hydride features and hence DHC initiation. Fabrication processes involve thermomechanical treatments that influence the grain morphology [Kass (1964) and Tong (2016)]. Notable examples include the Zircaloy-2 tubing ($f_l = 0.07$, $f_n = 0.33$ and $f_t = 0.70$) and hot rolled Zircaloy-4 plate ($f_l = 0.1$, $f_n = 0.3$ and $f_t = 0.6$). In other cases, the texture cannot be controlled such as in welded components that have an undesirable random texture [Strasser, Adamson, and Garzarolli (2008)].

Elastomechanics. The mechanical response of Zr alloys to external forces is perhaps the most important aspect of DHC experimental research. Classical mechanics is used to study the elastoplastic behaviour of a macroscopic Zr specimen which is treated in its entirety as a topologically continuous body. However the underlying microscale anisotropy and heterogeneity together lead to complex behaviour at the continuum scale, which is particularly evident for elastic properties of Zr components. This effect can be seen in measurements of the Young's modulus, Y , shear modulus, μ , and the Poisson's ratio, ν of Zr specimens, which are standard mechanical parameters that often assume isotropy.

As shown in FIG. 2.3, it is clear that Y is actually anisotropic for hot rolled Zircaloy-4 sheets as it differs along the x_l - and x_t -directions. This effect of anisotropy is stronger at lower temperatures. In particular, these Zircaloy-4 sheets are more stiff along the x_t -direction as opposed to the x_l -direction. This can be explained by considering the Kearns parameters for these Zircaloy-4 sheets; there is a significantly larger fraction of basal poles orientated towards to the x_t -direction. Deformation along the $\langle c \rangle$ -direction is more difficult than along the $\langle a \rangle$ -directions in a single crystallite [Akhtar (1973)]. Hence, deformation along the x_t -direction is more difficult because of the aggregate properties of the many crystallites whose basal poles coincide with this direction. Moreover, as the temperature increases, deformation along the $\langle c \rangle$ -direction becomes more energetically favourable so the stiffness along the x_t -direction is lowered. However, slip along $\langle a \rangle$ -directions is enhanced even more so at these higher temperatures, and hence, the degree of anisotropy is lowered. Accordingly, it is useful to unify the Young moduli along each direction so as to capture the underlying

FIG. 2.2

Texture of zirconium clad

Kearns parameters for the textures of various clad materials.

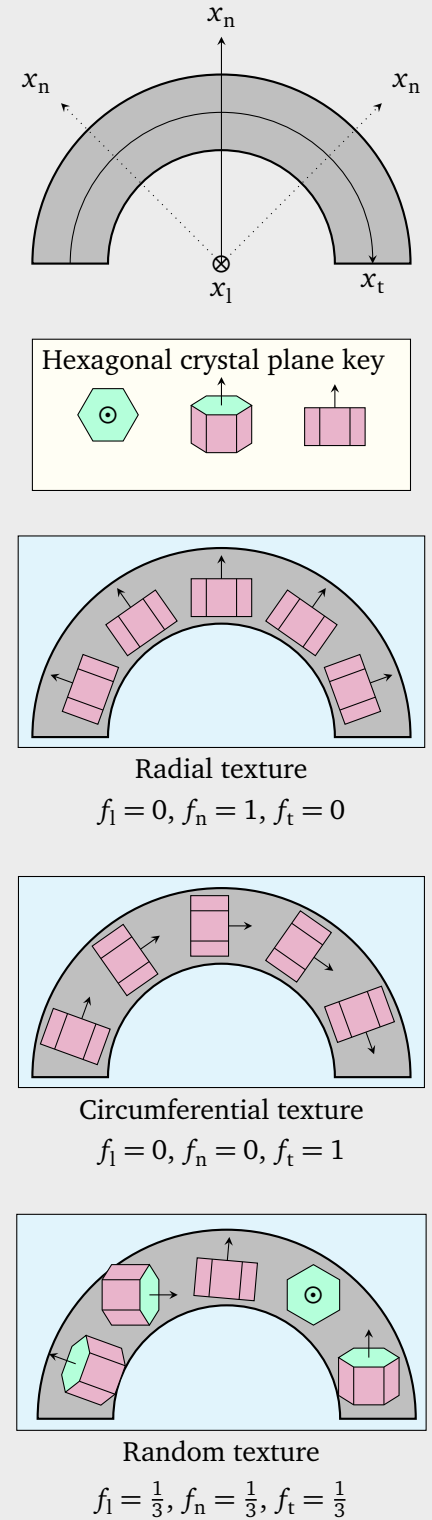
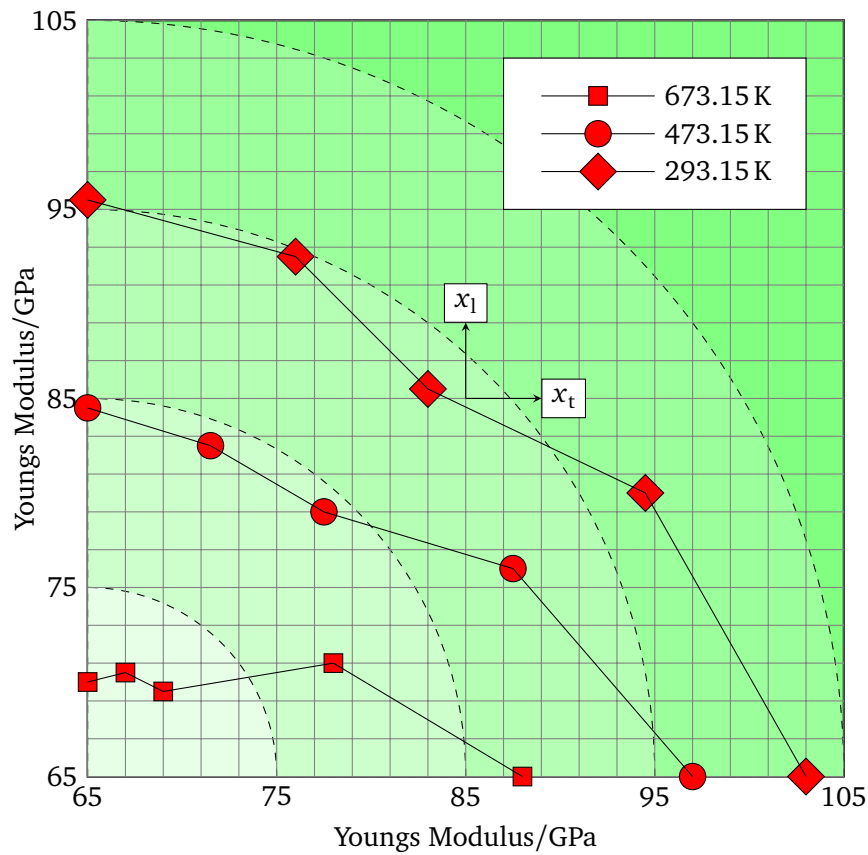


FIG. 2.3

Young's modulus of zirconium
The anisotropic nature of the Young's modulus of a highly-textured Zr specimen as measure along the normal and transverse directions, and how it varies with the temperature. Observe that at low temperatures, the degree of anisotropy, as defined by the ratio of the respective normal and transverse values at a given temperature, is greater because of the preferred directionality of slip modes. Adapted from Akhtar (1973).



symmetry of the constituent crystallite.

Owing to its crystal anisotropy, Y on its own is not a sufficient gauge for the elastic properties of a Zr alloy. It is necessary to use the fully anisotropic fourth-rank elastic stiffness constant tensor $C_{[4]}$ and compliance tensor $S_{[4]}$, which capture the hexagonal symmetry. For a hexagonal material, there are five independent elastic stiffness components, $\{C_{11}, C_{12}, C_{13}, C_{33}, C_{44}\}$, which may be determined directly from standard mechanical tests as well as first-principles electronic structure calculations [Akhtar (1973) and Burr (2014)]. Experimental values are listed in TAB. 2.1 from it can be seen that the isotropic Y values are not suitable at any temperature.

TAB. 2.1

The elastic stiffness constants of hexagonal zirconium
The elastic stiffness constants are given in units of GPa at various temperatures. It is clear that Young's modulus does not truly convey the anisotropy of deformation that is crucial for hexagonal materials in general. Adapted from Akhtar (1973).

T/K	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	Y	μ
298 K	143.4	72.8	65.3	164.8	32.0	96.9	36.4
573 K	130.10	78.60	65.70	155.9	28.2	81.7	30.2
773 K	121.4	81.2	65.9	149.3	25.7	71.8	26.2

2.1.2 Defect Microstructure

The manufactured alloys of Zr contain a rich diversity of defects at various length scales. The defect microstructure of the Zr clad material can drastically influence the mechanistics of the DHC sub-processes [Puls (2012)]. The aim here is to showcase the most important defects that are present in commercial Zr alloys and appreciate their role in DHC initiation. This serves as useful starting point for the development of mechanistic models of the multi-defect stress state of Zr alloys.

Defects in Zr alloys have been observed using a broad range of experimental characterisation techniques that operate at different length scales. The most relevant examples are listed in **TAB. 2.2**, which includes field ion microscopy (FIM), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and optical micrography [Carpenter (1973), Cui et al. (2009), and Puls (2012)]. Note that the typical resolutions are only listed here should only be used as generic guide. Many other variants of these techniques have been applied to study the defect microstructure of Zr alloys in the context of DHC research; this includes electron back-scatter diffraction (EBSD) and atom probe tomography (APT) [Tong (2016) and Barrera et al. (2018)]. The present work focuses primarily on TEM and SEM observations for reasons that will become clear in later discussions.

It is also important at this point to distinguish pure Zr as considered in the preceding discussions from its various commercial alloys. In the nuclear industry, the primary reasons for alloying Zr are to increase the mechanical strength and corrosion resistance. The various commercial Zr alloys are primarily defined by solute content and their concentrations; the effects of various solute species in Zr are listed in **TAB. 2.3** towards the end of this section.

Resolution	Characterisation Technique	Observable Defects
ℓ [atomic]	Field Ion Microscopy (FIM)	Interstitials
ℓ [nanoscopic]	Transmission Electron Microscopy (TEM)	Dislocations Inclusions Micro-precipitates
ℓ [microscopic]	Scanning Electron Microscopy (SEM)	Grain boundaries Macro-precipitates
ℓ [macroscopic]	Optical Micrography	Notches and cracks

TAB. 2.2

Characterisation of defect microstructures
Experimental techniques for observing various defects in Zr alloys. Note that the typical resolutions are only given as estimates and serve as convenient references in the present work.

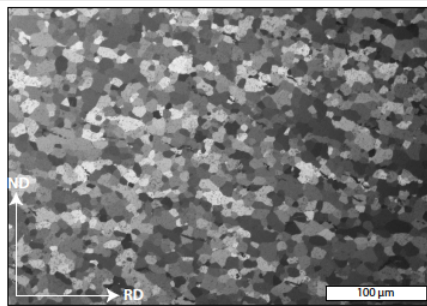
FIG. 2.4

Defects in zirconium

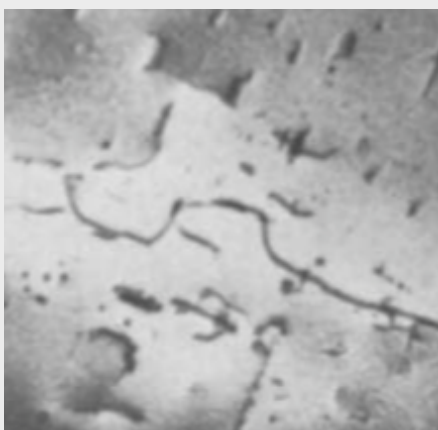
(a) A secondary DHC flaw as seen in an optical micrograph. (b) An EBSD map showing the grains in polycrystalline Zr. (c) Dislocation networks using TEM.



(a) [Puls (2012)]



(b) [Weekes (2015)]



(c) [Carpenter, Watters, and Gilbert (1973)]

Volumetric Flaws. The free surfaces of the Zr component are nominally smooth, but they may contain flaws such as notches or cracks. These flaws can be relatively large, that is, their sizes could be of the order of $100\text{ }\mu\text{m}$ or greater. A flaw whose size is comparable to that of the component is an important geometrical feature that must be considered at the continuum scale. Furthermore, during reactor operation, the swelling of the fuel creates hoop stresses in the fuel clad. Any existing flaw is then subject to these loading conditions. The inter-atomic bonds at the flaw tip are stretched apart to point of slip or rupture. The region ahead of the flaw is thus under tension and is prone to deformation via plastic yielding, and ultimately, separation via brittle fracture.

The tensile state ahead of the flaw depends on its geometry and loading conditions as well as the local microstructure. This tensile state influences H diffusion and hence hydride precipitation. Therefore flaw geometries are the subject of considerable investigation to experimental DHC test programs. It is industry practice to use handbook solutions that parametrize DHC initiation as a function of various flaw geometries including V-notches, U-notches, penny-shaped voids and sharp cracks. Additionally, DHC initiation creates secondary flaws via the fracture of the hydrogen-enhanced and hydride-rich regions. The propagation of these DHC flaws through the component is vital to failure criteria of Zr alloys [Puls (2012), Schofield (2002), and Martin (2013)].

Grains. Heterogeneity plays an important role in the micromechanics of Zr components because every interface between two homogeneous regions is an energetic surface. The polycrystalline nature of Zr alloy components is crucial because of anisotropy of Zr crystallites. A boundary between two grains is an interface between the misorientated crystallites along which the atomic structure is locally disordered. Hence, a grain boundary is a localised stress-raiser; certain areal pockets on the crystallographically-mismatched interface may be under either extreme tension or compression. Hence, the intrinsic energetics at grain boundaries can also influence H diffusion and hydride precipitation but at a more localised scale. In this sense, grain boundaries are secondary stress-raisers to the loaded flaw. The effect of grain boundaries is more noticeable for fine grain specimens in which there is a higher density of grains and, hence, grain boundaries [Chamaa et al. (2018)].

Regardless of the average grain size, grains are understood to be the largest spatial regions of crystallographic homogeneity in the metal. However, in reality, grains have a complex substructure and their homogene-

ity is rarely preserved, even for the smallest crystallites. Grains not only contain a conglomeration of smaller intra-granular defects, such as atomic scale interstitials and vacancies, microscale dislocation pile-ups and precipitate features, that disrupt the regularity of the crystal lattice, but they may also be divided into smaller crystallites whose interfaces are not as energetic as those between grains. These low energy intra-granular crystallite interfaces may be twin boundaries, laths, stacking faults or two-phase interfaces [Puls (2012)]. These smaller scale surface defects are then tertiary stress-raisers.

Dislocation Networks. The evolution of dislocation microstructure of a polycrystalline specimen of Zr underpins its plastic deformation. Each dislocation is like a soliton, that is, a localised wave packet that represents a mobile distortion in an otherwise perfect crystallite. In general, the soliton dynamics of dislocations in metals leads to the formation of energetically favourable networks of dislocations. However, the complex configurations of such dislocations networks bestows a certain irreversibility to the dislocation dynamics. This complexity is attributed to the many-soliton interactions between dislocations and their sources as well as with other defects, which involves the nucleation and annihilation of dislocation loops, the impedance to dislocation motion by barriers, the pinning of dislocations to obstacles and, ultimately, the growth of dislocation forests.

This irreversible complexity of dislocation dynamics plays an important role in the local scale elastoplastic behaviour of Zr alloy components. Plastic deformation in Zr can be attributed to both homogeneous and heterogeneous mechanisms. Homogeneous mechanisms involve the activation of slip via sources such Frank-Read sources. Heterogeneous mechanisms involve the channelling of radiation-induced prismatic loops in narrow intra-granular bands. There are typically high densities of dislocations in Zr alloys; for example, in cold worked Zr-2.5Nb tubes, the dislocation density is as high as 10^{15} m^{-2} [Schofield (2002)]. At high temperatures, a dense dislocation microstructure can be annealed so as to clear the memory of the plastic deformation. Dislocations are thought to play an important role in hydride nucleation as they can affect the solid solubility of H in Zr alloys [Darby, Martin, and Scarth (2013) and Puls (2012)].

Irradiation Damage. The high neutron flux environment of the reactor can lead to the formation of point defect clusters in the Zr alloys through the Frenkel pair mechanism. These point defects cluster to form interstitial and vacancy loops that impede dislocation motion. The irradiation damage then increases the density of defects within the Zr matrix. In turn, this can also have an affect on the solid solubility of H in Zr alloys [Darby, Martin, and

Scarth (2013)].

Intermetallic Second-Phase Particles. The typical alloying additions of Fe, Cr, Ni and Nb second-phase particles (SPPs) are heterogeneously distributed throughout the grains. In general, this distribution will vary according to heat treatment and compositions. The SPPs can be thought of as inclusions but they are very small in size relative to typical grain sizes. For example, Fe and Cr solutes form SPPs whose sizes are of the order of ~ 100 nm and smaller. The two-phase interface between parent matrix and SPPs is a tertiary stress-raiser to the loaded flaw and grain boundaries in the sense that it is a (less potent) nucleation site for hydrides [Chamaa et al. (2018)].

Hydrogen and Hydrides. It is worth emphasising H interstitials and hydride precipitate features are indeed themselves defects whose stresses distort the Zr matrix, and the ensuing discussions will expand upon this perspective.

TAB. 2.3

The effects of alloying additions to zirconium

Commercial alloys can be categorised according to the typical compositions of these constituent solute additions. It is important to the improvement to waterside corrosion resistance that is offered by Sn is only true for the older generation of Zr alloys; for current Zr-Nb alloys, the addition of Sn is detrimental. Note that H is an undesirable solute.

Solute Addition	Alloying Effects
Chromium (Cr)	▶ Formation of second-phase particles ▶ Stabilisation of β-phase: - see Iron - large weight percentage ▶ Improvement of corrosion resistance
Hydrogen (H)	▶ Formation of brittle hydride features ▶ Implicated in DHC failure
Iron (Fe)	▶ Formation of second-phase particles ▶ Stabilisation of β-phase: - Chromium - large weight percentage ▶ Improvement of corrosion resistance
Oxygen (O)	▶ Stabilisation of α-phase: - Raises α-β phase transus in Zr - Enhances the β-phase field ▶ Interstitial solution strengthening
Nickel (Ni)	▶ Formation of second-phase particles ▶ Enhancement of hydrogen pick-up ▶ Improvement of corrosion resistance
Niobium (Nb)	▶ Stabilisation of β-phase ▶ Lowering of corrosion kinetics ▶ Reduction in H pick-up
Tin (Sn)	▶ Stabilisation of α-phase ▶ Enhancement of creep resistance ▶ Improvement of (waterside) corrosion resistance

2.2 Hydrogen in Zirconium

The second theme of this literature review concerns the behaviour of H solute atoms as point defects in solid solution within α -Zr, and there is a breadth of research around this specific topic [Puls (2012)]. In the context of DHC, these studies can be sub-categorised into four main areas: (i) the pick-up of H atoms; (ii) the electronic structure of the Zr-H system; (iii) the diffusion of H atoms in the bulk Zr matrix; and (iv) the thermodynamics of Zr-H phases.

Considerable industrial effort is directed towards reducing H pick-up in the first instance because H ingress is the gateway to DHC initiation. However, once H atoms have been introduced into the Zr alloy component, it is crucial to understand the behaviour of these point defects. Fundamentally, a H atom is a quantum mechanical particle whose electronic structure determines its energetics in the Zr unit cell. The atomistic scale anisotropy of Zr suggests that H interstitial atoms occupy preferential sites that are energetically favourable [Khoda-Bakhsh and Ross (1982)].

Moreover, these energetics dictate how H interstitial atom can transition from one site to another; this step-by-step atomistic scale transport of H atoms through the Zr lattice towards flaws underpins the first sub-mechanism of DHC, namely, stress-driven diffusion. This interconnects directly with the second sub-mechanism of DHC, diffusion-controlled precipitation, because the flaw-tip accumulation of H atoms instigates the evolution of Zr-H system hydride phases that are more thermodynamically favourable than the Zr-H system dilute solid solution phase [Puls (2012)].

The thermodynamics of the Zr-H is described by the partial eutectoid group IV metal-hydrogen phase diagram shown in FIG. 2.5, which shows the existence several distinct Zr-H phases. The conditions for phases transformation between the solid solution phase to the hydride phases is characterised by terminal solid solubility (TSS), which is the critical concentration at a given temperature for both the solid solution and hydride phases to exist in equilibrium. Unifying the findings of H ingress, interstitialcy, transport and solubility in Zr alloys is important to the early stages of DHC initiation.

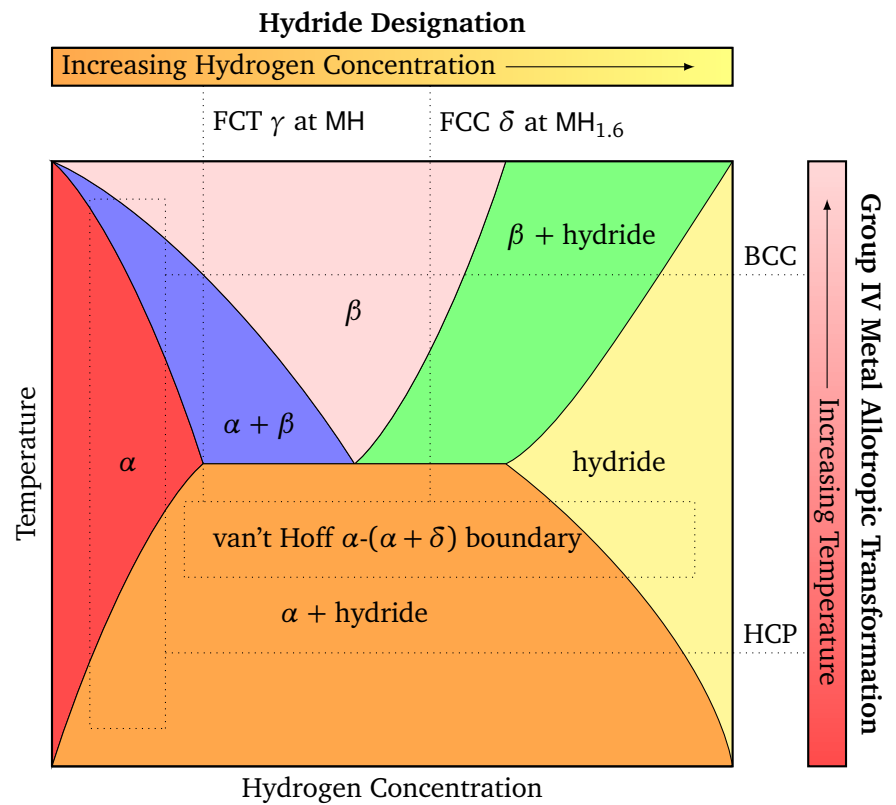
The following discussion is a review of the theoretical and experimental studies on H in Zr divided into the four aforementioned sub-categories. The ideas presented here also extend to the hydrogenic isotopes, deuterium (D) and tritium (T), whose behaviour in Zr alloys is subtly different. Collectively these mechanistic discussion topics will prove useful in developing a multiscale model of fracture-driven diffusion of H in Zr alloys. Note that the paradigm of multiscale has so far focused solely on length scales; now it will be important to also address the various time scales.

FIG. 2.5

Group IV metal-hydrogen partial eutectoid phase diagram

At reactor operating conditions, the α -phase is the most relevant, which leads to a range of zirconium-hydride phases with distinct stoichiometric properties and crystallographic structures. Note that this phase diagram should really portray a third axis pertaining to the system pressure. From this it would be clear that the varying temperatures and pressures in the reactor cause the thermodynamic system to alternate between the solid solution and hydride phases.

Adapted from Coleman (2003).



2.2.1 Ingress

The pick-up of H atoms by Zr alloy components, and the subsequent introduction into the bulk solid solution, is attributed to a range of pre-service manufacturing processes as well as the reactor environment. Following industrial manufacturing guidelines, pre-service H pick-up can be restricted to relatively low concentrations,

$$c_{\text{H}}[\text{manufacturing}] \simeq [5, 15] \text{ ppm}, \quad (2.4)$$

which is then supplemented with H picked up from the reactor environment over the operation lifetime of the component. The lifetime of Zr alloy components is expected to be of the order of years and so it is useful to introduce the time scale

$$\tau[\text{year}] \simeq \mathcal{O}(10^7 \text{ s}) \quad (2.5)$$

in order to quantify the annual elevation of the bulk H concentrations. In modern reactors, H generation and ingress can be caused by four pick-up processes: (i) aqueous corrosion at the metal oxide-coolant water interface; (ii) radiolysis of coolant water; (iii) oxidation of the nuclear fuel; and (iv) absorption of the H concentration dissolved in the coolant water. The H

concentration absorbed by the component over operation time T due to the pick-up process $\mathcal{P}$ is given by the general formula

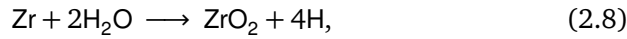
$$c_H[\text{ingress}](T) = \int_0^T dt \left(p_H[\text{ingress}; \mathcal{P}](t) r_H[\text{generated}; \mathcal{P}](t) \right), \quad (2.6)$$

where $r_H[\text{generated}; \mathcal{P}](t)$ is the total rate of H production within the reactor environment and $p_H[\text{ingress}; \mathcal{P}](t)$ is the fraction of H that is subsequently absorbed by the component. Note that the integral over time t in Eq. (2.6) accounts for the fact that H pick-up varies over time. The total bulk H concentration in the Zr alloy component over operation time T is then given by

$$c_H[\text{component}](T) = c_H[\text{manufacturing}] + \sum_{\mathcal{P}} c_H[\text{ingress}; \mathcal{P}](T) \quad (2.7)$$

Although all four processes contribute to H pick-up, the summation in the second term in Eq. (2.7) is dominated by the contribution from corrosion [Strasser, Adamson, and Garzarolli (2008)].

Aqueous Corrosion. The exterior of Zr alloy component is in contact with the coolant water. But, as previously mentioned, the electronic structure of Zr allows for multiple oxidation states. Hence, the coolant is able to react with Zr to form an oxide via the chemical reaction



that is, H is a by-product of the oxidation. But, in operation, only a small fraction of the corrosion by-product H, which is alloy dependent, enters the component; this is the corrosion H pick-up fraction

$$p_H[\text{corrosion}] = \frac{c_H[\text{ingress}; \text{corrosion}]}{c_H[\text{generated}; \text{corrosion}]} \simeq [0.05, 0.20]. \quad (2.9)$$

where $c_H[\text{generated}; \text{corrosion}]$ and $c_H[\text{ingress}; \text{corrosion}]$ are usually assumed to be constant over time. In modern reactors, then annual increase

$$c_H[\text{ingress}; \text{corrosion}](\tau[\text{year}]) \simeq [1, 2] \text{ ppm}, \quad (2.10)$$

and so the end-of-life $c_H[\text{component}](t)$ values are typically of the order of tens of parts per million. However, bulk H concentrations have been measured to be hundreds of parts per million for components in BWRs and PWRs as well [Schofield (2002) and Strasser, Adamson, and Garzarolli (2008)].

2.2.2 Interstitialcy

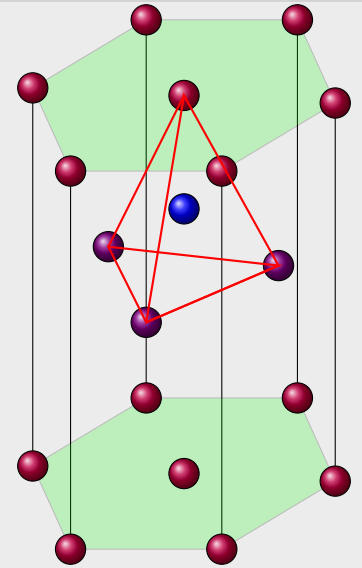
Once a H atom is in solid solution, it is an extrinsic point defect that occupies specific interstitial sites. The properties of the interstices are directly related

FIG. 2.6

Hydrogen as a tetrahedral interstitial in hexagonal close-packed zirconium

The interstitial environment of H in Zr has a trigonal symmetry.

Adapted from Patel (2014).



- Zr atom in HCP stacking layer A
- Zr atom in HCP stacking layer B
- H atom in tetrahedral site

to the electronic structure properties of Zr and the Zr-H system. Theoretical and experimental work seem to suggest that H atoms occupy preferential tetrahedral sites in hexagonal Zr owing to the anisotropy of the crystal structure. As shown in [FIG. 2.6](#), the tetrahedral sites have a trigonal symmetry; the H atoms forms three equivalent bonds with the Zr atoms on the basal plane and one non-equivalent bond with the Zr atom along the axial $\langle c \rangle$ -direction.

Interaction Energy. The elastic interaction energy mediates stress-driven diffusion. The mobile diffusing species creates a localised elastic distortion as it is a misfit in the crystallographic interstitial sites. This distortion interacts with other sources of elastic fields in the lattice, such as those caused by dislocations and cracks, to define an interaction energy. The usual chemical potential-driven diffusive hops are then biased by the need to reduce the interaction energy in the system.

All theoretical studies thusfar treat the H interstitials as misfitting spheres in an isotropic continuum; these ideas are based on previous work on hydrogen in iron [[Puls \(1985\)](#)]. Experimental studies indicate that distortion created by hydrogen in zirconium is that of a prolate sphere in tetrahedral sites which theoretically agrees with the notion of an isotropic basal plane and differing elastic effects along the $[0001]$ -direction [[Khoda-Bakhsh and Ross \(1982\)](#)]. Furthermore, there is continuum anisotropy and hence stress fields of dislocations and cracks must also account for this deviation from isotropy [[Steeds \(1973\)](#) and [Barnett and Asaro \(1972\)](#)].

The H-H interaction can be taken as negligible; this can be argued as follows. Firstly, in isotropic elasticity, the direct interaction energy between point defects is zero as each defect only produces shear stresses in the surrounding matrix. However, in anisotropic elasticity, the interaction is non-zero but is very short ranged; specifically, the defect stresses decay with the cube of the radial distance from its centre and hence the interaction between two defects would decay in a sextic manner. Hence, in a dilute solution, H-H interactions in anisotropic Zr are negligible as the interstitials would be too far apart on average [[Puls \(2012\)](#), [Eshelby \(1956\)](#), and [Eshelby \(1976\)](#)].^{Note 1}

Some work on the interaction energy of H with dislocations in Zr indicate that there are tensile regions near dislocation cores where the interaction energy is highly favourable. These regions have the potential to act as nucleation sites as they may contain a sufficiently large concentration of H that exceeds the critical solvus. For practical temperatures associated with DHC, this may indeed be the case in certain situation [[Puls \(2012\)](#)].

Note 1

Hydrogen-hydrogen interactions in zirconium

Additionally, the assumption of ignoring the hydrogen-hydrogen interaction is further supported of DFT studies on H interstitials in Zr indicate that two H atoms tend to repel each other in a dilute system [[Burr et al. \(2013b\)](#), [Burr et al. \(2013a\)](#), and [Lumley \(2013\)](#)].

2.2.3 Transport

The ability of H interstitials to be mobile in Zr depends on a variety of factors, including temperature and pressure, as well as impedance and trapping due to other intrinsic defects. The long-range transport of H atoms is assumed to be an interstitial diffusion mechanism that is biased by the local microstructure. This is best understood through transition state theory at the atomic scale as shown in **FIG. 2.7**. Theoretical justification of experiments of bulk diffusion in metals via this direct interstitial mechanism are usually based on phenomenological force-flux relations in the framework of linear irreversible thermodynamics [Callen (1960), Groot and Mazur (1961), and Balluffi, Allen, and Carter (2005)]. Treating the system as not too far from thermodynamical equilibrium is a simple way of constructing a macroscopic theory of diffusion that includes the effects of the gradients of stress and temperature [Puls (2012)].

Migration. A stress gradient provides a bias in the diffusive hops of the H interstitials in the Zr crystal. Considering the elastic energy of the misfit, a H atom would avoid compressive regions and accumulate in tensile regions; the rate of this process will be controlled, in part, by the elastic interaction energy between (i) the stress fields created by the H misfit in an interstitial site in Zr and (ii) any non-uniform local distortion due to stress-raisers in the system. In general, a typical Zr alloy clad sample will contain many sources of stress between the atomic and microstructural scales; alongside the loaded notch, these also include any plastic zone dislocation distributions, crystallographic dislocations, grain boundaries, second-phase particles and, of course, hydrides.

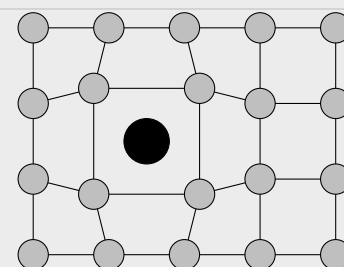
During the operation of the reactor and in dry-storage casks, H diffusion will also be affected by temperature gradients; generally, local temperatures become higher traversing along cladding material in the direction of the nuclear fuel pin. The H atoms tend to gather in low-temperature regions located towards the interface between metal-(oxide) cladding surface and coolant; the tensile fields of a surface notch will coincide with such regions [Puls (2012)]. Thermal diffusion of hydrogen in zirconium is not a well-studied experimental problem. Few studies involve working with a sample held with a constant temperature gradient but this alone did not produce hydrogen-enhanced regions where the concentration exceeded the solvus in the time required to achieve a steady-state solution [Puls (2012)].

In principle, several other diffusion mechanisms would need to be considered in a more full treatment of the kinetics of H diffusion in the Zr alloy. Firstly, diffusion along grain boundaries and the existence of fast diffusion paths could play an important role in the equilibrium concentration profiles.

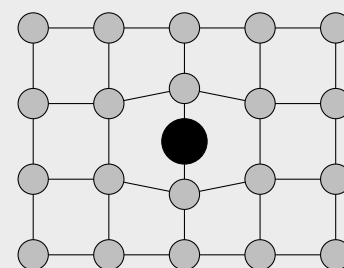
FIG. 2.7

Diffusive transition state

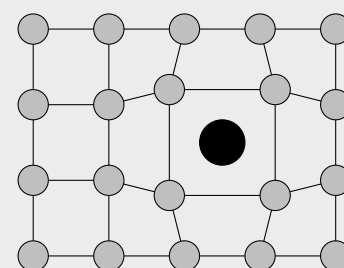
An atomic scale transition state model of interstitial diffusion in a crystal.



Initial state



Transition state



Final state

TAB. 2.4

Experimentally-measured diffusivities of hydrogen isotopes in zirconium

Note that the quote values are the Arrhenius diffusivity coefficients. Adapted from Puls (2012).

System	Diffusivity/($10^7 \text{ m}^2 \text{ s}^{-1}$)
H in Zr	{0.714, 1.09, 7.0, 40.0}
T in Zr	1.53
H in Zircaloy-2	{2.17, 7.0}
T in Zircaloy-2	{0.21, 1.04}
H in Zr-2.5Nb	1.17
T in Zr-2.5Nb	{0.18, 2.4, 3.5, 5.2}

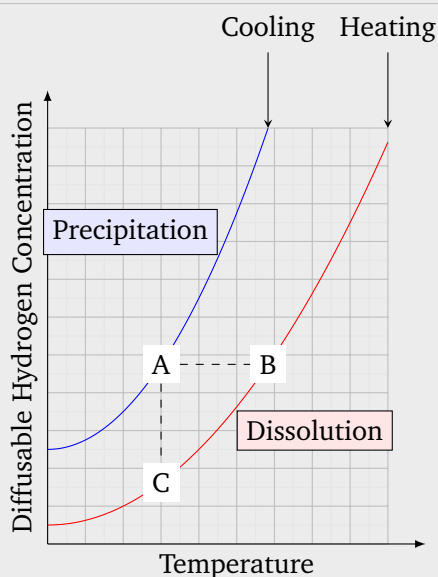
Secondly, an irradiated sample will contain a non-negligible density of defects that act as trapping sites, which will impede the motion of the diffusing species. On the other hand, H is a quantum mechanical particle which can tunnel through such barriers, even at lower temperatures. Thirdly, bulk hydride diffusion may need to be considered in regions of elevated equilibrium concentration such as mobile H in hydrides. Finally, the role of anisotropy is also important with diffusivities being dependent on direction.

Diffusivity. There have been many experimental studies on the diffusion of hydrogen, deuterium and tritium in zirconium and its alloys [Geleznas, Conn, and Price (1963), Gulbransen and Andrew (1954), Mallet and Albrecht (1957), Mazzolai and Ryll-Nardzewski (1976), Skinner and Dutton (1990), Kearns (1972), Watanabe, Ashida, and Sonobe (1990), Austen, Elleman, and Verghese (1974), Cupp and Flubacher (1962), and Greger et al. (1980)]. Measurements of diffusivities in dilute systems involve methods to determine tracer diffusion coefficients as well as their Arrhenius relationship with temperature. As shown in TAB. 2.4, the variance of obtained values is quite large but appear to be of a similar order of magnitude.

FIG. 2.8

Hydrogen solvi for zirconium-niobium alloy

The points A and C are separated by $\sim 50 \mu\text{g/g}$ for this particular example. Adapted from Eadie, Metzger, and Léger (1993).



2.2.4 Solubility

The terminal solid solubility (TSS) provides a temperature boundary for the phase transition, that is, the temperature at which either (i) the first hydrides have just begun to precipitate in the forwards phase-transition or (ii) the last remaining hydrides have just begun to dissolve. Observe that this definition of the TSS is only valid for a closed system with a constant hydrogen content; in the field of DHC, the TSS is further classified into the terminal solid solubility for precipitation (TSSp) and the terminal solid solubility for dissolution (TSSd) for the ensuing reasons [Puls (2012)].

Hysteresis. Between the stages of precipitation and dissolution of the hydrides, an important observed effect is the large and reproducible hysteresis in the solvus which, in part, can be explained by high mobility of H atoms as opposed to the Zr atoms. (In general, hysteresis in phase transformations are a consequence of the existence of a barrier to the transformation itself which can only be overcome only by a threshold driving force as opposed to random thermal fluctuations alone.) This affects the rate of phase transition in a particular direction depending on the extent to which it relies on the mobility of the Zr atoms and accessibility to intermediate metastable phases [Puls (2012)]. The precipitation-dissolution curve in FIG. 2.8 is a manifestation of this TSSp/d hysteresis [Eadie, Metzger, and Léger (1993) and Darby, Martin, and Scarth (2013)].

2.3 Hydrides in Zirconium

The third theme of this literature review focuses on the hydrided microstructure of Zr alloy components, which is central to DHC initiation. Therefore, experimental characterisation of hydrides in α -Zr has featured prominently in DHC research. Neutron and X-ray diffraction techniques are used to probe the crystallographic structure of hydrides [Balagurov, Bashkin, and Kolesnikov (1991) and Kolesnikov, Balagurov, and Bashkin (1994)]. Micrographs obtained from TEM, SEM and optical experiments are routinely used to study the morphology and topography of hydride features [Puls (2012), Bailey (1963), Bradbrook, Lorimer, and Ridley (1972), Carpenter (1973), Carpenter, Watters, and Gilbert (1973), and Carpenter (1978)]. These studies on hydrides in Zr have revealed the existence of distinct phases and non-simple morphologies.

However, the lifecycle of hydride precipitates is subject of considerable debate [Mueller, Blackledge, and Libowitz (1968) and Puls (2012)]. It is not known exactly how hydrides nucleate, grow and dissolve because there is no direct evidence from the aforementioned experimental studies. Such information can only be inferred from *in situ* TEM and SEM studies, which has led to various theories but no conclusive consensus. It is for this reason industrial safety assessments use very conservative (worst-case scenario) estimates of the hydride microstructures that are based on simulations of flaw-tip H profiles [Martin (2013)]. In such models, the nucleation, growth and dissolution of hydrides is not simulated explicitly. From the standpoint of modelling, this conservatism can be both inaccurate and inefficient. For the purpose of this investigation, it is then essential to deduce with care the important length and time scales associated with hydride precipitation in Zr so that they may be used more effectively in a multiscale model.

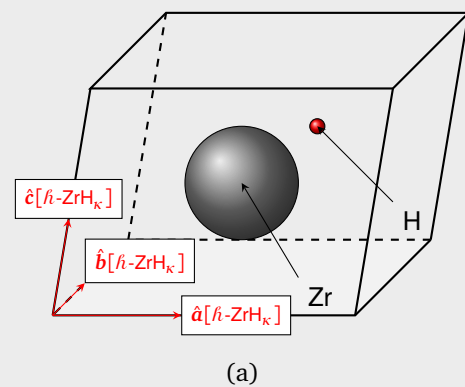
As before, it is also useful to divide this review on hydrides in Zr into three sub-categories: (i) the properties of bulk hydride phases; (ii) morphologies of hydride precipitates; and (iii) hypotheses concerning the mechanisms of nucleation and growth. The well known ideas from the first and second topics underpin DFT and PF models of hydrides, and the speculative ideas from the third topic is the focus of a later theoretical discussion on diffusion-controlled precipitation.

Before commencing this section of the review, it is worth commenting on the H isotope effect. The chemistry that underpins the Zr-H phase system is very similar to Zr-D and Zr-T phase systems. On the most part, hydrides share many properties with their deuteride and tritide counterparts in Zr alloys. However, there are very subtle differences between hydrides, deuterides and tritides [Mueller, Blackledge, and Libowitz (1968)].

FIG. 2.9

Zirconium hydride unit cell

The Wigner-Seitz crystallographic unit cell of a hydride phase.



2.3.1 Bulk Hydride Phases

The first topic of this review on hydrides in Zr concerns the properties of pure hydride phases across different length scales. At the atomic scale, a hydride phase, h -ZrH $_{\kappa}$, can be distinguished from the parent α -Zr metal and the α -Zr-H dilute solid solution by its H stoichiometric composition, κ , and crystallographic structure as defined by the Wigner-Seitz unit cell in FIG. 2.10. At the microscale, the morphology and orientation relationships of hydride precipitates in α -Zr can be deduced from experimental micrographs. At the continuum scale, the differences in the elastomechanical properties between pure Zr and hydrogenated or hydrided Zr become more apparent.

Phase Characterisation. Four distinct hydride phases have been discovered to date. In order of H stoichiometry, these are commonly labelled as the ζ -ZrH $_{0.50}$, γ -ZrH $_{1.00}$, δ -ZrH $_{1.66}$ and ϵ -ZrH $_{2.00}$ phases. The formation of precipitates of each phase depends not only on H concentration but also the temperature and the cooling rate. Their respective properties of each phase are summarised in TAB. 2.5, from which it is clear that more is known about the γ -ZrH $_{1.00}$ and δ -ZrH $_{1.66}$ phases. This is because γ -ZrH $_{1.00}$ and δ -ZrH $_{1.66}$ precipitates are more commonly observed in Zr alloys when subject to reactor-like conditions [Lemaignan (2012), Blackmur et al. (2015), and Carpenter (1978)]. For example, in Zircaloy-4, γ -ZrH $_{1.00}$ and δ -ZrH $_{1.66}$ precipitates are observed when the bulk H concentration exceeds the solubility limit of 50 at.% at 773 K or 0.7 at.% at 573 K, the latter case being more relevant here.

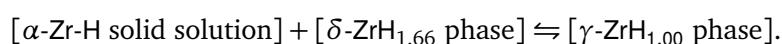
The most recently discovered ζ -ZrH $_{0.50}$ phase is the subject of much speculation and much less is known about it in comparison to the other phases, especially from an experimental standpoint. It is typically not observed in Zr alloys subject to typical reactor conditions. However, the existence of such a metastable ζ -ZrH $_{0.50}$ phase had been predicted prior to its discovery because of the theoretical necessity of an intermediate transitional phase between the α -Zr-H solid solution and the γ -ZrH $_{1.00}$ or δ -ZrH $_{1.66}$ phases [Zhao et al. (2008a)]. It is now believed that the metastable ζ -ZrH $_{0.50}$ phase features can transform into the (meta-)stable γ -ZrH $_{1.00}$ phase features during fast cooling or the stable δ -ZrH $_{1.66}$ phase features during slow cooling [Zhao et al. (2008a), Zhao et al. (2008b), Zhu et al. (2016), Steuwer et al. (2009), and Zheng et al. (2015)].

Alongside the γ -ZrH $_{1.00}$ and δ -ZrH $_{1.66}$ phases, a third stable ϵ -ZrH $_{2.00}$ phase is also observed in Zr alloys subject to reactor conditions. However, the formation of ϵ -ZrH $_{2.00}$ precipitates requires a very large H composition and so they occur less frequently in experimental studies than their γ -ZrH $_{1.00}$ and δ -ZrH $_{1.66}$ counterparts. In the context of DHC, γ -ZrH $_{1.00}$ and δ -ZrH $_{1.66}$

precipitates are, therefore, more relevant; the remainder of the discussion will focus more on these particular phases.

Phase Stability. The thermodynamic stability of ϵ -ZrH_{2.00} phases is well known but there is no general agreement in the literature regarding the thermodynamic stability of the ζ -ZrH_{0.50}, γ -ZrH_{1.00} and δ -ZrH_{1.66} phases. One measure of the stability of the reduction in the free energy associated with the enthalpy of formation; a greater (more negative) formation enthalpy, ΔH_f , is indicative of greater stability. As shown in **TAB. 2.5**, the greater ΔH_f values for the δ -ZrH_{1.66} and ϵ -ZrH_{2.00} phases is partly indicative of a higher stability.

Given the significance of γ -ZrH_{1.00} precipitates in DHC failure, several competing ideas have been proposed regarding its stability [Puls (2012), Mishra, Sivaramakrishnan, and Asundi (1972), Motta and Chen (2012), and Nath, Lorimer, and Ridley (1975)]. There are two schools of thought: (i) the γ -ZrH_{1.00} precipitates constitute a metastable phase; or (ii) the γ -ZrH_{1.00} precipitates constitute an equilibrium phase formed via the peritectoid reaction:



As previously mentioned, it is generally understood that the formation of γ -ZrH_{1.00} and δ -ZrH_{1.66} phases is influenced by the cooling rate. However, experimental studies also show that γ -ZrH_{1.00} precipitates are continuously observed regardless of the cooling rate [Nath, Lorimer, and Ridley (1975)]. In these experiments, an ageing effect was observed at low H concentrations where γ -ZrH_{1.00} features are replaced by δ -ZrH_{1.66} features. Conversely, there was no ageing effect on δ -ZrH_{1.66} features in the low temperature regime at H concentrations below 500 wppm, implying that the δ -ZrH_{1.66} phase is in equilibrium at these temperatures and suggesting that the hypothesised peritectoid reaction does not occur for these conditions. Additional studies at room temperature and 421 K also confirm the absence of a transition from the δ -ZrH_{1.66} phase to the γ -ZrH_{1.00} phase [Lanzani and Ruch (2004) and Colas et al. (2010)]. Furthermore, γ -ZrH_{1.00} precipitates form more readily at higher H concentration, which indicates that there may be a critical H transus for γ -ZrH_{1.00} precipitation [Colas et al. (2010) and Daum, Chu, and Motta (2009)]. From these experimental studies, it can be concluded to some extent that the γ -ZrH_{1.00} phase is then metastable. ^{Note 2}

The corresponding deuterides and tritide phases are generally less stable than their hydride counterparts. This is most easily seen by comparing ϵ -ZrH_{2.00} phase and the ϵ -ZrD_{2.00} phase, the latter having a lower (less negative) formation enthalpy than the former [Mueller, Blackledge, and Libowitz (1968)]. This isotope effect is understood as follows. The D gas

Note 2

Experiments on Bulk Specimens

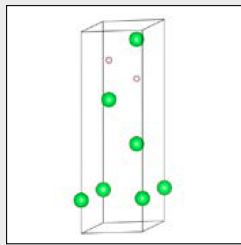
The hydrogenation of Zr to the relevant compositional range of the γ -ZrH_{1.00} phase has to date not produced any bulk γ -ZrH_{1.00} phase features, which is a further indication of its metastability.

FIG. 2.10

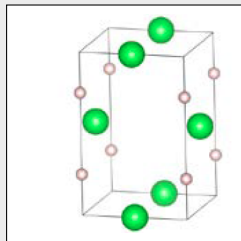
Zirconium hydride crystallography

The experimentally determined crystal structures of the four known hydride phases: (a) the trigonal hcp structure of the ζ -ZrH_{0.50} phase; (b) the tcp structure of the γ -ZrH_{1.00} phase; (c) the fcc structure of the δ -ZrH_{1.66} phase; (d) the fct structure of the ϵ -ZrH_{2.00} phase.

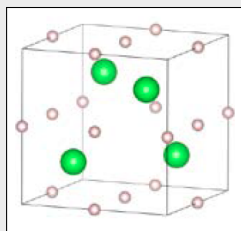
Adapted from Zhu et al. (2016).



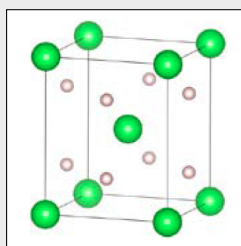
(a)



(b)



(c)



(d)

generally has a larger absolute entropy due to the larger mass and, hence, greater moment of inertia of D atoms. Therefore, the entropy of formation of deuterides is slightly greater (more negative) and so their dissolution (dissociation) pressures are slightly higher.

Phase Crystallography. The crystal structures of the γ -ZrH_{1.00}, δ -ZrH_{1.66} and ϵ -ZrH_{2.00} phases are well known from experimental observations, whereas the ζ -ZrH_{0.50} phase crystallography is still subject to considerable debate [Zhao et al. (2008a), Zhao et al. (2008b), and Puls (2012)].

The γ -ZrH_{1.00} phase has an ordered tetragonal close-packed (TCP) structure belonging to the P4₂/n space group. The two lattice parameters at room temperature are given by

$$a[\gamma\text{-ZrH}_{1.00}] = 4.586 \text{ \AA} \quad \text{and} \quad c[\gamma\text{-ZrH}_{1.00}] = 4.948 \text{ \AA}, \quad (2.11)$$

but other very similar values are also found in the literature [Puls (2012)]. The Zr atoms are found at the $\langle \frac{1}{4} \frac{1}{4} \frac{1}{4} \rangle$ sites whereas the H atoms occupy tetrahedral interstitial sites on alternating (1 1 0) planes, that is, the $\langle 000 \rangle$ and $\langle 00 \frac{1}{2} \rangle$ sites.

The δ -ZrH_{1.66} phase has a disordered face-centred cubic (FCC) structure of the CaF₂ prototype belonging to the Fm $\bar{3}$ m space group. The lone lattice parameter at room temperature is given by

$$a[\delta\text{-ZrH}_{1.66}] = 4.768 \text{ \AA} \quad (2.12)$$

but, again, other similar values are reported in the literature. The H atoms also occupy tetrahedral sites [Puls (2012)].

The ϵ -ZrH_{2.00} phase has a distorted face-centred tetragonal (FCT) structure of the space group I4/mmm, which resembles the CaF₂ prototype. However, unlike the similar tetragonal γ -ZrH_{1.00} phase, its room temperature lattice parameters

$$a[\epsilon\text{-ZrH}_{2.00}] = 4.969 \text{ \AA} \quad \text{and} \quad c[\epsilon\text{-ZrH}_{2.00}] = 4.450 \text{ \AA} \quad (2.13)$$

define an axial ratio, $c[\epsilon\text{-ZrH}_{2.00}]/a[\epsilon\text{-ZrH}_{2.00}]$, that is less than one.

The ζ -ZrH_{0.50} phase is found to have a metastable HCP structure of the trigonal crystal class system belonging to the P3m1 space group. As expected given the observations for H atoms in the α -Zr-H solid solution and the γ -ZrH_{1.00} and δ -ZrH_{1.66} phases, the H atoms in the ζ -ZrH_{0.50} phase also occupy tetrahedral sites.

Phase Stoichiometry. The γ -ZrH_{1.00} phase is stoichiometric whereas the δ -ZrH_{1.66} and ϵ -ZrH_{2.00} phases are non-stoichiometric. The defined ratios of the Zr atoms to H atoms in either phase is, however, only a typical representation.

In reality, the H occupancy throughout the spatial extent of a given phase is not uniform. For example, stable δ -ZrH_{1.66} phase features can have an average H/Zr atom ratio ranging from 1.56 to 1.70, which is a fairly large deviation in the chemical composition at the atomic scale [Puls (2012)].

In order to see how the average stoichiometric composition, κ for ZrH _{κ} , may be related to the actual H content of a hydride precipitate, it is useful to first evaluate the Wigner-Seitz primitive unit crystal volume of a given hydride phase

$$\Omega[h\text{-ZrH}_\kappa] = \frac{a[h\text{-ZrH}_\kappa] \cdot (b[h\text{-ZrH}_\kappa] \times c[h\text{-ZrH}_\kappa])}{N_{\text{Zr}}[h\text{-ZrH}_\kappa]} \quad (2.14)$$

where the atomic scale vectors $\{a[h\text{-ZrH}_\kappa], b[h\text{-ZrH}_\kappa], c[h\text{-ZrH}_\kappa]\}$ define the edges of the parallelepiped, as shown in FIG. 2.10, and $N_{\text{Zr}}[h\text{-ZrH}_\kappa]$ is the number of Zr atoms in each unit cell. For the case of γ -ZrH_{1.00} and δ -ZrH_{1.66} phases, the respective primitive cell volumes are given by

$$\begin{aligned} \Omega[\gamma\text{-ZrH}_{1.00}] &\simeq \frac{|a[\gamma\text{-ZrH}_{1.00}]|^2 |c[\gamma\text{-ZrH}_{1.00}]|}{N_{\text{Zr}}[\gamma\text{-ZrH}_{1.00}]} = \frac{(4.586)^2 (4.948)}{4.00} \\ &= 26.02 \text{ \AA}^3 / \gamma\text{-ZrH}_{1.00} \text{ basis} \\ &= 15.62 \times 10^{-6} \text{ m}^3 / \gamma\text{-ZrH}_{1.00} \text{ mol} \end{aligned} \quad (2.15)$$

$$\begin{aligned} \Omega[\delta\text{-ZrH}_{1.66}] &\simeq \frac{|a[\delta\text{-ZrH}_{1.66}]|^3}{N_{\text{Zr}}[\delta\text{-ZrH}_{1.66}]} = \frac{(4.768)^3}{4.00} \\ &= 27.09 \text{ \AA}^3 / \delta\text{-ZrH}_{1.66} \text{ basis} \\ &= 16.42 \times 10^{-6} \text{ m}^3 / \delta\text{-ZrH}_{1.66} \text{ mol} \end{aligned} \quad (2.16)$$

using which it is possible to estimate the hydrogen concentration in a homogeneous hydride precipitate of a given volume.

Phase Metallography. Extensive experimental studies on γ -ZrH_{1.00} and δ -ZrH_{1.66} precipitate microstructures have understand the nature of the interfaces between α -Zr-H solid solution and the microscopic γ -ZrH_{1.00} and δ -ZrH_{1.66} phase features [Carpenter, Watters, and Gilbert (1973), Carpenter (1973), Carpenter (1978), Perovic, Weatherly, and Simpson (1982), Perovic, Weatherly, and Simpson (1983), Perovic and Weatherly (1984), and Puls (2012)]. The matrix-hydride interfaces are defined by the following orientation relationships:

$$\{0001\}_{\alpha\text{-Zr-H}} \parallel \{111\}_{h\text{-ZrH}_\kappa} \quad \text{and} \quad \langle 11\bar{2}0 \rangle_{\alpha\text{-Zr-H}} \parallel \langle 1\bar{1}0 \rangle_{h\text{-ZrH}_\kappa} \quad (2.17)$$

$$\{0001\}_{\alpha\text{-Zr-H}} \parallel \{001\}_{h\text{-ZrH}_\kappa} \quad \text{and} \quad \langle 11\bar{2}0 \rangle_{\alpha\text{-Zr-H}} \parallel \langle 1\bar{1}0 \rangle_{h\text{-ZrH}_\kappa} \quad (2.18)$$

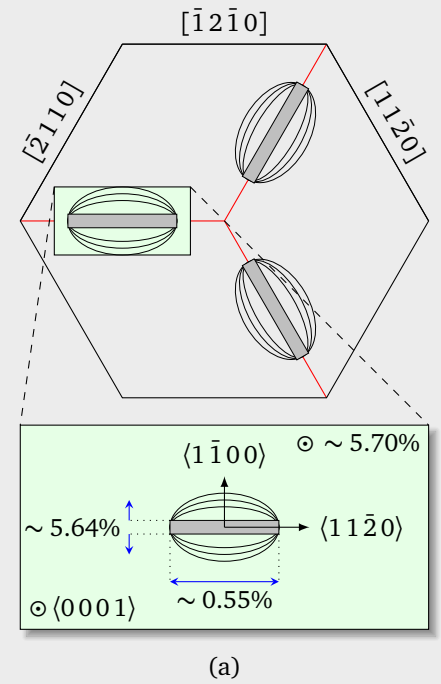
These orientation relationships correspond to preferred crystallographic planes on which the hydride precipitates reside, namely, the habit planes. The commonly-observed preferred habit plane for γ -ZrH_{1.00} and δ -ZrH_{1.66} phase

FIG. 2.11

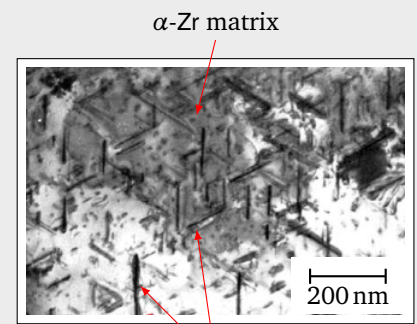
Hydride orientation on the basal plane of hexagonal zirconium

The morphology and orientations of microscopic hydride precipitates on the basal habit planes.

Adapted from Carpenter, Watters, and Gilbert (1973).



(a)



Hydrides

(b)

is on the near-basal plane; in pure α -Zr, these include: (i) the basal plane $\{0001\}$ and (ii) the $\{10\bar{1}1\}$ family of planes that are $\sim 14^\circ$ from the basal plane. The preference of a habit plane is again a manifestation of anisotropy at the nanoscopic scale.

These anisotropic orientation relationships provide a crucial insight into the nature of two theoretical concepts: (i) the matrix-precipitate interfacial energies; and (ii) the stress-free transformation strains in the matrix due to the misfit precipitate particle. Both of these concepts will be formalised more rigorously in later discussions but it is worth introducing them here. The interfacial energy per unit area of the two-phase surface is generally higher if the crystallographic lattice mismatch is greater at the atomic scale. The stress-free transformation strains provide a measure of the elastic deformation in the lattice around the precipitate defect as a result of the (in)coherency. The interfacial energy is difficult to measure via experiment but its effects can be inferred indirectly; the stress-free transformation strains, on the other hand, have been deduced for γ -ZrH_{1.00} and δ -ZrH_{1.66} precipitates. For the case of γ -ZrH_{1.00} precipitates, it is possible to express the transformation strain tensor:

$$[e_T]_{ij}[\gamma\text{-ZrH}_{1.00}] = 10^{-3} \begin{bmatrix} 5.51 & 0 & 0 \\ 0 & 5.64 & 0 \\ 0 & 0 & 5.70 \end{bmatrix} \quad \text{with} \quad \begin{cases} x_1 \parallel [1\bar{2}10] \\ x_2 \parallel [10\bar{1}0] \\ x_3 \parallel [0001] \end{cases} \quad (2.19)$$

which suggests that there is coherency along the $\langle 0001 \rangle$ direction but semi-coherency or incoherency along the $\langle 1\bar{2}10 \rangle$ and $\langle 10\bar{1}0 \rangle$ directions. The values are very similar for δ -ZrH_{1.66} precipitates [Carpenter (1973), Carpenter, Watters, and Gilbert (1973), and Puls (2012)].

The main consequence of this anisotropy is manifest in the morphology of the hydride precipitates. On the basal plane, the γ -ZrH_{1.00} features are observed to be needle-like or platelet-like, as shown in FIG. 2.13, with preferred orientations along the three hexagonal crystallographic axes [Carpenter (1978) and Puls (2012)]. Evidence suggests that these hydrides continue to grow in this needle-like manner, that is, faster along their length than their (cross-sectional) thicknesses. This effect is due to the interfacial elastic coherency along the length and a considerable misfit strain along the thicknesses both on and out of the basal plane [Carpenter, Watters, and Gilbert (1973) and Puls (2012)].

The other consequence of the anisotropic interfacial energies and misfit strain energies concerns the size and shape of the precipitates. The interfacial energy increases as the two-phase surface area of the incoherent

increases. The misfit strain energy increases with the volume of the precipitate. As a result, there is a critical size and shape attained by the growing hydride particles. For example, the lengths of the γ -ZrH_{1.00} needles are typically of the order of $\sim \ell$ [microscopic] whereas their cross-sectional and axial thicknesses are typically smaller by a factor of ten or a hundred [Carpenter (1973), Carpenter (1978), and Puls (2012)].

In typical microstructures, microscopic hydride needles are not usually found alone but in colonies or packets. For example, a staircase-like stacking of γ -ZrH_{1.00} needles has been observed as shown in FIG. 2.12. The possible reasons for this phenomena is the topic of a forecoming discussion on hydride morphologies but it can be explained somewhat by the current state of understanding. It is evident from the previous discussion on Wigner seitz cells that a large concentration of H atoms is then required to form these microscopic γ -ZrH_{1.00} hydride needles, that is, a volume of pure hydride phase whose dimensions extend to $\sim \ell$ [microscopic] in one direction. The diffusion of H atoms to the site of a growing hydride precipitate is thermodynamically favourable but as the hydride size is limited, it is reasonable to assume that secondary hydride needles may precipitate in the vicinity of the original that surplus H atoms. This precipitation process is then termed sympathetic [Perovic, Weatherly, and Simpson (1983)].

Mechanical Properties. It has proved very difficult to isolate the hydride phases in experimental studies and so there is no conclusive understanding on the deformation mechanics of bulk hydrides. As listed in TAB. 2.5, this is where electronic structure simulations can be used to calculate the elastic stiffness constants and moduli of each of the phases in isolation [Zhu et al. (2016)].

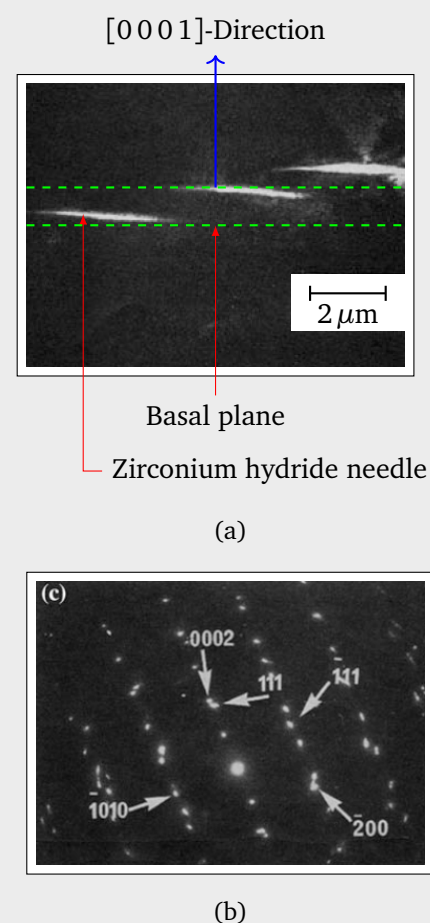
There exists extensive experimental research on the mechanical properties of the Zr alloys containing δ -ZrH_{1.66} and ϵ -ZrH_{2.00} precipitates. Such studies typically involve mechanical tests that determine the elastic moduli, uniaxial deformation and fracture toughness parameters of the hydrided Zr alloy specimens. It is then possible to deduce the H composition- and temperature-dependent brittleness of the hydrides [Beck and Mueller (1960), Barraclough and Beevers (1969a), and Barraclough and Beevers (1969b)]. Tensile tests on bulk Zr hydride specimens showed that plastic deformation was not present in larges pieces of single phase δ -ZrH_{1.66} and ϵ -ZrH_{2.00} compositional ranges. Furthermore, the brittle nature of the hydrides was confirmed as specimens that were crack-free could not be produced experimentally [Puls (2012)].

FIG. 2.12

A micrograph of the hydride stacking group effect

(a) The staircase-like stacking of micro-hydrides needles. (b) Networks of micro-hydride needles that constitute the substructure of macro-hydride colonies.

Adapted from Perovic, Weatherly, and Simpson (1983).



TAB. 2.5

Hydride phases in zirconium

The four known hydride phases are described in terms of their thermodynamic, crystallographic, microscopic and mechanical properties. Regarding the thermodynamic properties: the phase stability of the ζ -ZrH_{0.50} and γ -ZrH_{1.00} phases is the subject of considerable debate; the stoichiometric compositions are only a reference as generally the composition across a hydride precipitate can vary; the formation enthalpies at 0K are obtained from DFT simulations. Regarding the crystallographic properties: the crystal structure and lattice parameters are known from experimental studies and have been confirmed by DFT simulations as well; the H atoms are known to occupy the tetrahedral sites in the hydride phases as well. Regarding the metallographic properties: the orientation relationships of the hydride phases in the α -Zr matrix have been deduced from TEM and SEM studies; the preferred habit planes and transformation strains of the misfit precipitate particles are indicative of the needle-like or platelet-like morphologies that the γ -ZrH_{1.00} and δ -ZrH_{1.66} phases are known to form. Regarding the mechanical properties: the anisotropic elastic stiffness constants and the isotropic bulk, shear and Young moduli have been determined at 0K using DFT simulations. These properties are discussed further in the text.

This tabulated data draws upon various sources in the literature: Puls, 2012; Lumley, 2013; Zhao et al., 2008a; Zhu et al., 2016; Steuwer et al., 2009; Zheng et al., 2015; Lemaignan, 2012; Blackmur et al., 2015; Carpenter, 1978; Barrow et al., 2013.

Hydride Phase	ζ -ZrH _{0.50}	γ -ZrH _{1.00}	δ -ZrH _{1.66}	ϵ -ZrH _{2.00}
THERMODYNAMICS				
Phase stability	metastable	metastable	stable	stable
Stoichiometry	ZrH _{0.50}	ZrH _{1.00}	ZrH _{1.66}	ZrH _{2.00}
ΔH_f /eV	-0.178	-0.430	-0.503	-0.573
CRYSTALLOGRAPHY				
Ordering	-	ordered	disordered	-
Structure	HCP	TCP	FCC	FCT
Space group	P3m1	P4 ₂ /mmc	Pn $\bar{3}$ m	I4/mmm
Group number	-	86	225	159
Pearson number	-	tP6	cF12	tI6
Lattice parameters:				
a [$\hbar$ -ZrH _{κ}]/Å	3.270	4.586	4.768	4.969
c [$\hbar$ -ZrH _{κ}]/Å	10.83	4.948	4.768	4.450
Interstitialcy	tetrahedral	tetrahedral	tetrahedral	-
METALLOGRAPHY				
Habit Planes	-	$\{10\bar{1}0\}$ $\{10\bar{1}7\}$	$\{10\bar{1}0\}$ $\{10\bar{1}7\}$	-
Transformation strains:				
$\langle 0001 \rangle$ direction	4.1%	4.1%	5.5%	-
$\langle 11\bar{2}0 \rangle$ direction	0.9%	0.6%	3.1%	-
$\langle \bar{1}100 \rangle$ direction	0.9%	0.5%	0.5%	-
Morphologies:				
Size range/ μ m	$[10^{-3}, 10^{-1}]$	$[10^{-2}, 1]$	$[10^{-2}, 1]$	-
Shape	cluster deposit	needle platelet	needle platelet	-
MECHANICAL				
Elastic stiffness:				
C_{11} /GPa	119	116	160	174
C_{12} /GPa	96.1	112	139	147
C_{13} /GPa	96.1	97	103	104
C_{33} /GPa	119	183	115	153
C_{44} /GPa	59.8	49	58.6	31.6
B /GPa	104	113	23.7	66.5
G /GPa	31.1	119	29.0	80.3
Y /GPa	85.0	133	31.5	87.6

2.3.2 Lifecycle of Hydrides

The second topic of this review on hydrides concerns the exact nature of the precipitation process, which is more speculative than the previous topic. The typical stages of a precipitate lifecycle include nucleation, growth, coarsening and dissolution [Cahn and Haasen (1996)]. Hydride nucleation can be understood at the atomic scale in terms of the phase transition processes by which crystallographic structure and stoichiometric composition transform from the α -Zr-H solid solution to the ζ -ZrH_{0.50}-phase and then to the γ -ZrH_{1.00} or δ -ZrH_{1.66} phases. Hydride nucleation may also be described at the microscopic scale in terms of preferred sites in the microstructure at which precipitation is more favourable. The process of growth involves the evolution of the hydride morphology through the migration of matrix-hydride interfaces and the overall rate of transformation of the hydride microstructure [Sutton and Balluffi (1995)]. The dissolution process is the reverse phase transition in which the hydride precipitates are annealed out of the matrix and the H atoms return to the solid solution. Evidence of the lifecycle of a hydride precipitate feature can only be inferred from characterisation experiments, which is how the following discussion will proceed.

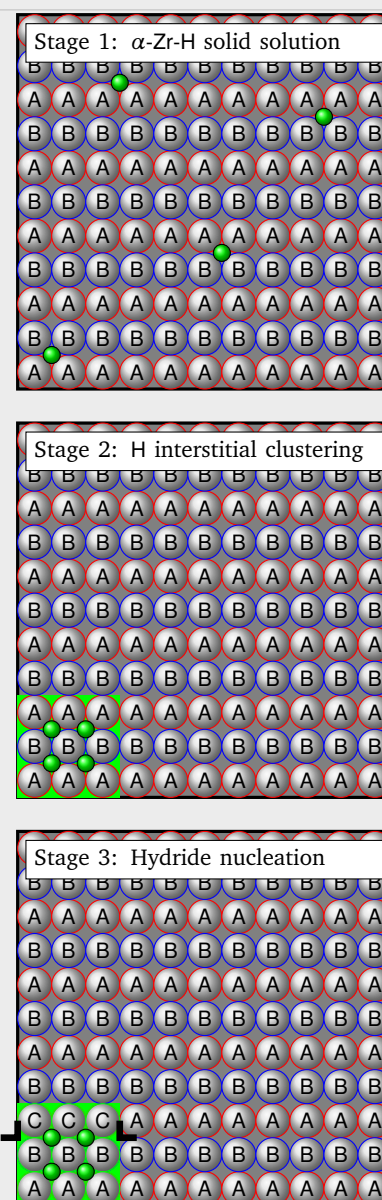
Nucleation. The phase transformation from the α -Zr-H to the β -ZrH_k phase is first order; there is an energy barrier that must be overcome for the sub-nanoscale hydride nuclei to form. Therefore, nucleation is more favourable at certain sites within the α -Zr matrix where this energy (transus) barrier is lower [Cahn and Haasen (1996)]. The local atomistics govern the thermodynamic stability of each hydride nucleus and whether the precipitate can grow to a discernable size.

The nucleation steps of such sub-nanoscale nuclei of a hydride phase are poorly understood [Cassidy and Wayman (1980b), Cassidy and Wayman (1980a), Bradbrook, Lorimer, and Ridley (1972), and Puls (2012)]. But considering the difference between pure α -Zr matrix and a generic hydride phase β -ZrH_k, it is evident that both H and Zr atoms must move as the matrix-hydride interface migrates. Firstly, as previously discussed, there is the long range transport of H via a thermally activated diffusion process, which is biased by stress and temperature gradients. Secondly, there is the mid-to-short range dense clustering of H atoms in the vicinity of a precipitation site. Thirdly, there is the short range motion of Zr atoms that transforms the parent HCP α -Zr lattice to the crystal structure of the β -ZrH_k phase, which is accompanied by short-range H reordering if needed. The time scales for H clustering and the crystallographic reconfiguration of Zr atoms are much faster than the thermally activated diffusive hops of H atoms. In this sense, it is possible to then say the time scales for hydride nucleation are controlled

FIG. 2.13

The formation of a hydride nucleus

The proposed three-stage mechanism of hydride nucleation. The first stage involves the long range transport of H atoms in solid solution. The second stage involves the short-to-mid range clustering of H atoms. The third stage involves the short range reconfiguration of Zr atoms.



entirely by H diffusion in the bulk.

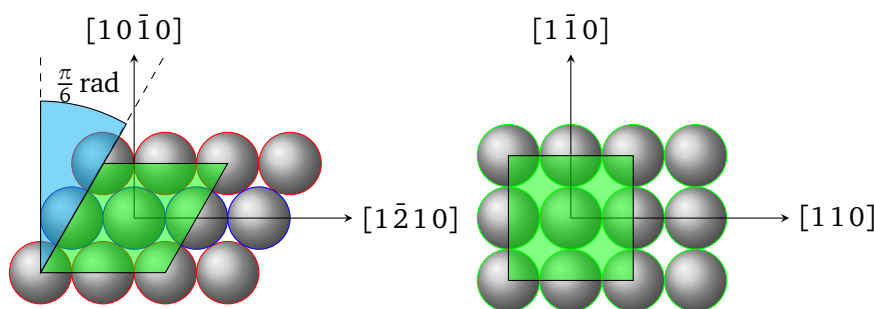
It is hypothesised that the formation of the hydride nuclei is linked to the dissociation of dislocations into multiple partial dislocations in the α -Zr matrix that provide trapping sites for the diffusing H atoms [Carpenter (1973)]. The propagation of stacking faults—or the motion of partial dislocations—can then transform the HCP configuration of Zr atoms in the α -Zr phase into, say, the FCC configuration of δ -ZrH_{1.66} phase.

The formation of the hydride nuclei causes a misfit expansion in the surrounding α -Zr lattice. Accordingly, the matrix-hydride migrates as the Zr atoms move whilst the H atoms continue to occupy tetrahedral interstitial sites. Two possible mechanisms have been proposed for the short range motion of Zr atoms, namely, the pure lattice transformation (PLT) and the pure shear transformation (PST), which are respectively based on the assumption that either the volume per Zr atom changes or the lattice expansion is solely along the habit plane normal [Bradbrook, Lorimer, and Ridley (1972)].

For the case of a γ -ZrH_{1.00} precipitate, its nuclei is believed to form via an invariant plane strain transformation. The resultant transformation would involve (i) a dilatational strain normal to the invariant habit plane and (ii) shear strains parallel to this habit plane. The minimum-energy precipitate geometry for such a transformation is a platelet shape with a small thickness-to-length ratio, which agrees with experimental observations [Bradbrook, Lorimer, and Ridley (1972), Puls (2012), and Carpenter (1973)]. The stresses in the plate-normal direction are negligible along most of the length of such a precipitate. However, the dilatational transformation strains would generate large Poisson contraction stresses in the in-plate directions.

A somewhat alternative to this theory is that γ -ZrH_{1.00} nuclei form in a similar fashion to bainite in steels, which can be summarised as follows. The hydride formation may be completed by (i) first the civilian or diffusive motion of H atoms occupying tetrahedral sites and (ii) subsequently the military or diffusionless martensitic motion of Zr atoms in a shear transformation to their appropriate positions to complete the face-centred tetragonal configuration. Such a process may not normally be possible in homogeneous nucleation process in a one-component system; however, since H atoms are very mobile, they can occupy the desired interstitial sites in α -Zr to form a metastable H profile cluster. This configurational transformation is accessible in successive steps [Bradbrook, Lorimer, and Ridley (1972), Puls (2012), and Bhadeshia (2001)].

Analogous to other martensitic transformation processes, the elastic misfit strains associated with hydride nucleation are suggestive of an autocatalytic or sympathetic nucleation process, whereby multiple hydride fea-



tures form in the vicinity of each other. The formation of such hydride colonies helps reduce the elastic strain energy as the hydride network helps screen the misfit strains associated with individual hydrides. The observed staircase-like stacking is one such example of a minimum strain energy network. Note that martensitic transformation hypothesis is supported by the experimental observations of twinning and shape changes at free surfaces for both γ -ZrH_{1.00} and δ -ZrH_{1.66} phases, which is characteristic of martensitic transformations [Cahn and Haasen (1996), Perovic, Weatherly, and Simpson (1983), and Puls (2012)].

Growth. The morphological growth of a hydride nucleus involves the migration of the matrix-hydride interfaces. The rate of precipitate growth is then determined by the speeds at which the interfaces migrate along different crystallographic directions. This rate is also controlled almost entirely by the long-range diffusion of H atoms to the vicinity of the growing hydride nucleus, as the mid-range clustering of H atoms and the short-range reconfiguration of Zr atoms is generally assumed to be much faster than thermally activated diffusive transitions. Note that advancing two-phase interface must also require the short-range partitioning of H atoms into appropriately distributed tetrahedral interstitial sites, but this process is also assumed to be much faster than long-range diffusion [Banerjee and Mukhopadhyay (2010), Perovic, Weatherly, and Simpson (1983), and Puls (2012)].

As the hydride nuclei grows, it may eventually reach the sizes that are necessary for it to be distinguished in conventional micrographs as a metallographic feature of a different phase. At the scale of TEM studies, individual nanoscopic γ -ZrH_{1.00} precipitates whose sizes are $\sim \mathcal{O}(100 \text{ nm})$ have been observed [Bradbrook, Lorimer, and Ridley (1972) and McRae and Coleman (2017)]. Fully-formed stable microscopic γ -ZrH_{1.00} precipitates are known to attain typical sizes $\sim [1, 3] \mu\text{m}$ in length [Carpenter (1973)]. Due to the anisotropic energetics of the matrix-hydride interfaces, these micro-hydride precipitates have a lenticular needle-like or platelet-like geometry. Each

FIG. 2.14

Hydride nucleation process

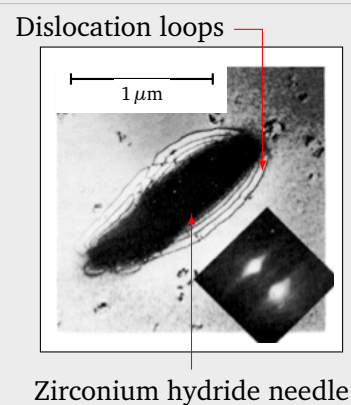
The shearing of the HCP crystal into a FCC crystal which results in the creation of a stacking fault.

FIG. 2.15

Dislocation loops around a micro-hydride

A TEM image of prismatic loops around a γ -ZrH_{1.00} needle.

Adapted from Carpenter, Watters, and Gilbert (1973).

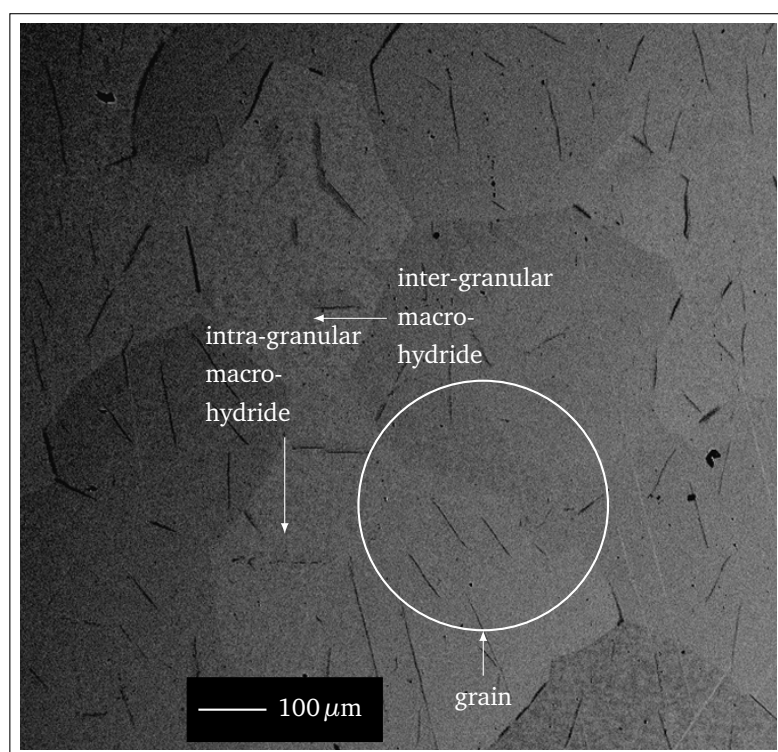


micro-hydride needle is often treated as a mono-phase entity which is an elastic misfit that is accommodated in the Zr matrix. This assumption will be applied to this work but it is worth noting that there is a complex substructure to these micro-hydride features, which includes the existence of defects such as dislocations, H vacancies and multi-hydride phase interfaces [McRae and Coleman (2017) and Mueller, Blackledge, and Libowitz (1968)].

The hydride precipitate continues to grow until it reaches some critical shape and size. At this point, the misfit may exert enough force on the surrounding matrix to plastically deform it. This plastic relaxation is postulated to be accompanied by the punch-out of dislocations. In TEM studies of γ -ZrH_{1.00} needles, as shown in FIG. 2.15, prismatic loops are observed around the micro-precipitate feature [Carpenter, Watters, and Gilbert (1973), Carpenter (1973), and Puls (2012)].

Beyond these critical shapes and sizes, the micro-hydride growth is restricted, most likely due to the local elastic strain energetics. This also suppresses coarsening so that larger hydride entities cannot form in the matrix. That is, its growth at these stages is energetically less favourable than the formation of a new hydride nuclei. As previously explained, individual micro-hydride precipitates stack together in colonies to macroscopic hydride features [Perovic, Weatherly, and Simpson (1983), McRae and Coleman (2017), and Puls (2012)]. The growth of these macro-hydride features is attributed to an autocatalytic or sympathetic nucleation process. The rate of growth of these macro-hydride features corresponds to both the rate of micro-hydride precipitate growth as well as the rate of autocatalytic nucleation events. Macro-hydride features also grow by absorbing or coalescing with other smaller colonies. For these reasons, the macro-hydride growth rate is not controlled entirely by H diffusion.

The macro-hydride features are composites of the parent Zr matrix and the hydride phase micro-precipitates. These macroscopic structures can extend to sizes of $\sim [10, 100] \mu\text{m}$ and their morphology depends on the local microstructure, loading conditions and thermomechanical cycling [Coleman (2003), McRae and Coleman (2017), and Puls (2012)]. In SEM studies as shown in FIG. 2.16, macro-hydride features can be identified to be intergranular, intra-granular or trans-granular [Chamaa et al. (2018)]. The hydride microstructure is then a complex multi-phase system containing networks of large macro-hydride features that are themselves composite assemblies of smaller micro-hydride precipitates in the Zr matrix.



(a) Chamaa et al., 2018

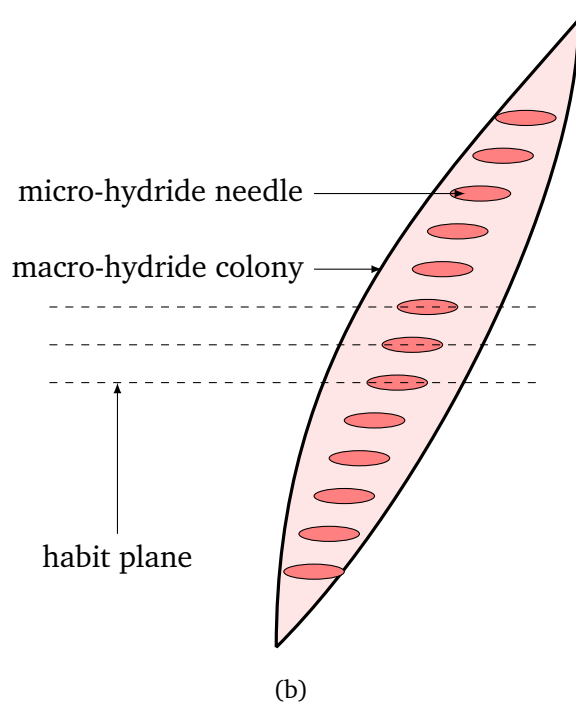


FIG. 2.16

Macro-hydrides in polycrystalline zirconium

(a) A SEM of a hydrided Zr alloy specimen containing macroscopic hydride colonies within grains and at grain boundaries. Observe the manner which inter-granular macro-hydride colonies follow the path of the grain boundary. It is also important to note that not all grain boundaries act as nucleation sites; this is possible due to the combined effects of crystalline anisotropy and polycrystalline heterogeneity; specific grain boundaries are more energetically favourable nucleation sites than others. (b) The substructure of a macro-hydride colony as a staircase-like stack of micro-hydride needles residing on preferred crystallographic habit planes. This is a very simplistic two-dimensional representation of a macro-hydride colony. However, these assemblies are typically more complicated.

FIG. 2.17

Summary of DHC models.

A two-step breakdown of the two proposed theories of the DHC mechanism. The third step of precipitate-induced embrittlement and fracture is the same for both models.

Diffusion-First Model*Step 1: Stress-Driven Diffusion*

Stress gradients ahead of the SCF generates a thermodynamic potential that encourages H diffusion.

Step 2: Diffusion-Controlled Precipitation

The accumulation of H in the vicinity of the SCF eventually leads to the formation of hydride features when the transus is exceeded.

(a)

Precipitation-First Model*Step 1: Stress-Induced Precipitation*

Stress gradients ahead of the SCF allow the formation of a precipitate feature.

Step 2: Precipitation-Controlled Diffusion

The resulting concentration gradient encourages H diffusion.

(b)

2.4 Crack Initiation

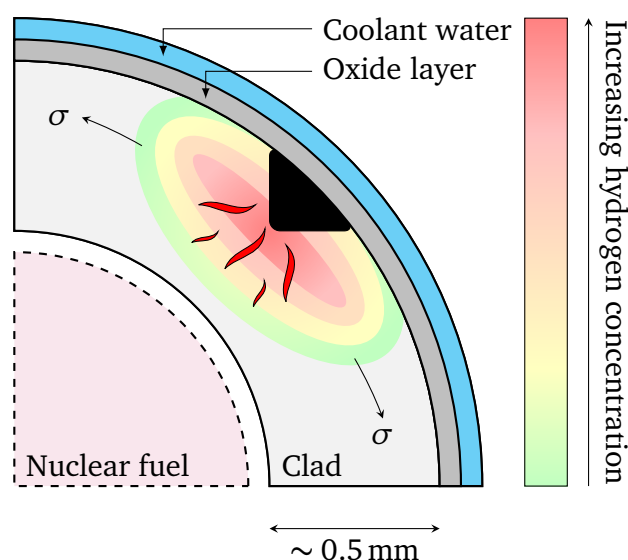
The final theme of this literature review focuses on DHC initiation in Zr alloy fuel clad material. In the nuclear industry, DHC is often described as a thermally-assisted intermittent cracking process which is time-dependent and sub-critical [Puls (2012)]. As previously stated, the qualities of time dependence and sub-criticality refer to the sub-processes of H diffusion and hydride precipitation. That is, there is some relationship between the fracture criteria and the hydrided microstructure in the vicinity of stress-concentrating features (SCFs) such as cracks and notches. However, the exact details of this relationship are the subject of much speculation and uncertainty. It is inevitable that hydrides will accumulate ahead of SCFs during normal reactor operating conditions provided that H ingress is sufficiently high. But what is less clear is which processes must take place for the fracture criteria to be met and the time scales over which these processes occur.

In the recent history of DHC research, two conflicting theories have been put forward to address such questions; these theories are respectively known as the diffusion-first model and the precipitation-first model [McRae, Coleman, and Leitch (2010)]. These two theories are distinguished by their hypothesis concerning the initial step of the DHC mechanism. In the diffusion-first model, H diffusion is assumed to precede hydride precipitation, whereas, in the precipitation-first model, hydride precipitation is assumed to precede H diffusion. A brief description of these two models is presented in FIG. 2.17 from which it is evident that the precipitation-first model requires there to be an effect of the stress around the SCF on the H solubility.

The precipitation-first model assumes that precipitation occurs more readily in the vicinity ahead of the SCF because the local hydrostatic stresses reduce the solvus of phase transition. There is limited experimental evidence that supports this assumption [McRae and Coleman (2017)]. The diffusion-first model does not require such an assumption. Moreover, the diffusion-first model appears to describe a more logical sequence of events as precipitation of hydrides near the SCF must invariably require the migration of H atoms. For these reasons, this discussion will continue to operate under the diffusion-first model, which has been implicitly assumed thusfar.

2.4.1 Ratchetting

The initiation of DHC is usually preceded by a series of thermomechanical cycles during which hydrides repeatedly precipitate and dissolve. Over the course of these thermomechanical cycles, the hydrided microstructure evolves into a complex multi-phase system comprising a large and dense population of macro-hydride colonies in the vicinity of the loaded flaw in the



Zr alloy component. It is understood that this evolution process is governed by the flaw acuity and microstructural properties as well as temperature and load histories [Schofield (2002), Coleman (2003), Cui et al. (2009), Motta and Chen (2012), and Puls (2012)]. This thermal cycle-induced evolution of the hydrided microstructure is often referred to as ratchetting [Puls (2012)]. Broadly speaking, the likelihood of DHC initiation is exacerbated by the consequences of ratchetting.

Hydride Process Zones. Ratchetting causes an increase in the hydride volume fraction at flaw tips. This is attributed to the TSSp/d hysteresis [Eadie, Metzger, and Léger (1993)]. That is, re-precipitation occurs much more readily. As shown in FIG. 2.18 and FIG. 2.19, this eventually leads to the formation of hydride process zones emanating from the flaw tip. These hydride process zones provide the gateway for DHC initiation but the crack dynamics are far more complicated than the predictions offered by standard cohesive zone models of non-linear fracture [Puls (2012), Scarth and Smith (2001), and Scarth (2002)].

Hydride Reorientation. Ratchetting also causes the (apparent) radial reorientation of circumferential macro-hydride colonies towards the flaw. This is postulated to be the result of the simultaneous operation of two mechanism: (i) a memory effect caused by repeated precipitation-dissolution cycles in which dissolving hydrides create a residual distortion that acts a new precipitation site (ii) the effect of cyclic loading in which the re-assembling of macro-hydride colonies is gradually biased by the hoop stresses [Puls (2012) and Patel and Stopher (2017)].

FIG. 2.18

Flaw-tip hydrogen profile and hydrided microstructure

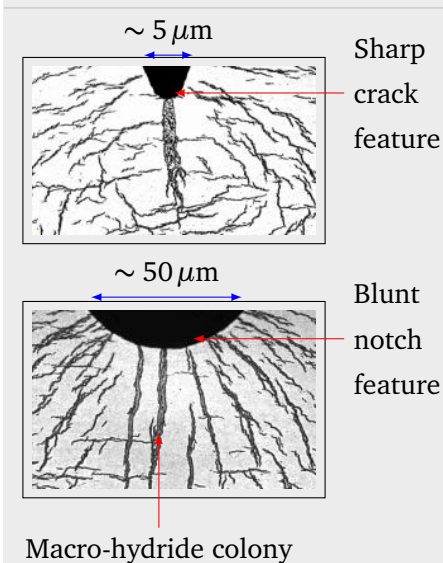
Schematic of the clad and the hydride process zone at the flaw tip. The hoop stresses bias the re-assembling of macro-hydride colonies, which leads to the formation radial features that are directed towards the flaw. This makes DHC initiation more likely as the reorientated hydrides can provide a more convenient pathway for crack dynamics.

FIG. 2.19

Flaw-tip hydrided microstructures

Micrographs of the hydrided microstructures for (a) a sharp crack and (b) a blunt notch.

Adapted from Cui et al. (2009).



2.4.2 Stress Intensity Factor

From the standpoint of past and current nuclear safety assessments, the complexity of H diffusion and hydride precipitation in Zr alloys can be encapsulated in one standalone macroscopic parameter for describing DHC threshold as a function of notch acuity, microstructure and thermomechanical cycling. This DHC threshold parameter is the stress intensity factor, K_{IH} , which is the minimum loading stress required for DHC flaw propagation. In the nuclear industry, it is standard practice to use conservative handbook solutions for K_{IH} that have been obtained from long-running experimental test programs [Puls (2012) and Martin (2013)].

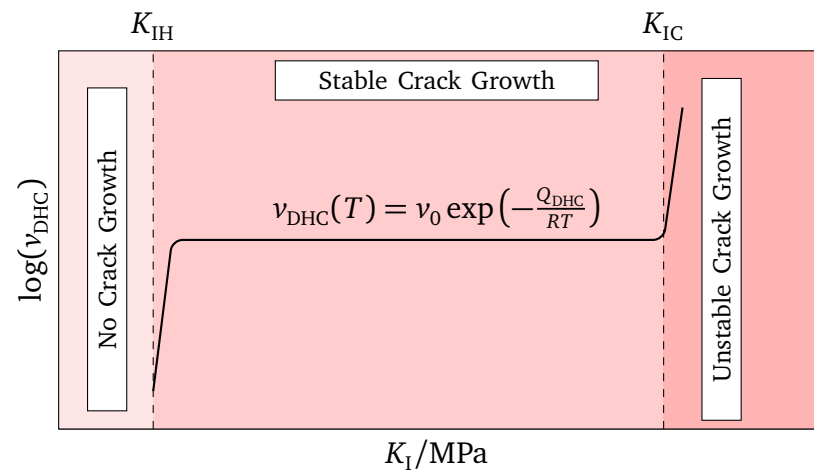
The rate of DHC flaw propagation is given by the DHC growth velocity, v_{DHC} , which defines three distinct regimes of DHC failure. These three regimes are depicted in FIG. 2.20 and, in worst case scenarios, a DHC flaw can propagate at speeds of up to ~ 1 mm/day in typical reactor conditions. So DHC failure can be a relatively quick process following initiation.

FIG. 2.20

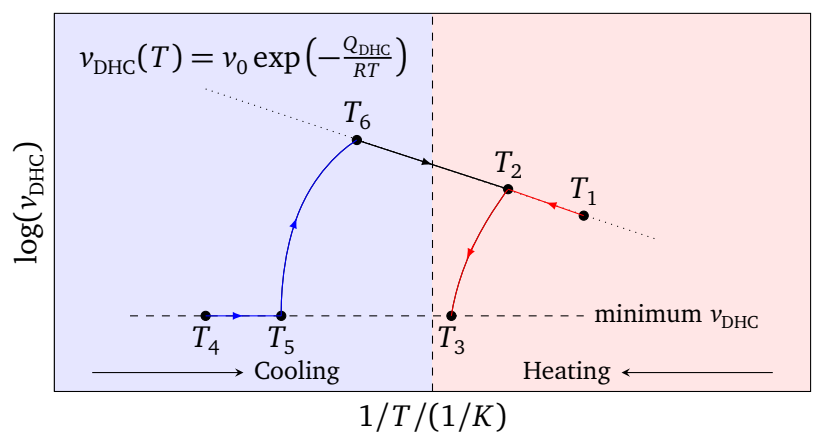
Regimes of DHC failure

(a) The DHC flaw growth rate velocity as a function of the mode I stress intensity factor. There is a three stage dependence that is common to other similar environmentally assisted sub-critical crack growth mechanisms. The present work focuses on the first regime in which no crack growth occurs because modelling the mechanics of rapid crack dynamics at the later stages is not particularly useful in this context; the best measure is instead a preventative one (b) The effect of the temperature history on the DHC flaw growth rate velocity. The DHC flaw velocity follows the sequence $T_1 \rightarrow T_2 \rightarrow T_3 \rightarrow T_4$ upon heating and the sequence $T_4 \rightarrow T_5 \rightarrow T_6 \rightarrow T_2$ upon cooling. The maximum growth rate can only be achieved by cooling from a sufficiently high temperature.

Adapted from Puls (2012).



(a)



(b)

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3

Modelling Strategy

Chapter Overview

In light of the overwhelming breadth of experimental research on DHC, it is important to conceive a modelling strategy based on two primary considerations. Firstly, it is important to recognise the industrial requirements for safety analysis software, which regard the physical barriers to radiotoxic release as the most critical components [[International Atomic Energy Agency \(2003\)](#)]. Secondly, it is necessary to ask whether—and to what extent—these requirements can be satisfied by the application of standard computational methodologies to the problem DHC in Zr components.

The purpose of DHC modelling is clearly outlined by the industrial regulatory standards: to develop a mechanistic and, thereby, predictive framework for DHC initiation—as a function of notch acuity, microstructure and thermomechanical cycling—that is to be used alongside experimental test programmes at the component scale [[Strasser, Adamson, and Garzarolli \(2008\)](#) and [Puls \(2012\)](#)]. In the industrial setting, computational models must not only be accurate but also efficient. That is, the computational expenditure should be minimised and the simulation runtime should be fast. Computational speed is vital because of the need to treat a statistical ensemble of simulations and, therefore, average out any stochastic variations arising from deviations within manufacturing tolerances, randomness of the defect microstructure, and fluctuations in the reactor operating conditions. This statistical approach is central to modern safety cases of Zr alloys.

The proposed strategies for realising this vision within modern nuclear fuel performance codes are highly contingent on three particular computational methodologies, namely, DFT, PF and FE methodologies [[Tonks et al. \(2017\)](#) and [Aybar and Ortega \(2005\)](#)]. Answering the key question of whether these strategies are actually effective requires an assessment of the DFT, PF and FE methodologies in terms of their individual and combined capabilities.

Consider first the individual capabilities. In the field of computational materials science as a whole, DFT, PF and FE methodologies have emerged as very popular general-purpose simulation techniques for modelling mate-

rials [Payne et al. (1992), Chen (2002), Zienkiewicz (1977), Janssens et al. (2007), and Vvedensky (2004)]. The versatility of DFT, PF and FE methodologies can be both enabling and crippling. Their ability to simulate a diverse spectrum of materials phenomena is often offset by the computational overheads associated with their generality; the simulation runtime scales unfavourably with increasing system sizes and finer spatial resolutions. For this reason, DFT, PF and FE models are usually confined to one specific sub-domain or length scale of the physical description: DFT methodologies are used in electronic structure solvers; PF methodologies are used in microstructural solvers; and FE methodologies are used in continuum solvers. The conventional DFT, PF and FE methodologies work well at the electronic, microstructural and continuum length scales for which they were respectively designed. But the challenge of modelling DHC is that the constituent sub-mechanisms of stress-driven diffusion, diffusion-controlled precipitation and precipitation-induced fracture are operative concurrently across these length scales. Therefore, standalone DFT, PF and FE models cannot capture the multiscale complexity of DHC or even its constituent sub-mechanisms.

Consider next the combined capabilities: an appropriate combination of DFT, PF and FE models can provide a multiscale framework for modelling Zr-H systems of various sizes and resolutions. In nuclear fuel performance codes, the pathway towards multiscale modelling has usually involved two main strategies. The first strategy is a rudimentary approach in which the results of separate DFT, PF and FE simulations are integrated and analysed together. The second strategy is a sequential parametrisation approach in which FE models are informed by findings from DFT and PF studies. Both strategies have been proposed for modelling the early stages of DHC in the regime of no crack growth [Tonks et al. (2017), Bair, Zaeem, and Tonks (2015), Jernkvist and Massih (2014), and Jernkvist (2014)].

However, the problem of computational expenditure persists for both strategies. In the case of the first strategy, standalone DFT, PF and FE simulations of the Zr-H system are computationally intensive, and repeating simulations for statistical averaging would, therefore, be a laborious task. For example, it would be impractical—if not impossible—to use only these three techniques to explore the variable parameter space of alloy composition, grain size distribution, texture and irradiation damage. In the case of the second strategy, the multiscale FE models must incorporate, either explicitly or implicitly, findings from small scale simulations, which would typically require a greater number of state variables as well as a finer spatial resolution. Inevitably this increases the simulation runtimes and, quite possibly, decreases the system sizes that could be modelled. In addition, the

parametrisation procedure would involve DFT and PF simulations of system sizes that are larger than their current capabilities, and this could be costly to implement if there is an extensive need for high performance computing [Tonks et al. (2017), Bair, Zaeem, and Tonks (2015), Jernkvist and Mas-sih (2014), and Jernkvist (2014)]. Such multiscale models would then be computationally encumbered for practical day-to-day use on standard work-stations and over commercial time frames.

The premise of these two strategies is quite simple and,—acknowledging the widespread availability of well established and legacy bounded DFT, PF and FE codes—, this does appear to be a convenient starting point for mul-tiscale modelling. However, it has been established that proceeding with either strategy in the long term is not a viable option from the standpoint of statistical modelling in industrial safety cases. For this reason, the present work adopts a third alternative strategy that is not based on the standard DFT, PF and FE methodologies so as to avoid the computational overheads associated with these general-purpose codes and difficulties of transferring information between them.

The third strategy is then a more innovative approach that involves formulating a bespoke multiscale model of DHC and its constituent sub-mechanisms. This would ideally be a leapfrog theoretical and computa-tional methodology that surpasses the standard methodologies in terms of the accuracy-efficiency balance. The philosophy of this approach is founded on the intersection of computational science and computer science. For the purposes of this work, computational science addresses the notion of accu-racy whereas computer science addresses the notion of efficiency. From the perspective of computational science, the simulation scope must convey the essential physics of DHC and its constituent sub-mechanisms. From the per-spective of computer science, the algorithmic workflow must be optimised so that the simulation runtimes are sufficiently fast for statistical modelling. The challenge is then to identify the principal sub-domains or length scales that most holistically describe DHC initiation. It is best to begin to do so by first considering the possible inputs and outputs of an idealised multiscale model of DHC that can be compared directly with empirical studies on DHC initiation.

In empirical studies, the complexity of DHC initiation is encapsulated within the threshold stress intensity factor, which a critical parameter that denotes the minimum load for crack propagation. The importance of this standalone threshold criterion in nuclear fuel pin technology cannot be over-stated. In fact, it is common practice in the nuclear industry to employ handbook solutions of this critical parameter. These handbook solutions are quantified through expensive long-running experimental test programmes

on Zr alloy components and are systematically organised into an easy-to-use reference table for different scenarios [Schofield (1993), Puls (2012), and Martin (2013)]. As previously stated, the DHC initiation threshold depends on flaw acuity, microstructure and thermomechanical cycling, all of which have an effect on H diffusion and hydride precipitation [Shek (1998), Schofield (2002), and Puls (2012)]. Therefore a multiscale model of DHC should be able to simulate stress-driven diffusion of H and diffusion-controlled precipitation of hydrides in various Zr alloys as a function of flaw acuity, microstructure and thermomechanical cycling.

To this end, the simulation cell should be a simulated multiscale micrograph that capable of depicting the geometries, morphologies and contours of key metallographic features. This simulated micrograph should portray, at relevant length scales, the defect microstructure in the vicinity of a flaw tip of a hydrided Zr alloy specimen. This includes larger defects such as the flaws, grains and macro-hydride colonies as well as smaller defects such as micro-hydride needles, second-phase particles and dislocation networks. Considering the typical dimensionalities of these metallographic features, the principal sub-domains of interest to this work are those that are intermediate to the microscopic and macroscopic length scales. However, the model input should be appropriately informed by smaller scale electronic structure and atomistic simulations of the Zr-H system where possible and the model output should be adaptable into larger scale continuum simulations of the Zr alloy component. The development of such a multiscale model of DHC is the overarching aim of this investigation.

In order to effectively follow through with this strategy, it is worthwhile to first review the DFT, PF and FE studies of Zr-H systems. In the following, a brief summary of each methodology is given alongside its usage in the context of DHC research. This will be a demonstration of the limitations of these standard methodologies in obtaining the accuracy-efficiency balance required by industrial safety assessments. Moreover, this will also be an instructive exercise as it will provide a list of the essential physical details that must be considered at the atomic, microstructural and continuum length scales within a multiscale model. This list will then be used to outline a novel multiscale modelling strategy that underpins this investigation.

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3.1 Electronic Structure and Atomistic Modelling

At the atomic scale, it is important to consider the role played by quantum nature of electrons. Supposing the fundamental postulates of quantum mechanics, it is possible to determine the behaviour such many-atom systems from first-principles or *ab initio* calculations in which the input parameters are mostly fundamental physical constants. The premise of electronic structure solvers is to determine the total energy of a system of electrons and nuclei. Such calculations are useful because many— or rather, nearly all— material properties are related to either the total energy or the difference between total energies. These include quantities such as equilibrium lattice parameters, bulk moduli and phase transition temperatures [Payne et al. (1992)].

The information obtained from electronic structure solvers that is used to perform *ab initio* atomistic simulations can be scaled up to larger systems of hundreds of thousands of atoms. These atomistic simulations use atomic potentials to approximate the force fields created the collective assembly of atoms. Due to the high computational expenditure associated with electronic structure and atomistic methodologies even at these smaller length and time scales, it is not practical to simulate the larger system sizes that are of interest to engineering design. For example, a system of hundreds of atoms represents less than $10^{-20}\%$ of a typical Zr alloy fuel clad component. Nevertheless, it is very useful to extract fundamental information about such systems that can be used to guide larger scale simulations as well as parametrise physical quantities that are needed in practical engineering design.

There are various *ab initio* methodologies but DFT is the most widely used across computational material science. This section presents the main ideas behind the DFT methodology followed by the application of DFT to the Zr-H system.

3.1.1 Density Functional Theory

The total energy calculation problem that is explored by Kohn-Sham DFT is formalised as follows. Consider an interacting electron gas consisting of N_e electrons in the presence of atomic nuclei. In the Schrödinger equation for this system, the Hamiltonian operator $\hat{H}$ includes five contributions: (i) the kinetic energy of the electrons; (ii) the kinetic energy of the nuclei; (iii) the classical electron-electron Coulomb interaction; (iv) the classical electronic-nuclear Coulomb interaction; and (v) the classical nuclear-nuclear Coulomb interaction. The total energy of the system can be evaluated by first determining its quantum mechanical wavefunction, which is a computation-

ally intensive task, even for the simplest cases; it is impossible to solve the Schrödinger equation directly for a solid because the quantum mechanical wavefunction is a function of $\sim O(10^{23})$ variables.

Approximations. In the first instance, it appears that the intractability of many-particle Schrödinger equation can be circumvented by employing a series of approximations. The three most widely used modelling simplifications are the Born-Oppenheimer approximation, pseudopotential approximation and periodic cell approximation.

The Born-Oppenheimer approximation involves the adiabatic treatment of the electrons and so the electron dynamics can be parametrised by fixed nuclear positions. This approximation is based on the fact that electrons are much lighter than the nuclei. The characteristic time scale for nuclear dynamics is a typical phonon period of $\sim O(10^{-13} \text{ s})$, which is about three orders of magnitude greater than electronic time scale defined by a plasmon period. It is, therefore, reasonable to assume that electrons can remain in their ground-state over the time scales of nuclear dynamics. That is, the electrons respond almost instantaneously to the movements of the nuclei.

The pseudopotential approximation exploits the notion that the valence electrons are more influential from the standpoint of physical chemistry than the tightly-bound core electrons. Chemical bonding, crystal structures, elastic constants, phonon frequencies and defect energetics are all determined by valence electrons that occupy the outermost shells of the atom. Core electrons, which are closer to the nucleus in filled shells, play little or no role in any of these solid state properties. However, a small error in the treatment of the core electrons produces a large error in the total energy because they are so much closer to the nucleus. There are, therefore, two good reasons to try to exclude core electrons from the calculation of the electronic structure. The pseudopotential approximation excludes the core electrons by treating the nuclei and core electrons as ionic cores with potentials that reproduce accurately the wave functions of the valence electrons of the free atom outside its core. Pseudopotentials do not reproduce the correct valence electron wavefunction inside the core, but this does not matter for the purposes stated above.

The periodic cell approximation is an application of Bloch's theorem in which larger crystalline systems can be represented by periodically repeating arrays of unit cells. Periodic supercells containing hundreds of atoms can be used to model defects, such as point defects, dislocations and grain boundaries. They have the advantage of avoiding the surface of a free cluster of atoms used to model a defect, but the periodicity introduces electronic and elastic interactions between defects in the supercell and its periodic im-

ages.

Although these approximations reduce to original problem to a many (valence) electron Schrödinger equation, the explicit computation of the many-electron wavefunction is still impractical [Payne et al. (1992)].

Electron Density Functionals. The Kohn-Sham electron density functional formalism recasts the intractable many-electron Schrödinger equation in terms of the electron (number) density $\rho(\mathbf{x})$, which is a continuous spatially-varying function satisfying the normalisation constraint

$$\iiint_V d^3\mathbf{x} [\rho(\mathbf{x})] = N_e. \quad (3.1)$$

For any physical variable operator $\hat{O}$ that is bounded below, the associated Levy density functional is defined as

$$O[\rho(\mathbf{x})] \equiv \text{Min}_{\Psi \rightarrow \rho} [\langle \Psi | \hat{O} | \Psi \rangle], \quad (3.2)$$

which is evaluated for a given density $\rho(\mathbf{x})$ by checking all possible totally-antisymmetric (Fermionic) electronic wavefunctions $\{\Psi\}$ that yield the aforementioned density to find the one that minimises the expectation value of the operator.

In accordance with the quantum mechanical variational principle, the ground state energy E_0 is given by the total energy Levi density functional as

$$\begin{aligned} E_0 \equiv E[\rho(\mathbf{x})] &\equiv \text{Min}_{\Psi \rightarrow \rho} [\langle \Psi | \hat{H} | \Psi \rangle] \\ &= F[\rho(\mathbf{x})] + E_{\text{EN}}[\rho(\mathbf{x})] + E_{\text{NN}}, \end{aligned} \quad (3.3)$$

where $F[\rho(\mathbf{x})]$ is the universal electron functional, $E_{\text{EN}}[\rho(\mathbf{x})]$ is the electron-nuclear Coulomb interaction energy functional and the constant E_{NN} is the classical nuclear-nuclear Coulomb interaction energy.

Universal Electron Functional. In theory, the universal electron functional can be calculated once and for all to describe the energetics of any system of interacting electrons. However, this is not the case in practice because the exact form of $F[\rho(\mathbf{x})]$ is unknown. Nevertheless, it is possible to deconstruct $F[\rho(\mathbf{x})]$ as a sum of identifiable contributions as

$$F[\rho(\mathbf{x})] \stackrel{!}{=} T_{\text{KS}}[\rho(\mathbf{x})] + E_{\text{H}}[\rho(\mathbf{x})] + E_{\text{XC}}[\rho(\mathbf{x})], \quad (3.4)$$

where universal functional $T_{\text{KS}}[\rho(\mathbf{x})]$ is the ground-state kinetic energy of the fictitious Kohn-Sham system of non-interacting electrons with a density of $\rho(\mathbf{x})$, the Hartree energy $E_{\text{H}}[\rho(\mathbf{x})]$ is the expectation value of the classical electron-electron Coulomb interaction, and the exchange-correlation

energy $E_{\text{xc}}[\rho(\mathbf{x})]$ embeds the small but unknown contributions so that the statement of identity (!) holds. The kinetic energy of the Kohn-Sham electrons is not the same as the kinetic energy of the fully interacting electron gas. The error in the kinetic energy falls within the exchange-correlation energy, which really is a rubbish bin term where everything resides that is unknown in the DFT model.

First-Principles Molecular Dynamics. A total energy DFT calculation gives the minimum-energy electron density parametrised by the position of atomic nuclei. The resultant force acting on each atomic nucleus (or ionic core) is the vector summation of the repulsive Coulomb interaction from all other nuclei as well as the attractive Coulomb interaction due to the charge distribution of the electron density. Within the Born-Oppenheimer approximation, it is possible to treat the nuclei as classical Newtonian particles whose acceleration is then related to spatial derivatives of the total energy functional. This approach can be used to perform *ab initio* molecular dynamics by iterating over DFT total energy calculations.

Computational Implementation. The traditional DFT methodologies typically scale as $\sim O(N_e^3)$ with the system size. This is entirely due to the orthogonalisation procedure required to compute $T_{\text{KS}}[\rho(\mathbf{x})]$ exactly. Moreover there are a variety of choices for pseudopotentials and exchange-correlation functionals depending on the system under investigation. These choices are usually informed based on available knowledge of physical chemistry of the system or adopted based on desired outputs. Therefore, although DFT is branded as an *ab initio* methodology, in practice, it often requires more input than just the fundamental physical constants.

3.1.2 Application to Zirconium

It is not straightforward to apply conventional DFT codes to pure Zr crystals because of the unique chemistry of transition metals. This is because the distinction between valence and core electrons on which the pseudopotential approximation relies is less clear in transition metals. That is because the *d*-shell is filled before the *s* and *p* shell across the series, leading to some orbitals being designated as semi-core states. This means that the pseudopotential and the exchange-correlation functional are typically chosen based on the desired accuracy of certain physical properties.

In order to more accurately describe Zr chemistry, it is common to use the projector augmented wave (PAW) or ultrasoft pseudopotentials that treat the semi-core 4*s* and 3*d* electrons as valence states. From the standpoint of engineering mechanics, the choice of the exchange-correlation func-

Simulation	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	Ref.
PP-LDA	140.0	55.0	67.0	155.0	24.0	[Lumley (2013)]
PP-PW-PBE	141.9	65.4	68.0	148.7	30.2	[Burr (2014)]
PAW-PW-PBE	141.1	67.6	64.3	166.9	25.8	[Burr (2014)]
PP-PW-PBE	139.4	71.3	66.3	162.7	25.5	[Burr (2014)]
FP-LMTO-LDA	153.1	63.4	76.5	171.2	22.2	[Burr (2014)]
Experimental	155.4	67.2	64.6	172.5	36.3	[Akhtar (1973)]

tional is based on the accuracy to which the elastic stiffness constants must be computed. As shown in **TAB. 3.1**, the DFT results are benchmarked against experimental values [Burr (2014) and Lumley (2013)]. The standard local density approximation (LDA) is often unsuitable for DFT studies of pure Zr because its use results in the overestimation or underestimation of certain elastic constants. Accordingly the Perdew-Burke-Erzenhof (PBE) generalised gradient approximation is used for more accurate the elastomechanical computations [Perdew, Burke, and Ernzerhof (1996)].

The use of a non-standard pseudopotential and exchange-correlation functional contributes to the overall expenditure of DFT simulations of Zr crystals. In the state-of-the-art DFT studies of Zr, the largest simulation cells have consisted of ~ 500 atoms [Burr (2014)]. Although these simulations are incredibly time-consuming given the current-most capabilities of DFT, they can provide a gateway into understanding the behaviour of H and hydrides in Zr so as to inform computational studies of the larger Zr-H systems simulated in PF and FE models.

3.1.3 Application to Hydrogen in Zirconium

The DFT studies of H interstitials in Zr provide a useful insight into the electronic structure and energetics of the interstitialcy as well as the concentration distribution [Lumley (2013), Burr (2014), Burr et al. (2013), Varvenne et al. (2013), and Majeবাদia (2014)].

Interstitialcy. The DFT results indicate that there is a more negative solution enthalpy for a HCP α -Zr crystal in which the H atom occupies a tetrahedral site as opposed to a octahedral site [Lumley (2013) and Burr (2014)]. This was also shown to be case for the FCC lattice so this effect can be attributed to the relative sizes of the interstitial sites. This strongly agrees with the experimental understanding of H atoms occupying preferential tetrahedral sites in the Zr matrix [Khoda-Bakhsh and Ross (1982)]. As shown in **FIG. 3.1**,

TAB. 3.1

A comparison of DFT computations of the elastic constants of zirconium

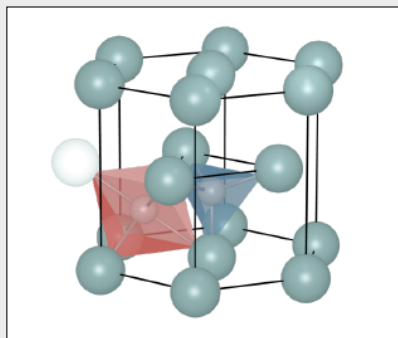
It is important to ensure that the elastic response of the system is congruent with experimental studies, which underpins the choice of more intensive DFT computation over traditional approaches with standard pseudopotentials and exchange correlation functionals.

FIG. 3.1

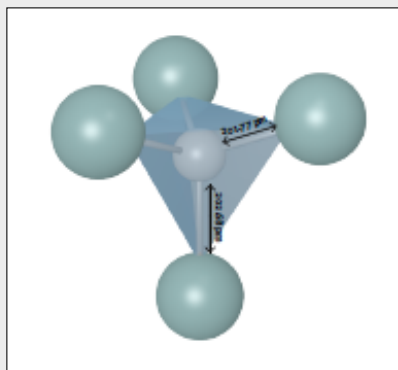
Hydrogen interstitials in hexagonal zirconium

(a) A visualisation of the atomic environments of octahedral and tetrahedral sites. (b) The configuration of a hydrogen anion occupying a tetrahedral site formed by four neighbouring zirconium atoms.

Adapted from Burr (2014).



(a)



(b)

a H atom in a tetrahedral site forms three equivalent bonds with the Zr atoms on the basal plane and one non-equivalent bond with the Zr atom along the basal pole. This trigonal symmetry is a manifestation of atomic scale anisotropy.

These DFT findings have several important implications for larger scale simulations of the Zr-H system. Firstly, it is necessary to account for the tetrahedral interstitialcy and trigonal symmetry in some capacity within microstructural and continuum scale models. This paradigm appears in the computation of the elastic interaction between H point defects and other sources of stress in the Zr alloy component. This elastic interaction energy mediates the long-range transport of H in the Zr via stress-driven diffusion. Secondly, the elastic interaction energy provides a coupling between the atomic scale and continuum scale, and so the anisotropic treatment of H interstitials in HCP α -Zr at the atomic must be reflected by the anisotropic treatment of the higher dimensional defects in the hexagonal metal. This is an important point for self-consistency.

Concentration Distribution. The DFT studies of H-H interactions suggest that H prefers a bimodal concentration distribution within the Zr lattice. Initially H atoms prefer to maintain a sparse concentration, exhibiting a high energetic barrier for hydride formation. However, as more H atoms are absorbed by the Zr matrix, this barrier is overcome and hydride precipitation becomes energetically favourable [Lumley et al. (2014) and Lumley (2013)].

The concentration of the H solute atoms required to initiate precipitation in DFT studies is much greater than observed experimentally. This disparity is in part due to the experimental differences in the respective local and global chemical compositions corresponding to pure phase micro-hydride features that possess a high H stoichiometry and the macro-hydride microstructures that evolve following relatively low hydrogenation. For example, γ -ZrH_{1.00}-hydride features are observed in Zr specimens that are charged to H concentrations of 200 ppm, but each individual pure phase γ -ZrH_{1.00} micro-hydride needle would require the local concentration in the excess of 500,000 ppm [Puls (2012)].

These DFT findings suggest that there may be more fundamental mechanisms at play which enhance the local H concentrations to drive precipitate nucleation and growth. It is postulated that localised stress-raisers can then act as nucleation sites at the atomic scale [Lumley et al. (2014) and Lumley (2013)]. The mid-range clustering of H atoms at these nucleation sites is driven by gradients in the chemical potential. The local concentration of H appears in the chemical potential, and so does the local interaction energy with the elastic field of higher dimensional defects. Diffusion-controlled

precipitation is also governed by this chemical potential, that is, the α -Zr-H solid solution and the hydride phases coexist when the chemical potential of H in the hydride phase equals the chemical potential of H in the solid solution phase.

This mid-ranged clustering is not a standard feature of most continuum scales model that couple stress-driven diffusion and diffusion-controlled precipitation [Janssens et al. (2007)]. This is because continuum scale models are based on a linear diffusion theory in which the dilute solution approximation is made [Coleman (2003), Jernkvist and Massih (2014), and Jernkvist (2014)]. In this dilute limit, the chemical potential of H in solid solution is assumed to vary linearly with its concentration. But this assumption does not hold in the vicinity of precipitates where the concentrations far exceed the dilute limit. This suggests that a simplistic coupling of the such continuum scale models of stress-driven diffusion and diffusion-controlled precipitation does constitute a self-consistent approach, especially for modelling flaw-tip H profiles and hydrided microstructures in the context of DHC failure.

3.1.4 Application to Hydrides in Zirconium

Although the DFT simulations are limited to 500 or so atoms, it is still possible to invoke the periodic supercell approximation to model certain properties of the bulk hydride phases. In particular, it is useful to employ such DFT findings as a guide for understanding the nanoscale crystallography and stability of hydride features. These DFT studies investigate both the experimentally confirmed hydride phases—including the ζ -ZrH_{0.50}-, γ -ZrH_{1.00}-, δ -ZrH_{1.66}- and ϵ -ZrH_{2.00}-hydrides—as well as some speculative hydride phases [Lumley (2013), Zhu et al. (2016), Zheng et al. (2015), Zhu et al. (2010), and Lumley et al. (2014)].

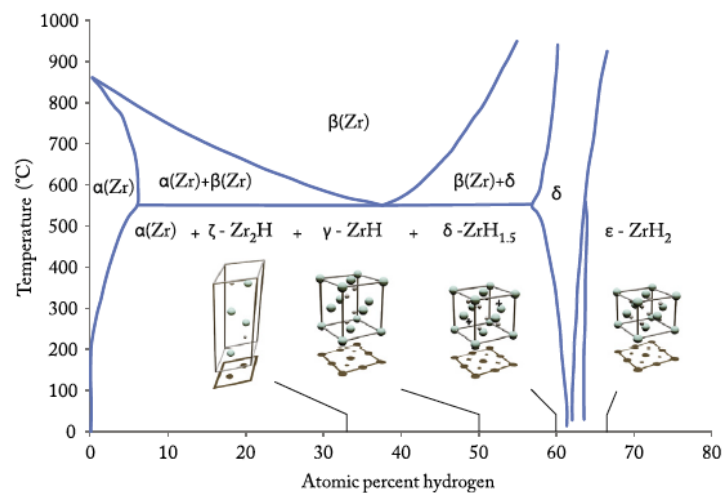
In order to apply DFT to study the properties of bulk hydride phases, assumptions have to be made about the chemical potential of H and hence the free energy of the system. That is, these electronic structure predictions cannot be made in isolation without certain thermodynamic considerations. Therefore, the following results must be viewed in the context of these assumptions as presented in the respective studies.

Crystallography. Many of the hydride phases are generally disordered but the γ -ZrH_{1.00}-hydride and ϵ -ZrH_{2.00}-hydride are somewhat more ordered. As previously stated, the DFT studies do not agree completely with the experimentally known stoichiometry of certain hydride phases. For example, the δ -ZrH_{1.66}-hydride is often assumed as ZrH_{1.66} but the first-principles atomistic simulations suggest there are two H atoms for every Zr atom. This im-

FIG. 3.2

Crystallography of hydrides in zirconium
Structures and formulae of different hydrides found in the Zr-H system. The Zr and H atoms are represented by the larger and smaller spheres, respectively.

Adapted from Lumley et al. (2014).



plies that over the spatial extent of a $\delta\text{-ZrH}_{1.66}$ -hydride feature, there is only a partial occupancy of H interstitials; however it is not known if there is a particular pattern to this partial occupancy [Lumley et al. (2014) and Bair, Zaeem, and Tonks (2015)]. Again this stoichiometric mismatch is important in relating the H concentration predicted by a dilute solution diffusion model to the computational treatment of nucleation events that require a large H content at local scale.

Moreover the H atoms prefer tetrahedral sites in the $\zeta\text{-ZrH}_{0.50}$, $\gamma\text{-ZrH}_{1.00}$ and $\delta\text{-ZrH}_{1.66}$ -phases [Lumley et al. (2014)]. This has important implications on the mechanism that governs the phase transition process from H being in the solid solution of $\alpha\text{-Zr}$ to the formation of ZrH compounds. This lends some support to the postulated multi-stage mechanism in which the more mobile H atoms diffuse to the energetically favourable tetrahedral sites and, once a sufficient concentration of H has accumulated, the Zr atoms undergo a shear (displacive) Martensitic transformation to complete the phase transition [Puls (2012) and Bair, Zaeem, and Tonks (2015)].

Phase Stability. The DFT studies indicate that $\gamma\text{-ZrH}_{1.00}$ and $\epsilon\text{-ZrH}_{2.00}$ -hydrides are thermodynamically stable, while the $\delta\text{-ZrH}_{1.66}$ -hydride phase is close in energy, it is not quite as favourable, and thus, not as stable. The $\zeta\text{-ZrH}_{0.50}$ -phase, and speculative phases consisting of a high concentration of H atoms or containing H interstitials in octahedral sites were significantly less stable [Zhu et al. (2016), Zhu et al. (2010), Lumley et al. (2014), and Lumley (2013)]. There is a tenuous evidence for clustered H atoms in the hydride phases to be more stable when sparsely positioned, which agrees with aforementioned analysis in the solid solution phase [Lumley (2013) and Lumley et al. (2014)].

The distinct crystallography of the stable hydride phases supports the experimental observation of sharp parent metal-hydride interfaces and specific orientation relationships [McRae and Coleman (2017)]. But the exact computation of interfacial energies is beyond the scope of conventional DFT studies. These interfacial energies are explicitly needed in larger scale simulations including microscale PF models of hydrides; the absence of DFT data here means that best-estimate guesses have to be used [Bair, Zaeem, and Tonks (2015)]. It seems then far more appropriate to deduce the hydride orientation relationships from TEM experiments, and strategically use this information in larger scale models because these experimental findings implicitly contain the details of the interfacial energies.

Elastomechanics. As previously stated, the elastic constants of pure hydride phase features can only be determined by DFT computations [Zhu et al. (2010)]. The key point here is that there is not a considerable difference between the elastic constants of the parent metal and those of the pure hydride phases. This greatly facilitates the explicit treatment of hydride features as elastic inhomogeneities within the framework of elastic field theory.

In DFT models of strained hydrides, it was determined that H atoms prefer tetrahedral sites under tension but they transition to octahedral sites under compression. The increase in solution energy with tension agrees well with the diffusion-first hypothesis [Bair, Zaeem, and Tonks (2015), Lumley (2013), and McRae, Coleman, and Leitch (2010)].

In addition, DFT simulations also suggest that ζ -ZrH_{0.50}- and γ -ZrH_{1.00}-hydrides are actually more ductile than α -Zr but δ -ZrH_{1.66}-hydride is significantly more brittle. This agrees well with experimental studies that indicate that the fracture toughness of Zr specimens is severely compromised by δ -ZrH_{1.66}-hydrides [Puls (2012)].

3.2 Microstructural Modelling

Microstructural evolution constitutes a broad spectrum of phenomena. For the case of phase transformations in materials, the microstructures are composed of distinct thermodynamic phases, different crystallographic structures, misorientated grains, inhomogeneities and other lower-dimensional structural defects [Callen (1960) and Cahn and Haasen (1996)]. There are two main challenges faced by conventional theoretical and computational physics-based approaches to simulating processes at the length and time scales typical of microstructural evolution. On the one hand, atomistic and electronic structure calculations are computationally expensive and hence the system sizes are limited by the computational resources available. On the other hand, an approach based purely on the mechanics and thermodynamics of continua cannot truly capture the microstructural details of the systems and processes unless empirical and constitutive relationships are used [Gurtin, Fried, and Anand (2010)].

To this end, the PF method provides a powerful computational framework to describe the microstructure using a set of conserved and non-conserved field variables, whose temporal and spatial evolution is governed by the Cahn-Hilliard non-linear diffusion equation and the Allen-Cahn relaxation equation [Chen (2002) and Janssens et al. (2007)]. As the PF method is able to predict arbitrarily complex morphologies, it is a natural starting point for treating the problem of hydrides in Zr in the context of DHC [Ma et al. (2002), Ma et al. (2006), Guo et al. (2008), and Bair, Zaeem, and Tonks (2015)]. In the following, the PF method is introduced, and its applications to the DHC problem are discussed by highlighting the key successes and drawbacks.

3.2.1 Phase Field Method

The premise of the PF method is that the microstructural evolution takes place to minimise the thermodynamical free energy that may include a range of local and global contributions: (i) bulk chemical free energy; (ii) interfacial energies between distinct phases; (iii) elastic strain energy of inhomogeneities and defects; (iv) external variables such as applied stress and temperature fields across the system [Chen (2002)]. Such a system could be simulated numerically using conventional interface-tracking models that describe mathematically sharp interfaces. In these interface-tracking models, the local interfacial velocities are determined by various means such as driving forces for particle mobility, surface motion and boundary conditions. Such a strategy requires—as the name suggests—explicitly tracking all interfaces and, due to the geometrical complexity, this is very computationally

expensive in problems beyond one-dimensional systems [Chen (2002)].

In contrast, a PF model takes advantage of the concept of a van der Waals diffuse interface [van der Waals (1894), Cahn and Hilliard (1958), and Chen (2002)]. By incorporating the effects of random thermal noises, the stochastic temporal evolution of the microstructure in a PF model is described by two continuum thermodynamical equations: the Cahn-Hilliard non-linear diffusion equation and the Allen-Cahn time-dependent Ginzburg-Landau equation [Chen (2002), Janssens et al. (2007), and Vvedensky (2004)].

There are two types of PF models: (i) the field variables are known and phase fields are introduced to avoid the complex explicit treatment of thermodynamic phase interfaces; and (ii) the field variables are not known but they correspond to well-defined physical order parameters, in which the thermodynamics and kinetics of the system can be described by its microscopic properties. The latter type is of interest to the problem of DHC as such models can be used treat simultaneously solid-state phase transformations, multi-component diffusion, defect-solute interactions, dislocation dynamics and crack-propagation [Chen (2002), Ma et al. (2002), Ma et al. (2006), and Guo et al. (2008)].

Free Energy Functional. Consider a heterogeneous microstructure which is a system of volume $\mathcal{V}$ described by a set of N_f field variables, of which N_c are conserved variables and $(N_f - N_c)$ are non-conserved field variables, that is,

$$\{c_a \mid a = 1, 2, \dots, N_c\} \quad \text{and} \quad \{c'_{a'} \mid a' = 1, 2, \dots, (N_f - N_c)\} \quad (3.5)$$

respectively. Representing all phase boundaries in the material as diffuse interfaces, the total free energy of the system can be expressed in a general form as

$$\begin{aligned} F_{\text{PF}} = & \iiint_{\mathcal{V}} d^3r \left[f_{\text{PF}}(\{c_a\}, \{c'_{a'}\}) + \sum_{a=1}^{N_c} \mathfrak{A}_a (\nabla c_a)^2 \right. \\ & \left. + \mathfrak{B}_{ij} \sum_{a'=1}^{N_f-N_c} (\nabla c'_{a'})_i (\nabla c'_{a'})_j \right] \\ & + \iiint_{\mathcal{V}} d^3r \iint_{\mathcal{V}} d^3r' G(\mathbf{r} - \mathbf{r}'), \end{aligned} \quad (3.6)$$

where the function f_{PF} is the local chemical free energy density, the $(N_c \times 1)$ matrix $\mathfrak{A}_a$ and (3×3) matrix $\mathfrak{B}_{ij}$ contain gradient energy coefficients, and the function G describes long-range interactions. The explicit form of the RHS of Eq. (3.6) marks the distinction from one phase field model to another, and the main challenge is bestowing expressions to the various contributions to the total free energy. On the RHS of Eq. (3.6), there are the following contributions: (i) the first volume integral concerns all local con-

tributions to F_{PF} from short-range chemical interactions, which includes interfacial energies originating from gradient energy terms that are non-zero only in the vicinity of the interfaces; and (ii) the second volume integral contains non-local contributions to F_{PF} that arise from a number of long-range interactions such as the elastic interactions, electric dipole-dipole interactions and electrostatic interactions [Chen (2002)].

Consider first the local free energy density whose form depends on the system in question. Typical variants of expressions for f_{PF} are given in TAB. 3.3. For many solid state phase transformations, the field variables correspond to physical parameters; for such cases, the form of f_{PF} is that of a Landau-type polynomial of the order parameters [Chen (2002)].

The next important feature of real microstructures are interfaces; the heterogeneity is associated with an excess free energy, which is the interfacial energy. The interfacial energy is assumed to be given by the gradient energy that appears in Eq. (3.6), and usually the interfacial energy must be evaluated numerically. In general, interfacial energies are anisotropic due to the underlying crystallography of metallic solids. For solid state phase transformations, this anisotropy can be introduced through gradient terms [Chen (2002)].

The final component of the phase field is the contributions from long-range interactions. In general, solid state phase transformations involve the formation of coherent interfaces at the early stages of microstructure evolution. Usually, the lattice planes and directions are continuous across the interfaces and lattice mismatches between phases and domains are accommodated by elastic distortions. The role of the elastic energy in adding to F_{PF} can be incorporated directly by either (i) introducing an expression for the elastic strain energy as function of the field variables or (ii) coupling the field variables and the elastic displacement gradients in the f_{PF} function [Khachaturyan (1983)]. One possible means to account for the elastic heterogeneity is to introduce a spatial dependence in the elastic stiffness tensor. Once a form for the stress-free strain is postulated, the stress state of the material can be determined by solving the usual mechanical equilibrium conditions subject to appropriate boundary conditions. Subsequently the total elastic strain energy of the system can be calculated through the usual expression, which can also include contributions from external stresses. It is important to note that direct numerical approaches for incorporating heterogeneities—for example, using conjugate gradients methods or FE methodologies—are usually computationally expensive. It is possible to add, say, a FE overhead to a PF model to compute the elastic fields. But it has been suggested that first-order approximations should be employed for weaker heterogeneities [Chen (2002)].

Local Free Energy Density	Field Variables	Example Form
Double-well form	ϕ	$4\Delta f \left(-\frac{1}{2}\phi^2 + \frac{1}{4}\phi^4 \right)$
Double-obstacle form	ϕ	$\Delta f (1 - \phi^2) + I(\phi)$
Crystalline energy	ϕ	$\Delta f \sin^2(\pi\phi)$
Extended double-well form	$\{\phi_a\}$	$4\Delta f \left(-\frac{1}{2}\sum_a \phi_a^2 + \frac{1}{4}\sum_a \phi_a^4 \right) + c \sum_a \sum_{b>a} \phi_a^2 \phi_b^2$
Landau polynomial	$c, \{c'_{a'} \mid a' = 1, 2, 3\}$	$f_d(c, T)$ $+ \frac{1}{2}A_1(c, T) \sum_{a'} c_{a'}'^2$ $+ \frac{1}{3}A_3(c, T) \prod_{a'} c_{a'}'$ $+ \frac{1}{4}A_{41}(c, T) \sum_{a'} c_{a'}'^4$ $+ \frac{1}{8}A_{42}(c, T) \epsilon_{a'b'c'} c_{b'}'^2 c_{c'}'^2$

Equilibration. The temporal evolution of the field variables is given by the Cahn-Hilliard non-linear diffusion equations and the Allen-Cahn (or Ginzburg-Landau) relaxation equations:

$$\frac{\partial c_a(\mathbf{r}, t)}{\partial t} = \nabla_i \left[\mathfrak{M}_{ab} \nabla_i \left(\frac{\delta F_{\text{PF}}}{c_b(\mathbf{r}, t)} \right) \right] \quad (3.7)$$

$$\frac{\partial c'_{a'}(\mathbf{r}, t)}{\partial t} = \mathfrak{L}_{a'b'} \left(\frac{\delta F_{\text{PF}}}{\delta c'_{b'}(\mathbf{r}, t)} \right), \quad (3.8)$$

where the coefficients matrices $\mathfrak{M}$ and $\mathfrak{L}$ are related to the atom or interface mobility.

In general, PF models require fundamental thermodynamic and kinetic information from either experiments or electronic structure and atomistic models. However several parameters that are very important to PF modelling are not directly known. An important example is the aforementioned interfacial energy between two phases, which is usually difficult to deduce directly from experiment and cannot be obtained from conventional DFT simulations due to the computational limitations. Hence such parameters must often be quantified without any *a priori* physical basis in order to proceed with the PF analysis.

Computational Implementation. Due to the mathematically complex nature of the coupled thermodynamics, the Cahn-Hilliard and Allen-Cahn relaxation equations must be solved numerically on a discretised spatial grid. Even two-dimensional PF models can be computationally intensive if there are many variables and components in the free energy functional of the system of interest. Furthermore, the evaluation of the elastic fields of defects with nonsimple interfaces may involve resorting to intensive numerical computational steps, including prospective FE overheads. Generally, PF simulations output a qualitative or phenomenological demonstration of the evolution

TAB. 3.3

Phase field local free energy density forms

Variants of the Landau polynomial are common to structural phase transformation models, and several expressions have been put forward for the problem of hydride precipitation in Zr alloys.

Adapted from [Chen \(2002\)](#).

of the microstructure. The system sizes vary from application to application; in the context of hydrides precipitation, the two-dimensional PF models are typically limited to system sizes of $10\ \mu\text{m} \times 10\ \mu\text{m}$ with a spatial resolution of $0.1\ \mu\text{m}$ set by the choice of 100×100 grid points.

3.2.2 Application to Hydride Precipitation

The PF methodology is a popular choice for treating the complexity of H diffusion-controlled precipitation of micro-hydrides and subsequent morphological evolution of the hydride-matrix interfaces [Ma et al. (2002), Ma et al. (2006), and Bair, Zaeem, and Tonks (2015)]. There has been extensive work on simulating two-dimensional $\gamma\text{-ZrH}_{1.00}$ -hydride microstructures on the basal plane using various PF models [Bair, Zaeem, and Tonks (2015)]. In such models, it is common to use a free energy functional of the form

$$F_{\text{PF}} = F_{\text{c}} + F_{\text{el}} \quad (3.9)$$

with

$$F_{\text{c}} = \iiint d^3\mathbf{r} \left[f(C, \eta_p) + \sum_{p=1}^v \frac{\alpha_p}{2} (\nabla \eta_p)^2 + \frac{\beta}{2} (\nabla C)^2 \right] \quad (3.10)$$

$$f(C, \eta_p) = \frac{A_1}{2} (C - C_1)^2 + \frac{A_2}{2} (C - C_2)^2 \sum_{p=1}^v \eta_p^2 - \frac{A_3}{4} \sum_{p=1}^v \eta_p^4$$

$$- \frac{A_4}{6} \sum_{p=1}^v \eta_p^6 + A_5 \sum_{p \neq q} \eta_p^2 \eta_q^2 + A_6 \sum_{p \neq q, r} \eta_p^4 (\eta_q^2 + \eta_r^2)$$

$$+ A_7 \sum_{p \neq q \neq r} \eta_p^2 \eta_q^2 \eta_r^2 \quad (3.11)$$

where F_{c} is the chemical free energy and F_{el} is the elastic energy. In the chemical free energy, η_p represents the order parameter for each of the three possible orientations of $\gamma\text{-ZrH}_{1.00}$ -hydride needles on the basal plane, C is the concentration of diffusible H, and C_1 and C_2 are the concentrations of H in the matrix and precipitate respectively. The gradient energy coefficients α_p and β and the prefactors $\{A_n\}$ are (generic) physical constants that govern the microstructural evolution and so must be chosen to reflect empirical findings. It is often convenient to simulate with dimensionless PF models because the qualitative information is still retained [Bair, Zaeem, and Tonks (2015)].

The elastic energy differs in various PF models of $\gamma\text{-ZrH}_{1.00}$ -hydrides and several forms for F_{el} have been proposed based on the theory of strain-induced phase transformations [Khachaturyan (1983)]. Most variants of F_{el} include contributions from the $\gamma\text{-ZrH}_{1.00}$ -hydride transformation strains and

H diffusion interaction energy, as determined by experiments, and the elastic constants of Zr to define the (purely) elastic portion of the free energy equation. In addition, PF models that also include continuum elastoplasticity have been developed to treat the plastic relaxation around hydrides [Guo et al. (2008)]. Coupled FE-PF models have been applied to study flaw-tip hydride microstructures [Ma et al. (2002) and Ma et al. (2006)]. However, in most cases, isotropic elasticity is employed and the FE overhead for stress analysis of the non-simple topology of the hydride-matrix interfaces adds computational expenditure. Therefore, it is not straightforward to upscale the PF models to macroscopic systems that are more relevant to the DHC mechanism [Tonks et al. (2017)].

Hydrided Microstructures. The two-dimensional PF studies usually involve simulation cells of dimensions $10\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$ resolved on a 100×100 discretised grid. As shown in FIG. 3.3, the simulated microstructures can typically show several individual micro-hydride needles with a resolution that is on the nanoscale [Bair, Zaeem, and Tonks (2015) and Tonks et al. (2017)]. This means that the simulated thickness of the hydride-matrix interfaces is approximately one or two orders of magnitude than the atomically sharp interfaces observed in experiments [McRae and Coleman (2017) and Puls (2012)].

Despite this shortcoming, the simulated microstructures from PF models do indeed resemble their experimental counterparts at least qualitatively. That is, these PF simulations can demonstrate the known orientation relationships and morphologies of micro-hydride needles as well as the staircase-like stacking effect [Bair, Zaeem, and Tonks (2015)]. This is arguably the main benefit of PF models in which the relevant contributions to the system free energy have been clearly identified. However, as previously stated, they only depict a very small area of the entire flaw-tip H-enhanced region. For this reason, it is impossible to use the PF method to study the effect of the microstructure on hydride precipitation at the larger length scales that are relevant to DHC failure.

Prior to these recent studies, dimensionless PF models had also been investigated [Ma et al. (2002) and Ma et al. (2006)]. In such models, the physical length scales are either reduced or chosen according to convenience [Janssens et al. (2007)]. As shown in FIG. 3.3, the dimensionless PF models appear to simulate a larger region consisting of more hydride features than their counterparts. But due the absence of any explicit length scales, this cannot be said with any certainty and there is no obvious use for these results in, say, FE models.

As PF simulations often involve an optimisation procedure, the time

scales for the kinetics of hydride precipitation can only be inferred. In particular, only a snapshot of the final equilibrium state is determined. For this reason, it has not been possible to show the iterative steps for the hypothesised autocatalytic nucleation mechanism. This is because the precipitate nuclei are randomly dispersed within the simulation cell so it is unclear whether these are separate nucleation events or those triggered by a sympathetic mechanism [Bair, Zaeem, and Tonks (2015)].

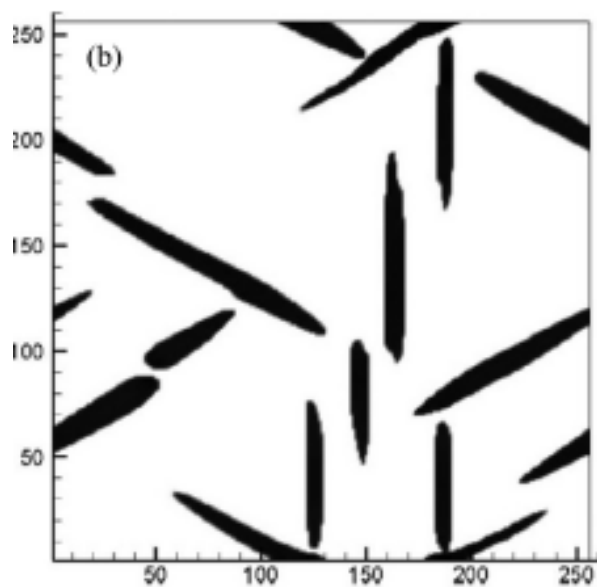
Diffuse Multi-Phase Interfaces. In addition to limited system size, another drawback of applying the PF methodology to the study of hydrides in Zr is the assumption of an diffuse interface [Bair, Zaeem, and Tonks (2015)]. This is in contrast to the DFT and experimental studies which indicate that the hydride-matrix interface is atomically sharp [Lumley et al. (2014), Britton (*Nuclear Materials: Zirconium*), and Puls (2012)]. In this respect, the treatment of the hydride distribution as a spatially varying field is both physically inaccurate and far too computationally expensive, given the fact the micro-hydride nucleation and growth is highly localised to the order of microns.

Furthermore, certain PF models do replicate the growth of micro-hydride needle on the basal along one of the three preferred directions, which agrees with experimental studies. However, this information is usually put into the PF model beforehand through the order parameters chosen to mimic the experimentally measured misfit strains of fully-formed micro-precipitates. So there is not much new information to be gained from such simulations. More to the point, this strategy is quite circular and somewhat inefficient if experimental observations are to be translated into complicated expressions for energies. This is particularly true for the interfacial energies used in PF models [Bair, Zaeem, and Tonks (2015) and Shi and Xiao (2015)].

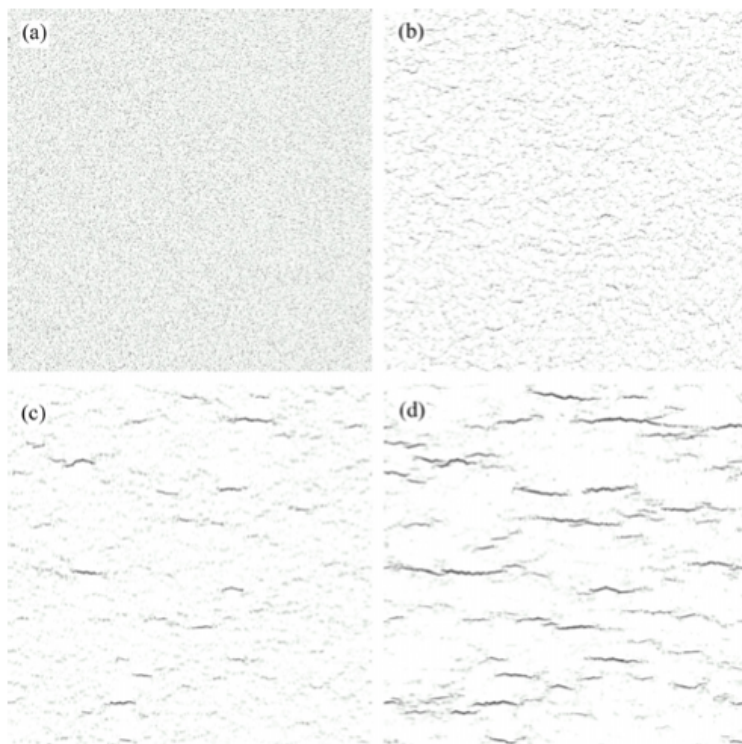
In conjunction with dimensionless analysis, the diffuse-interface assumption also means that a cut-off must be introduced to visualise the micro-hydride geometry. This cut-off corresponds to a critical H concentration that must be exceeded for a given grid point to be in the hydride phase as opposed to the solid solution phase. This cut-off is often not quoted in the literature, and it is a computational artefact that can be chosen to qualitatively replicate experimental findings [Bair, Zaeem, and Tonks (2015) and Janssens et al. (2007)].

As evident, the simulated micro-hydride morphologies have non-simple geometries due to the use of the diffuse-interface approximation. Therefore, the computation of their elastic fields would generally require some numerical calculations. Given that a large density of such micro-hydrides that would need be treated in a macroscopic region around the flaw tip,

this would be a very computationally expensive procedure. This is yet another reason why PF models are limited in terms of their system sizes. It then seems appropriate to simplify the micro-hydride morphology so that the system stress analysis can be performed efficiently.



(a) Shi and Xiao, 2015



(b) Ma et al., 2006

FIG. 3.3

Simulated hydrided microstructures using the phase field method

(a) A PF simulation of γ -ZrH_{1.00}-phase micro-hydride needles on the basal plane. Here the order parameters in the PF model are chosen meticulously so that the simulated micro-hydrides are determined to reside along the three preferred orientations on the basal plane. The main finding from this particular simulation is the existence of energetically favourable networks of micro-hydride needles whose formation is dictated by the elastic contributions to the free energy. However, even this model, the hydride-matrix interfaces are diffuse which does not agree with experimental observations. (b) A dimensionless PF simulation of hydride features. There is some qualitative agreement with experimental micrographs in the sense that hydrides are discretised entities but there is no explicit notion of length in these images. The temporal evolution is demonstrated from (a) to (d) but there is no explicit notion of time because this is really an optimisation procedure.

3.3 Continuum Scale Modelling

At the component scale, it is often of practical interest to be able to examine—over extended periods of time—the entire component as a whole or at least some macroscopic region of it. The materials phenomena at these length and time scales can often be conveyed without any explicit reference to the underlying atomic, electronic or even microstructural details.

The underlying structure of matter is essentially homogenised into a topologically continuous and pointwise differentiable mass density. In this coarse description of the material, physical quantities can be described by spatially varying fields. Using these pointwise fields, the physical quantities can be related to each other through a set of partial differential equations (PDEs) that can be formulated using basic physical principles, such as conservation laws or the tenets of classical mechanics and thermodynamics, or adapting empirical observations. These PDEs can then be solved using computational libraries of numerical methods [[Gurtin, Fried, and Anand \(2010\)](#) and [Vvedensky \(2004\)](#)].

The most well known method for solving deterministic PDEs in the context of engineering sciences is the FE method [[Zienkiewicz \(1977\)](#) and [Suli \(2012\)](#)]. The FE method is a general-purpose PDE solver that is widely used in the field of solid mechanics because of its ability to treat complex geometries and non-linear relationships as well as material heterogeneity and anisotropy. For this reason, it is a very popular tool in the industrial setting for continuum scale stress analysis. In the nuclear industry, FE models of DHC have received a considerable amount of attention and several models have been validated against experimental test programmes [[Martin \(2013\)](#), [Jernkvist and Massih \(2014\)](#), [Jernkvist \(2014\)](#), [McRae, Coleman, and Leitch \(2010\)](#), [Tonks et al. \(2017\)](#), and [Aybar and Ortega \(2005\)](#)]. Therefore, it is only sensible to explore the most recent and most advanced of these FE models in depth.

3.3.1 Finite Element Method

In order to solve PDEs, the FE method draws upon various approximate numerical techniques, such as the variation methods, weighted residuals and piecewise continuous trial functions. The FE method is particularly suited for problems in which the PDEs cannot be solved by analytical or semi-analytical approaches as well as cases for which the standard integral domain transformations, such as Laplace and Fourier transformations, or power series methods do not converge. The general premise of FE modelling involves dividing the physical system into a finite number of contiguous components known as elements whose individual behaviour and prop-

erties can be understood much more straightforwardly. The original system is reconstructed by piecing together the constituent elements [Zienkiewicz (1977) and Suli (2012)].

Discretisation. As shown in FIG. 3.4, the physical system is tessellated with a uniform or non-uniform mesh. Each cell in the tessellation defines the element which is a surface in the two-dimensional case or a volume in the three-dimensional case. This division procedure forms imaginary boundaries that are lines in the two-dimensional case or planes in the three-dimensional case. The elements are assumed to be interconnected at a number of nodal points that are positioned within the elements or on the boundaries. Computers can store the spatially varying fields at these nodal points; the physical quantities can be interpolated within each element. In this way, a PDE is discretised on the nodal points and effectively replaced by a set of algebraic equations. These equations are solved for the values of the solution at the nodal points.

Computational Implementation. The FE method constitutes the foundation of well established and legacy bounded software packages such as ABAQUS [ABAQUS]. As stated earlier, the FE method is designed to treat macroscopic regions within a material or even the entire component if necessary. But the FE method relies heavily on the ability to generate quality meshes that convey arbitrarily complex geometries to a suitable degree of accuracy. This initialisation procedure can be time consuming and, in transient problems where the geometries evolve in time, re-meshing can be a major computational bottleneck. The FE methods scales, in part, with the system size and the total number of elements as well as the number and order of PDEs. Therefore, the computational expenditure of FE models can be quite high, especially for multi-field problems.

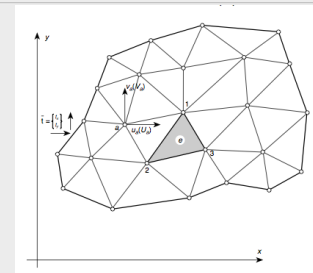
3.3.2 Application to Stress Analysis

The FE method is readily applicable to numerical stress analysis of notched specimens under a (quasi-static) tensile loading, and so it is a natural choice for modelling the stress state ahead of flaws in Zr alloy components. In the context of DHC, various flaw acuties are considered including sharp cracks, circular holes, V-notches and U-notches [Puls (2012), Schofield (2002), and Martin (2013)]. It is, however, entirely possible to determine the stress fields for these particular flaw geometries to a reasonable accuracy using analytical and semi-analytical techniques within the framework of planar elasticity [Bilby, Cottrell, and Swinden (1962), Bilby and Eshelby (1968), Chell (1976), Lardner (1975), Lardner (1970), Muskhelishvili (1977), and

FIG. 3.4

Finite element meshing

An example of a two-dimensional region tessellated by a spatial mesh. The elements are triangles in case. Adapted from Zienkiewicz (1977).



Vitek (1975)]. The main benefit of the FE approach here is the ability to represent non-trivial flaw geometries and capture surface effects in three-dimensional simulations, but these cases are seldom explored in the context of DHC research because of the difficulties associated with quality mesh creation.

Isotropic Elasticity. One drawback of standard FE models of Zr is the common assumption of isotropic elasticity. The continuum scale anisotropy of Zr is ignored because the FE models do not account for the anisotropic crystallography of the Zr lattice at the atomic scale or the anisotropic polycrystallinity of the (textured) Zr microstructure at the microscale. This is an obvious oversight because of the significance of distinguishing different Zr alloy textures. This requires the use of more sophisticated FE-based crystal plasticity models in which the compatibility stresses due to misoriented HCP crystallites can be computed [Dunne and Petrinic (2005)].

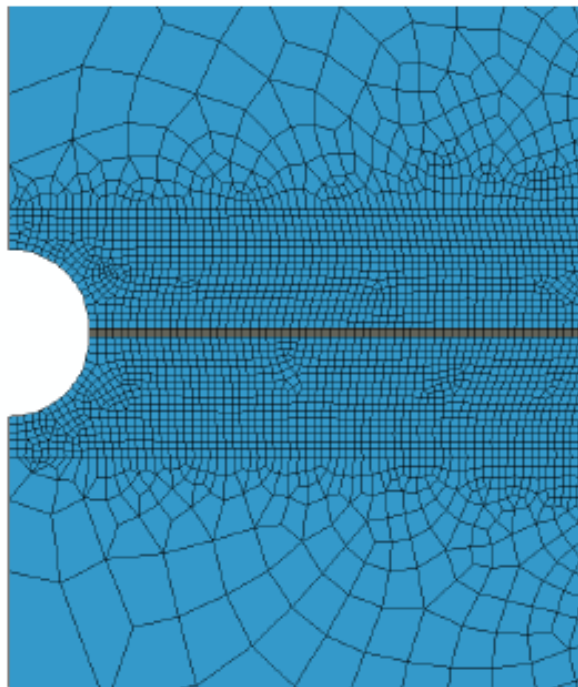
Process Zone Modelling. The FE method provides convenient backdrop for studying the DHC initiation as the gradual separation of the hydrided process zone [Martin (2013), Puls (2012), Scarth and Smith (2001), Scarth (2002), and Matvienko (2004)]. This process zone approach falls within the framework of cohesive zone modelling, which is based on the strip yield theory [Park and Paulino (2011), Bilby, Cottrell, and Swinden (1962), and Dugdale (1960)]. The aim of the process zone model is to predict the (isothermal) threshold stress for DHC initiation, which defines the critical process zone displacement,

$$d_{\text{crit}} = \frac{K_{\text{IH}}^2}{E_0 p_{\text{crit}}} \quad \text{with} \quad E_0 = \frac{E}{1 - \nu^2}, \quad (3.12)$$

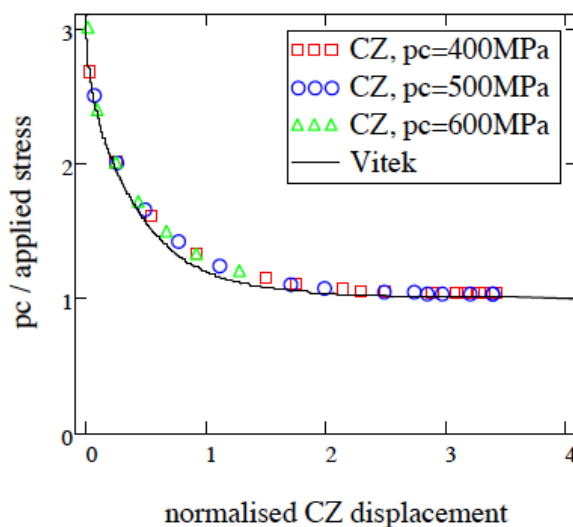
where p_{crit} is threshold hydride fracture stress. In this engineering model, the non-linearity associated with the hydride fracture is contained within an infinitesimally thin region of constant cohesive strength radiating from the notch root [Martin (2013), Bilby, Cottrell, and Swinden (1962), and Dugdale (1960)]. It is taken that this is a good assumption for cracks and sharp notches where hydrides have been observed to concentrate at the notch root [Martin (2013), Scarth (2002), and Scarth and Smith (2001)]. This is, however, difficult to justify for the blunter notches with finite root-radii because the notch-tip hydrided microstructure is found to be more disperse in experimental studies [Cui et al. (2009)].

An application of the process zone approach to case of a circular hole is shown in FIG. 3.5 which shows the complexity of mesh in the vicinity of the notch and adjacent to the hydride process zone [Martin (2013)]. This model is very practical from the standpoint of day-to-day engineering because it requires a very minimalistic input. It is also important to highlight

here the quantitative agreement between the FE-based cohesive models and the semi-analytical model derived using the theory of planar elasticity [Martin (2013) and Vitek (1975)]. Note also the use of isotropic elastic constants E and ν in the process zone approach, and hence the absence of any real microstructural information.



(a)



(b)

FIG. 3.5

Hydride process zone modelling

(a) A FE-based cohesive zone model of a notched $40 \text{ mm} \times 40 \text{ mm}$ square plate specimen with a circular hole of radius 1 mm and single narrow process zone between two adjacent regions under plane strain. Notice the complexity of the meshing in the vicinity of the notch and the process zone. (b) A comparison in the variation of the normalised cohesive zone displacement with the cohesive strength as determined through this FE-based cohesive model and a semi-analytical solution. The response of the cohesive zone model closely matches the semi-analytical solution.

Adapted from Martin (2013).

3.3.3 Application to Stress-Diffusion Analysis

The FE method is capable of treating multiple spatially varying fields and so multi-field FE models provide a convenient framework in which to simulate stress-driven diffusion of H in a notched specimen under tension by coupling the system stress fields and the H concentration field. In the present work, this paradigm is referred to as the stress-diffusion analysis, which constitutes one aspect of a multiscale DHC model. The main output of the stress-diffusion analysis is the notch-tip H concentration profile as a function of the flaw acuity as well as other microstructural defects that can operate as localised stress generators.

Various continuum PDEs have been derived to describe the long-range transport of interstitials under the influence of stress gradients; these PDEs assume the general postulates of linear irreversible thermodynamics and fundamentally Fickian diffusion equations with a field that biases the kinetics [Balluffi, Allen, and Carter (2005), Callen (1960), and Khachaturyan (1983)]. Assuming no H production within the material, the local continuity equation of the H concentration $c_H(\mathbf{x}, t)$ and its flux vector $\mathbf{J}_H(\mathbf{x}, t)$ is given by

$$\frac{\partial c_H(\mathbf{x}, t)}{\partial t} + \nabla \cdot \mathbf{J}_H(\mathbf{x}, t) = 0, \quad (3.13)$$

in which a widely used constitutive relationship is used to describe the diffusional flux in terms of stress gradients as

$$[\mathbf{J}_H]_i(\mathbf{x}, t) = -D \left[\frac{\partial c_H(\mathbf{x}, t)}{\partial x_i} + \frac{c_H(\mathbf{x}, t) \Delta V_H}{RT} \frac{\partial P(\mathbf{x})}{\partial x_i} \right], \quad (3.14)$$

$$P(\mathbf{x}) = -\frac{1}{3} \text{Tr}[\boldsymbol{\sigma}]_{ij}(\mathbf{x}), \quad (3.15)$$

where the scalar field $P(\mathbf{x})$ is the hydrostatic pressure, D and ΔV_H are diffusivity and the volume of transport for H in Zr respectively, and R is the molar gas constant. Note that temperature gradients can also be included in a similar way but these are not considered in the scope of this investigation [Jernkvist and Massih (2014) and Jernkvist (2014)]. Observe that there is no time variation in $P(\mathbf{x})$, that is, this is a model of H equilibration in the static elastic fields around the notch tip. This is a reasonable assumption given the high mobility of H at temperatures that are relevant to reactor operation [Puls (2012)].

It is again worth highlighting that this approach assumes an isotropic coupling between the H interstitials and the stress-raisers in the Zr specimen. This is because of the so called $P(\mathbf{x})\Delta V_H$ elastic interaction energy, which is based on the application of the spherical misfit model of point defects to case of H interstitials. However, this is not compatible with experimental

and DFT findings of H atoms occupying tetrahedral interstitial sites. This effect of anisotropy within the stress-diffusion analysis is explored at a later stage in this investigation.

3.3.4 Application to Diffusion-Precipitation Analysis

In a similar vein to PF models, it is possible to apply the concept of multi-field FE modelling to study problem of H diffusion-controlled hydride precipitation in the vicinity of the flaw tip. In the present work, this paradigm will be referred to as the diffusion-precipitation analysis. These FE models are far more simplistic in their treatment of precipitation and precipitates than their PF counterparts, but they cover a much larger region of the Zr alloy component [Tonks et al. (2017), Aybar and Ortega (2005), Jernkvist and Massih (2014), and Jernkvist (2014)].

The multi-field FE models can incorporate precipitation by first decomposing the total H concentration into the free diffusible H atoms that resides in solid solution and the H atoms that are chemically bonded to a particular hydride phase:

$$c_H(\mathbf{x}) = (1 - \kappa)c_H^{(1)}(\mathbf{x}) + \kappa[c_H^{(2)}(\mathbf{x}) + c_H^{(3)}(\mathbf{x})] \quad (3.16)$$

where, on the RHS, the first term describes the mobile H concentration in solid solution in the metal, and the second term concerns the H that is within the spatial domain of a hydride phase, both mobile and chemically bound to the hydride phase. The distinction made to include the mobile H within the hydride phase is an unique feature of this particular model and so the J_H is generally non-zero in the hydride precipitates [Jernkvist and Massih (2014)]. The parameter $\kappa \in [0, 1]$ controls the volume fraction of hydrides, that is, when κ is unity, the system is in pure hydride phase. A point-kinetics approach is applied to express κ in terms of a local rate of change as

$$\frac{\partial \kappa}{\partial t} + \frac{1}{\tau}(\kappa - \kappa_{\text{final}}), \quad (3.17)$$

where τ is a characteristic time scale and κ_{final} is the hydride volume fraction that would be reach after an infinite time. In practice, κ_{final} must be deduced from the Zr-H phase diagram and then put in by hand. This forces the FE diffusion-precipitation analysis to be completely deterministic; there is no stochastic variation that is central to microstructural evolution. Therefore, this approach is not suitable for any statistical modelling of the hydrided microstructure.

The most sophisticated of these multi-field FE models integrates the process zone stress analysis, the constitutive stress-diffusion analysis and the point-kinetics based diffusion-precipitation analysis [Jernkvist and Massih (2014)]. The algorithmic workflow for this methodology is depicted in

FIG. 3.6, which shows how the respective analyses are coupled into a two-loop structure.

In order to convey some of the experimental findings of the Zr-H system, this multi-field FE model extends the previous FE analyses in the following ways: (i) the stress-diffusion analyses is modified to also include the effects of temperature gradients; (ii) the point-kinetics model is extended to include both precipitation and dissolution with a hysteresis that reproduces the ratchetting phenomenon; (iii) the hydride volume fraction is vectorised to account for the average directionality of the hydrides and thereby capture hydride reorientation; and (iv) process zones of more complex geometries are described using decohesion laws [Jernkvist and Massih (2014)].

This is an ambitious strategy that attempts to unify—albeit in a very simplistic manner—all three stages of DHC within one self-consistent framework. The real benefits of this study are that it is based on real experimental evidence, it is validated, and it essentially provides a list of the key physics that must be included in an engineering model of DHC failure [Martin (2014) and Jernkvist (2014)].

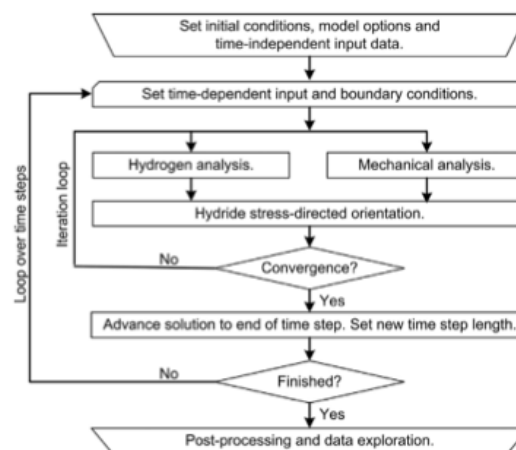
In spite of these benefits, multi-field FE modelling still falls short of ideal standard. These models do not accurately account for the anisotropic atomic environment of H interstitials in HCP α -Zr and hence the anisotropic diffusion of H in polycrystalline Zr microstructures, the morphologies of micro-hydride needles and their thermodynamically favourable assembly into macro-hydride colonies at heterogeneous nucleation sites, or local scale mechanisms such as the discrete dislocation plastic relaxation around hydrides which underpins the ratchetting phenomenon. Moreover these multi-field FE models of DHC would be far too computationally expensive for any efficient statistical modelling.

FIG. 3.6

A multi-field finite element methodology for DHC

A strategy for coupling stress analysis, stress-diffusion analysis and diffusion-precipitation analysis with a FE framework. This is a two-loop convergence structure in which every iterative step requires a potentially expensive FE computation.

Adapted from Jernkvist and Massih (2014).



3.4 Multiscale Modelling

After having reviewed the experimental findings and having learnt about the capabilities of state-of-the-art electronic structure, atomistic, microstructural and continuum scale modelling methodologies, it is now possible to put forward a multiscale modelling strategy. This is a bespoke model of the early stages of DHC failure, that is, stress-driven diffusion of H and diffusion-controlled precipitation of hydrides in Zr alloy microstructures within the DHC regime of no crack initiation. At this stage, it is essential to establish the simulation scope as well as the desired accuracy in terms of the simulated physics and the desired efficiency in terms of the simulation runtime.

Simulation Scope. The primary input to this model are parameters that quantify the notch acuity, specimen microstructure and thermomechanical cycles. The computations are categorised into three analyses: (i) stress analysis which involves computations of the stress state of the multi-defect microstructure; (ii) stress-diffusion analysis which involves computations of the H profile in the static elastic fields of the system; and (iii) diffusion-precipitation analysis which involves computations of the morphological growth of micro-hydride needles and macro-hydride colonies at heterogeneous nucleation sites. As shown in FIG. 3.7, the output of this model is a simulated micrograph that depicts the geometries, morphologies and contours of key metallographic features:

- ▶ *Geometries.* This includes the geometries of the flaw as well as the hierarchy of inter-granular and intra-granular nucleation sites.
- ▶ *Morphologies.* This includes the morphologies of micro-hydride needles and macro-hydride colonies as well as grains.
- ▶ *Contours.* This includes the contours of the flaw-tip H enhancement and depletion as well as the contours of hydride-rich and denuded zones.

Therefore, the simulated system size must be ~ 1 mm in each direction with a resolution of $\sim 0.1 \mu\text{m}$ in order capture these metallographic features.

Accuracy. In reference to the respective analyses, the following is list of the essential multiscale physics that should be incorporated within this bespoke model:

- ▶ *Stress Analysis.* This involves the treatment of the individual and interacting elastic fields of H point defects, various classes of dislocations in HCP α -Zr, micro-hydride needles and macro-hydride colonies, second-phase particle inclusions, grain boundaries and the flaw under a tensile loading. These computations of the elastic fields must

incorporate separate or combined effects of crystalline anisotropy and polycrystalline heterogeneity of Zr alloy microstructure.

- ▶ *Stress-Diffusion Analysis.* This involves the treatment of the long-range transport of H atoms to the flaw tip in the dilute solution limit within the framework of linear irreversible thermodynamics. These computations must account for the atomic scale anisotropy of the point defect environment because the H diffusion occurs via an interstitial mechanism in which H preferentially occupy tetrahedral sites in the HCP α -Zr crystal; this atomic scale anisotropy corresponds to a trigonal symmetry.
- ▶ *Diffusion-Precipitation Analysis.* This involves the explicit treatment of micro-hydride needle formation at heterogeneous nucleation sites and their thermodynamically favourable assembly into macro-hydride colonies whilst implicitly accounting for the steps that are necessary for the phase transformation: (i) the mid-range clustering H to heterogeneous nucleation sites and (ii) subsequent the short-range martensitic motion of Zr atoms and reordering of H atoms. The first step requires a H mass balance self-consistency, that is, there must be a sufficient amount of H atoms to form a micro-hydride needle of a given shape and size with a specific H stoichiometry. The second step requires the interfacial energetics that lead to the known orientation relationships and an update to the local stress state due to the presence of a newly formed micro-hydride needle. The autocatalytic (sympathetic) nucleation must also be treated by considering prospect of adjacent or secondary nucleation events in the neighbourhood of successful nucleation events.

Unifying these three separate analyses into one framework is the central premise of this investigation. The degree of accuracy to which the essential physics is simulated must, however, be weighed against the resulting computational expenditure. This strategy is motivated by the need for statistical modelling, and so its overall efficiency is of equal value.

Efficiency. An important point has to be made here about the notion of efficiency in computational modelling. In theory, the DFT, PF and FE methodologies can individually capture all of the essential multiscale physics that is listed above; but this is impossible in practice. There is one common reason for this non-feasibility: all three methodologies involve, at their most simplest level, a representation of the essential physics through either spatially varying fields or coefficients in PDEs that then have to be solved numerically. While it is understandably true that PDEs can offer a mathematically elegant representation of the physics, re-expressing experimental observations

exclusively in terms of PDEs is somewhat restrictive. The best example here is the need for interfacial energies in PF models to reproduce experimental observations of the micro-hydride orientation relationships. Computers provide an assortment of other tools that may be more efficient for directly incorporating experimental observations. In the present work, one such tool is introduced to this field of research; this is computer vision and its applications to the problem at hand will become clear in due course. For now, the efficiency is address in three ways:

- ▶ *Analytical Approximations.* The stress analysis and stress-diffusion analysis should focus primarily on analytical or semi-analytical techniques. If the analysis requires numerically solving PDEs, a set of one-off PDE solutions should be used to inform the model and an alternative computing tool should be used to implement these findings.
- ▶ *Geometrical Simplifications.* The notch geometries and hydride morphologies should be represented by simple shapes whereas the H profile contours should be represented by smooth curves.
- ▶ *Algorithmic Optimisations.* Given that time scales for H diffusion are much longer than the time scales for hydride precipitation, there is no need to perform stress-diffusion analysis and diffusion-precipitation analysis at every simultaneous step.

In its concurrent treatment of accuracy and efficiency, the present work intersects computational science and computer science.

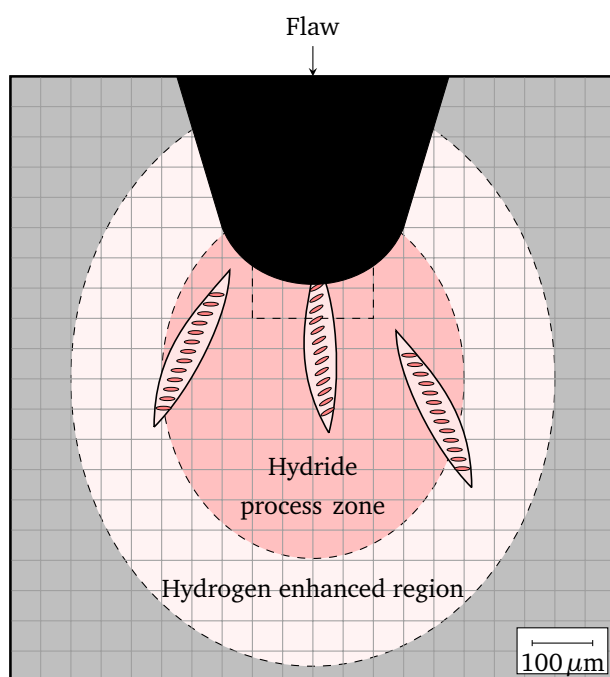


FIG. 3.7

Metallographic features in a simulated micrograph

A high level representation of the simulation cell of the bespoke model that is proposed in this investigation. The geometries of the notch and the grains are represented by simple shapes. The contours of the H enhanced region and hydride process zone are represented by smooth curves. Macro-hydride colonies and their composite substructure of micro-hydride needles can also be seen, but the exact representation of these features is detailed in later discussions. This simulated micrograph conveys all of the essential physics of the Zr-H at the atomic, electronic, microstructural and continuum scales.

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Part II

Mechanistic Modelling

4

Stress Analysis

Chapter Overview

The first module of this hybrid multiscale model of DHC is a fast and efficient framework for performing stress analysis. The repetition of numerical computations of the system stress state is a major bottleneck in the conventional microstructural models of hydride precipitation as well as the continuum scale models of the flaw-tip H enhancement. In addition, these models assume isotropic elasticity, which does not accurately reflect the hexagonal crystallography of α -Zr and the trigonal environmental symmetry of Zr-H point defect system. Therefore, the present work seeks to derive and use analytical closed-form expressions for the elastic fields around different classes of defects in transversely isotropic continua. This chapter serves as a handbook for the derivations of these analytical formulae. The derivations are particularly important here for establishing the necessary toolkit for extending these formulae beyond what is presented in this body of work.

The problem of determining the exact micromechanical behaviour of hydrogenated Zr is intractable even within a small region, let alone the entire component. This is because the complex evolution of the hydrided microstructure is governed by the simultaneity of the various interactions between all of the different classes of crystalline defects that are present in the system. For the purpose of modelling the micromechanics here, it is, therefore, necessary to reduce this complexity by decomposing the early stages of DHC into a sequence of steps and then identifying the relevant defects whose interactions mediate each step.

This step-by-step breakdown of the early stages of DHC begins with the long-range transport of H atoms to the tensile state ahead of the loaded notch, which is mediated by the interactions between the H point defects and volumetric flaws in the component. This is followed by the mid-ranged clustering of H atoms to nucleation sites, which is mediated by the interactions between the H point defects and more localised microstructural defects such as grain boundaries, twin boundaries, SPP inclusions, dislocation networks, and vacancy loops. The subsequent nucleation and growth of the microhydride needles is defined by the migration of the two-phase interfaces be-

tween the α -Zr-H solid solution and the hydride phase through the short-ranged martensitic motion of Zr atoms and the reordering of H atoms, which is mediated by the interaction between the precipitates and the surrounding matrix. The subsequent formation of the networks of macro-hydride colonies is determined by the optimised configurations of the micro-hydride needles, which is mediated by the complex many-body interactions amongst the precipitates in the microstructure ahead of the flaw tip under a remote loading.

Considering the free energy, one substantial contribution to the overall mechanics that emerge as a result of these complicated interactions is due to the long-range elastostatic fields that are present around each defect [Chen (2002), Khachaturyan (1983), Guo et al. (2008), Bair, Zaeem, and Tonks (2015), Ma et al. (2002), and Ma et al. (2006)]. That is, the evolution of the hydrided microstructures can be approximated by a quasi-static minimisation of the elastic interaction energy between the relevant defects at each step whilst assuming that the chemical free energy is also minimised. In the linear elastic regime, the sole requirement for computing this elastic interaction energy is the knowledge of the elastic fields of each defect in isolation; the system stress state can be determined by the linear superposition of the isolated elastic fields at any iteration of the quasi-static evolution. Thus it is clear how the elastic interaction energy can be computed in either a sequential or concurrent treatment of the steps listed earlier.

It is then important to establish the topological accuracy to which each defect is described because this is the limiting factor in the efficient computation of elastic interaction energy. In the case of PF models, the arbitrarily complex morphologies of the simulated hydrides creates the problem of complicated boundary conditions. In the case of FE models, a similar problem exists due to the non-trivial flaw geometries as well as the surface effects due to the finiteness of the simulated specimen. In both cases, the numerical corrections to the system stress state add to the simulation runtime, and this is undesirable because of the need to routinely evaluate the elastic interaction energies. In this work, the Zr alloy component is represented as a (semi-)infinite homogeneous continuum under plane strain conditions, which is mathematically simpler but still of practical relevance to modelling in the context of DHC failure [Puls (2012) and Martin (2013)]. In addition, all crystalline defects are modelled using the several classes of topological continuum defects for which closed-form elastic fields are available.

In the following, four categories of defects are considered in the planar framework, and they are categorised according to their dimensionality. The first category pertains to zero-dimensional point defects for modelling H interstitials occupying tetrahedral sites in α -Zr. The second category per-

tains to one-dimensional line defects for modelling edges dislocations corresponding to basal and prismatic slip in Zr crystals. The third category pertains to two-dimensional surface defects for modelling grain boundaries as potent nucleation sites in polycrystalline Zr alloys as well as free surfaces. The fourth category pertains to three-dimensional volume defects for modelling precipitates as well as cracks and notches. At relevant stages, the expressions for isotropic continua and transversely isotropic continua are compared. This comparison highlights the importance of elastic anisotropy in the treatment of Zr and the Zr-H system, a detail that is often omitted from PF and FE models.

In order to demonstrate the importance of anisotropy—and hence the deviations from isotropy—this chapter begins by first considering fundamental distortions that can be evaluated using the elastostatic Green tensor function of the continuum. This is a useful starting point because the elastic fields of any defect are fundamentally connected to the form of the Green tensor function of that medium. The availability of the closed-form expressions for the Green tensor function has implications on the availability of analytical or semi-analytical expressions for the elastic fields of certain defects [[Mura \(1987\)](#)].

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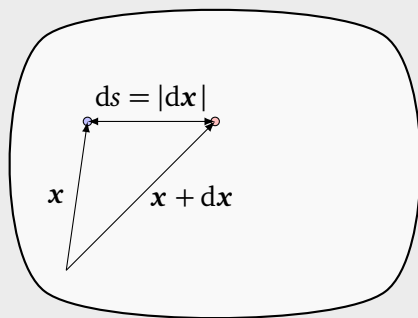
4.1 Fundamental Distortions

A brief exposition to some standard concepts in elastic field theory is given here in order to introduce the mathematical preliminaries for treating continuum anisotropy and heterogeneity, and clarify how these absent symmetries are related to crystalline anisotropy and polycrystalline heterogeneity. In addition, this provides an opportunity to relate the coarse-grained continuum concepts to the detailed atomic picture. This groundwork culminates in the representation of the Zr alloy component as a transversely isotropic continuum through its elastostatic Green tensor function.

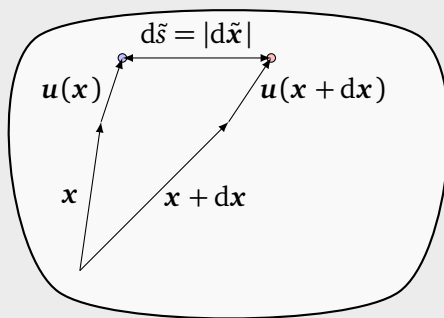
FIG. 4.1

Deformation of a continuum

Configuration of a continuum undergoing an elastic deformation as marked by the change in the position and, hence, the separation of two adjacent points. (a) Reference configuration. (b) Deformed configuration.



(a)



(b)

4.1.1 Elastic Field Theory

Consider an infinite continuum whose reference configuration is defined by a vector space of a set of coordinates, $\mathcal{X} \equiv \{\mathbf{x}\}$, that describe points on the body. Now, upon a deformation, as shown in FIG. 4.1, the reference configuration is mapped onto a deformed configuration $\tilde{\mathcal{X}} \equiv \{\tilde{\mathbf{x}}\}$ by a linear transformation:

$$\mathbf{u} : \mathcal{X} \mapsto \tilde{\mathcal{X}} \quad \text{with} \quad \tilde{\mathbf{x}} = \mathbf{x} + \mathbf{u}(\mathbf{x}) \quad (4.1)$$

where the vector mapping function $\mathbf{u}(\mathbf{x})$ is the displacement field that captures the pointwise translational transformation that interconnects points in the reference and deformed states. The application of elastic field theory to an actual material requires that the underlying atomic scale description be replaced with this coarse-grained continuum scale representation; but it is important to note that the points in the continuum do not generally correspond to the discrete atomic positions.

In the standard continuum mechanical models of the Zr alloy component, the material is assumed to be a homogeneous, isotropic, linear elastic continuum [Jernkvist and Massih (2014), Jernkvist (2014), and Puls (2012)]. The assumptions of linearity and elasticity are sensible—at least macroscopically—because of the high Σ_{UTS} relative to the loading conditions in the reactor environment so the entire component is not expected undergo large plastic deformations. (There is some localised plasticity around the flaw-tip and near hydride features.) The assumptions of homogeneity and isotropy are, however, not suitable for an explicit treatment of the defect microstructure. Homogeneity is reflected in the translational invariance of material tensors whereas isotropy is reflected in the rotational invariance of the material tensors. The removal of either assumption complicates considerably the mathematical treatment, and so a sensible compromise has to be met.

Strain and Compatibility. In the small deformation regime, a metric for quantifying the distortion can be derived by considering the transformation of an infinitesimal unit of length from the reference configuration to the deformed configuration, that is,

$$\begin{aligned} (d\tilde{s})^2 &= d\tilde{x}_i d\tilde{x}_i \\ &= (ds)^2 + \left[u_{j,k}(\mathbf{x}) + u_{k,j}(\mathbf{x}) + u_{i,j}(\mathbf{x}) u_{i,k}(\mathbf{x}) \right] dx_j dx_k, \end{aligned} \quad (4.2)$$

where the spatial derivatives of $\mathbf{u}(\mathbf{x})$ constitute the distortion tensor. Rearranging Eq. (4.2) for the ratio $d\tilde{s}/ds$ can be used to define the second-rank strain tensor field, $e_{[2]}(\mathbf{x})$, as

$$\frac{d\tilde{s}}{ds} = 1 + n_j e_{jk}(\mathbf{x}) n_k \quad \text{with} \quad n_i \equiv \frac{dx_i}{|d\mathbf{x}|} \quad (4.3)$$

where the components of $\mathbf{n}$ are the direction cosines. Evidently, Eq. (4.3) captures the fractional deformation in terms of (i) normal strains or elongation transformations and (ii) shear strains or angular transformations. In the linearised regime for small deformations, the spatial variations of the displacement are treated as small, allowing for the simplification of the definition of the small (or linear) strain tensor field to the symmetrisation of the distortion tensor, that is,

$$e_{ij}(\mathbf{x}) \stackrel{!}{=} u_{(i,j)}(\mathbf{x}) = \frac{1}{2} \left[u_{i,j}(\mathbf{x}) + u_{j,i}(\mathbf{x}) \right]. \quad (4.4)$$

There are two important properties of this tensor. Firstly, $e_{[2]}(\mathbf{x})$ is indeed a tensorial object in the sense that it obeys the linear coordinate transformation law as prescribed by Jacobian transformation matrices; for a coordinate transformation

$$\mathfrak{T} : \mathbf{x} \mapsto \mathbf{x}'(\mathbf{x}) \quad \text{with} \quad \mathfrak{T}_{i'i} = \frac{\partial x'_{i'}}{\partial x_i}, \quad (4.5)$$

the usual linear coordinate transformation law for second-rank tensors applies as

$$e'_{i'j'}(\mathbf{x}') = \mathfrak{T}_{i'i} \mathfrak{T}_{j'j} e_{ij}(\mathbf{x}) \quad (4.6)$$

Secondly, $e_{[2]}(\mathbf{x})$ is defined in the reference state of the continuum, and hence its domain is restricted to the undeformed configuration $\mathcal{X}$ for finite continua; this is implicitly assumed here for the small strain regime.

Naively, it appears that the index symmetry of $e_{[2]}(\mathbf{x})$ bestows it six independent components; however, there are compatibility relations which contain the interdependency between these components arising from the fact that they are related directly to the three-component displacement vector field. These compatibility relationships can be written compactly as

$$\epsilon_{pmk} \epsilon_{qnj} e_{jk,nm} = 0. \quad (4.7)$$

In practice, the compatibility criteria in Eq. (4.7) is often re-expressed in terms of the continuity of the displacement vector field and its spatial derivative. The compatibility criteria features heavily in the treatment of heterogeneous media in which the continuity conditions have to be satisfied across any internal boundaries between two homogeneous regions [Dunne and Petrinic (2005)]. This problem is discussed further in due course.

The concept of strain may be extended to the atomic scale but there is also an analogous notion of compatibility. Suppose that the reference configuration is defined by a triad of non-coplanar lattice vectors, $\{A_a | a = 1, 2, 3\}$, at some local scale. Compatibility is satisfied if there exists a local transformation between these reference lattice vectors and the corresponding lattice vectors, $\{A'_a | a = 1, 2, 3\}$, defined in the deformed configuration. Then the local distortion tensor can be expressed as

$$u_{i,j}[\text{atomic}] = (A'_{ai} - A_{ai})A_{aj} \quad (4.8)$$

which is defined exclusively at atomic sites. Incompatibility arises for the cases where the local transformation is not topologically possible because of, say, missing atoms or extra atoms [Stoneham (1975)].

Stress and Equilibria. In the reference configuration, the arrangement of points in the continuum correspond to some mechanical equilibrium. As a deformation occurs, internal forces arise that attempt to restore the continuum to its original equilibrium state; these body forces are attributed as sources of internal stresses. A complete specification of the stress state of a continuum requires knowledge of the three independent components of areal intensity of force vector on the three planes whose outward normals are mutually perpendicular; mathematically, this information is conveyed by the symmetric second-rank stress tensor field $\sigma_{[2]}(\mathbf{x})$ whose component $\sigma_{ij}(\mathbf{x})$ provides the force per unit area in the x_i -direction at the point $\mathbf{x}$ acting on a plane whose outward normal is in the x_j -direction.

For a continuum in mechanical equilibrium, every infinitesimal volume element exhibits Newtonian stationarity. Consider a volume $V(\mathbf{x})$ enclosed by a surface $S(\mathbf{x})$ with an outward normal $\mathbf{n}(\mathbf{x})$ which is subject to (i) a distribution of stress-related surface tractions $t_i(\mathbf{x}) = \sigma_{ij}(\mathbf{x})n_j(\mathbf{x})$ acting over the surface area and (ii) a distribution of body forces per unit volume $f_i(\mathbf{x})$ representing external force fields.

Now, resolving forces in, say, the x_i -direction gives the corresponding

component of the resultant force as

$$\begin{aligned}
 [F_{\text{res}}]_i &= \oint_S dS(\mathbf{x}) t_i(\mathbf{x}) + \iiint_V dV(\mathbf{x}) f_i(\mathbf{x}) \\
 &= \oint_S dS(\mathbf{x}) \sigma_{ij}(\mathbf{x}) n_j(\mathbf{x}) + \iiint_V dV(\mathbf{x}) f_i(\mathbf{x}) \\
 &= \iiint_V dV(\mathbf{x}) [\sigma_{ij,j}(\mathbf{x}) + f_i(\mathbf{x})]. \tag{4.9}
 \end{aligned}$$

Mechanical equilibrium is defined by the absence of a (non-zero) resultant force: $[F_{\text{res}}]_i = 0$ and this statement must hold for any arbitrarily small volume; hence it must hold point-wise, thereby giving the equilibrium condition

$$\sigma_{ij,j}(\mathbf{x}) + f_i(\mathbf{x}) = 0 \quad \forall i. \tag{4.10}$$

This set of equations describes how the divergence of the stress tensor field is related to the distribution of the body forces. Furthermore, for mechanical equilibrium, there must be no net moment about any point. The resultant torque in the x_i -direction about the origin is given by

$$\begin{aligned}
 [M_{\text{res}}]_i &= \oint_S dS(\mathbf{x}) \epsilon_{ijk} x_j t_k(\mathbf{x}) + \iiint_V dV(\mathbf{x}) \epsilon_{ijk} x_j f_k(\mathbf{x}) \\
 &= \iiint_V dV(\mathbf{x}) \epsilon_{ijk} \sigma_{jk}(\mathbf{x}). \tag{4.11}
 \end{aligned}$$

Again, the requirement that $[M_{\text{res}}]_i = 0$ at the point-wise scale implies the symmetry of the stress tensor, which, therefore, has six independent components.

The concept of stress is far more useful at the atomic scale than the concept of strain. This is because it is always possible to compute the stress at discrete atomic sites even if there is no obvious reference configuration. At the atomic site N , position at $\mathbf{r}_N$, the atomic stress tensor can be obtained by considering the change in the energy to first order due to the application of a virtual strain to take the form

$$\sigma_{Nij}[\text{atomic}] = \frac{1}{2V_{(N)}} \left(\frac{dv(r)}{dr} \right) \bigg|_{r_{NM}} \cdot \sum_{M \neq N} \frac{[\mathbf{r}_M - \mathbf{r}_N]_i [\mathbf{r}_M - \mathbf{r}_N]_j}{r_{NM}}, \tag{4.12}$$

where $r_{NM} = |\mathbf{r}_N - \mathbf{r}_M|$ is the distance between atomic sites, $V_{(N)}$ is the volume associated with site N , and $v(r)$ is a pairwise interatomic potential [Stoneham (1975)].

Thermodynamics of Deformation. Suppose that the volume is subject to a small incremental displacement, $\Delta \mathbf{u}(\mathbf{x})$, which is virtual in the sense that it does not disrupt equilibrium. Then the (virtual) elastic work done on the volume due to the distribution of surface tractions and body forces is given by

$$\begin{aligned}\Delta W &= \oint_S dS(\mathbf{x}) t_i(\mathbf{x}) \Delta u_i(\mathbf{x}) + \iiint_V dV(\mathbf{x}) f_i(\mathbf{x}) \Delta u_i(\mathbf{x}) \\ &= \frac{1}{2} \iiint_V dV(\mathbf{x}) \sigma_{ij}(\mathbf{x}) \Delta e_{ij}(\mathbf{x}),\end{aligned}\quad (4.13)$$

where it must be noted that only the (ij) -symmetric part of the infinitesimal distortion tensor, $\Delta u_{i,j}$, corresponding to the infinitesimal strain Δe_{ij} , contributes to the work done, whereas the $[ij]$ -antisymmetric part of $\Delta u_{i,j}$ corresponds to rotations. Hence, the stress tensor may be expressed as the functional derivative of the elastic work density as

$$\sigma_{ij}(\mathbf{x}) = \frac{\delta W}{\delta e_{ij}(\mathbf{x})}, \quad (4.14)$$

which is general beyond linear elasticity [Sadd (2005) and Balluffi (2012)]. If this deformation is small and irreversible as well as slow enough for thermodynamic equilibrium to be maintained, then it is possible to show that

$$\sigma_{ij}(\mathbf{x}) = \left(\frac{\delta F}{\delta e_{ij}(\mathbf{x})} \right)_T, \quad (4.15)$$

where F is the Helmholtz free energy in V , and the functional derivative is taken at a constant temperature. Therefore, the thermodynamic evolution of the defect microstructure involves, in part, the minimisation of the elastic strain energy as expected [Gurtin, Fried, and Anand (2010) and Balluffi, Allen, and Carter (2005)].

Elastic Stiffness and Compliance. The equilibrium condition in Eq. (4.10) provides a set of three equations for the six unknowns of the stress tensor. In order to uniquely specify the problem, the relationship between $\sigma_{[2]}(\mathbf{x})$ and $e_{[2]}(\mathbf{x})$ must be considered. The stress-strain relationship is commonly idealised as linear, which is a constitutive material property that is assumed in addition to the linearity of the (small) strain tensor. This constitutive material property is encapsulated within two fourth-rank material tensors that each contain $3^4 = 81$ proportionality constants that relate each stress (or strain) component to every strain (or stress) component. These two material tensors are the elastic stiffness tensor, $C_{[4]}$, and the elastic compliance tensor, $S_{[4]}$, respectively; they satisfy the inverse identity relationship

$$C_{ijkl} S_{klmn} = \frac{1}{2} (\delta_{im} \delta_{jn} + \delta_{in} \delta_{jm}) \quad (4.16)$$

so that complete knowledge of $C_{[4]}$ can be used to determine $S_{[4]}$, and vice versa. The absence of any rotational and translational symmetries of $C_{[4]}$ reflect the anisotropy and heterogeneity of the continuum. If the continuum is isotropic, then $C_{[4]}$ exhibits rotational invariance. If the continuum is homogeneous, then $C_{[4]}$ exhibits translational invariance.

For an anisotropic heterogeneous continuum, the linear dual field response can be expressed through the pointwise Hooke's law as

$$\sigma_{ij}(\mathbf{x}) = C_{ijkl}(\mathbf{x}) e_{kl}(\mathbf{x}) \quad \text{and} \quad e_{ij}(\mathbf{x}) = S_{ijkl}(\mathbf{x}) \sigma_{kl}(\mathbf{x}), \quad (4.17)$$

in which it is important to highlight the spatial dependence of the material tensors because this is not the norm in elementary stress analysis. This pointwise stress-strain relationship holds in the small distortion regime at the atomic scale if it is possible to approximate the aforementioned pairwise potential, $v(r)$, as a quadratic in the interatomic distances [Stoneham (1975)].

The number of independent constants in $C_{[4]}$ is smaller than 81 due to the minor and major symmetries. The minor symmetries are a consequence of the symmetries of the strain and stress tensors which imply that

$$C_{ijkl} = C_{(ij)(kl)} \quad \text{with} \quad C_{ijkl} = C_{jikl} \quad \text{and} \quad C_{ijkl} = C_{ijlk} \quad (4.18)$$

everywhere. The major symmetry of C_{ijkl} arises due to the definition of the stress in terms of the elastic strain work density in Eq. (4.14) used in conjunction with Hooke's Law in Eq. (4.17), implying that

$$C_{ijkl} = C_{(ij)(kl)} \quad \text{with} \quad C_{ijkl} = \frac{\partial^2 W}{\partial e_{ij} \partial e_{kl}} \quad (4.19)$$

due to the irrelevance of the order of differentiation. The combination of minor and major symmetries reduces the number of independent elastic stiffness constants to 21 at most for an anisotropic homogeneous continuum or within some anisotropic homogeneous region inside a general anisotropic heterogeneous continuum. However, the pointwise relationship in Eq. (4.17) is still far too complicated to manipulate mathematically in most cases; this is, in part, because of the compatibility criterion [Dunne and Petrinic (2005)]. The aim is then to restrict attention to anisotropic heterogeneous continua that are both physically relevant but also mathematically simpler in that the spatial dependency in $C_{[4]}$ can be removed.

Anisotropy and Heterogeneity. Consider a division of the anisotropic heterogeneous continuum, $\mathcal{X}$, into a set of distinct homogeneous regions, $\{\mathcal{X}_\alpha | \alpha \in \mathbb{N}\}$, so that

$$\mathcal{X} = \bigcup_{\alpha} \mathcal{X}_{\alpha} \quad (4.20)$$

where each division, $\mathcal{X}_\alpha$, is assigned a stiffness tensor, $C_{[4]}[\mathcal{X}_\alpha]$, which is generally anisotropic. In the most coarse-grained continuum description, $\mathcal{X}$ can be treated as an aggregate of $\{\mathcal{X}_\alpha\}$, and so the stiffness of the continuum, $C_{[4]}[\mathcal{X}]$, can be loosely thought of as some average of $\{C_{[4]}[\mathcal{X}_\alpha]\}$ if the effects of the interfaces between two homogeneous sub-divisions are ignored. (This aggregate average is not strictly true but it is simply assumed for the purpose of the argument.) If $\mathcal{X}$ is composed entirely of the same material, that is, each $\mathcal{X}_\alpha$ is composed of the same material, then each $C_{[4]}[\mathcal{X}_\alpha]$ differs only due to the orientation of the corresponding $\mathcal{X}_\alpha$ relative to some global coordinate system.

There are several special cases where the spatial dependency in $C_{[4]}$ can then be removed. In the case that each $\mathcal{X}_\alpha$ is isotropic, then the orientation of $\mathcal{X}_\alpha$ does not matter to fourth-order tensors, and so $C_{[4]}[\mathcal{X}_\alpha]$ and therefore $C_{[4]}[\mathcal{X}]$ are rotationally invariant; here, $\mathcal{X}$ is called an isotropic heterogeneous medium. In the case that the orientations of each $\mathcal{X}_\alpha$ are identical, then the sub-divisions are arbitrary from the standpoint of Eq. (4.20) and so the divisions can be ignored altogether; here, $\mathcal{X}$ is called an anisotropic homogeneous medium. There is a further degenerate case in which each $\mathcal{X}_\alpha$ are isotropic and identically orientated; here, $\mathcal{X}$ is called an isotropic homogeneous medium. All of these special cases are referred to as elastically homogeneous media.

It is important to clarify that the rotational invariance of $C_{[4]}[\mathcal{X}_\alpha]$ only corresponds to the elastic isotropy of $\mathcal{X}_\alpha$ with respect to the limited symmetry transformations that are available for this particular fourth-order tensor. Other physical properties, which are described using higher-order tensors, may not exhibit rotational symmetries and $\mathcal{X}_\alpha$ is then not wholly isotropic. ^{Note 3}

Note 3

Continuum and crystalline symmetry

The significance of this subtle difference between elastic isotropy and crystalline rotational symmetries will become clear in the treatment of the anisotropic micro-hydride needle orientation relationships on the elastically isotropic basal plane of a HCP α -Zr crystal.

Crystal Symmetries. The number of elastic stiffness constants can be reduced further from 21 by considering the point group symmetries of individual crystallites. This is a consequence of Neumann's principle which states that the symmetry elements of any material tensor must include the symmetry elements of the point group of the crystal [Nye (1957)]. This is most easily seen by first vectorising Eq. (4.17) into Voigt notation as

$$\sigma_I(\mathbf{x}) = C_{\alpha IJ}(\mathbf{x}) e_J(\mathbf{x}) \quad \text{with } \mathbf{x} \in \mathcal{X}_\alpha \quad (4.21)$$

where $\mathcal{X}_\alpha$ now labels a crystallite within the continuum representation of a polycrystalline material, $\mathcal{X}$, and $C_{\alpha IJ}$ is the elastic stiffness matrix for $\mathcal{X}_\alpha$ as usual. The forms of the elastic stiffness matrix C_{IJ} for three relevant crystal classes are given in TAB. 4.1.

Crystal Class	Elastic Stiffness Matrix	Examples
Cubic	$\begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{bmatrix}$	β -Zr δ -ZrH _{1.66} - hydride
Isotropic	$\begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{66} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{66} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix}$	—
Hexagonal	$\begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix}$	α -Zr ζ -ZrH _{0.50} - phase hydride
Tetragonal	$\begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & C_{16} \\ C_{12} & C_{11} & C_{13} & 0 & 0 & C_{26} \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ C_{26} & 0 & 0 & 0 & C_{44} & 0 \\ C_{16} & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix}$	γ -ZrH _{1.00} - phase hydride

TAB. 4.1

Elastic stiffness matrix symmetries

Independent elastic stiffness constants for cubic, isotropic, hexagonal and tetragonal crystals. For cubic, isotropic and hexagonal crystals, $C_{66} \equiv \frac{1}{2}(C_{11} - C_{12})$ is a shear modulus measuring the resistance to shear on the $\{110\}$ -plane; the ratio of C_{44} to C_{66} defines the anisotropy ratio, which is unity for isotropic crystals. For tetragonal crystals, $C_{16} = -2C_{26}$ and C_{66} is an independent constant. From the standpoint of linear elastic field theory, hexagonal crystals are transversely isotropic; the six-fold rotational symmetry of basal plane is not conveyed in the rotational symmetries of the elastic stiffness tensor, which is invariant to rotational transformations around the basal pole.

Polycrystalline Zirconium. A single HCP α -Zr crystallite is transversely isotropic within the framework of linear elasticity. In the two-dimensional projection of a polycrystalline Zr specimen, there are two special cases for which $C_{[4]}$ is translationally invariant as listed above; these both require modelling polycrystalline Zr as a transversely isotropic continuum.

4.1.2 Transversely Isotropic Continua

The Zr alloy component is modelled as an infinite elastically homogeneous transversely isotropic continuum, $\mathcal{X} \equiv \{\mathbf{x}\}$, and it is assumed to be a linear Hookean system with the (compactified) anisotropic elastic stiffness tensor

$$\begin{aligned} C_{ijkl} = & C_{12}\delta_{ij}\delta_{kl} + \frac{1}{2}(C_{11} - C_{12})(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) \\ & + (C_{11} + C_{33} + 2C_{12} - 4C_{44})h_{3i}h_{3j}h_{3k}h_{3l} \\ & + (C_{13} - C_{12})(h_{3i}h_{3j}\delta_{kl} + h_{3k}h_{3l}\delta_{ij}) \\ & + [C_{44} - \frac{1}{2}(C_{11} - C_{12})](h_{3i}h_{3k}\delta_{jl} + h_{3j}h_{3l}\delta_{ik}) \\ & + [C_{44} - \frac{1}{2}(C_{11} - C_{12})](h_{3i}h_{3l}\delta_{jk} + h_{3j}h_{3k}\delta_{il}), \end{aligned} \quad (4.22)$$

where the unit vectors $\{\mathbf{h}_n \mid n = 1, 2, 3\}$ establish a Cartesian coordinate system for a hexagonal crystal in which these vectors are aligned along the following crystallographic axes:

$$\mathbf{h}_1 \parallel [1\bar{1}20], \quad \mathbf{h}_2 \parallel [1\bar{1}00] \quad \text{and} \quad \mathbf{h}_3 \parallel [0001], \quad (4.23)$$

that is, $\mathbf{h}_1$ and $\mathbf{h}_2$ are chosen to lie on the basal plane and $\mathbf{h}_3$ lies along the hexad axis or the basal pole. This coordinate system is depicted in FIG. 4.2 and it is a natural choice for the problem at hand. The $(\mathbf{h}_1, \mathbf{h}_2)$ -plane corresponds to a basal plane with a six-fold rotational symmetry whereas $(\mathbf{h}_1, \mathbf{h}_3)$ -plane corresponds to a prism plane with a two-fold rotational symmetry. Given the crystallographic plane of interest, it is necessary to rotate C_{ijkl} into the coordinate system of the simulation cell $\{\mathbf{x}'_i\}$ by applying the tensor transformation law for fourth-rank tensors

$$C'_{i'j'k'l'} = \mathfrak{T}_{i'i}\mathfrak{T}_{j'j}\mathfrak{T}_{k'k}\mathfrak{T}_{l'l}C_{ijkl} \quad \text{with} \quad \mathfrak{T} = \prod_{n=1}^3 \Omega_n(\theta_n) \quad (4.24)$$

where the transformation matrix $\mathfrak{T}$ can be specified by the usual $\mathcal{SO}(3)$ matrices

$$\Omega_1(\theta_1) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos \theta_1 & -\sin \theta_1 \\ 0 & \sin \theta_1 & \cos \theta_1 \end{bmatrix} \quad (4.25a)$$

$$\Omega_2(\theta_2) = \begin{bmatrix} \cos \theta_2 & 0 & \sin \theta_2 \\ 0 & 1 & 0 \\ -\sin \theta_2 & 0 & \cos \theta_2 \end{bmatrix} \quad (4.25b)$$

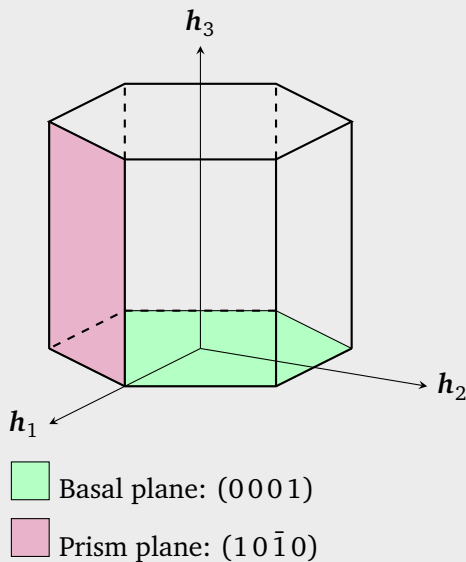
$$\Omega_3(\theta_3) = \begin{bmatrix} \cos \theta_3 & -\sin \theta_3 & 0 \\ \sin \theta_3 & \cos \theta_3 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \quad (4.25c)$$

for rotations about the $\mathbf{h}_1$, $\mathbf{h}_2$ and $\mathbf{h}_3$ axes respectively.

FIG. 4.2

Crystallographic planes of the hexagonal unit cell

The natural choice of a Cartesian coordinate system for the hexagonal unit cell. In the planar setting, the simulation cell projects the basal plane by choosing the basal pole to lie along the normal to the simulation plane. Alternatively, the simulation cell projects the prism plane by choice of the basal pole to lie along one of the directions on the simulation plane.



Basal Plane. Observe that $C_{[4]}$ is invariant to any $\Omega_3(\theta_3)$ transformation. That is, the six-fold rotational symmetry about the hexad axis equates to the elastic isotropy of the fourth-rank material tensor [Nye (1957) and Steeds (1973)]. This is an important symmetry that considerably simplifies the mathematical treatment of the basal plane in the planar setting. If the (x_1, x_2) -plane of the simulation cell is chosen to project (0001) , it is more convenient to use isotropic elastic stiffness tensor

$$C_{ijkl}^* = \mu \left[\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} + \left(\frac{2\nu}{1-2\nu} \right) \delta_{ij}\delta_{kl} \right] \quad (4.26)$$

where μ is the Shear modulus, ν is the Poisson ratio, and the superscript $*$ is adopted to distinguish the isotropic expressions. If the simulation cell projects the basal plane, it corresponds to the isotropic heterogeneous system.

Prism Plane. If the (x_1, x_2) -plane of the simulation cell is chosen to project (0001) , then the (x_1, x_3) -plane projects $(10\bar{1}0)$, and the coordinate transformation $\Omega_2(\pi/2)$ can be applied. If the simulation cell projects the prism plane, it corresponds to the anisotropic homogeneous system.

4.1.3 Elastostatic Green Tensors

The fundamental problem of classical elasticity may be formalised as follows: given a distribution of body forces in the continuum, the aim is to determine the response of the medium in terms of the displacement field for the system. The most general mathematical strategy is to employ the elastostatic Green tensor $G_{ij}(\mathbf{x}, \mathbf{y})$ which corresponds to the displacement along the x_i -direction at $\mathbf{x}$ in response to a point force along the x_j -direction at $\mathbf{y}$ [Mura (1987)]. There are a series of several appropriate simplifications about the nature of this Green function: (i) for an infinite homogeneous medium, it depends only the relative displacements between the points and (ii) Maxwell's reciprocity condition holds for the symmetry of the tensor field, that is,

$$G_{ij}(\mathbf{x}, \mathbf{y}) \stackrel{!}{=} G_{ij}(\mathbf{x} - \mathbf{y}) \quad \text{and} \quad G_{ij}(\mathbf{x} - \mathbf{y}) \stackrel{!}{=} G_{ji}(\mathbf{x} - \mathbf{y}) \quad (4.27)$$

respectively. The displacement field at $\mathbf{x}$ in response to a point force $\mathbf{F}$ acting at $\mathbf{y}$ in the infinite homogeneous continuum is then given by

$$u_i(\mathbf{x}; \mathbf{y}) = G_{ij}(\mathbf{x} - \mathbf{y}) F_j(\mathbf{y}). \quad (4.28)$$

Therefore, employing Hooke's Law in Eq. (4.17) and invoking the definition of the strain tensor field in Eq. (4.4), the stress tensor field can be expressed as

$$\sigma_{ij}(\mathbf{x}; \mathbf{y}) = C_{ijkl} G_{km,l}(\mathbf{x} - \mathbf{y}) F_m(\mathbf{y}). \quad (4.29)$$

Now, suppose that the system is in mechanical equilibrium; then, within a volume V enclosing the point $\mathbf{y}$, the point force $\mathbf{F}$ is cancelled by the distribution of stress-related surface tractions along the surface S enclosing V , that is,

$$\begin{aligned} 0 &\stackrel{!}{=} F_i(\mathbf{y}) + \oint_S dS(\mathbf{x}) \sigma_{ij}(\mathbf{x}; \mathbf{y}) n_j(\mathbf{x}) \\ &= \oint_V dV(\mathbf{x}) [\delta_{im} \delta^{(3)}(\mathbf{x} - \mathbf{y}) + C_{ijkl} G_{km,lj}(\mathbf{x} - \mathbf{y})] F_m(\mathbf{y}). \end{aligned} \quad (4.30)$$

Now this equilibrium statement (!) must hold for any arbitrary point force distribution, which leads to the defining partial differential equation for the elastic Green tensor:

$$C_{ijkl} G_{km,lj}(\mathbf{x} - \mathbf{y}) + \delta_{im} \delta^{(3)}(\mathbf{x} - \mathbf{y}) = 0. \quad (4.31)$$

Setting $\mathbf{y}$ to be the origin for convenience and taking the (forward) Fourier transform of Eq. (4.31) into the reciprocal $\mathbf{k}$ -space produces the matrix-inversion problem for the Fourier transform of the elastostatic Green's tensor as given by the statement of identity:

$$K_{ij}(\mathbf{k}) \mathfrak{F}[G_{jk}(\mathbf{x})](\mathbf{k}) = \delta_{ik} \quad \text{with} \quad K_{ij}(\mathbf{k}) \equiv C_{ijkl} k_k k_l. \quad (4.32)$$

Therefore, the elastostatic Green tensor for any isotropic continuum is given explicitly by the inverse Fourier transform:

$$G_{ij}(\mathbf{x}) = \mathfrak{F}^{-1}[(K^{-1})_{ij}(\mathbf{k})](\mathbf{x}) \quad \text{with} \quad (K^{-1})_{ij}(\mathbf{k}) = \frac{(\text{adj}[K])_{ij}(\mathbf{k})}{(\det[K])(\mathbf{k})}. \quad (4.33)$$

The elastostatic Green function $G_{ij}(\mathbf{x})$ is the fundamental tensor of an elastic continuum. The components of $G_{ij}(\mathbf{x})$ are parametrised solely by the elastic stiffness or compliance constants of material. Therefore it is entirely possible to parametrise $G_{ij}(\mathbf{x})$ using first-principles electronic structure calculations. Through this knowledge of $G_{ij}(\mathbf{x})$, it would then be relatively straightforward to determine the elastic fields around any topological defect at the continuum scale [Mura (1987)]. This would be one multiscale method for performing stress analysis of crystalline defects as a function of crystalline anisotropy and polycrystalline heterogeneity.

As intuitively anticipated, there appears to be no general analytical expression for the solution of Eq. (4.33) given the form of the elastic stiffness tensor for the continuum. In general $G_{ij}(\mathbf{x})$ must be evaluated numerically for either homogeneous or heterogeneous continua. But there are a few special cases for which analytical closed-form expressions for $G_{ij}(\mathbf{x})$ are known.

Fortunately, two of these cases happen to be for isotropic heterogeneous continua and transversely isotropic homogeneous continua [Willis (1964), Mura (1987), Steeds (1973), and Teutonico (1970)]. Knowing $G_{ij}(\mathbf{x})$ for Zr will prove to be immensely powerful from the standpoint of computational micromechanics because it will optimise the evaluation of the stress states around networks of defects.

Basal Plane. In the isotropic limit, the individual components of $G_{ij}^*(\mathbf{x})$ are explicitly given by the closed-form analytical expressions for the (x_1, x_2) -plane as the elastically isotropic basal plane:

$$G_{11}^*(x_1, x_2, 0) = \frac{1}{16\pi\mu(1-\nu)(x_1^2 + x_2^2)^{1/2}} \left[(3-4\nu) + \frac{x_1^2}{x_1^2 + x_2^2} \right] \quad (4.34a)$$

$$G_{12}^*(x_1, x_2, 0) = \frac{1}{16\pi\mu(1-\nu)(x_1^2 + x_2^2)^{1/2}} \left[\frac{x_1 x_2}{x_1^2 + x_2^2} \right] \quad (4.34b)$$

$$G_{22}^*(x_1, x_2, 0) = \frac{1}{16\pi\mu(1-\nu)(x_1^2 + x_2^2)^{1/2}} \left[(3-4\nu) + \frac{x_2^2}{x_1^2 + x_2^2} \right] \quad (4.34c)$$

Considering FIG. 4.3, it is clear that $G_{ij}^*(\mathbf{x})$ exhibits invariance under any rotational transformations about the basal pole. That is, $G_{ij}^*(\mathbf{x})$ does indeed reflect the elastic isotropy of the basal plane [Mura (1987)].

Prism Plane. The isotropic limit does not distinguish between the basal and prism planes. In order to treat defects on the prism plane, it is necessary to resort to the fully anisotropic elastostatic Green tensor function. The strategy for solving this problem is not presented here but it requires the inversion of a sextic (sixth-order polynomial) equation; the coefficients of this polynomial are functions of the elastic stiffness constants. The inversion is analytical for two cases of symmetry in which the sextic can be factorised into either a bicubic (the square of a cubic) or the product a quadratic and a quartic. In accordance with Galois theory, both cases yield analytical roots for the polynomial, which has implications on the availability of closed-form expressions for $G_{ij}(\mathbf{x})$ for different crystal classes and, more specifically, different planes of rotational symmetries. For hexagonal crystals or transversely isotropic continua, complete expressions for $G_{ij}(\mathbf{x})$ are well known [Willis (1964), Mura (1987), Steeds (1973), Ting (1996), and Teutonico (1970)].

In the transversely isotropic limit, the relevant individual components of $G_{ij}(\mathbf{x})$ are explicitly given by the closed-form analytical expressions for

the (x_1, x_3) -plane as the two-fold symmetric prism plane:

$$G_{11}(x_1, 0, x_3) = 2d_1\Delta_1 \left\{ \frac{1}{(x_1^2 + d_1^2 x_3^2)^{1/2} + d_1^2 x_3^2} - \frac{x_1^2}{(x_1^2 + d_1^2 x_3^2)^{1/2} [(x_1^2 + d_1^2 x_3^2)^{1/2} + d_1 x_3]^2} \right\} + 2d_2\Delta_2 \left\{ \frac{1}{(x_1^2 + d_2^2 x_3^2)^{1/2} + d_2^2 x_3^2} - \frac{x_1^2}{(x_1^2 + d_2^2 x_3^2)^{1/2} [(x_1^2 + d_2^2 x_3^2)^{1/2} + d_1 x_3]^2} \right\} + D_3 \left\{ \frac{1}{(x_1^2 + d_3^2 x_3^2)^{1/2} + d_3 x_3} \right\} \quad (4.35a)$$

$$G_{13}(x_1, 0, x_3) = \frac{(d_1 D_1 + d_2 D_2)x_1}{(x_1^2 + d_1^2 x_3^2)^{1/2} [(x_1^2 + d_1^2 x_3^2)^{1/2} + d_1 x_3]} \quad (4.35b)$$

$$G_{33}(x_1, 0, x_3) = -\frac{C_{11}\bar{D}_1 + C_{44}d_1^2 D_1}{(C_{13} + C_{44})(x_1^2 + d_1^2 x_3^2)^{1/2}} - \frac{C_{11}\bar{D}_2 + C_{44}d_2^2 D_2}{(C_{13} + C_{44})(x_1^2 + d_2^2 x_3^2)^{1/2}} \quad (4.35c)$$

where

$$\left. \begin{aligned} d_1 &= \left\{ \frac{[(C_{11}C_{33})^{1/2} - C_{13}]^{1/2} [(C_{11}C_{33})^{1/2} + C_{13} + 2C_{44}]^{1/2}}{(4C_{33}C_{44})^{1/2}} + \frac{[(C_{11}C_{33})^{1/2} + C_{13}]^{1/2} [(C_{11}C_{33})^{1/2} - C_{13} - 2C_{44}]^{1/2}}{(4C_{33}C_{44})^{1/2}} \right\} \\ d_2 &= \left\{ \frac{[(C_{11}C_{33})^{1/2} - C_{13}]^{1/2} [(C_{11}C_{33})^{1/2} + C_{13} + 2C_{44}]^{1/2}}{(4C_{33}C_{44})^{1/2}} - \frac{[(C_{11}C_{33})^{1/2} + C_{13}]^{1/2} [(C_{11}C_{33})^{1/2} - C_{13} - 2C_{44}]^{1/2}}{(4C_{33}C_{44})^{1/2}} \right\} \\ d_3 &= \left(\frac{C_{66}}{C_{44}} \right)^{1/2} \end{aligned} \right\} \quad (4.36a)$$

$$\left. \begin{aligned} D_1 &= -\bar{D}_1 = \frac{1}{d_1} \left\{ \frac{C_{13} - C_{44}}{4\pi C_{33}C_{44}(d_2^2 - d_1^2)} \right\} \\ D_2 &= -\bar{D}_2 = \frac{1}{d_2} \left\{ \frac{C_{13} - C_{44}}{4\pi C_{33}C_{44}(d_2^2 - d_1^2)} \right\} \\ D_3 &= -\bar{D}_3 = \frac{1}{4} \pi C_{44} d_3 \end{aligned} \right\} \quad (4.36b)$$

$$\left. \begin{aligned} \Delta_1 &= -\frac{C_{44} - C_{33}d_1^2}{8\pi C_{33}C_{44}(d_1^2 - d_2^2)d_1^2} \\ \Delta_2 &= -\frac{C_{44} - C_{33}d_2^2}{8\pi C_{33}C_{44}(d_1^2 - d_2^2)d_2^2} \end{aligned} \right\} \quad (4.36c)$$

Evidently, these expressions are far more complicated than their isotropic counterparts. The latter two components are visualised in [FIG. 4.4](#).

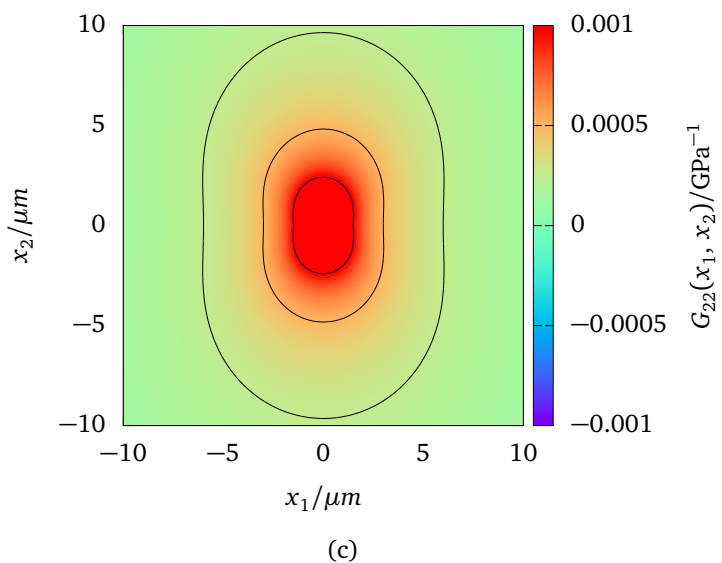
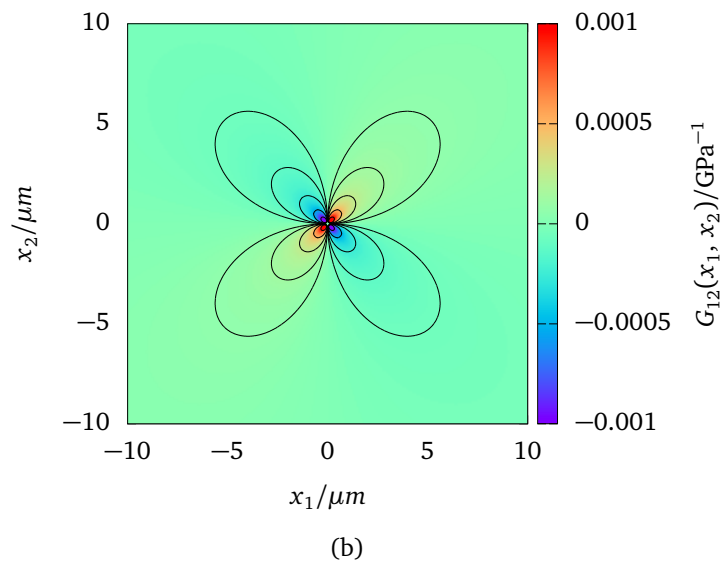
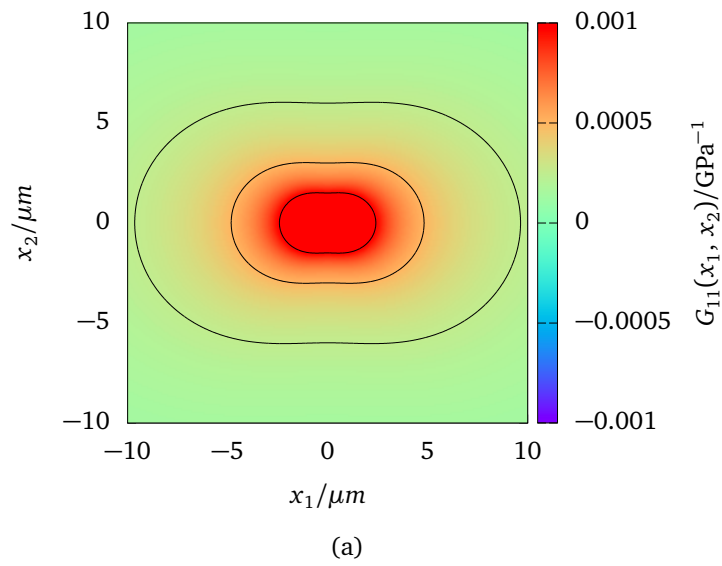


FIG. 4.3

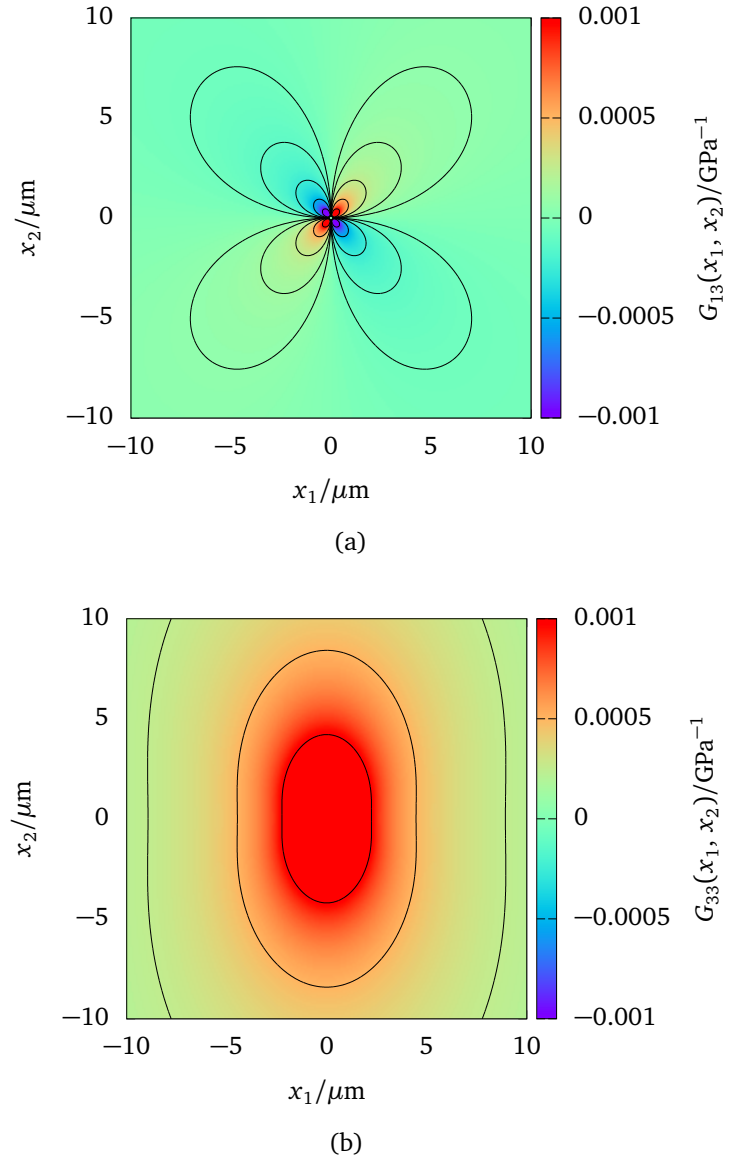
Green tensor for isotropic zirconium

The components of the elastostatic Green tensor for an infinite isotropic continuum with the elastic properties of Zr. The simulation cell projects the basal plane. Using these formulae, it is possible to compute the stress state around various topological defects in the isotropic heterogeneous system that represents the random in-plane basal texture; this isotropic heterogeneous system is used to represent the weld textures in which the grains are randomly misorientated and so aggregate elastic properties may be considered at the continuum scale.

FIG. 4.4

Green tensor for transversely isotropic zirconium

The components of the elastostatic Green tensor for an infinite transversely isotropic continuum with the elastic properties of Zr. The simulation cell projects the prism plane. There are noticeable qualitative and quantitative differences in the fundamental distortion in comparison to the isotropic case for the basal plane.



Displacement Responses. Substituting $C_{ijkl}\tilde{u}_{k,\tilde{l}j}(\mathbf{y}) + f_i(\mathbf{y}) = 0$ into Eq. (4.31) leads to the general expression for the displacement field

$$u_i(\mathbf{x}) = \iiint_V dV(\mathbf{y}) G_{ij}(\mathbf{x} - \mathbf{y}) f_j(\mathbf{y}) + \iint_S dS(\mathbf{y}) C_{j\tilde{k}l\tilde{m}} u_{l,\tilde{m}}(\mathbf{y}) G_{ij}(\mathbf{x} - \mathbf{y}) n_{\tilde{k}}(\mathbf{y}) - \iint_S dS(\mathbf{y}) C_{j\tilde{k}l\tilde{m}} u_k(\mathbf{y}) G_{il,\tilde{m}}(\mathbf{x} - \mathbf{y}) n_{\tilde{k}}(\mathbf{y}), \quad (4.37)$$

where the terms on the RHS respectively describe (i) the displacement due to a continuous distribution of body forces, (ii) the displacement due to a continuous distribution of surface tractions and (iii) the displacement due to a distribution of displacements on the surface; it is the third integral which is of tremendous importance for the theory of dislocations.

4.2 Zero-Dimensional Defects

The first category of defects concerns zero-dimensional point defects and, in particular, H interstitial atoms occupying tetrahedral sites in the HCP α -Zr matrix. The atomic structure of this point defect system exhibits a trigonal symmetry; the H interstitial forms three equivalent bonds with the Zr atoms on the basal plane but one non-equivalent bond with the Zr atom along the basal pole. There are other point defects in the defect microstructure of Zr such as vacancy clusters and self-interstitials created by irradiation damage, but the focus here is on the Zr-H point defect system.

Stress analysis of interstices is complicated because it involves unifying the quantum mechanical atomic scale and classical continuum scale descriptions of point defects. In the atomic picture, the interstitial atom occupies a non-lattice site within the crystal structure and it exerts forces on the neighbouring host atoms, distorting their positions. In the continuum picture, the interstitial atom is a (small) misfitting inclusion that generates a distortion field within the medium. Therefore, it is necessary to relate the discrete forces exerted by the interstitial atom to the continuous displacement field generated by the corresponding misfit [Teodosiu (1982) and Stoneham (1975)].

Adhering to the elastostatic Green tensor formalism, it is possible to bridge the atomic scale and continuum scale descriptions by expressing the displacement field due to a point defect, $\mathbf{u}_p(\mathbf{x})$, in terms of a discrete distribution of defect forces, $\{\mathbf{f}_p(\mathbf{R}_A) | A \in \mathbb{N}\}$, as

$$\begin{aligned} [u_p]_i(\mathbf{x}) &= \sum_A G_{ij}(\mathbf{x} - \mathbf{R}_A) [f_p]_j(\mathbf{R}_A) \\ &\simeq \sum_A \left[G_{ij}(\mathbf{x}) + R_{Ak} G_{ij,k}(\mathbf{x}) \right. \\ &\quad \left. + R_{Ak} R_{Al} G_{ij,kl}(\mathbf{x}) + \dots \right] [f_p]_j(\mathbf{R}_A), \end{aligned} \quad (4.38)$$

which is a discretisation of Eq. (4.37) and the Taylor expansion is analogous the multipolar expansion in electrostatics [Teodosiu (1982)]. Suppose that the index A labels a neighbouring atom at some position $\mathbf{R}_A$ in the host matrix, and the summation over A is over closed shells of neighbouring atoms. If the system is in mechanical equilibrium, then the leading term in this expansion is given by

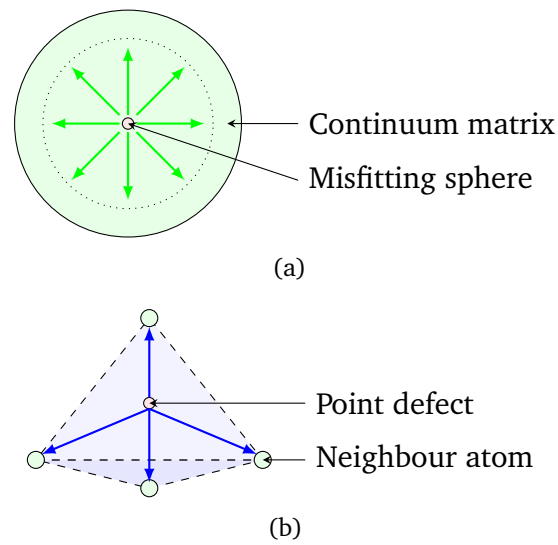
$$[u_p]_i(\mathbf{x}) \simeq G_{ij,k}(\mathbf{x}) \rho_{kj} \quad \text{with} \quad \rho_{kj} \equiv \sum_A R_{Ak} [f_p]_j(\mathbf{R}_A), \quad (4.39)$$

where $\rho_{[2]}$ is the elastic dipole tensor, and it is a central quantity in the present work. Observe the $\rho_{[2]}$ is exclusively a property of the atomic structure of the point defect system. It provides a connection between this atomic

FIG. 4.5

Comparison of models of point defects

(a) The standard misfitting sphere model in which the point defect exerts a continuous and isotropic distribution of forces on the surrounding continuum. (b) The atomic structure of an anisotropic point defect system in which the point defect exerts discrete and anisotropic forces on neighbouring host atoms.



structure and the continuum long-range elastic fields. Note also that $\rho_{[2]}$ only differs from the atomic scale stress tensor by a factor of the inverse of the volume associated with the defect site.

In the following, $\{f_p(\mathbf{R}_A) | A \in \mathbb{N}\}$ is treated into ways. The first is the widely used misfit model in which a point defect is assumed to be a spherical misfit in an isotropic continuum. The second is the multipole model in which a point defect is represented by a multipolar expansion of forces exerted on discretely-positioned neighbouring atoms. These models are compared in FIG. 4.5. In the context of DHC, it will become clear why the misfit model is inadequate for H in Zr and why the multipole model is more appropriate for modelling H diffusion in Zr alloy microstructures.

4.2.1 Spherical Misfit

The simplest model of a point defect is to suppose that it is a misfitting sphere in an infinite homogeneous linear elastic continuum. This is a spherically symmetric system; transferring to spherical polar coordinates (r, θ, ϕ) , it is possible to write the point defect forces as a continuous distribution

$$f_p^*(\mathbf{r}) \propto -\Delta V \nabla \delta(\mathbf{r}) \quad (4.40)$$

where ΔV is a (small) volume change in the medium. In this case, $\rho_{[2]}^*$ is rotationally invariant, that is,

$$\rho_{ij}^* = \rho_{11} \delta_{ij}, \quad (4.41)$$

where the non-zero constant ϱ_{11} is the only independent component of the isotropic elastic dipole tensor. It is then straightforward to deduce that

$$\mathbf{u}_p^*(r, \theta, \phi) = \begin{pmatrix} [u_{pd}^*]_r(r, \theta, \phi) \\ [u_{pd}^*]_\theta(r, \theta, \phi) \\ [u_{pd}^*]_\phi(r, \theta, \phi) \end{pmatrix} = \begin{pmatrix} [u_{pd}^*]_r(r) \\ 0 \\ 0 \end{pmatrix}, \quad (4.42)$$

that is, there are no angular dependencies and the angular displacements are zero. It is then straightforward to show that solution for Navier's equation reads

$$\mathbf{u}_p^*(r) = \left(\frac{\Delta V}{4\pi} \right) \frac{1}{r^2} \hat{\mathbf{r}}, \quad (4.43)$$

where the prefactor containing ΔV is a measure of the strength of the point defect. It is possible to compute the non-zero components of the strain and stress fields of the system as

$$[e_p^*]_{rr}(r) = [u_{pd}^*]_{r,r}(r) = -\left(\frac{\Delta V}{2\pi} \right) \frac{1}{r^3} \quad (4.44)$$

$$[\sigma_p^*]_{rr}(r) = 2\mu[e_p^*]_{rr}(r) + \lambda\delta_{rr}[e_p^*]_{ii}(r) = -\mu\left(\frac{\Delta V}{\pi} \right) \frac{1}{r^3}, \quad (4.45)$$

noting that the dilatation of the system, $[e_p^*]_{ii}(r)$, is zero. In the plane strain setting, Eq. (4.45) simply reads

$$[\sigma_p^*]_{rr}(x_1, x_2) = -\mu\left(\frac{\Delta V}{\pi} \right) \left(\frac{1}{\sqrt{x_1^2 + x_2^2}} \right)^3 \quad (4.46)$$

which is a spherically symmetric stress profile around the point defect. This isotropic model forms the basis for standard continuum scale stress-diffusion analysis of flaw-tip H enhancement in the Zr alloy component [Jernkvist and Massih (2014) and Jernkvist (2014)]. However, as this model cannot distinguish between the respective projections of the atomic structure of the Zr-H system as viewed from the basal or prism planes, it is not suitable for describing the effects of texture on H diffusion within a polycrystalline Zr specimen.

4.2.2 Multipolar Forces

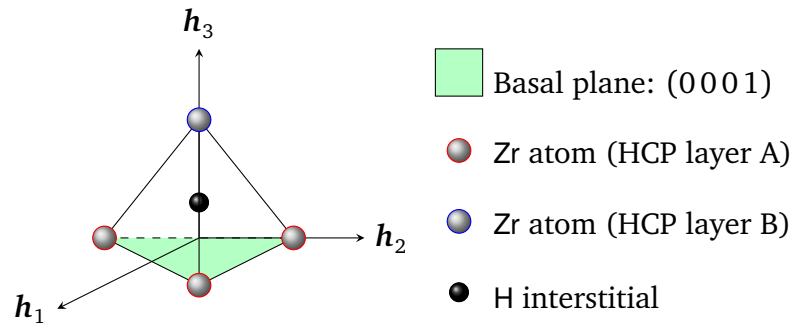
In the anisotropic elastic multipole model of H interstitials occupying tetrahedral sites in HCP α -Zr, the components of $\rho_{[2]}$ must be computed explicitly. Considering the coordinate system shown in FIG. 4.6, it is evident that $\rho_{[2]}$ captures the trigonal symmetry by taking the form

$$\rho_{ij} = \delta_{ij}\varrho_{11} + (\varrho_{33} - \varrho_{11})h_{3i}h_{3j} \quad \text{with} \quad \varrho_{11} \neq \varrho_{33} \quad (4.47)$$

FIG. 4.6

Hydrogen interstitial in a tetrahedral site in hexagonal zirconium

The choice of the Cartesian axes for trigonally symmetric point defect system. This is the coordinate system in which the elastic dipole tensor is naturally expressed. This anisotropic elastic dipole tensor then varies according to the orientation of every crystallite in a polycrystalline specimen.



where the constants ϱ_{11} and ϱ_{33} are the only two (non-zero) independent components of the elastic dipole tensor. Again note that ρ_{ij} is invariant to $\mathcal{D}_3(\theta_3)$ transformations, which is a manifestation of the elastic isotropy of the basal plane. Most importantly, it is the non-equivalence of ϱ_{11} and ϱ_{33} that distinguishes this model from its isotropic counterpart.

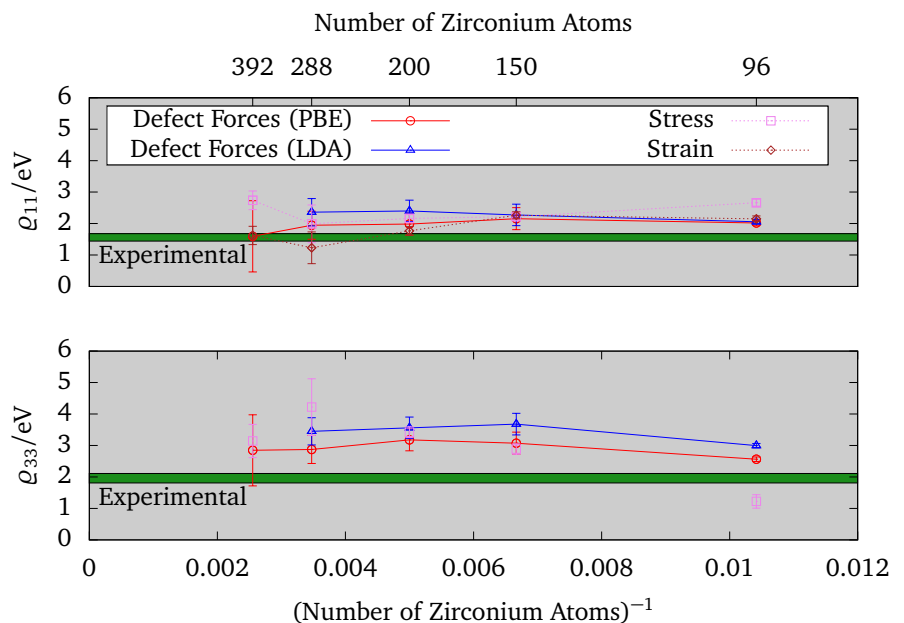
In order to determine ϱ_{11} and ϱ_{33} for the H in α -Zr, first-principles electronic structure calculations can be used to explicitly determine the point defect forces or to compute the atomic scale stress tensor. For the purpose of this work, $\rho_{[2]}$ has been calculated within the framework of DFT using several different strategies [Nazarov et al. (2016)]. Details are not given here but the results are shown in FIG. 4.7 from which the relationship $\varrho_{11} < \varrho_{33}$ has been found. These results are invoked in the stress-diffusion analysis.

FIG. 4.7

Elastic dipole tensor of tetrahedral hydrogen interstitials in hexagonal zirconium

The values of the two independent components of the elastic dipole tensor computed using various DFT methods and compared to the values deduced from experimental studies. There is reasonable agreement between the different DFT studies with the experimental values. Three different DFT methods are used to evaluate the elastic dipole tensor: the defect forces method, the strain method and the stress method. As the simulation cell size becomes larger, more complete shells of nearest neighbours feature in the summation, leading to some convergence.

Adapted from Nazarov et al. (2016).



4.3 One-Dimensional Defects

The second category of defects concerns one-dimensional line defects and, in particular, dislocations in crystals. Dislocations are a very important class of crystalline defects as they are responsible for various mechanical phenomena such as plastic deformation and forest hardening. And, much like point defects, stress analysis of dislocations involves both a quantum mechanical treatment of the core and a classical treatment of the long-range elastic field.

In this work, dislocations take on a more significant role. The elastic fields of a crystalline dislocation, outside of the dislocation core, can be modelled by a topological Volterra-Somigliana (or Volterra) dislocation in a continuum [Mura (1987) and Hirth and Lothe (1982)]. More importantly, Volterra dislocations are a fundamental type of defect in a continuum, and higher-dimensional defects can effectively be constructed using distributions of Volterra dislocations; the elastic fields around Volterra dislocations can themselves be used as elastostatic Green tensor functions for computing the elastic fields around higher-dimensional defects [Weertman (1996)]. This is the premise of distributed dislocation technique, which features prominently in this work as a strategy for efficient analytical and semi-analytical computations of the system stress state.

As shown in FIG. 4.8, several classes of crystalline defects can be modelled using Volterra edge dislocations. These dislocation models will be formalised after deriving the elastic fields of the constituent Volterra edge dislocations.

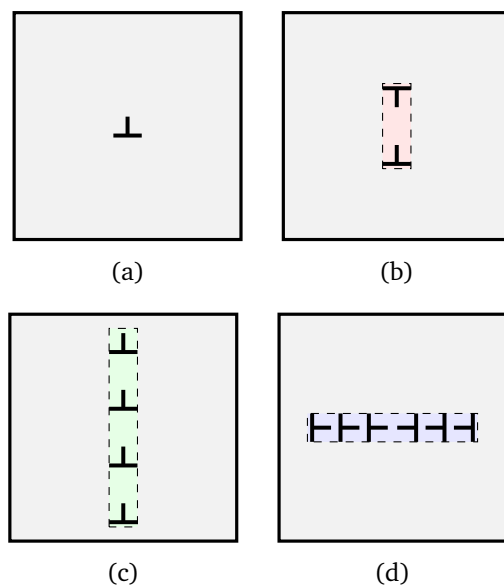


FIG. 4.8

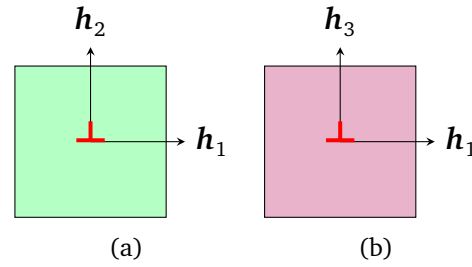
Dislocation models of higher-dimensional defects

(a) An edge dislocation. (b) A needle-like precipitate as a dipole of edge dislocations. (c) A low-angle symmetric tilt (grain) boundary as an array of edge dislocations. (d) A mode I slit crack as a double pile-up of climbing edge dislocations.

FIG. 4.9

Classes of edge dislocations in hexagonal crystals

(a) Prismatic slip with the edge dislocation line direction parallel to the basal pole. (b) Basal slip with the edge dislocation line direction parallel to the prism plane normal.



Using the elastostatic Green tensor function, it is straightforward to write down a generic expression for the stress fields around a Volterra dislocation with a Burgers vector $\mathbf{b}$ as

$$\begin{aligned} [\sigma_d]_{ij}(x_1, x_2) &= C_{ijkl} \oint_L dl(\mathbf{y}) \left[\varepsilon_{lno} C_{pqmn} b_m v_o \frac{\partial G_{kp}(\mathbf{x} - \mathbf{y})}{\partial x_q} \right] \\ &= \frac{1}{8\pi^2} \left[\oint_{\mathbb{S}_1} dS(\xi) [K^{-1}]_{kp}(\xi) \right] \cdot \\ &\quad \cdot C_{ijkl} \oint_L dl(\mathbf{y}) \left[\varepsilon_{lno} C_{pqmn} b_m v_o \frac{\partial}{\partial x_q} \left(\frac{1}{|\mathbf{x} - \mathbf{y}|} \right) \right], \quad (4.48) \end{aligned}$$

where the line integral is around dislocation loop L and $\mathbf{v}$ is the unit normal to the surface of the slip plane bounded L as usual [Mura (1987) and Bal-luffi (2012)]. This integral effectively depends only on the elastic stiffness $C_{[4]}$ whose symmetries dictate the availability of analytical solutions. It is clear that a closed-form expression for $G_{ij}(\mathbf{x})$ is a necessary precursor for a closed-form expression for a Volterra dislocation and hence any higher-dimensional defect composed of Volterra dislocations. Closed-form expressions are known for isotropic continua but considerable effort has been directed towards the application of Eq. (4.48) to special cases of anisotropic continua [Willis (1964), Mura (1987), Teutonico (1970), and Steeds (1973)].

In general, it is well known that analytical solutions to Eq. (4.48) can be obtained if the dislocation line is either: (i) parallel to an axis of rotational symmetry; or (ii) normal to an axis of evenfold rotational symmetry [Steeds (1973)]. In the case of hexagonal crystals, every direction in the basal plane is a diad axis corresponding to the two-fold rotational symmetry of the prism plane; this statement only holds for the transversely isotropic $C_{[4]}$ in the framework of linear elasticity. Therefore, closed-form expressions are available for all classes of dislocations in transversely isotropic continua.

Using the transversely isotropic $C_{[4]}$, Eq. (4.48) can be solved for the two relevant classes of Volterra edge dislocations corresponding to prismatic slip and basal slip. The choices of Cartesian axes for these two classes of HCP dislocations are shown in FIG. 4.9, and it is possible to write down compact

expressions for both cases in which the symmetries are more apparent as

$$[\sigma_d]_{11}(x_1, x_2; b_d) = \alpha_{11}[\mathbb{P}] b_d \left[\frac{x_2 (\omega_{11}[\mathbb{P}] x_1^2 + \Omega_{11}[\mathbb{P}] x_2^2)}{x_1^4 + v_{11}[\mathbb{P}] x_1^2 x_2^2 + \Upsilon_{11}[\mathbb{P}] x_2^4} \right] \quad (4.49a)$$

$$[\sigma_d]_{12}(x_1, x_2; b_d) = \alpha_{12}[\mathbb{P}] b_d \left[\frac{x_1 (\omega_{12}[\mathbb{P}] x_1^2 + \Omega_{12}[\mathbb{P}] x_2^2)}{x_1^4 + v_{12}[\mathbb{P}] x_1^2 x_2^2 + \Upsilon_{12}[\mathbb{P}] x_2^4} \right] \quad (4.49b)$$

$$[\sigma_d]_{22}(x_1, x_2; b_d) = \alpha_{22}[\mathbb{P}] b_d \left[\frac{x_2 (\omega_{22}[\mathbb{P}] x_1^2 + \Omega_{22}[\mathbb{P}] x_2^2)}{x_1^4 + v_{22}[\mathbb{P}] x_1^2 x_2^2 + \Upsilon_{22}[\mathbb{P}] x_2^4} \right] \quad (4.49c)$$

where b_d is the slip vector component in the x_1 -direction, and the (non-tensorial) coefficients $\{\alpha_{ij}, \omega_{ij}, \Omega_{ij}, v_{ij}, \Upsilon_{ij}\}$ are chosen according to the type of slip, labelled by the plane $\mathbb{P}$ as follows. For prismatic slip, $\mathbb{P}$ is (0001) and the isotropic $C_{[4]}^*$ can be used for convenience. For basal slip, $\mathbb{P}$ is (10 $\bar{1}$ 0) and the fully anisotropic $C_{[4]}$ is required.

4.3.1 Prismatic Dislocations

For the prismatic edge dislocation whose line direction is parallel to the basal pole, the coefficients take their well known isotropic forms:

$$\alpha_{11}[(0001)] = -\frac{\mu}{2\pi(1-\nu)} \quad (4.50a)$$

$$\alpha_{12}[(0001)] = \frac{\mu}{2\pi(1-\nu)} \quad (4.50b)$$

$$\alpha_{22}[(0001)] = \frac{\mu}{2\pi(1-\nu)} \quad (4.50c)$$

$$\omega_{11}[(0001)] = 3 \quad (4.50d)$$

$$\omega_{12}[(0001)] = 1 \quad (4.50e)$$

$$\omega_{22}[(0001)] = 1 \quad (4.50f)$$

$$\Omega_{11}[(0001)] = 1 \quad (4.50g)$$

$$\Omega_{12}[(0001)] = -1 \quad (4.50h)$$

$$\Omega_{22}[(0001)] = -1 \quad (4.50i)$$

$$v_{11}[(0001)] = 2 \quad (4.50j)$$

$$v_{12}[(0001)] = 2 \quad (4.50k)$$

$$v_{22}[(0001)] = 2 \quad (4.50l)$$

$$\Upsilon_{11}[(0001)] = 1 \quad (4.50m)$$

$$\Upsilon_{12}[(0001)] = 1 \quad (4.50n)$$

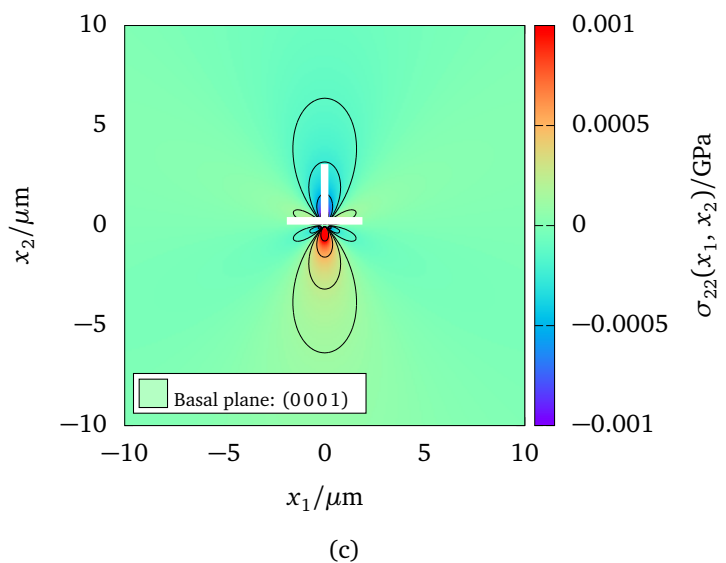
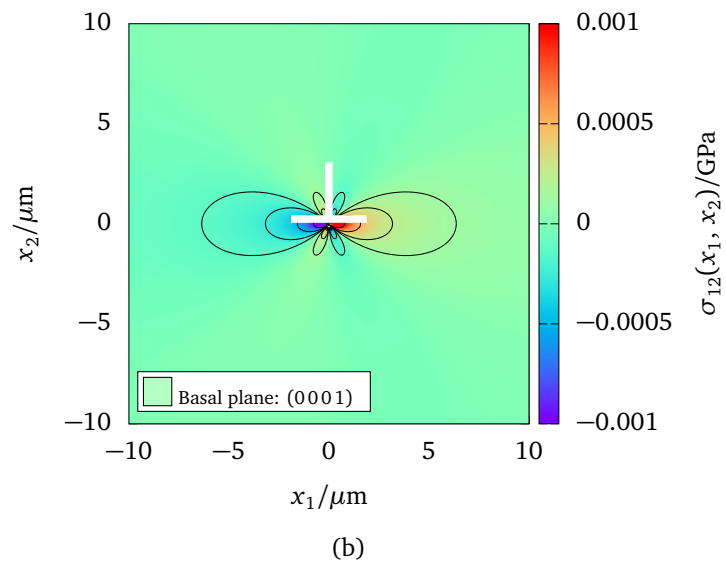
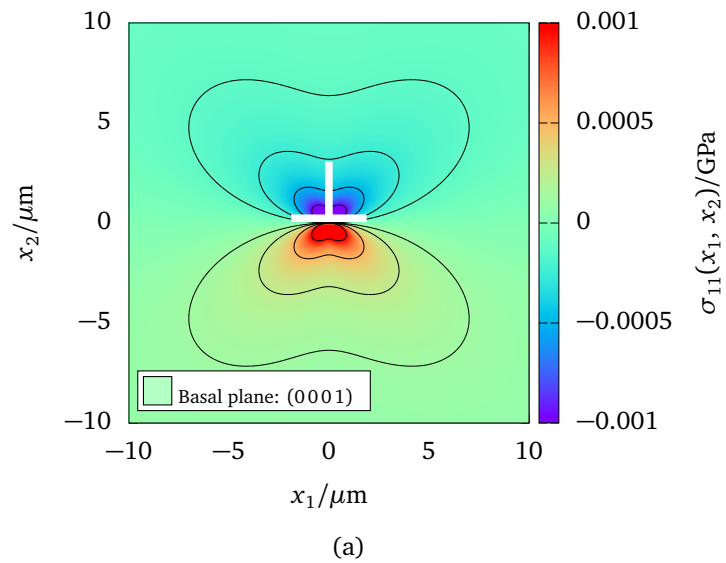
$$\Upsilon_{22}[(0001)] = 1. \quad (4.50o)$$

The contours of the prismatic edge dislocation can be visualised on the basal plane as shown in **FIG. 4.10**.

FIG. 4.10

The stress fields around a prismatic edge dislocation

The contours of the stresses around a Volterra edge dislocation in an isotropic continuum that has the elastic properties of Zr with the (x_1, x_2) -plane corresponding to the (h_1, h_2) -plane. These stress fields represent the stress state around a prismatic edge dislocation outside of its core. The core cut-off is approximately specified by the Burgers vector; here the Burgers vector is $1\text{\AA}$, that is, the order of the lattice constants.



4.3.2 Basal Dislocations

For the basal edge dislocation whose line direction is parallel to the prism plane normal, the coefficients are given in terms of the transversely isotropic $C_{[4]}$ and $S_{[4]}$ as

$$\alpha_{11}[(10\bar{1}0)] = -\frac{1}{2\pi(S_{11} - S_{13}^2/S_{33})} \cdot \left[\left(\frac{2C_{11}}{C_{33}} \right)^{1/2} - \frac{C_{13}^2 + 2C_{13}C_{44} - C_{11}C_{33}}{C_{33}C_{44}} \right]^{-1/2} \quad (4.51a)$$

$$\alpha_{12}[(10\bar{1}0)] = \frac{1}{2\pi(S_{11} - S_{13}^2/S_{33})} \cdot \left[\left(\frac{2C_{11}}{C_{33}} \right)^{1/2} - \frac{C_{13}^2 + 2C_{13}C_{44} - C_{11}C_{33}}{C_{33}C_{44}} \right]^{-1/2} \quad (4.51b)$$

$$\alpha_{22}[(10\bar{1}0)] = \frac{1}{2\pi(S_{11} - S_{13}^2/S_{33})} \cdot \left[\left(\frac{2C_{11}}{C_{33}} \right)^{1/2} - \frac{C_{13}^2 + 2C_{13}C_{44} - C_{11}C_{33}}{C_{33}C_{44}} \right]^{-1/2} \quad (4.51c)$$

$$\omega_{11}[(10\bar{1}0)] = \left(\frac{C_{11}}{C_{33}} \right)^{1/2} - \frac{C_{13}^2 + 2C_{13}C_{44} - C_{11}C_{33}}{C_{33}C_{44}} \quad (4.51d)$$

$$\omega_{12}[(10\bar{1}0)] = 1 \quad (4.51e)$$

$$\omega_{22}[(10\bar{1}0)] = 1 \quad (4.51f)$$

$$\Omega_{11}[(10\bar{1}0)] = \frac{C_{11}}{C_{33}} \quad (4.51g)$$

$$\Omega_{12}[(10\bar{1}0)] = -\left(\frac{C_{11}}{C_{33}} \right)^{1/2} \quad (4.51h)$$

$$\Omega_{22}[(10\bar{1}0)] = -\left(\frac{C_{11}}{C_{33}} \right)^{1/2} \quad (4.51i)$$

$$v_{11}[(10\bar{1}0)] = -\frac{C_{13}^2 + 2C_{13}C_{44} - C_{11}C_{33}}{C_{33}C_{44}} \quad (4.51j)$$

$$v_{12}[(10\bar{1}0)] = -\frac{C_{13}^2 + 2C_{13}C_{44} - C_{11}C_{33}}{C_{33}C_{44}} \quad (4.51k)$$

$$v_{22}[(10\bar{1}0)] = -\frac{C_{13}^2 + 2C_{13}C_{44} - C_{11}C_{33}}{C_{33}C_{44}} \quad (4.51l)$$

$$\Upsilon_{11}[(10\bar{1}0)] = \frac{C_{11}}{C_{33}} \quad (4.51m)$$

$$\Upsilon_{12}[(10\bar{1}0)] = \frac{C_{11}}{C_{33}} \quad (4.51n)$$

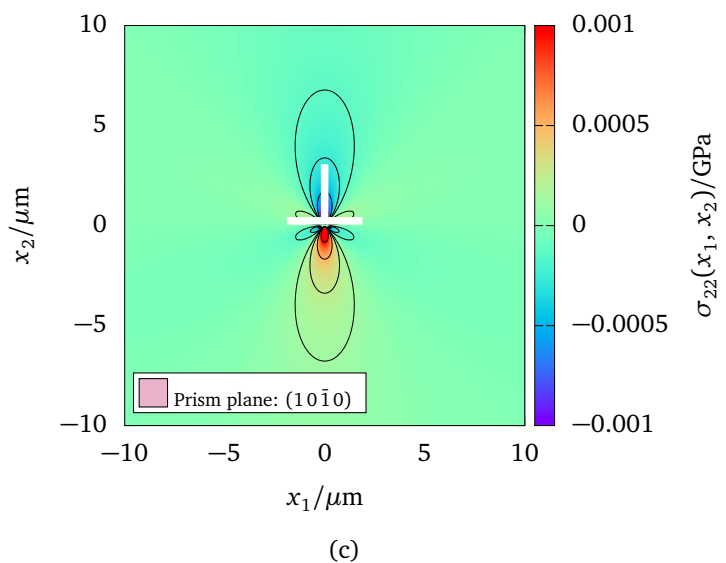
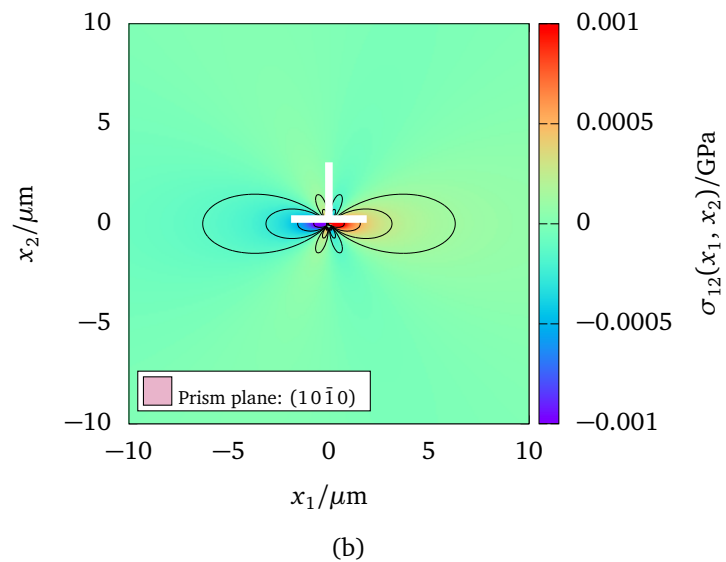
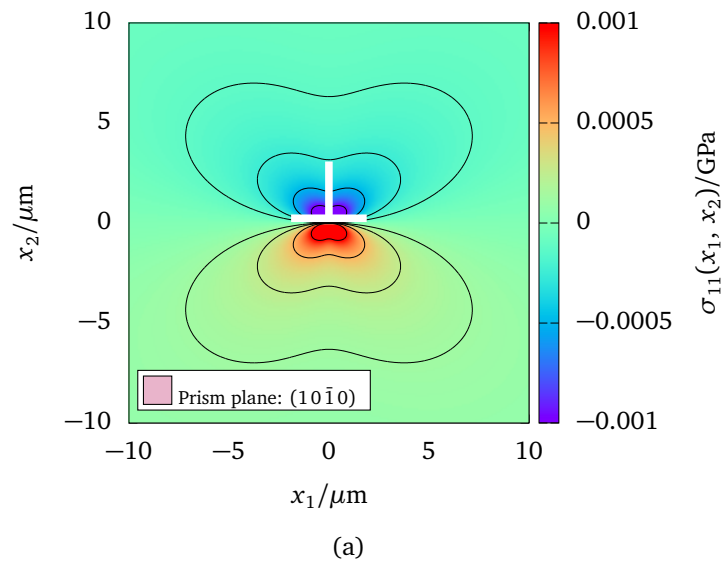
$$\Upsilon_{22}[(10\bar{1}0)] = \frac{C_{11}}{C_{33}}. \quad (4.51o)$$

Although these expressions appear more complicated than isotropic counterparts, the isotropic limit can be formally recovered by taking $C_{11} \rightarrow C_{33}$ as required. The contours of the basal edge dislocation can be visualised on the prism plane as shown in [FIG. 4.11](#) and compared in [FIG. 4.12](#).

FIG. 4.11

The stress fields around a basal edge dislocation

The contours of the stresses around a Volterra edge dislocation in a transversely isotropic continuum that has the elastic properties of Zr with the (x_1, x_2) -plane corresponding to the (h_1, h_3) -plane. These stress fields represent the stress state around a basal edge dislocation outside of its core. The core cut-off is approximately specified by the Burgers vector; here the Burgers vector is $1\text{\AA}$, that is, the order of the lattice constants.



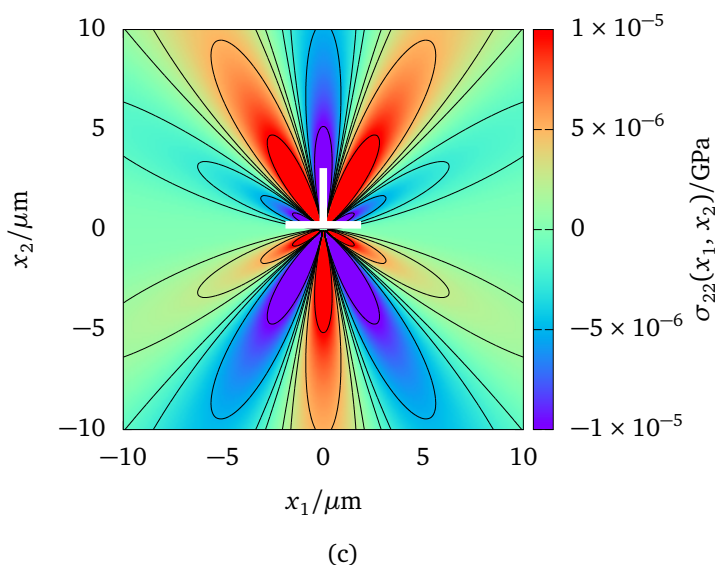
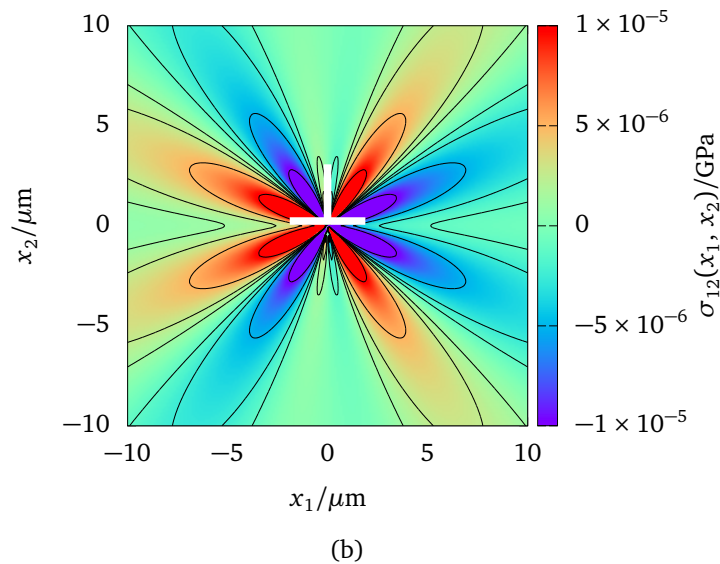
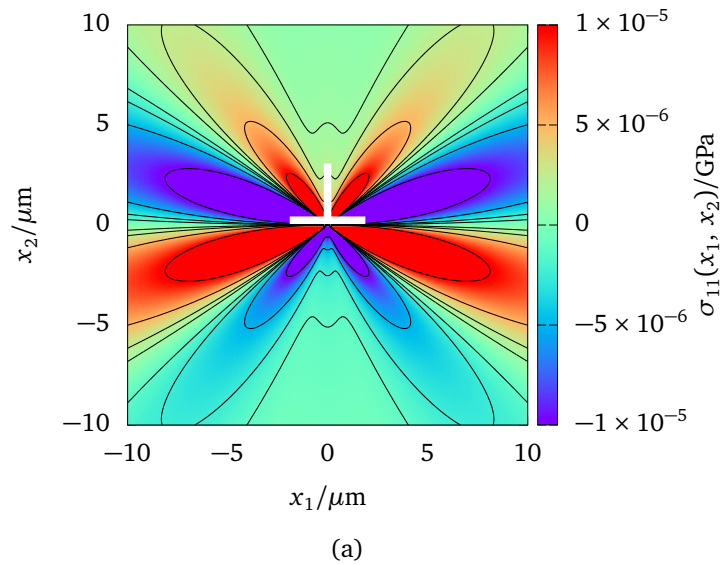


FIG. 4.12

A comparison of prismatic and basal slip
 A contour map of the differences between the isotropic and transversely isotropic expressions for the stress fields around a Volterra dislocation. There is up to $\sim 10\%$ correction to the stress profile within a radius of $\sim 5 \mu\text{m}$ of the dislocation core. This justifies the need to use anisotropic elasticity because these Volterra dislocations are constituents of higher-dimensional defects. This correction does not appear in the standard isotropic stress analysis in which there is no mathematical distinction between prismatic and basal slip.

4.4 Two-Dimensional Defects

The third category of defects concerns two-dimensional planar defects and, in particular, internal interfaces and free surfaces. The microstructure of a hydrided Zr alloy component consists of many different interfaces that demarcate regions of different crystal structure and orientation. Internal interfaces include heterophase boundaries between the Zr matrix, intermetallic second-phase particles and the different hydride phases as well as homophase boundaries such as grain boundaries between the hexagonal crystallites, twin boundaries and stacking faults. Free surfaces are also prominent because of the context of this work; the region of interest to DHC initiation is in the vicinity of a volumetric flaw near the outer edge of the Zr alloy component.

The existence of these planar defects has several important consequences to the stress analysis because of the imposed elastic heterogeneity. The correct mathematical treatment of these planar defects requires spatial variation in $C_{[4]}$ in order to account for different material properties and crystal orientations across the internal interfaces as well as voids and gaps across the free surfaces. This elastic heterogeneity complicates the evaluation of $G_{[2]}(\mathbf{x})$ because Eq. (4.31) must be generalised to the form

$$C_{ijkl}(\mathbf{x})G_{km,lj}(\mathbf{x} - \mathbf{y}) + \delta_{im}\delta^{(3)}(\mathbf{x} - \mathbf{y}) = 0, \quad (4.52)$$

where $C_{[4]}(\mathbf{x})$ must incorporate every internal interface and free surface. In practice, Eq. (4.52) is a mathematical boundary value problem that is difficult to solve analytically, even for the very simple cases that are of relevance to this work, the main examples being a hexagonal bicrystal and a semi-infinite transversely isotropic continuum. Owing to this difficulty, the solution to Eq. (4.52) generally requires a numerical approach that increases in complexity as the planar defects become more numerous and irregular. This numerical treatment extends to the evaluation of $[\sigma_d]_{[2]}(\mathbf{x})$ using $G_{[2]}(\mathbf{x})$, and this can become computationally expensive if distributions of Volterra dislocations are used to model higher-dimensional defects.

In addition to this mathematical boundary value correction, internal interfaces are generators of intrinsic stresses due to the local distortions in the atomic arrangement and, more importantly, they can control other micromechanical processes that shape the global stress state of the system by acting as a source, sink or barrier for lower-dimensional defects. These physical effects depend on the type of interface as well as interfacial properties such as sharpness and coherency. On the one hand, it is necessary to account for both the physical effects and the mathematical corrections to the stress analysis. But, on the other hand, a direct computation of these stresses is

neither tractable nor efficient. Therefore, an alternative strategy is required to account for the stresses near these planar defects and how they influence H diffusion and hydride precipitation. Proceeding here with the usual assumption of elastic homogeneity, it is then worth briefly discussing how the (partial) omission of planar defects in the stress analysis can be rectified in the stress-diffusion analysis and diffusion-precipitation analysis.

4.4.1 Interfaces

The internal interfaces play a central role in the evolution of the hydrided microstructure and effectively underpin DHC initiation. There are, however, far too many different types of interfaces to provide a complete specification here. So attention is restricted to grain boundaries because they are the largest of the internal planar defects and hence arguably the most potent contributors to the global stress state. This is true at least for a pure polycrystalline specimen of α -Zr prior to any hydride formation.

In terms of the stress analysis, grain boundaries alter the evolution of the global stress profile through the following effects. Firstly, a grain boundary between two misorientated α -Zr crystallites generates intrinsic stresses due to the distorted atomic structure in its vicinity. These intrinsic stresses are bound to the incompatibility of the plastic deformation between the neighbouring grains, and they vary with the degree of anisotropy of the crystal structure, geometry of the grain boundary, the relative misorientation and the boundary conditions that define the continuity of the elastic fields across the interface [Dunne and Petrinic (2005), Peralta, Schober, and Laird (1993), and Rey (1988)]. These incompatibility stresses do not feature in traditional models of an isotropic heterogeneous continuum because the assumption of elastic homogeneity does not enforce any boundary conditions. But, in reality, these intrinsic stresses always exist at the grain boundaries—even in the supposed elastically homogeneous media—because of the atomic degrees of freedom.

Secondly, dislocation sources can be activated by large stresses due to singularities along grain boundaries such as ledges. The resulting local dislocation networks then harden the region around the grain boundaries [Rey (1988) and Hull and Bacon (2011)]. Thirdly, grain boundaries can act as an obstacle to plastic glide, that is, barriers to dislocation motion which lead to the formation of dislocation pile-ups [Hirth and Lothe (1982)]. In the low temperature regime, such grain boundaries ensure the cohesion of grains with different slip systems [Dunne and Petrinic (2005)]. Finally, grain boundaries are sinks for segregants and nucleation sites for precipitates [Neumann (1995), Rey (1988), and Sutton and Balluffi (1995)].

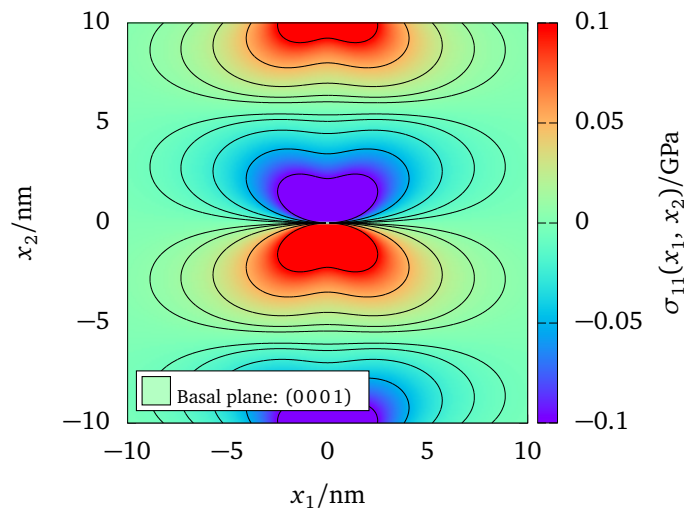
Evidently, the stress profile near grain boundaries is far too complicated to compute accurately and efficiently. Therefore, these stresses are not explicitly considered here. That is, the continuum is assumed to be elastically homogeneous, but grain boundaries are modelled to describe other microstructural processes. For illustrative purposes, consider the low-angle symmetric tilt boundary shown in **FIG. 4.13** whose intrinsic stress fields can be represented by an infinite co-planar array of Volterra dislocations as

$$\begin{aligned}
 [\sigma_g]_{11}(x_1, x_2; d_g, \phi_g) &= \sum_{n=-\infty}^{\infty} [\sigma_d]_{11}(x_1, x_2 - nd_g; b_g) \\
 &= -\frac{\mu b_g}{2\pi(1-\nu)d_g} \cdot \sum_{n=-\infty}^{\infty} \left(\frac{x_2}{d_g} - n \right) \left[\frac{3(x_1/d_g)^2 - [(x_2/d_g) - n]^2}{[(x_1/d_g)^2 + (x_2/d_g - n)^2]^2} \right] \\
 &= -\frac{\mu b_g}{2\pi(1-\nu)d_g} \frac{\sin(2\pi x_2/d_g)}{[\cosh(2\pi x_1/d_g) - \cos(2\pi x_2/d_g)]^2} \cdot \left\{ \cosh(2\pi x_1/d_g) - \cos(2\pi x_2/d_g) \right. \\
 &\quad \left. + 2\pi(x_1/d_g) \sinh(2\pi x_1/d_g) \right\} \quad (4.53a)
 \end{aligned}$$

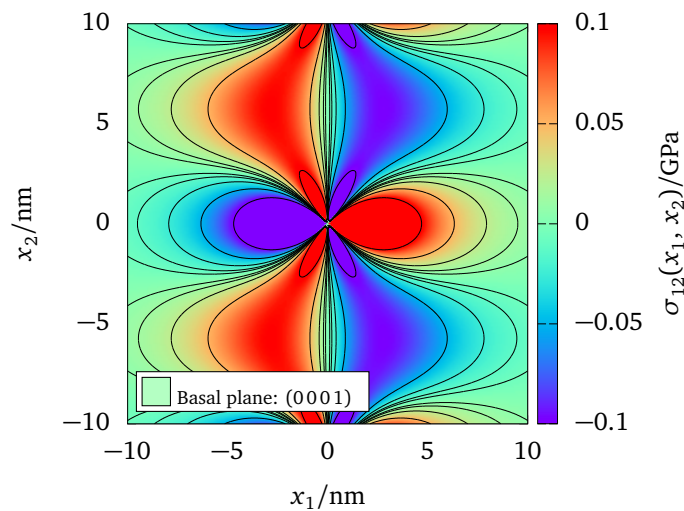
$$\begin{aligned}
 [\sigma_g]_{12}(x_1, x_2; d_g, \phi_g) &= \sum_{n=-\infty}^{\infty} [\sigma_d]_{12}(x_1, x_2 - nd_g; b_g) \\
 &= \frac{\mu b_g}{2\pi(1-\nu)d_g} \cdot \sum_{n=-\infty}^{\infty} \left(\frac{x_1}{d_g} \right) \left[\frac{(x_1/d_g)^2 - [(x_2/d_g) - n]^2}{[(x_1/d_g)^2 + (x_2/d_g - n)^2]^2} \right] \\
 &= \frac{\pi \mu b_g}{(1-\nu)d_g} \frac{x_1/d_g}{[\cosh(2\pi x_1/d_g) - \cos(2\pi x_2/d_g)]^2} \cdot \left\{ \cosh(2\pi x_1/d_g) \cos(2\pi x_2/d_g) - 1 \right\} \quad (4.53b)
 \end{aligned}$$

$$\begin{aligned}
 [\sigma_g]_{22}(x_1, x_2; d_g, \phi_g) &= \sum_{n=-\infty}^{\infty} [\sigma_d]_{22}(x_1, x_2 - nd_g; b_g) \\
 &= \frac{\mu b_g}{2\pi(1-\nu)d_g} \cdot \sum_{n=-\infty}^{\infty} \left(\frac{x_2}{d_g} - n \right) \left[\frac{(x_1/d_g)^2 - [(x_2/d_g) - n]^2}{[(x_1/d_g)^2 + (x_2/d_g - n)^2]^2} \right] \\
 &= -\frac{\mu b_g}{2(1-\nu)d_g} \frac{\sin(2\pi x_2/d_g)}{[\cosh(2\pi x_1/d_g) - \cos(2\pi x_2/d_g)]^2} \cdot \left\{ \cosh(2\pi x_1/d_g) - \cos(2\pi x_2/d_g) \right. \\
 &\quad \left. - 2\pi(x_1/d_g) \sinh(2\pi x_1/d_g) \right\} \quad (4.53c)
 \end{aligned}$$

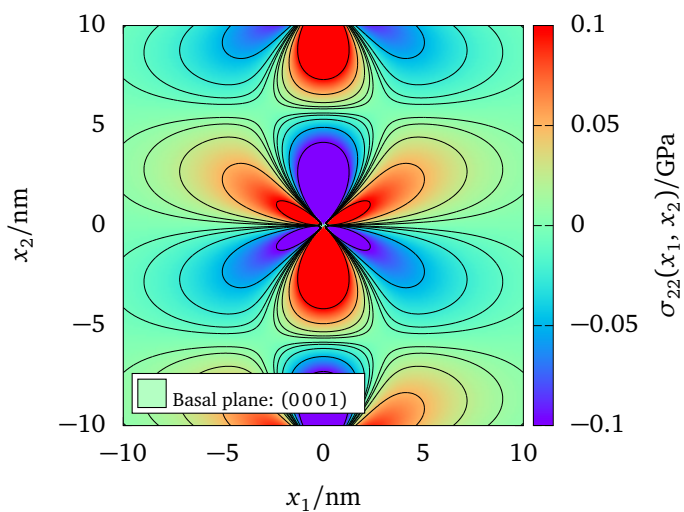
where $b_g = 2d_g \sin(\phi_g/2)$ in which ϕ_g is the misorientation angle and d_g is the spacing between dislocations [Hirth and Lothe (1982)].



(a)



(b)



(c)

FIG. 4.13

Stress fields near a low-angle symmetric tilt boundary

A model of the intrinsic stresses around a low-angle tilt boundary in an infinite isotropic continuum. The tilt boundary is represented as an infinite vertical array of Volterra edge dislocations. An angle of $\pi/180$ is chosen for the relative misorientation. There is a periodic repetition of tensile and compressive regions. The tensile regions can act as sinks for H atoms and hence nucleation sites for hydride precipitation. It is important to appreciate that this local stress profile corresponds to an ideal bicrystal and so this is of limited practical use to a polycrystalline material in which many grain boundaries interact with each other. In reality, the periodicity would not be present and, more generally, the stress profile will vary from grain boundary to grain boundary. That is, certain grain boundaries will be more potent sinks for H atoms and hence more energetically favourable nucleation sites for hydride precipitation. This agrees with experimental evidence of inter-granular macro-hydride colonies that form at specific grain boundaries.

4.4.2 Surfaces

In the vicinity of the flaw tip, the infinite continuum assumption must be corrected due to the presence of the free surface at the edge of the Zr alloy component as well as the surface of the volumetric flaw. The former can be treated by supposing instead a semi-infinite continuum with a free surface defined by the straight line $x_1 = 0$, and imposing the necessary boundary conditions, namely, the condition of a traction-free surface. This requires a correction to the stress fields around any defects that are near the free surface. The boundary correction becomes more significant the closer the defect is to the free surface [Balluffi (2012)].

The traction-free surface condition can be directly built into the elastostatic Green tensor function. But it is more convenient to use the method of images for dislocation models. The method of images involves the placement of a virtual (image) dislocation with an equal and opposite Burgers vector on the other side of the free surface to cancel the traction generated by a real dislocation [Hirth and Lothe (1982) and Balluffi (2012)]. Although this eliminates all normal stresses, this naïve image construction is, however, not sufficient for cancelling the shear stresses on the surface. A supplementary field is needed to enforce the boundary condition, and the image corrected stress fields are then a superposition of the stress fields of the real dislocation and the virtual dislocation with the supplementary field. Analytical solutions for this supplementary field are not straightforward to obtain for even this simple setup [Hirth and Lothe (1982)]. For example, in an isotropic half-continuum, the image corrected stress fields for a dislocation at a position $(-l, 0)$ take the form

$$[\widetilde{\sigma}_d]_{11}(x_1, x_2; b_d) = -\frac{2\mu b_d l x_1 x_2}{\pi(1-\nu)(l^2 + x_2^2)^3} [3(l - x_1)^2 - x_2^2] \quad (4.54a)$$

$$[\widetilde{\sigma}_d]_{12}(x_1, x_2; b_d) = -\frac{\mu b_d l}{\pi(1-\nu)(l^2 + x_2^2)^3} [(l - x_1)^4 + 2x_1(l - x_1)^3 + 6x_1 x_2^2(l - x_1) - x_2^4] \quad (4.54b)$$

$$[\widetilde{\sigma}_d]_{22}(x_1, x_2; b_d) = +\frac{\mu b_d l}{\pi(1-\nu)(l^2 + x_2^2)^3} [4(l - x_1)^3 x_2 + 6(l - x_1)^2 x_1 x_2 + 4(l - x_1)x_2^3 - 2x_1 x_2^3], \quad (4.54c)$$

and it is clear that these expressions are not simply the sum of the real and virtual parts [Hirth and Lothe (1982)]. So the present work does not completely address surface corrections beyond the simple image construction. This approach is only acceptable because later analyses focus mainly on the normal stresses. The image corrections for dislocations near the volumetric flaw surface depend on the flaw geometry. These corrections are discussed further in due course.

4.5 Three-Dimensional Defects

The fourth and final category of defects concerns volumetric defects and, in particular, micro-hydride needle precipitates as well as a selection of volumetric flaws of different geometries, including slit cracks, elliptical holes and V-notches. The models of the precipitates and slit cracks are unique to this work and they will provide a powerful demonstration of the one-dimensional distributed dislocation technique as a computationally efficient strategy for stress analysis [Patel et al. (2017) and Patel et al. (2018)]. Although the distributed dislocation technique can be extended to the elliptical holes and V-notches, the mathematical treatment of a two-dimensional distribution of dislocations often results in a numerical solution, and so an alternative strategy is employed for these defects. This alternative strategy is the method of complex potentials in the mathematical theory of planar elasticity [Muskhelishvili (1977), Muskhelishvili (1992), and Sadd (2005)].

Before proceeding, it is worth reiterating that the present work assumes a planar framework. In the planar representation of three-dimensional defects, all three dimensional shapes are prisms with an infinite depth along the plane normal. Therefore, the three-dimensional geometries of the hydrides and the volumetric flaws must be interpreted as such.

4.5.1 Precipitates

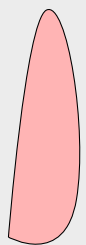
Consider first a micro-hydride needle precipitate, which is an inclusion in Zr matrix. The problem of a lone inclusion in an infinite continuum has been extensively studied in elasticity theory and analytical formulae for the system stress state are well known [Eshelby (1956), Eshelby (1957), Eshelby (1959), and Balluffi (2012)]. But this is certainly not the case for the more generalised problem of a large density of inclusions near a free surface, which is significantly more relevant for modelling the flaw-tip hydrided microstructure. It appears that this complex multi-phase system necessitates a computationally expensive representation of an elastically heterogeneous continuum. But here an original strategy to simplify this paradigm is conceived. This strategy exploits experimental knowledge of micro-hydride needles as well as first-principles simulations of bulk hydride phases. By making a sequence of approximations that are physically justified and mathematically sensible, it is possible to systematically reduce the stress analysis of the hydrided microstructure to a fully analytical solution.

Recall the DFT computations of elastomechanical properties of the pure hydride phases [Zhu et al. (2010), Zhu et al. (2016), Lumley (2013), and Lumley et al. (2014)]. These results indicate that the respective values for the elastic stiffness constants for a α -Zr crystal and the different bulk hy-

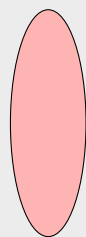
FIG. 4.14

Dislocation model of precipitates

The sequence of approximations in the stress analysis of a micro-hydride needle. (a) An arbitrarily complex precipitate. (b) An ellipsoidal inclusion. (c) A two-dimensional distribution of Volterra edge dislocations along the matrix-hydride interface. (d) A Volterra edge dislocation dipole.



(a)



(b)



(c)



(d)

hydride phases are within $\sim 30\%$ of each other. That is, there is not a large variation in the anisotropic elastic constants of the pure metal and the pure metal hydride systems. Assuming that $C_{[4]}$ is the same for α -Zr and the hydride phases, the problem is effectively reduced to an elastically homogeneous continuum. This is the first approximation, and it is specific to the Zr-H system.

Now recall the TEM images that depict the typical morphologies of individual micro-hydride needles [Carpenter (1978), Carpenter (1973), Carpenter, Watters, and Gilbert (1973), Perovic, Weatherly, and Simpson (1982), Perovic, Weatherly, and Simpson (1983), Perovic and Weatherly (1984), and Puls (2012)]. Although each hydride feature is invariably different in reality, the micrographs clearly show that they grow into lenticular platelets that are microscopic in size and reside on the basal plane. This lenticular morphology can be thought of as an extreme (near one-dimensional) limit of an ellipsoidal inclusion whose geometry is parametrised by one principle axis being much longer than the other two principle axes with one of these being negligible. The stress fields around such a lone ellipsoidal inclusion have well known analytical expressions in both isotropic and transversely isotropic continua [Eshelby (1956), Eshelby (1957), Eshelby (1959), Willis (1963), Mura (1987), and Ting (1996)]. These stress fields can be decomposed into a continuous distribution of Volterra dislocations. Here, the stress fields of Volterra dislocations act as elastostatic Green tensor functions whereas the dislocation distribution is specified along the boundary of the ellipsoid; these Volterra dislocations are interfacial stress generators [Sutton and Balluffi (1995)]. In the near one-dimensional limit, this dislocation distribution peaks at both ends of the longest principle semi-axis of the ellipsoid. This peak dominates the stress state in the Green function formalism, and the contributions due to the remainder of the distribution are essentially negligible. The stress state of an individual micro-hydride needle can then be represented by a dipole of Volterra edge dislocations [Patel et al. (2017) and Perovic, Weatherly, and Simpson (1982)]. This sequence of simplifications is illustrated in FIG. 4.14, which constitutes the second approximation.

The dislocation dipole model of a micro-hydride needle is analytical because the stress fields of Volterra dislocations have already been derived. The stress fields around a micro-hydride needle are simply given by a linear superposition of the stress fields due to the constituent dislocations. It is only necessary to configure (i) the distance separating the centre points of constituent dislocations, which defines the precipitate length, l_p , and (ii) the Burgers vector, b_p , which can be chosen according to the precipitate thickness, t_p , and its misfit strain.

On the basal plane, the stress fields of an individual precipitate positioned at the origin take the form

$$\begin{aligned}
 [\sigma_p]_{11}(x_1, x_2; l_p, t_p) &= [\sigma_d]_{11}(x_1, x_2 - l_p/2; -b_p) \\
 &\quad + [\sigma_d]_{11}(x_1, x_2 + l_p/2; b_p) \\
 &= \frac{\mu b_p}{2\pi(1-\nu)} \left\{ \frac{(x_2 - l_p/2)[3x_1^2 + (x_2 - l_p/2)^2]}{[x_1^2 + (x_2 - l_p/2)^2]^2} \right. \\
 &\quad \left. - \frac{(x_2 + l_p/2)[3x_1^2 + (x_2 + l_p/2)^2]}{[x_1^2 + (x_2 + l_p/2)^2]^2} \right\}, \quad (4.55a)
 \end{aligned}$$

$$\begin{aligned}
 [\sigma_p]_{12}(x_1, x_2; l_p, t_p) &= [\sigma_d]_{12}(x_1, x_2 - l_p/2; -b_p) \\
 &\quad + [\sigma_d]_{12}(x_1, x_2 + l_p/2; b_p) \\
 &= -\frac{\mu b_p}{2\pi(1-\nu)} \left\{ \frac{x_1[x_1^2 - (x_2 - l_p/2)^2]}{[x_1^2 + (x_2 - l_p/2)^2]^2} \right. \\
 &\quad \left. - \frac{x_1[x_1^2 - (x_2 + l_p/2)^2]}{[x_1^2 + (x_2 + l_p/2)^2]^2} \right\}, \quad (4.55b)
 \end{aligned}$$

$$\begin{aligned}
 [\sigma_p]_{22}(x_1, x_2; l_p, t_p) &= [\sigma_d]_{22}(x_1, x_2 - l_p/2; -b_p) \\
 &\quad + [\sigma_d]_{22}(x_1, x_2 + l_p/2; b_p) \\
 &= -\frac{\mu b_p}{2\pi(1-\nu)} \left\{ \frac{(x_2 - l_p/2)[x_1^2 - (x_2 - l_p/2)^2]}{[x_1^2 + (x_2 - l_p/2)^2]^2} \right. \\
 &\quad \left. - \frac{(x_2 + l_p/2)[x_1^2 - (x_2 + l_p/2)^2]}{[x_1^2 + (x_2 + l_p/2)^2]^2} \right\} \quad (4.55c)
 \end{aligned}$$

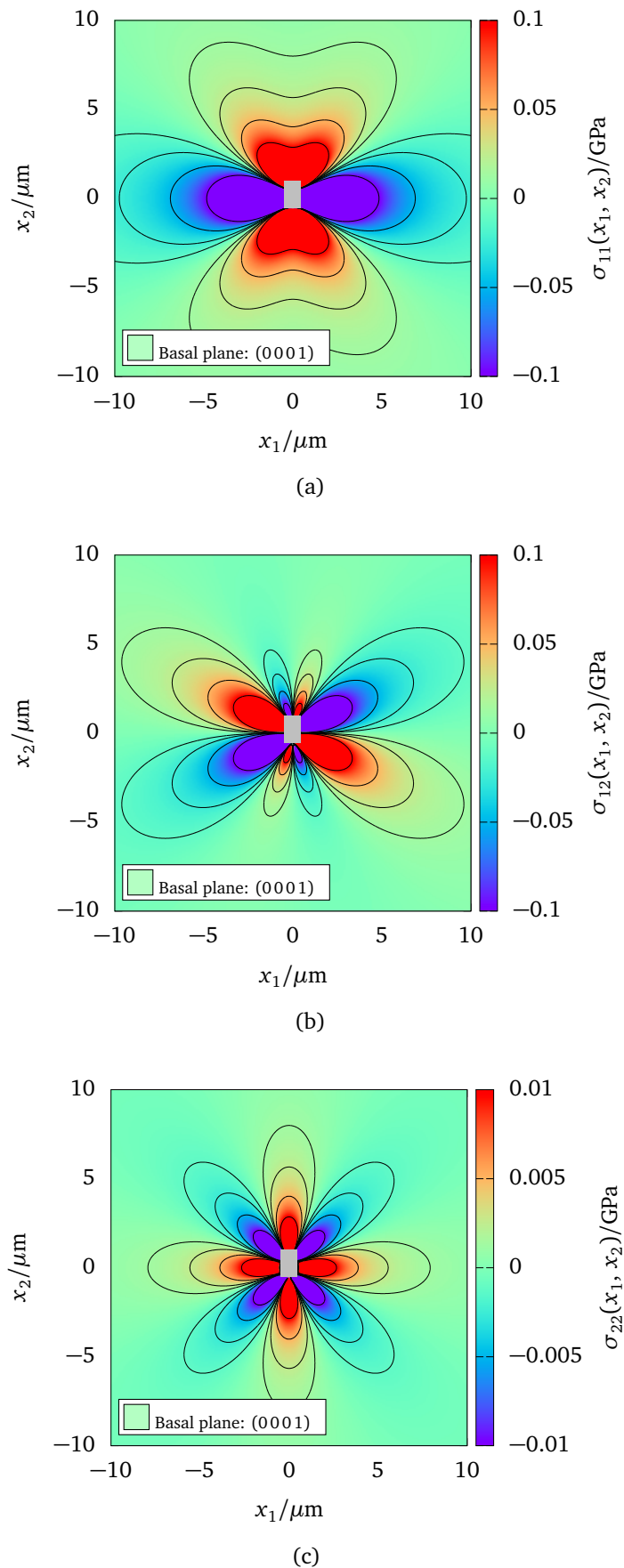
where the relationship $b_p = e_p t_p$ can be invoked to configure the Burgers vector according to experimentally measured misfit strain e_p of $\sim 5\%$ [Carpenter (1973) and Puls (2012)]. These stress fields are visualised in **FIG. 4.15**, and linear superposition is clearly evident in the contours.

In later discussions on diffusion-controlled precipitation, this dislocation dipole model of micro-hydride needles will be used to study the thermodynamically favourable assembly of multiple precipitates within the substructure of the larger macro-hydride colonies. This analytical model facilitates the rapid computation of the elastic strain energetics of a continuum containing multiple micro-hydride needles. It is this approximation of the hydrided Zr alloy microstructure that will allow the bespoke model to surpass, if not, transcend, the capabilities of analogous PF models with respect to the metrics of the accuracy-efficiency balance.

FIG. 4.15

Stress fields around a micro-hydride needle

The stress fields around a dipole of Volterra edge dislocations separated by the distance of $1\ \mu\text{m}$ and a Burgers vector that is 100 times larger than the typical Burgers vector of a crystallographic dislocation. The contours of the stresses clearly resemble a superposition of two Volterra dislocations with an equal and opposite sign.



4.5.2 Slit Cracks

Acute flaw geometries are hypothesised to be worst case scenarios from the standpoint of DHC initiation due to the relatively high stress intensity at the flaw tip [Schofield (2002) and Puls (2012)]. One important example is the sharp slit crack that features prominently in the analytical process (cohesive) zone approach [Puls (2012) and Scarth (2002)]. Such process zone analyses adapt the Dugdale-Bilby-Cottrell-Swinden (DBCS) model of an elastoplastic slit crack [Dugdale (1960), Bilby, Cottrell, and Swinden (1962), Barenblatt (1959), and Barenblatt (1962)]. In the DBCS model, a mode I slit crack and its narrow coplanar plastic zones are represented by a double pile-up of climbing edge dislocations as shown in FIG. 4.16, which forms the intellectual basis to dislocation-based fracture mechanics [Bilby, Cottrell, and Swinden (1962), Bilby and Eshelby (1968), Weertman (1996), Lardner (1975), Lardner (1970), and Chell (1976)].

However, the DBCS model is formulated exclusively within the framework of isotropic elasticity because of its inception in the study of slit cracks in steel sheets [Dugdale (1960) and Bilby, Cottrell, and Swinden (1962)]. In this isotropic setting, it is not possible to distinguish cracks that open on different crystallographic planes or determine the size of plastic zones as function of the dislocation class. However, the effects of anisotropy are evident in the HCP crystallography of α -Zr that permits the existence of several distinct classes of dislocations whose distortion fields cannot be adequately described by isotropic elasticity [Steeds (1973), Willis (1964), and Teutonico (1970)]. Accordingly, the applicability of the DBCS model to the case of Zr requires an extension to anisotropic hexagonal materials; this extension is pursued in the following and it is especially necessary as the isotropic DBCS model is still in active use to determine handbook solutions for the stress analysis of Zr alloys in the nuclear industry [Puls (2012)].

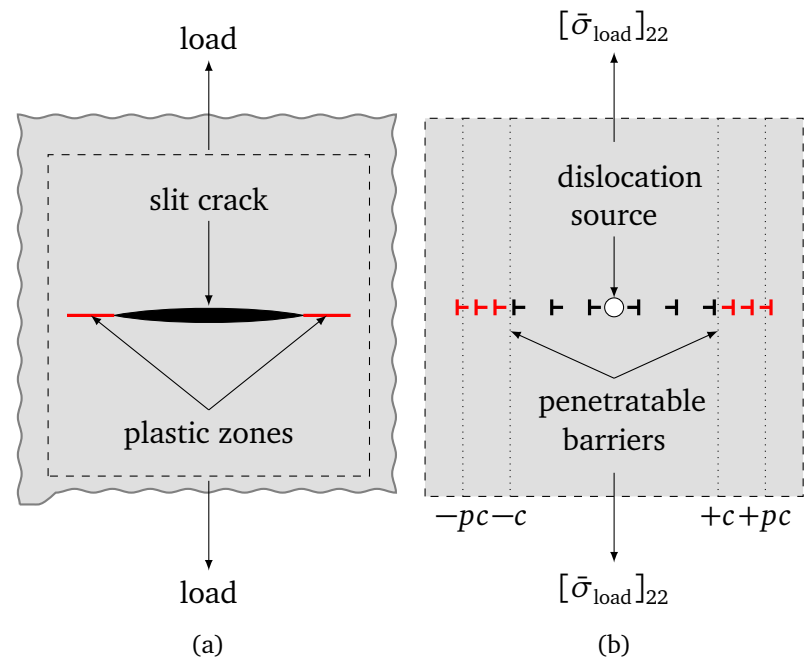
In the following, a model of a slit crack in an infinite linear, homogeneous anisotropic elastoplastic continuum is developed within the framework of dislocation-based fracture mechanics. Consider a crack whose front is confined to the interval $\mathbb{D}_c = [-c, +c]$ along the $\bar{x}_1$ -direction and whose plane is normal to the $\bar{x}_2$ -direction. The coplanar plastic zones ahead of the crack tips are confined to the intervals $\mathbb{D}_p^\pm = [\pm c, \pm pc]$ where the plastic zone ratio $p > 1$ defines the endpoints of the plastic zones. Under mode I loading by a constant external stress at infinity $[\sigma_{\text{load}}]_{22}$, the continuous Volterra dislocation distribution representation of the slit crack is depicted in FIG. 4.16

A standard dislocation distribution model requires four essential pieces of information: (i) a set of dislocation distribution functions; (ii) the stress

FIG. 4.16

Dislocation model of an elastoplastic slit crack

(a) A Dugdale-Barenblatt crack with a narrow coplanar plastic zone under a remote mode I loading. (b) The Dugdale-Bilby-Cottrell-Swinden distributed dislocation representation of a mode I elastoplastic slit crack as a double pile-up of climbing edge dislocations.



fields of individual dislocations; (iii) a point-wise mechanical equilibrium condition; and (iv) mathematical boundedness criteria. Together, these four components can be used to approximate the stress state of a higher-dimensional defect as follows. Firstly, the dislocation distribution $B(\mathbf{x})$ is a continuous function which quantifies at any given point $\mathbf{x}$ in the continuum the dislocation content of a given class (e.g. basal, prismatic, pyramidal), strength (Burgers vector magnitude) and character (e.g. edge, screw or mixed). Generally $B(\mathbf{x})$ is an unknown function which is determined by solving a set of singular integral equations, which convey the mechanical equilibrium condition of the system whilst simultaneously taking into account the geometry of the crack. Secondly, in order to formulate the mechanical equilibrium condition, the stress tensor field of individual constituent dislocations $[\sigma_d]_{[2]}(\mathbf{x})$ is required. However, if evaluating $B(\mathbf{x})$ is the sole requirement, then it is only necessary to have the relevant components of $[\sigma_d]_{[2]}(\mathbf{x})$ specific to the domain of the continuum where $B(\mathbf{x})$ is non-zero. Hence, one-dimensional dislocation distributions always satisfy the standard Cauchy-Hilbert singular integral equation in any anisotropic material [Barnett and Asaro (1972)]. Thirdly, the point-wise satisfaction of the mechanical equilibrium condition requires that there is no resultant force on any dislocation, which is given by the sum of the contributions from all other dislocations in $\mathcal{D}(\mathbf{x})$ in addition to loading and friction stresses. And finally, any specific restrictions on $B(\mathbf{x})$ can be accommodated by employing the appropriate inversion theorem for the singular integral equation

[Muskhelishvili (1992)].

For the purpose of outlining the theory, attention is restricted to one-dimensional dislocation distribution models. For an anisotropic continuum, it is possible to write the one-dimensional dislocation distribution $B(\bar{x}_1)$ for a crack opening on the crystallographic plane $\mathbb{P}$ as

$$B(\bar{x}_1) = \left(\frac{b_c}{\alpha[\mathbb{P}]} \right) B^*(\bar{x}_1), \quad (4.56)$$

where b_c is the Burgers vector of the constituent dislocation and $\alpha[\mathbb{P}]$ is a multiplicative coefficient that scales the function $B^*(\bar{x}_1)$, which is the solution to the standard Cauchy-Hilbert principle value integral equation in which the elasticity prefactors to the known function are appropriately normalised; most simply $B^*(\bar{x}_1)$ is the solution to the analogous isotropic problem in which the shear modulus μ is normalised to unity and the Poisson ratio ν is set to zero. It will become evident that $\alpha[\mathbb{P}]$ is not only dependent on the dislocation type, and thereby the mode of fracture, but it originates directly from the stress fields of the dislocations and hence embeds the anisotropy. Therefore, the aim here is to construct such Cauchy-Hilbert principal value integral equations, given by the form

$$\mathcal{P.V.} \int_{\mathbb{D}_c} d\bar{x}'_1 \left(\frac{B(\bar{x}_1)}{\bar{x}_1 - \bar{x}'_1} \right) = R(\bar{x}_1) \quad (4.57)$$

where $R(\bar{x}_1)$ is a function that contains information about the loading and frictional stresses that resist the motion of dislocation along the $\bar{x}_1$ -direction, whilst also incorporating the effects of the elastic stiffness properties of the continuum. As it stands, Eq. (4.57) describes the most general scenario. For the elastoplastic slit crack, $R(\bar{x}_1)$ is given by a rectangular function [Bilby, Cottrell, and Swinden (1962)]. With the foresight of incorporating the potential effects of anisotropy, this rectangular function can be more generally written as

$$R_{\text{DBCS}}(\bar{x}_1) = \begin{cases} \frac{\alpha[\mathbb{P}]}{b_c} (\gamma_c[\mathbb{P}] r_c^* - [\bar{\sigma}_{\text{load}}]_{22}) & \text{for } \bar{x}_1 \in \mathbb{D}_c \\ \frac{\alpha[\mathbb{P}]}{b_c} (\gamma_p[\mathbb{P}] r_p^* - [\bar{\sigma}_{\text{load}}]_{22}) & \text{for } \bar{x}_1 \in \mathbb{D}_p \\ 0 & \text{otherwise} \end{cases}, \quad (4.58)$$

where the frictional stresses r_c^* and r_p^* respectively correspond to the coplanar region of the crack and the plastic zone in the familiar isotropic DBCS model. In Eq. (4.58), the newly-introduced scaling prefactors $\alpha[\mathbb{P}]$, $\gamma_c[\mathbb{P}]$ and $\gamma_p[\mathbb{P}]$ incorporate the effects of anisotropy as follows.

First, consider an isotropic material with a shear modulus μ and Poisson ratio ν in which there is an elastoplastic slit crack with a mode II loading; now setting $\alpha^{(2)} = 2\pi(1 - \nu)/\mu$ and taking the limits $\gamma_c[\mathbb{P}] \rightarrow 1$ and

$\gamma_p[\mathbb{P}] \rightarrow 1$, the original isotropic DBCS model is recovered [Bilby, Cottrell, and Swinden (1962)]. Hence the constant $\alpha[\mathbb{P}]$ has dimensions of $[\text{stress}]^{-1}[\text{length}]^{-1}$ as it emerges directly from the stress fields of constituent dislocations; more specifically, $\alpha[\mathbb{P}]$ is related to the anisotropic energy factor of the dislocation. The scaling parameters $\gamma_c[\mathbb{P}]$ and $\gamma_p[\mathbb{P}]$ are dimensionless and provide a means of comparing isotropic values for r_c^* and r_p^* to the frictional stresses experienced by dislocations on different crystallographic planes and in different temperature regimes. While there is no physical reason to assume that $\gamma_c[\mathbb{P}]$ and $\gamma_p[\mathbb{P}]$ would be different, the flexibility to define these independently is retained.

The respective roles of $\alpha[\mathbb{P}]$, $\gamma_c[\mathbb{P}]$ and $\gamma_p[\mathbb{P}]$ are most easily seen by their effects on the dislocation distribution and the plastic zone ratio through a simple parametric study, which can be determined from solving Eq. (4.57) as follows. Using the general inversion theorem for singular integral equations, it can be shown that

$$\begin{aligned}
 B_{\text{DBCS}}(\bar{x}_1) = & - \left[\frac{\alpha[\mathbb{P}](\gamma_p[\mathbb{P}]r_p^* - [\bar{\sigma}_{\text{load}}]_{22})}{\pi^2 b_c} \right] (p^2 c^2 - \bar{x}_1^2)^{1/2} \\
 & \cdot \mathcal{P.V.} \int_{-pc}^{-c} d\bar{x}'_1 \left(\frac{1}{(p^2 c^2 - \bar{x}'_1{}^2)^{1/2}} \frac{1}{\bar{x}'_1 - \bar{x}_1} \right) \\
 & - \left[\frac{\alpha[\mathbb{P}](\gamma_c[\mathbb{P}]r_c^* - [\bar{\sigma}_{\text{load}}]_{22})}{\pi^2 b_c} \right] (p^2 c^2 - \bar{x}_1^2)^{1/2} \\
 & \cdot \mathcal{P.V.} \int_{-c}^{+c} d\bar{x}'_1 \left(\frac{1}{(p^2 c^2 - \bar{x}'_1{}^2)^{1/2}} \frac{1}{\bar{x}'_1 - \bar{x}_1} \right) \\
 & - \left[\frac{\alpha[\mathbb{P}](\gamma_p[\mathbb{P}]r_p^* - [\bar{\sigma}_{\text{load}}]_{22})}{\pi^2 b_c} (p^2 c^2 - \bar{x}_1^2)^{1/2} \right] \\
 & \cdot \mathcal{P.V.} \int_{+c}^{+pc} d\bar{x}'_1 \left(\frac{1}{(p^2 c^2 - \bar{x}'_1{}^2)^{1/2}} \frac{1}{\bar{x}'_1 - \bar{x}_1} \right) \\
 = & \left[\frac{\alpha[\mathbb{P}](\gamma_c[\mathbb{P}]r_c^* - \gamma_p[\mathbb{P}]r_p^*)}{\pi^2 b_c} \right] \ln \left| \frac{\bar{x}_1(p^2 - 1)^{1/2} + (p^2 c^2 - \bar{x}_1^2)^{1/2}}{\bar{x}_1(p^2 - 1)^{1/2} - (p^2 c^2 - \bar{x}_1^2)^{1/2}} \right| \\
 = & \left[\frac{\alpha[\mathbb{P}](\gamma_c[\mathbb{P}]r_c^* - \gamma_p[\mathbb{P}]r_p^*)}{\pi^2 b_c} \right] \cdot \left[\operatorname{arccosh} \left| \frac{1}{p} \left(\frac{p^2 - 1}{(c - \bar{x}_1)} + 1 \right) \right| \right. \\
 & \left. - \operatorname{arccosh} \left| \frac{1}{p} \left(\frac{p^2 - 1}{(c + \bar{x}_1)} + 1 \right) \right| \right], \quad (4.59)
 \end{aligned}$$

where the plastic zone ratio is defined by the mathematical condition that ensures the distribution is bounded at the extent of the plastic zone, that is,

$$p = \frac{1}{\sin \left[\frac{\pi}{2} \left(\frac{-\gamma_p[\mathbb{P}]r_p^* - [\sigma_{\text{load}}]_{22}}{\gamma_c[\mathbb{P}]r_c^* - \gamma_p[\mathbb{P}]r_p^*} \right) \right]}. \quad (4.60)$$

As evident from Eq. (4.59) and Eq. (4.60), the parameters $\gamma_c[\mathbb{P}]$ and $\gamma_p[\mathbb{P}]$ appear both explicitly and implicitly within the distribution via the size of the plastic zone. A simple parametric study of Eq. (4.59) is conducted in **FIG. 4.17** for demonstration purposes; the main result here is that the dislocation distribution is scaled by $\alpha[\mathbb{P}]$, which depends the dislocation class, and it is also parametrised by the dislocation mobility along specific crystallographic planes in the plastic zone whose size varies with $\gamma_c[\mathbb{P}]$ and $\gamma_p[\mathbb{P}]$ [Patel et al. (2018)]. These effects of crystalline anisotropy are not captured by the isotropic DBCS model or even the earlier anisotropic variants of the distributed dislocation technique [Bilby, Cottrell, and Swinden (1962) and Barnett and Asaro (1972)].

In order to apply this theory, it is useful to define $\gamma_p[\mathbb{P}]r_p^*$ as the total frictional resistance to the motion of (real) dislocations in the plastic zone. A typical material specimen would be heterogeneous, containing a rich variety of obstacles that impede dislocations. Accordingly, the choice of the anisotropy parameter $\gamma_p[\mathbb{P}]$ should reflect the texture and obstacle density as well as the loading regime. Consider first a polycrystalline material whose average grain size is larger than $(p-1)c$, that is, the entire plastic zone is confined to a single grain in the low stress regime. In this case $\gamma_p[\mathbb{P}]$ may be directly related to how dislocation motion on a particular crystalline plane is impeded by intrinsic lattice resistances (Peierls-Nabarro stresses) as well as obstacles such as precipitates and other immobile dislocations. Most importantly, $\gamma_p[\mathbb{P}]$ can be different depending on the orientation of the glide plane relative to the loading, with Eq. (4.60) providing the mathematical relationship between the size of the coplanar plastic zone and the effects of anisotropy on the total frictional resistance.

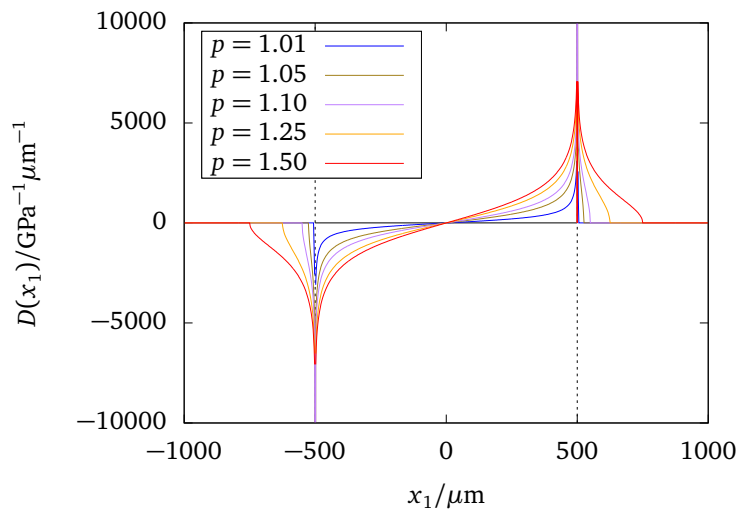
This anisotropic framework is readily applicable to extend the isotropic process zone analysis of DBCS cracks in hexagonal α -Zr by using $\gamma_p[\mathbb{P}]$ to account for the average grain orientation: (i) in the extreme soft texture limit, the $\langle c \rangle$ -direction of every grain is perpendicular to the loading, causing extensive plastic deformation; and (ii) in the extreme hard texture limit, the $\langle c \rangle$ -direction of every grain is parallel to the loading, restricting plastic yield. Therefore, $\gamma_p[\mathbb{P}]$ would be smaller for the $\langle a \rangle$ prismatic slip than for the $\langle a \rangle$ basal slip. Referring to **FIG. 4.17**, this implies that the plastic zones would always be larger for soft texture case as opposed to the hard texture for any loading stress, which agrees with experimental observations [Gong

et al. (2015)]. In practice, the respective values for $\gamma_p[\mathbb{P}]$ can then calibrated to the known physical parameters such as the relative slip strengths.

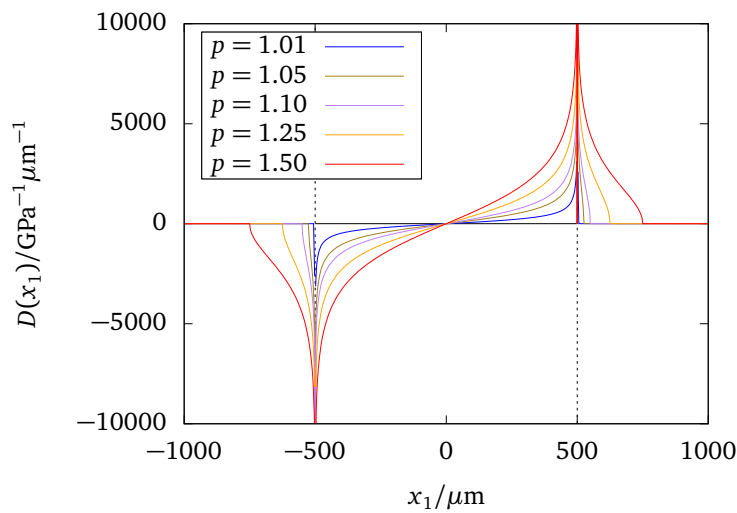
Now consider a polycrystalline material with relatively small grains in which the plastic zone traverses multiple grains in the high stress regime. Here $\gamma_p[\mathbb{P}]r_p^*$ would be dominated by the contribution from grain boundaries. Moreover $\gamma_p[\mathbb{P}]$ would account for the relative mismatch in the orientation of neighbouring anisotropic grains. For certain cases of highly textured materials in which there is a greater compatibility between neighbouring grains, it may be easier for dislocations to cross grain boundaries, and therefore $\gamma_p[\mathbb{P}]$ would be smaller. In applying this to the aforementioned example of DBCS cracks in pure α -Zr, $\gamma_p[\mathbb{P}]$ can be chosen according to Kearns parameters. For highly texture materials ($f_r = 1$ with $f_n = 0$ and $f_t = 0$), the isotropic limit $\gamma_p[\mathbb{P}] \rightarrow 1$ applies for DBCS cracks composed of prismatic dislocations, with r_p^* defining the obstacle strength of grain boundaries. Conversely, for a random weld texture ($f_n = f_r = f_t = 1/3$), the high degree of grain misorientation would make it more difficult for dislocations to travel across grain boundaries; hence $\gamma_p[\mathbb{P}]$ would be larger and the plastic zones would be smaller.

Evidently $\gamma_c[\mathbb{P}]$ and $\gamma_p[\mathbb{P}]$ embed the complexity of anisotropy, and so their role is important in comparing elastoplastic cracks in anisotropic materials. It is equally important to note that $\gamma_c[\mathbb{P}]$ and $\gamma_p[\mathbb{P}]$ are also relevant to two-dimensional plastic zones. Given the apparent difficulties of relating $\gamma_p[\mathbb{P}]r_p^*$ to the climb resistance for tensile cracks, a more realistic geometry for the plastic zone is given by two inclined planes of glide dislocations emanating from each crack tip [Lardner (1975)]. In this paradigm, $\gamma_p[\mathbb{P}]$ would correspond to the glide resistance as opposed to the climb resistance, and therefore $\gamma_p[\mathbb{P}]r_p^*$ is able to provide a more meaningful physical interpretation for tensile cracks in anisotropy [Lardner (1975)].

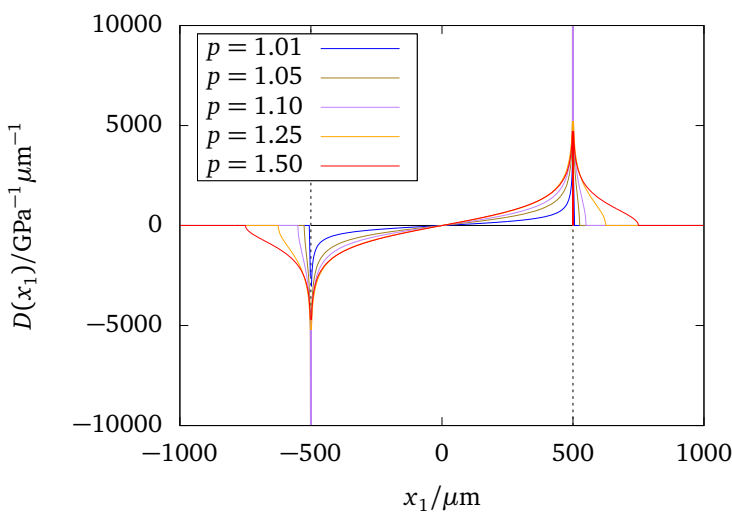
Finally, it is worthwhile to note that $\gamma_p[\mathbb{P}]$ can also incorporate the effects of temperature. It may be that the temperature is too low for the activation of the slip systems necessary for dislocation motion along the coplanar plastic zone. In this instance, the limit $\gamma_p[\mathbb{P}] \rightarrow \infty$ can be applied to Eq. (4.58) to ensure that the crack tip is an impenetrable barrier with $p \rightarrow 1$ as expected. This would apply for the case of slit cracks composed of, say, pyramidal dislocations in α -Zr at low temperatures; there would be no plastic zone and the dislocation distribution would need to be evaluated using the unbounded inversion theorem [Muskhelishvili (1992), Lardner (1975), and Lardner (1970)].



(a)



(b)



(c)

FIG. 4.17

Dislocation distribution functions in anisotropic continua

The anisotropic extension of the Dugdale-Bilby-Cottrell-Swinden dislocation distribution function for an elastoplastic slit crack of length $1000\mu\text{m}$ with various plastic zone sizes in the Zr component. (a) The usual isotropic DBCS model in which the plastic zone size is chosen independently of the dislocation class and slip plane. Here a constant $\alpha[\mathbb{P}]$ is chosen independently of p , which would be mathematically true if dislocations of all classes experienced the same resistive stresses on all crystalline slip planes. (b) and (c) The modified DBCS model in which the anisotropic dislocation distribution scaling is intrinsically related to the material properties; in (b) increasing $\alpha[\mathbb{P}]$ reduces p and in (c) increasing $\alpha[\mathbb{P}]$ increases p , with either case being dependent on the material properties, temperature, crack orientation and plastic zone crystallography.

After configuring $\gamma_c[\mathbb{P}]$ and $\gamma_p[\mathbb{P}]$, the stress state of a DBCS crack can be computed. Using the stress fields for prismatic and basal dislocations, it is straightforward to write down analytical formulae for $\alpha[\mathbb{P}]$ for cracks composed of prismatic and basal dislocations as

$$\alpha[\mathbb{P}] = \begin{cases} 1/\alpha_{22}[(0001)] &= 2\pi(1-\nu)/\mu \\ 1/\alpha_{22}[(10\bar{1}0)] &= 2\pi(S_{11} - S_{13}^2/S_{33}) \cdot \left[\left(\frac{2C_{11}}{C_{33}} \right)^{1/2} - \frac{C_{13}^2 + 2C_{13}C_{44} - C_{11}C_{33}}{C_{33}C_{44}} \right]^{1/2} \end{cases} \quad (4.61)$$

respectively. For these two elastoplastic slit cracks, compact semi-analytical formulae for the stress fields can then be written as

$$\begin{aligned} [\sigma_c]_{11}(x_1, x_2; c, p) &= \int_{-pc}^{pc} d\zeta [B_{\text{DBCS}}(\zeta) \cdot [\sigma_d]_{22}(x_2, \zeta - x_1; b_c)] \\ &= \int_{-pc}^{pc} d\zeta \left[\frac{\alpha[\mathbb{P}](\gamma_c[\mathbb{P}]r_c^* - \gamma_p[\mathbb{P}]r_p^*)}{\pi^2} \right] \cdot \ln \left| \frac{\zeta(p^2 - 1)^{1/2} + (p^2c^2 - \zeta^2)^{1/2}}{\zeta(p^2 - 1)^{1/2} - (p^2c^2 - \zeta^2)^{1/2}} \right| \alpha_{22}[\mathbb{P}] \cdot \\ &\quad \cdot \left[\frac{(\zeta - x_1)(\omega_{22}[\mathbb{P}]x_2^2 + \Omega_{22}[\mathbb{P}](\zeta - x_1)^2)}{x_2^4 + v_{22}[\mathbb{P}]x_2^2(\zeta - x_1)^2 + \Upsilon_{22}[\mathbb{P}](\zeta - x_1)^4} \right] \end{aligned} \quad (4.62a)$$

$$\begin{aligned} [\sigma_c]_{12}(x_1, x_2; c, p) &= \int_{-pc}^{pc} d\zeta [B_{\text{DBCS}}(\zeta) \cdot [\sigma_d]_{12}(x_2, \zeta - x_1; b_c)] \\ &= \int_{-pc}^{pc} d\zeta \left[\frac{\alpha[\mathbb{P}](\gamma_c[\mathbb{P}]r_c^* - \gamma_p[\mathbb{P}]r_p^*)}{\pi^2} \right] \cdot \ln \left| \frac{\zeta(p^2 - 1)^{1/2} + (p^2c^2 - \zeta^2)^{1/2}}{\zeta(p^2 - 1)^{1/2} - (p^2c^2 - \zeta^2)^{1/2}} \right| \alpha_{12}[\mathbb{P}] \cdot \\ &\quad \cdot \left[\frac{x_2(\omega_{12}[\mathbb{P}]x_2^2 + \Omega_{12}[\mathbb{P}](\zeta - x_1)^2)}{x_2^4 + v_{12}[\mathbb{P}]x_2^2(\zeta - x_1)^2 + \Upsilon_{12}[\mathbb{P}](\zeta - x_1)^4} \right] \end{aligned} \quad (4.62b)$$

$$\begin{aligned} [\sigma_c]_{22}(x_1, x_2; c, p) &= \int_{-pc}^{pc} d\zeta [B_{\text{DBCS}}(\zeta) \cdot [\sigma_d]_{11}(x_2, \zeta - x_1; b_c)] \\ &= \int_{-pc}^{pc} d\zeta \left[\frac{\alpha[\mathbb{P}](\gamma_c[\mathbb{P}]r_c^* - \gamma_p[\mathbb{P}]r_p^*)}{\pi^2} \right] \cdot \ln \left| \frac{\zeta(p^2 - 1)^{1/2} + (p^2c^2 - \zeta^2)^{1/2}}{\zeta(p^2 - 1)^{1/2} - (p^2c^2 - \zeta^2)^{1/2}} \right| \alpha_{11}[\mathbb{P}] \cdot \\ &\quad \cdot \left[\frac{(\zeta - x_1)(\omega_{11}[\mathbb{P}]x_2^2 + \Omega_{11}[\mathbb{P}](\zeta - x_1)^2)}{x_2^4 + v_{11}[\mathbb{P}]x_2^2(\zeta - x_1)^2 + \Upsilon_{11}[\mathbb{P}](\zeta - x_1)^4} \right] \end{aligned} \quad (4.62c)$$

These expressions are visualised in [FIG. 4.18](#) and [FIG. 4.19](#).

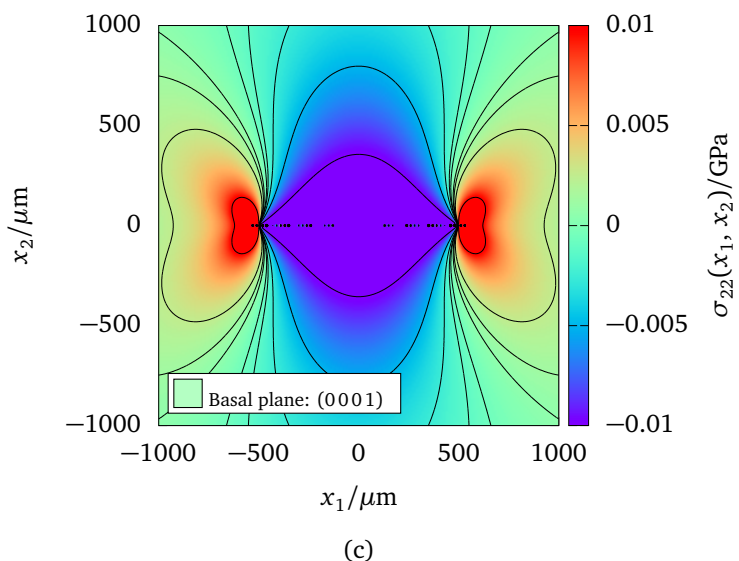
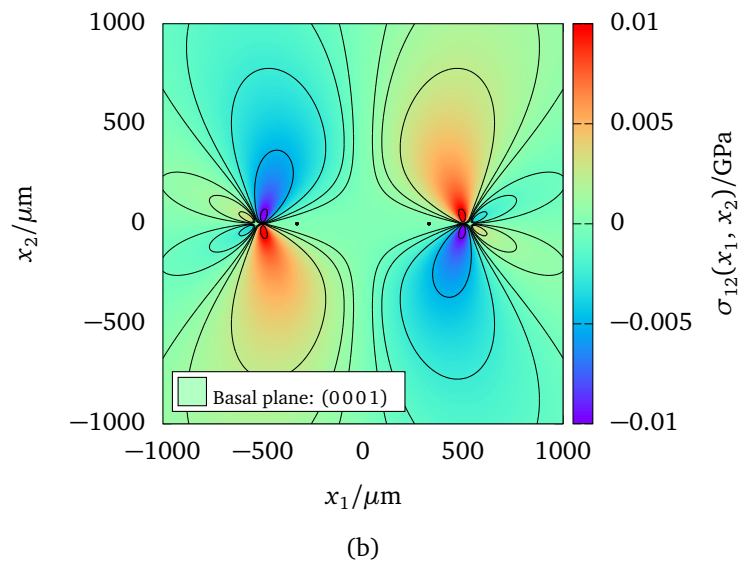
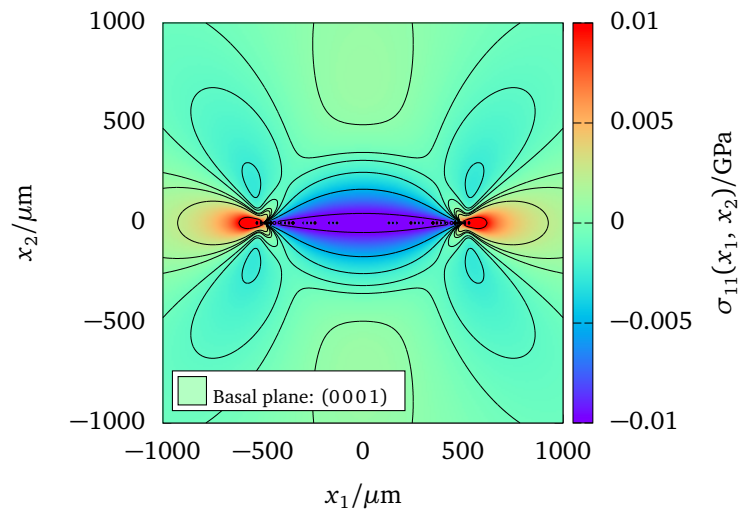


FIG. 4.18

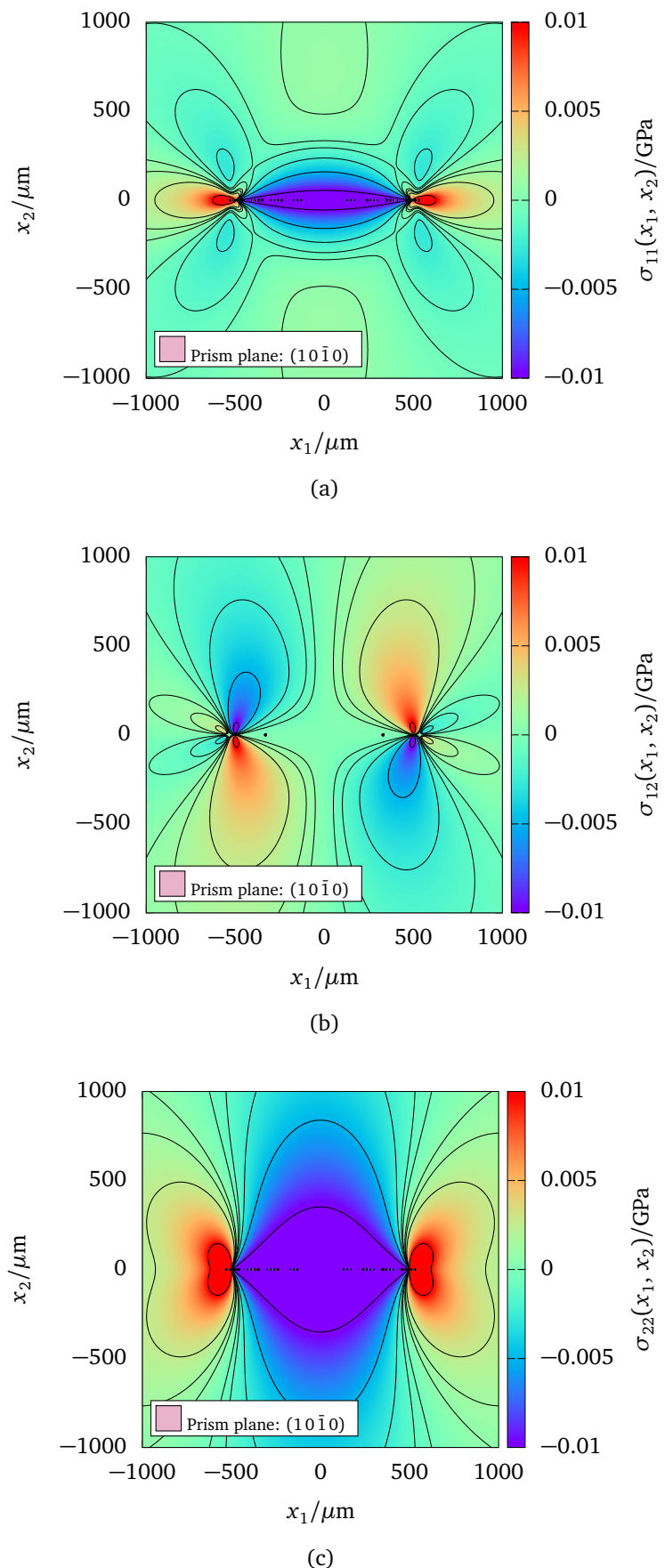
Stress fields of an elastoplastic slit crack whose front is on the basal plane

A DBCS crack with the crack length of $1000\mu\text{m}$, a plastic zone ratio of 1.1 and remote tensile loading of 10 MPa in an infinite continuum with the isotropic elastic properties of Zr. This crack is composed of prismatic dislocations. A cutoff chosen is chosen for both the distribution function and the dislocation core. A simplistic quadrature routine is used to evaluate integrals so the nature of the crack tip singularity is not accurately preserved. Nevertheless, the linear superposition of the dislocation stress fields is clear; the peak stress contours that emanate from the crack tip closely resemble the stress contours of individual dislocations as expected.

FIG. 4.19

Stress fields of an elastoplastic slit crack whose front is on the prism plane

A DBCS crack with the crack length of $1000\mu\text{m}$, a plastic zone ratio of 1.1 and remote tensile loading of 10MPa in an infinite continuum with the anisotropic elastic properties of Zr. This crack is composed of basal dislocations. In comparison to the elastoplastic slit crack composed of prismatic dislocations, the stress fields of this crack appear to be qualitatively different because of the stress fields of the constituent basal dislocations. These stresses are also quantitatively different because of the dislocation distribution scaling factor $\alpha[\mathbb{P}]$ being different for different crystallographic planes. There would generally be other differences due to the variations in the size of the plastic zone but this is not explored here. This is a unique consequence of the anisotropic extension of the DBCS model.



4.5.3 Elliptical Holes

Flaw acuity is a key factor in the DHC initiation threshold, and an elliptical flaw geometry provides one of the simplest quantifiers of sharpness or bluntness through the ratio of the major and minor semi-axes. In the present work, elliptical holes will serve as the primary flaw geometry for developing the bespoke model of simulated flaw-tip H profiles and hydrided microstructures because of its physical relevance, mathematical elegance and computational simplicity. This is in spite of the considerable effort that has been directed towards slit cracks in the previous discussion; the main limitation of the slit crack model is that lone geometrical parameter of the crack length does not permit any variation of the flaw acuity, which leads to very conservative DHC failure estimates.

Consider an infinite continuum containing an elliptical hole with major semi-axis c_1 and minor semi-axis c_2 as shown in FIG. 4.20. As previously stated, it is entirely possible to develop a distributed dislocation model of the stress fields around an elliptical hole but this would require a two-dimensional dislocation distribution function, which leads to an inconvenient numerical representation of the system stress state. It is instead more appropriate to employ the method of complex potentials in the mathematical theory of planar elasticity [Muskhelishvili (1977), Stevenson (1940), Sadd (2005), and Balluffi (2012)].

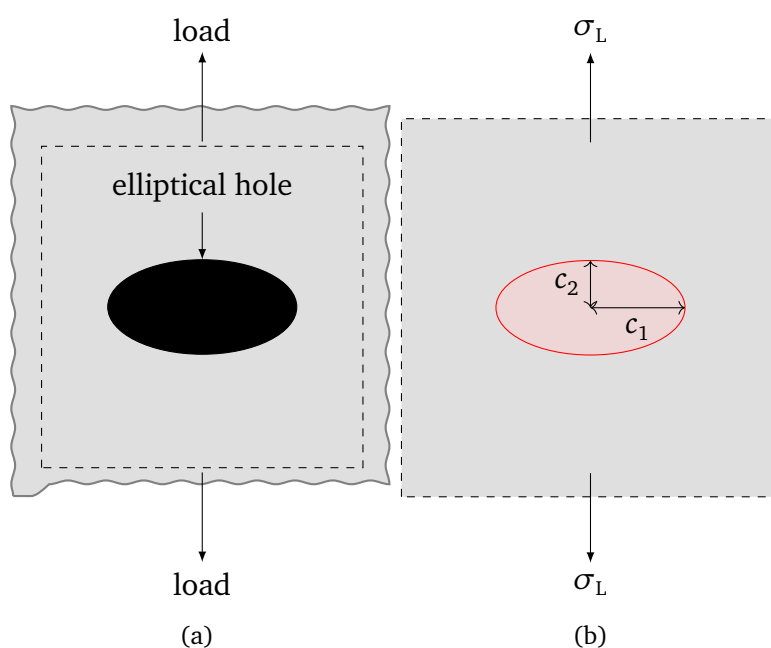


FIG. 4.20

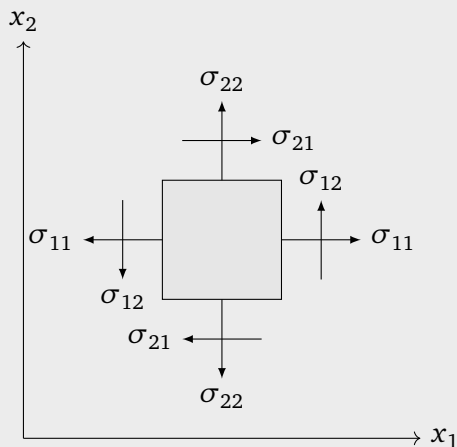
Elliptical hole in an infinite continuum

(a) An elliptical void embedded within an infinite continuum under uniform tension. (b) The geometry of the elliptical defect as specified by the major and minor semi-axes.

FIG. 4.21

Plane strain

The non-zero components of the stress tensor in the planar setting. Note that the σ_{33} component is not usually zero but it is also not independent because it is necessary to satisfy the condition $e_{33} = 0$.



Complex Potentials. Before proceeding with the stress analysis of the elliptical hole, it is worthwhile to establish the method of complex potentials and illustrate examples of practical problems in which the mathematical theory of planar elasticity is a useful theoretical counterpart to the method of elastostatic Green tensor functions. The first case is the case of plane strain. As shown in FIG. 4.21, an elastic continuum is said to be in plane strain parallel to the (x_1, x_2) -plane if (i) the displacement field components $u_1(\mathbf{x})$ and $u_2(\mathbf{x})$ depend only on x_1 and x_2 , and (ii) the displacement field component $u_3(\mathbf{x})$ is zero. The second case is that of an infinitely thin plate, such as a cylindrical disk, undergoing deformation due to coplanar forces.

For a continuum subject to a plane deformation parallel to the (x_1, x_2) -plane, the conditions for mechanical equilibrium explicitly read

$$\sigma_{11,1}(x_1, x_2) + \sigma_{12,2}(x_1, x_2) + f_1(x_1, x_2) = 0, \quad (4.63a)$$

$$\sigma_{21,1}(x_1, x_2) + \sigma_{22,2}(x_1, x_2) + f_2(x_1, x_2) = 0, \quad (4.63b)$$

which are two coupled partial differential equations for three to-be-determined components of the two-dimensional Cauchy stress tensor field. Additionally note that there is one non-trivial equation of compatibility for the plane theory of elasticity:

$$e_{11,22}(x_1, x_2) + e_{22,11}(x_1, x_2) - 2e_{12,12}(x_1, x_2) = 0, \quad (4.64)$$

which simply originates from the definition of the linear strain tensor field for a two-dimensional system.

Under the assumed condition of the absence of body forces, the statement of mechanical equilibrium in the plane theory is tremendously simplified to form

$$\sigma_{11,1}(x_1, x_2) = -\sigma_{12,2}(x_1, x_2) \quad (4.65a)$$

$$\sigma_{21,1}(x_1, x_2) = -\sigma_{22,2}(x_1, x_2). \quad (4.65b)$$

Now, these equations are mathematically equivalent to the necessary and sufficient condition for the existence of representation functions $\alpha(x_1, x_2)$ and $\beta(x_1, x_2)$ respectively such that

$$\alpha_{,1}(x_1, x_2) \stackrel{!}{=} -\sigma_{12}(x_1, x_2) \iff \alpha_{,2}(x_1, x_2) \stackrel{!}{=} \sigma_{11}(x_1, x_2), \quad (4.66a)$$

$$\beta_{,1}(x_1, x_2) \stackrel{!}{=} \sigma_{22}(x_1, x_2) \iff \beta_{,2}(x_1, x_2) \stackrel{!}{=} -\sigma_{12}(x_1, x_2). \quad (4.66b)$$

Note that Eq. (4.66a) and Eq. (4.66b) may be verified by supposing one of two relationships holds and then invoking the equilibrium conditions in Eq. (4.65a) to prove that the other statement is simultaneously true. Comparing Eq. (4.66a) and Eq. (4.66b), it is evident that the two representation

functions are related through

$$\alpha_{,1}(x_1, x_2) = \beta_{,2}(x_1, x_2), \quad (4.67)$$

which in turn implies the existence of yet another representation function $A(x_1, x_2)$ such that

$$\alpha(x_1, x_2) = A_{,2}(x_1, x_2) \iff \beta(x_1, x_2) = A_{,1}(x_1, x_2). \quad (4.68)$$

The unification of the statements in Eq. (4.68) with Eq. (4.66a) and Eq. (4.66b) establishes a crucial result: for the plane theory of elasticity, in the absence of a body force distribution, there exists some scalar function $A(x_1, x_2)$ which encapsulates all of the details of the stress tensor field through the relations

$$\sigma_{11}(x_1, x_2) = +A_{,22}(x_1, x_2), \quad (4.69a)$$

$$\sigma_{12}(x_1, x_2) = -A_{,12}(x_1, x_2) \quad (4.69b)$$

$$\sigma_{22}(x_1, x_2) = +A_{,11}(x_1, x_2). \quad (4.69c)$$

The representation function $A(x_1, x_2)$ is known as the Airy stress function. Since the stress tensor field components $\sigma_{11}(x_1, x_2)$, $\sigma_{12}(x_1, x_2)$ and $\sigma_{22}(x_1, x_2)$ and their second-order derivatives are single-valued and continuous functions in the domain of the continuum, the stress function $A(x_1, x_2)$ must satisfy the following properties: (i) $A(x_1, x_2)$ must have continuous derivatives up to and including the fourth order of differentiation and (ii) $A(x_1, x_2)$ must have single-valued derivatives onwards from the second order of differentiation. If $A(x_1, x_2)$ does indeed fulfil this criterion, then the stress tensor field components defined using the relations in Eq. (4.69a) will satisfy the equilibrium conditions in Eq. (4.65a).

It is important to note that a stress function $A(x_1, x_2)$ that captures the aforementioned relation may not necessarily describe a physically possible deformation that respects the properties of the continuum. Therefore, a physical stress function would have to satisfy additional conditions that also incorporate information on how elastic fields behave in the continuum. In particular, these supplementary details are incorporated by invoking the statement of compatibility in Eq. (4.64) into the definition of a physical stress function through the stress-strain relations for the continuum in question.

In an isotropic continuum, the Hookean stress-strain relations are explicitly given by the following expressions for the components of the strain

tensor field:

$$e_{11}(x_1, x_2) = \frac{1}{2\mu} \left[\sigma_{11}(x_1, x_2) - \frac{\lambda}{2(\lambda + \mu)} (\sigma_{11}(x_1, x_2) + \sigma_{22}(x_1, x_2)) \right], \quad (4.70a)$$

$$e_{22}(x_1, x_2) = \frac{1}{2\mu} \left[\sigma_{22}(x_1, x_2) - \frac{\lambda}{2(\lambda + \mu)} (\sigma_{11}(x_1, x_2) + \sigma_{22}(x_1, x_2)) \right], \quad (4.70b)$$

$$e_{12}(x_1, x_2) = \frac{1}{2\mu} \sigma_{12}(x_1, x_2). \quad (4.70c)$$

Therefore, the statement of compatibility in Eq. (4.64) can be expressed in terms of the stress tensor field components as

$$\sigma_{11,22}(x_1, x_2) + \sigma_{22,11}(x_1, x_2) - 2\sigma_{12,12}(x_1, x_2) - \frac{\lambda}{2(\lambda + \mu)} \nabla^2 (\sigma_{11}(x_1, x_2) + \sigma_{22}(x_1, x_2)) = 0. \quad (4.71)$$

Using the mechanical equilibrium conditions in Eq. (4.65a) to obtain the relation $-2\sigma_{12,12}(x_1, x_2) = \sigma_{11,11}(x_1, x_2) + \sigma_{22,22}(x_1, x_2)$, it is straightforward to simplify Eq. (4.71) to give the crucial result:

$$\nabla^2 (\text{Tr}[\sigma](x_1, x_2)) = 0 \quad \text{with} \quad \text{Tr}[\sigma](x_1, x_2) \equiv \sigma_{11}(x_1, x_2) + \sigma_{22}(x_1, x_2). \quad (4.72)$$

This is the statement that the trace of the two-dimensional stress tensor field is a harmonic function in isotropic elasticity. Following from this result, it is evident from Eq. (4.69a) that the associated stress function satisfies the biharmonic equation

$$\nabla^4 A(x_1, x_2) = 0 \quad \text{with} \quad \nabla^4 \equiv \frac{\partial^4}{\partial x_1^4} + 2 \frac{\partial^4}{\partial x_1^2 \partial x_2^2} + \frac{\partial^4}{\partial x_2^4}, \quad (4.73)$$

where ∇^4 is the biharmonic operator. As an ansatz to the general solution of this fourth-order partial differential equation, consider a new complex variable z that is defined as $z = x_1 + qx_2$ with q being an unknown parameter that would generally depend on the elastic constants. Upon substitution of a generic solution function $\bar{A}(z)$ into Eq. (4.73) leads to the condition

$$(1 + 2q^2 + q^4) \frac{d^4 \bar{A}(z)}{dz^4} \stackrel{!}{=} 0. \quad (4.74)$$

Supposing a non-trivial solution, that is, $\bar{A}(z)$ is not zero everywhere, then it is necessary that q satisfies the quartic algebraic equation $1 + 2q^2 + q^4 = 0$ for which there are degenerate solutions $+i$ and $-i$ that are notably independent of the elastic constants in isotropy. ^{Note 4} The solution may be corrected in spite of the degenerate roots by devising a modified version of Eq. (4.73)

Note 4

Anisotropic extension of the stress function

For the same problem in an anisotropic continuum, the roots would be the solution of a sextic algebraic equation and any degeneracies would reflect the symmetries of the continuum [Ting (1996)].

for which the degeneracy is lifted; that is, each root q is split into $q_{(1)}$ and $q_{(2)}$ and it is possible to write a linear combination of the basic solutions $\bar{A}_{(1)}(x_1 + q_{(1)}x_2)$ and $\bar{A}_{(2)}(x_1 + q_{(2)}x_2)$ respectively. Then the particular solution $[\bar{A}_{(1)}(x_1 + q_{(1)}x_2) - \bar{A}_{(2)}(x_1 + q_{(2)}x_2)]/[q_{(1)} - q_{(2)}]$ in limit of degeneracy $(q_1 - q_2) \rightarrow 0$ implies that a function of the form $x_2 \tilde{A}(z)$ is also a solution and then the general solution to the biharmonic equation is given by

$$A(z) = \Re[\tilde{A}(z) + x_2 \tilde{A}(z)]. \quad (4.75)$$

In the standard notation of planar elasticity theory, the solution in Eq. (4.75) may be written using two complex potentials $Q_{(1)}(z)$ and $Q_{(2)}(z)$ in the conventional format

$$A(z) = \Re \left[\int dz (Q_{(1)}(z)) + z^* Q_{(2)}(z) \right]. \quad (4.76)$$

The potentials may be easily connected to the physical fields of displacement, stress and resultant forces [Muskhelishvili (1977)].

For a certain choice of axes, the biharmonic equation is recovered for transversely isotropic continua [Ting (1996)]. This is most easily seen for a system in which the x_1 - and x_2 -directions are chosen to lie along the basal plane of a hexagonal crystal in which isotropy is preserved. Then the compatibility equations resemble that of the isotropic case except for the prefactors which now include the five independent elastic stiffness constants. Essentially, this is the plane theory of elasticity on the basal plane.

Following the analysis that led to Eq. (4.76) in an isotropic continuum, the fact that the stress function is biharmonic means that it may be deconstructed into an alternate representation through functions of a complex variable as

$$A(x_1, x_2) = \Re[\mathfrak{z}^* \varphi(\mathfrak{z}) + \psi(\mathfrak{z})] \quad \text{with} \quad \mathfrak{z} \equiv x_1 + ix_2, \quad (4.77)$$

where $\varphi(\mathfrak{z})$ and $\psi(\mathfrak{z})$ are the Kolosov-Muskhelishvili complex potentials [Muskhelishvili (1977)]. Through this complex representation, it can be shown that the stress fields satisfy the relations:

$$2 \left[\frac{d\varphi(\mathfrak{z})}{d\mathfrak{z}} + \left(\frac{d\varphi(\mathfrak{z})}{d\mathfrak{z}} \right)^* \right] = \sigma_{11}(x_1, x_2) + \sigma_{22}(x_1, x_2), \quad (4.78a)$$

$$2 \left[\mathfrak{z}^* \frac{d^2 \varphi(\mathfrak{z})}{d\mathfrak{z}^2} + \frac{d\psi(\mathfrak{z})}{d\mathfrak{z}} \right] = -\sigma_{11}(x_1, x_2) + \sigma_{22}(x_1, x_2) + 2i\sigma_{12}(x_1, x_2). \quad (4.78b)$$

In addition it is equally straightforward to relate these complex potentials to the components of the point-wise resultant forces $F(\mathbf{x})$

$$F_1(x_1, x_2) + iF_2(x_1, x_2) = -i \left[\varphi(\mathfrak{z}) + \left(\frac{d\varphi(\mathfrak{z})}{d\mathfrak{z}} \right)^* + \psi^*(\mathfrak{z}) \right] + \text{constant}, \quad (4.79)$$

as well as the displacement vector field $\mathbf{u}(\mathbf{x})$ as

$$u_1(x_1, x_2) + iu_2(x_1, x_2) = \frac{\left[\varphi(\mathfrak{z}) - \left(\frac{d\varphi(\mathfrak{z})}{d\mathfrak{z}} \right)^* - \psi^*(\mathfrak{z}) \right]}{2\mu/(3-4\nu)} \quad (4.80)$$

Given an appropriate set of boundary conditions, these complex potentials can be determined using the technique of analytic continuation in complex variable theory [Muskhelishvili (1977) and Sadd (2005)]. These potentials are typically subject to traction-prescribed boundary value problems; an intuitive ansatz can often be used to deduce the generic form the potentials, and then any unknown prefactors can be determined by imposing the boundary conditions.

It is also worth mentioning that this analysis can be straightforwardly extended to a transversely isotropic or a fully anisotropic continuum using several different mathematical formalisms [Ting (1996)]. However the present work only considers the isotropic continuum in consistency with the industrial models of DHC initiation ahead of a blunt notch feature [Martin (2013)].

Circular Void. In order to demonstrate the capabilities of the complex potential representation of the elastic fields, consider the simpler problem of a circular hole of radius w in an infinite continuum subject to a remote tensile load. This is simply an adaption of the scenario visualised in FIG. 4.20 with $c_1 = c_2 = w$ to define a circle. The generic forms of complex potentials can be deduced by considering the two boundary value problems: (i) the remote loading condition for which the faraway stresses approach the loading values; and (ii) traction-free condition on the free surface that marks the contours of the circular notch. These two boundary conditions lead to the following two requirements:

$$\left. \begin{aligned} \lim_{|\mathfrak{z}| \rightarrow \infty} [\sigma_{\text{CN}}]_{11}(x_1, x_2; w) &= 0 \\ \lim_{|\mathfrak{z}| \rightarrow \infty} [\sigma_{\text{CN}}]_{12}(x_1, x_2; w) &= 0 \\ \lim_{|\mathfrak{z}| \rightarrow \infty} [\sigma_{\text{CN}}]_{22}(x_1, x_2; w) &= \sigma_L \end{aligned} \right\} \quad \text{Remote} \quad (4.81a)$$

$$\left. \begin{aligned} \lim_{|\mathfrak{z}| \rightarrow w} [F_{\text{CN}}]_1(x_1, x_2; w) &= 0 \\ \lim_{|\mathfrak{z}| \rightarrow w} [F_{\text{CN}}]_2(x_1, x_2; w) &= 0 \end{aligned} \right\} \quad \text{Traction} \quad (4.81b)$$

Invoking Eq. (4.78a) and Eq. (4.78b) for the remote loading conditions whilst also applying Eq. (4.79) for the traction-free surface condition, it is

straightforward to show the complex potentials are given by

$$\varphi_{\text{CN}}(\mathfrak{z}; w) = \left(\frac{w\sigma_L}{2} \right) \left[\frac{\mathfrak{z}}{2w} - \frac{w}{\mathfrak{z}} \right], \quad (4.82a)$$

$$\psi_{\text{CN}}(\mathfrak{z}) = \left(\frac{w\sigma_L}{2} \right) \left[\frac{\mathfrak{z}}{w} - \frac{w}{\mathfrak{z}} - \left(\frac{w}{\mathfrak{z}} \right)^3 \right], \quad (4.82b)$$

and it is then straightforward to recycle these expressions back into Eq. (4.78a) and Eq. (4.78b) and rearrange for the components of stress tensor field of the system.

The central point here is again that neat analytical solutions are available for the stress state ahead of a blunt circular notch, and these formulae prove to be incredibly efficient in the mass generation of stress profiles that can be used in computational stress-diffusion analyses. This is worth repeating given that expensive FE simulations are routinely used in industrial models for notch geometries that can be approximated by a circular hole, but there is no inherent benefit as the FE methodologies require numerically solving similar PDEs, albeit with slightly more complicated boundary conditions. There is only one free geometric parameter in this case, namely, the radius of the circle, w , but these potentials are tremendously useful in their own right as a gateway for more complicated hole geometries [Muskhelishvili (1977)].

Elliptical Void. Now consider the problem at hand, as shown in FIG. 4.20, which is the elliptical hole in an infinite continuum under tension from a remote loading force. The previous solution to the circular hole can be transformed to an elliptical hole using conformal mapping.^{Note 5} The relevant conformal map for this problem involves an angle-preserving rescaling of a unit circle on the complex ζ -plane into the desired ellipse on the complex $\mathfrak{z}$ -plane, which is given by

$$\begin{aligned} \mathfrak{C} : \zeta \mapsto \mathfrak{z} \quad \text{with} \quad \mathfrak{z}(\zeta) &= \mathfrak{C}(\zeta) \\ &= \left(\frac{c_1 + c_2}{2} \right) \left[\zeta + \left(\frac{c_1 - c_2}{2\zeta} \right) \right] \end{aligned} \quad (4.83)$$

Noting that $\varphi_{\text{EN}}(\mathfrak{z}) = \varphi_{\text{EN}}(\mathfrak{C}(\zeta))$ and $\psi_{\text{EN}}(\mathfrak{z}) = \psi_{\text{EN}}(\mathfrak{C}(\zeta))$, the chain rule of differentiation provides the relationships

$$\frac{d\varphi_{\text{EN}}(\mathfrak{z})}{d\mathfrak{z}} = \frac{d\varphi_{\text{EN}}(\mathfrak{C}(\zeta))}{d\zeta} \bigg/ \frac{d\mathfrak{C}(\zeta)}{d\zeta}, \quad (4.84a)$$

$$\frac{d\psi_{\text{EN}}(\mathfrak{z})}{d\mathfrak{z}} = \frac{d\psi_{\text{EN}}(\mathfrak{C}(\zeta))}{d\zeta} \bigg/ \frac{d\mathfrak{C}(\zeta)}{d\zeta}, \quad (4.84b)$$

which can be substituted in the aforementioned boundary conditions for the remote loading and the traction free surface to yield the complex potentials

Note 5

Conformal mapping

In complex analysis, conformal maps are an important class of angle-preserving transformations. In the elasticity theory of fracture, the application of conformal mapping to circles is a powerful technique to obtain elastic fields [Muskhelishvili (1977) and Smirnov (1964)].

for the elliptical hole:

$$\varphi_{\text{EN}}(\zeta; c_1, c_2) = \frac{1}{4}\sigma_L \left(\frac{c_1 + c_2}{2} \right) \left[- \left(2 + \frac{c_1 + c_2}{c_1 - c_2} \right) \frac{1}{\zeta} + \zeta \right] \quad (4.85a)$$

$$\begin{aligned} \psi_{\text{EN}}(\zeta; c_1, c_2) = \frac{1}{4}\sigma_L \left(\frac{c_1 + c_2}{2} \right) & \left[\left(\frac{c_1 - c_2}{c_1 + c_2} \right) \frac{1}{\zeta} + \zeta - \frac{c_1 + c_2}{c_1 - c_2} \right. \\ & \left. \cdot \left(1 + \frac{(c_1 - c_2)^2}{(c_1 + c_2)^2} \right) \left(1 + \frac{c_1 - c_2}{c_1 + c_2} \right) \left(\frac{\zeta}{\zeta^2 - \frac{c_1 - c_2}{c_1 + c_2}} \right) \right] \end{aligned} \quad (4.85b)$$

As before, the stress fields can easily be computed using these potentials. Again it is worth commenting on the elegance of the analytical expressions. Now there are two geometrical parameters, the major and minor semi-axes as represented by c_1 and c_2 respectively. It is now possible to simulate the simplest effects of notch acuity through the changes in the stress profile as a function of the ratio, c_2/c_1 , which will henceforth serve the main template for most subsequent calculations.

As visualised in [FIG. 4.22](#), the opening stress tensor field component bears a striking resemblance to the corresponding fields for the elastic slit crack as modelled using the distributed dislocation technique. This similarity is most obvious in the extreme limit of the ratio c_2/c_1 approaching zero for the elliptical notch nears the geometry of a thin line. As c_2 increases and the notch becomes larger, it is also clear that the areal size of tensile region, as marked by a particular contour, also grows. This point will prove crucial in later explanations of how the size of hydrided zones may be influenced by notch acuity.

In order to model the hydrides ahead of this notch, it is necessary that stress fields generated around the Volterra dislocations used to represent the micro-hydride needles are also corrected in accordance with the traction-free criterion. These corrections are addressed in a later discussion.

Of course, it must also be stated there are several avenues for extending these results to the transversely isotropic continuum. As previously stated, there are several well known mathematical formalisms that generalise the method of complex potential to anisotropic continua [[Ting \(1996\)](#)]. But another more nuanced approach would be to determine the dislocation distribution function that replicates the results in [FIG. 4.22](#), and then apply the rescaling technique as discussed in the preceding section.

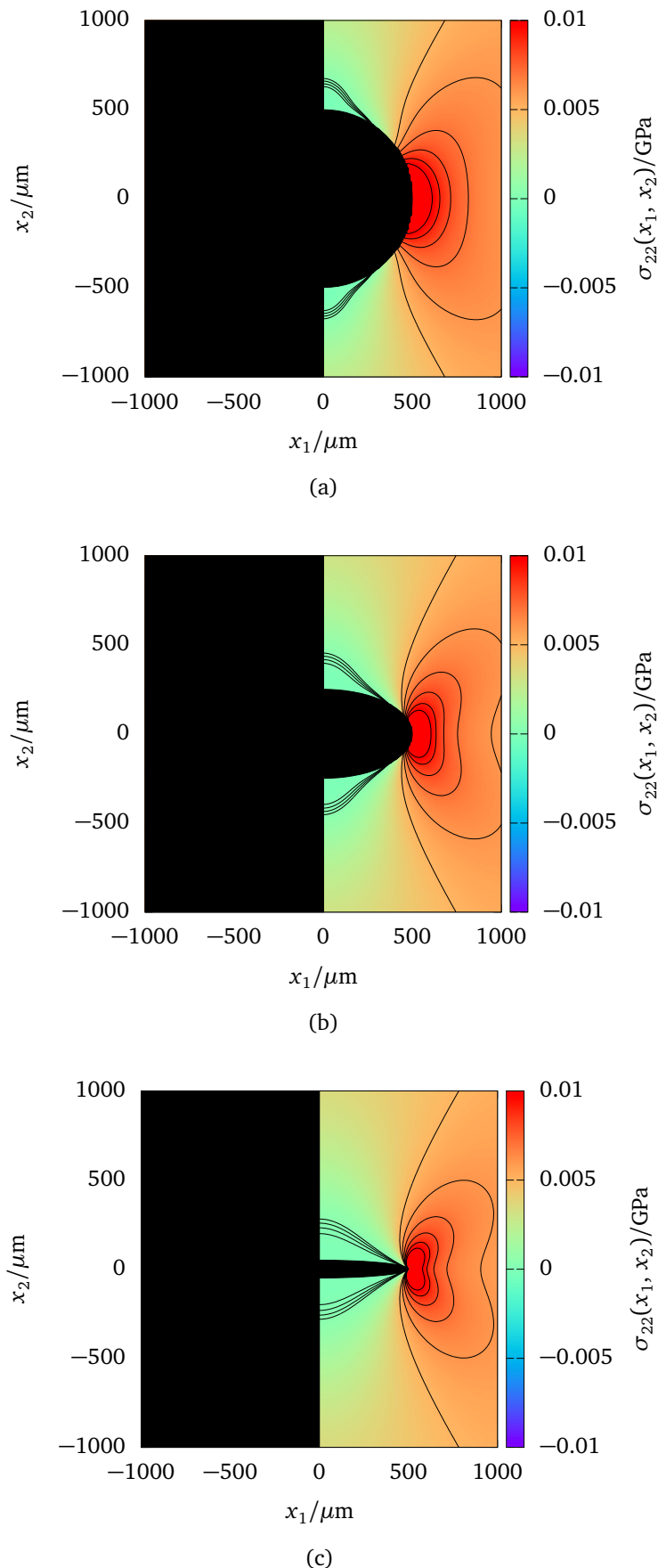


FIG. 4.22

Stress fields of an elliptical notch

The opening stress field around an elliptical hole in an infinite continuum subject to a remote tensile load of 5 MPa with the major semi-axis $c_1 = 500 \mu\text{m}$ and varying minor semi-axis. (a) $c_2 = 450 \mu\text{m}$ which is very close to the circular geometry. (b) $c_2 = 250 \mu\text{m}$, which is an intermediate case that is perhaps more representative of typical notch geometries that would be of interest in the nuclear industry. (c) $c_2 = 50 \mu\text{m}$ which is the extreme sharp geometry case. It is clear that as the notch approaches the extreme sharp geometry case, the stress profile approaches that of the elastic slit crack as modelled using the distributed dislocation technique. Note that half-space corrections are not made for the generation of these particular profiles but such corrections are straightforward to implement if necessary.

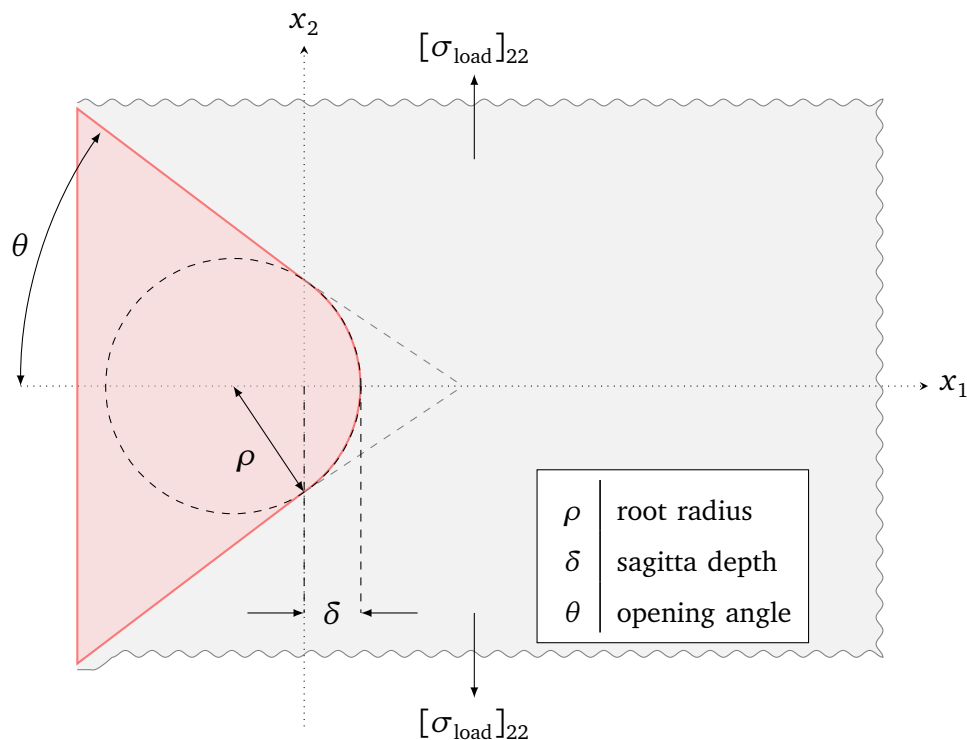
4.5.4 V-Notches

The remainder of this investigation will use the elliptical hole as the primary notch geometry for developing and testing the essential features of the multiscale model of DHC because it is a simple but powerful starting point. However, a fitting conclusion to the mathematical labours of the preceeding discussions would naturally be a preview of a more complicated notch geometry. The V-notch is one such geometry that is of great industrial concern [Schofield (2002)]. This demonstration of the method of complex potentials to the V-notch is depicted in FIG. 4.23, although it is worth noting that there are other ways of mathematically describing the geometry of a V-notch.

Curvilinear coordinate transformations can be used to approximate the V-notch geometry, which has been outlined in earlier studies that use the method of complex potentials to reproduce FE simulations of the stress profile around the same non-trivial notch geometries [Lazzarin and Tovo (1996) and Filippi, Lazzarin, and Tovo (2002)]. For brevity, these known results are summarised here through the mathematical expressions and the corresponding parameters in TAB. 4.2 and a visualisation of the stress fields in FIG. 4.24 which certainly resemble those of the elliptical hole. Generalisations to anisotropy may also be considered in the same vein as before.

FIG. 4.23

A geometrical representation of a V-Notch
A standard V-shape notch as defined by the opening (flank) angle, root radius and sagitta depth. These three geometrical parameters are not entirely independent in the complex potential representation because the curvilinear coordinate transformation that approximates this geometry interconnects these parameters through a set of simultaneous equations. As before, the V-notch is in an infinite continuum that is subject to a remote tensile load.



The complex potentials for the V-notch described can be obtained using a curvilinear coordinate transformation that approximates the geometry of the V-notch. These potentials take the rather simple form

$$\varphi_{VN}(z) = J_1 z^{Y_1} + J_3 z^{Y_2} \quad \text{and} \quad \psi_{VN}(z) = J_2 z^{Y_1} + J_4 z^{Y_2}, \quad (4.86)$$

where the to-be-determined coefficients, which embed the notch geometry as well as material dependence and loading conditions, are given by

$$\left. \begin{aligned} J_1 &= \frac{\sigma_{\max}}{Y_1 \delta^{(Y_1-1)} \left\{ 1 + Y_1 + \chi_2(1-Y_1) + \left(\frac{\pi-\theta}{2\pi} \right) \left[(1+Y_2)\chi_4 + \chi_3 \right] \left(\frac{\pi}{\pi-2\theta} \right) \right\}} \\ J_2 &= \chi_2(1-Y_1)J_1 \\ J_3 &= \left(\frac{\pi-\theta}{2(\pi-2\theta)} \right) \left(\frac{\chi_3}{Y_2} \right) J_1 \delta^{(Y_1-Y_2)} \\ J_4 &= \left(\frac{\pi-\theta}{2(\pi-2\theta)} \right) \left(\frac{\chi_4}{Y_2} \right) J_1 \delta^{(Y_1-Y_2)} \end{aligned} \right\} \quad (4.87a)$$

$$\left. \begin{aligned} \chi_2 &= \sin[(1-Y_1)(\pi-\theta)] / \sin[(1+Y_1)(\pi-\theta)] \\ \chi_3 &= \left[(1-Y_2)^2 - \frac{\pi}{2(\pi-\theta)}(1+Y_2) \right] \cdot \left[(3-Y_1) - \chi_2(1-Y_1) - (3-Y_2)\varpi \right] \\ \chi_4 &= \frac{\pi}{2(\pi-\theta)} \left(1 - \frac{2(\pi-\theta)}{\pi} \right) \cdot \left[3 - Y_1 - \chi_2(1-Y_2) \right] - \varpi \end{aligned} \right\} \quad (4.87b)$$

$$\begin{aligned} \varpi &= (1-Y_1)^2 + \chi_2(1-Y_1)^2 \\ &\quad - \left(\frac{\pi}{2(\pi-\theta)} \right) \left[(1-Y_1) - \chi_2(1-Y_2) \right] \end{aligned} \quad (4.87c)$$

These coefficients and exponents are tabulated in **TAB. 4.2**, and such a look-up table can be easily completed for later referencing using a series of one-off (one-time) numerical computations.

Flank Angle	Y_1	Y_2	χ_2	χ_3	χ_4	Notes
0	+0.5000	-0.5000	1.0000	4.0000	0.0000	
$\pi/6$	+0.5014	-0.4561	1.0707	3.7907	0.0632	
$\pi/4$	+0.5050	-0.4319	1.1656	3.5721	0.0828	
$\pi/3$	+0.5122	-0.4057	1.3123	3.2832	0.0960	
$\pi/2$	+0.5448	-0.3449	1.8414	2.5057	0.1046	
$2\pi/3$	+0.6157	-0.2678	3.0027	1.5150	0.0871	
$3\pi/4$	+0.6737	-0.2198	4.1530	0.9933	0.0673	
$5\pi/6$	+0.7520	-0.1624	6.3617	0.5137	0.0413	

TAB. 4.2

Complex potential parameters for the elastic fields of the V-notch

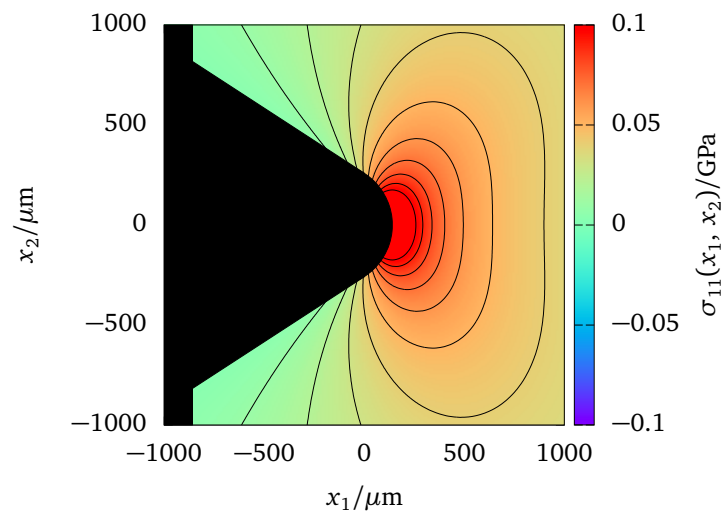
A tabulation of the key parameters, coefficients and exponents required for efficiently computing the stress fields of various V-notch geometries. These parameters are obtained numerically from solving self-consistency equations on a one-off basis, which is the main strength of analytical formulae in elasticity theory.

Adapted from [Filippi, Lazzarin, and Tovo \(2002\)](#).

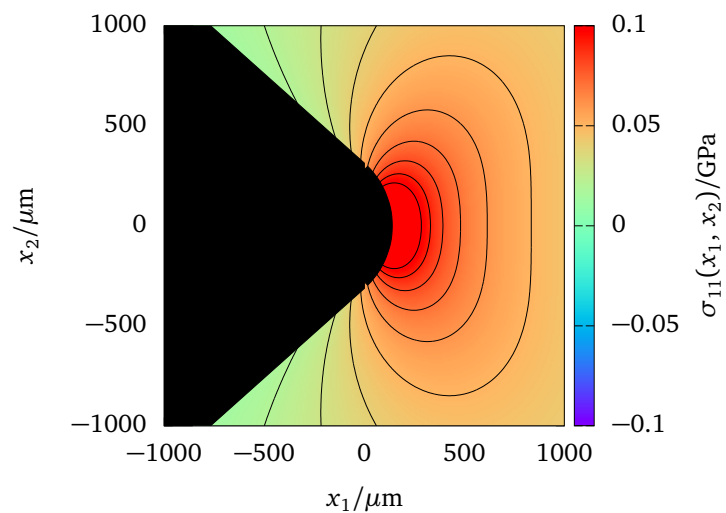
FIG. 4.24

The stress fields around a V-notch

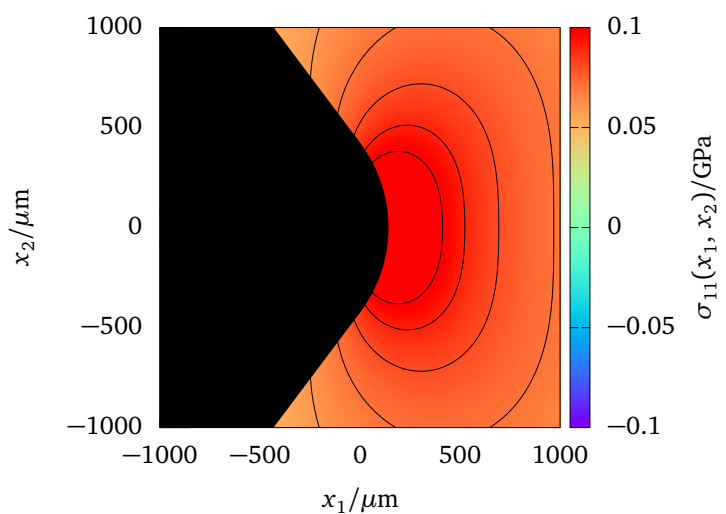
The opening stress state around V-notches in an infinite continuum subject to a remote tensile load. The sagitta depth is kept constant whilst the flank angle (and accordingly the root radius) are altered to give different notch geometries. It is worth noticing that all three notch geometries yield stress states whose contours resemble those of the slit crack or the elliptical hole. In addition, there is a geometrical optimisation that occurs when the geometrical parameters that define the V-notch are varied. It appears that there is an optimal choice of flank angle for which the tensile region ahead of the notch is the greatest in areal size for a fixed sagitta depth. The V-notch is more complicated than necessary given that the elliptical hole can play the same role as the V-notch but with fewer geometrical parameters. Therefore, given that the slit crack offers a restrictive set of flaw acuities, the elliptical hole is the obvious choice in developing a model of the flaw-tip H profile and hydride microstructures due to its geometric simplicity; the slit crack and V-notch geometries can be described in terms of special cases of the elliptical hole.



(a)



(b)



(c)

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5

Stress-Diffusion Analysis

Chapter Overview

The second module of this hybrid multiscale model of DHC is an extension of the theory of stress-driven diffusion to an anisotropic heterogeneous system. This generalisation serves as the blueprint for modelling the long-range transport of H interstitials to SCFs in polycrystalline Zr alloy components whilst accounting for the hexagonal crystallography. This paradigm is referred to as the stress-diffusion analysis for the sake of brevity, and it builds on top of the stress analysis. This chapter establishes the theoretical foundation of anisotropic stress-driven diffusion at the atomic and continuum scales, and the strategy to bridge these two length scales using the elastic dipole tensor. It will become clear that the stress fields around higher-dimensional defects in anisotropic continua can be analytically converted into H profiles that represent the steady state equilibrium limit of the diffusion kinetics.

It is worthwhile to begin this discussion by introducing some standard concepts that underpin the theory of atomic diffusion in crystalline solids, which can then be used to motivate the necessary modifications that are required to incorporate the effects of a non-uniform stress distribution as well as crystalline anisotropy and polycrystalline heterogeneity. Diffusive transport of an atomic species in a crystalline solid is generally divided into two basic categories: (i) vacancy diffusion in which the diffusing species moves between lattice sites; or (ii) interstitial diffusion in which the diffusing species moves between non-lattice sites. For the purpose of this work, it is assumed that H is the sole diffusing species and that the long-range transport of H atoms occurs via an interstitial mechanism [Puls (2012), Coleman (2003), and McRae, Coleman, and Leitch (2010)]. The latter assumption is sensible in regions of the Zr matrix where the regular arrangement of Zr atoms is more or less undisturbed, that is, sufficiently far away from higher-dimensional defects.

In the context of classical transition state theory, —that is, a system in which the probability of quantum mechanical tunnelling through a potential barrier vanishes completely when the energy is insufficient to surmount it—

, a typical diffusive hop of a H interstitial in the Zr matrix can be simplified into three stages [Eyring (1935) and Balluffi, Allen, and Carter (2005)]. In the first or initial stage, the H atom occupies a tetrahedral site where it forms three equivalent bonds with the Zr atoms on the basal plane and one non-equivalent bond with the Zr atom along the basal pole; this is understood to be a local equilibrium state for the H atom. In the second or transition stage, the H atom is displaced from its equilibrium position after receiving energy from small-amplitude lattice vibrations of Zr atoms; such lattice vibrations are a manifestation of the thermal energy and this is the origin of the temperature dependence of the diffusive hops. In the third or final stage, the H atom experiences restoring forces as the bonds between itself and the Zr atoms are stretched or even broken; the associated energy cost provides an energy barrier that must be overcome for the diffusive hop to be successful. If the thermal energy transferred to the H atom is enough to surmount the energy barrier, the H atom successfully completes the transition to a new equilibrium state in an adjacent tetrahedral site.

It is the transition energy barrier that contains information of the non-uniform stress distribution as well as the crystalline anisotropy and polycrystalline heterogeneity. For example, the energy barrier is typically lower if the H atom transitions from a compressive site in which the Zr atoms are closer together to a tensile site in which the Zr atoms are further apart. In this way, the H atom would migrate along a gradient of stress whereby successive sites become more tensile and the transition energy barriers become lower. Here, the stress gradient is said to provide a bias that governs the diffusive hops. (This bias effect is also observed in the presence of other gradients such as temperature and electric fields.) Similarly, the energy barrier may be lower along certain crystallographic directions as opposed to others because of the anisotropic atomic environment of the H interstitial, and this is also how the heterogeneous microstructure could bias H diffusion. This complexity of stress gradients, anisotropy and heterogeneity to the H diffusion path is encapsulated by the dividing hypersurface that distinguishes the initial and final states in the configuration space of the surrounding Zr atoms. But a statistical computation of these dividing hypersurfaces is beyond the current capabilities of any first-principles methodology. Therefore, it is impractical to describe H diffusion in Zr entirely within the domain of atomic scale modelling.

An altogether different approach is then required to adapt the atomic scale effects of stress gradients, anisotropy and heterogeneity into the continuum scale description of H diffusion in the Zr alloy component. At the continuum scale, the kinetics of diffusion are most commonly described using a PDE whose solution gives the spatial and temporal dependence of the

concentration of the diffusing species [Crank (1979) and Balluffi, Allen, and Carter (2005)]. This PDE is the well known diffusion equation, and it is classified as a parabolic second-order linear PDE in its standard form. There are two widely used mathematical strategies for deriving this PDE, namely, the random walk and the continuity principle. The random walk supposes a discrete Markovian process and it involves evaluating the probability of the walker at a given position and time; the diffusion equation is recovered upon taking the continuum limit [Chandrasekhar (1943)]. The continuity principle is most simply an application of the divergence theorem in conjunction with a constitutive relationship between the concentration and its flux; the constitutive relationship is the basis of Fick's first law and its substitution into the continuity principle results in the diffusion equation, which is Fick's second law [Balluffi, Allen, and Carter (2005)].

Both mathematical strategies eventually lead to the same basic diffusion equation but they provide different perspectives on the diffusion mechanism. In order to extend the diffusion equation to incorporate the effects of stress gradients, anisotropy and heterogeneity, it is important to understand how these two strategies can be modified. In the following, two such modifications are considered. Firstly, the random walk is modified to account for generic biases, which will provide a key insight into what additional terms appear in the PDE for diffusion in the presence of a bias. Secondly, Fick's laws are modified within the framework of linear irreversible thermodynamics to construct a generalised diffusion potential that includes the elastic interaction energy and hence accounts for the stress gradients, crystalline anisotropy and polycrystalline heterogeneity [Patel (2014) and Patel et al. (2018)].

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5.1 Biased Random Walk

In order to understand the mathematical basis for stress-driven diffusion in an anisotropic heterogeneous medium, it is useful to begin with the more simpler problem of a one-dimensional random walk in which the walker represents a mobile solute atom as it transitions between interstitial sites that are positioned between solvent atoms. At this level of description, the effects of stress, anisotropy and heterogeneity can be collectively thought of as biases that influence the otherwise random steps of the walker. The aim here is formulate a probabilistic relationship for the discretised transition steps of the walker, and then take the continuum limit in order to transform this relationship into a PDE for the diffusive motion of the solute species.

In order to proceed with this analysis, several assumptions are required for two primary reasons: (i) to provide a more accurate but simplified treatment of H diffusion in Zr that accounts for the nuances of the early stages of DHC failure; and (ii) to facilitate the mathematical derivations and the subsequent computational implementation in a manner that is befitting to theme of efficiency. The first assumption concerns the small or linear strain regime, which carries over from the previous discussion on stress analysis; the great benefit of this assumption is that the spacing between solvent atoms is more or less the same in a given direction, that is, the interstitial sites are positioned at regular intervals along a particular crystallographic direction. The second assumption concerns the irregularity of the time intervals between the transition steps; this atomic scale stochasticism can be subsumed into an effective diffusion constant that conveys this regularisation through an average time step. The third assumption concerns the Markovian nature of this process, that is, the walker retains no memory of the sequence of steps; this ultimately means that the evolution of the H concentration profile is entirely deterministic because the probabilities of outcomes is identical for any given realisation of the initial state. The final assumption concerns the dilute concentration limit that imposes another layer of linearity that follows on the first assumption; the diffusing H atoms do not interact elastostatically (or electrostatically as they are charged anions) with each other, which is reflected in the ensemble motion of the walkers that has no pre-emptive effect on the individual motion of the walkers. Evidently, the first and final assumption do indeed work well together at distances that are sufficiently far away from stress sources such as dislocation cores, grain boundaries and flaw tips where the H concentration is dilute. But this theory breaks down at these potential nucleation sites, which is worth noting in lieu of later discussions on the diffusion-precipitation analysis.

Adopting these assumptions, the one-dimensional biased random walk

can be mathematically formalised as follows. Over time t , a diffusing solute atom completes a series of transitions between adjacent interstitial sites between solvent atoms as it moves along the x_1 direction. Suppose that the interstices are located at a set of specific positions, $\{\chi_n | n \in \mathbb{Z}\}$, where $\chi_n = n\Delta\chi$, that is, the interstices are separated by a regular spatial interval, $\Delta\chi$, as per the assumptions. This configuration is visualised in **FIG. 5.1**, which shows a generic system as well as the reduced approximations in the one-dimensional setting. In addition, suppose that the transitions occur after successive time steps, $\{\tau_k | k \in \mathbb{N}\}$, where $\tau_k = k\Delta\tau$ and that the transitional time interval, $\Delta\tau$, is an average measure that can be related to the macroscopic diffusivity coefficient.

In the most generic configuration, the diffusing solute atom is initially positioned at χ_0 at a time τ_0 , and after some time interval $(\tau_1 - \tau_0)$ it will transition to one of the two neighbouring sites that are located at positions $\chi_{\pm 1}$ with some respective probabilities, $p_{\pm}(\chi_0)$, for either possibility. Considering the sequence of steps taken for the diffusing solute atom to be situated at the position χ_n at time τ_k , it is straightforward to write down a recursion relation for the probability that the solute occupies this position at this time, denoted $C[\chi_n, \tau_k]$, as

$$C[\chi_n, \tau_k] = p_+(\chi_{n-1})C[\chi_{n-1}, \tau_{k-1}] + p_-(\chi_{n+1})C[\chi_{n+1}, \tau_{k-1}]. \quad (5.1)$$

This is a central mathematical relationship for the treatment of stress-driven diffusion of a solute in a stressed anisotropic heterogeneous crystalline material. In the approximated case that the interstitial sites are equally spaced along a given crystallographic direction and that transitions occur at regular time intervals, the probability prefactors $p_{\pm}(\chi_n)$ fully incorporate the effects of stress and heterogeneity; in the multi-dimensional equivalent of Eq. (5.1), the probability prefactors would also incorporate the effects of anisotropy. The computational application of Eq. (5.1) is cumbersome. Instead it is more appropriate to convert this recursion relationship into a PDE by first replacing the discrete variables $\{\chi_n, \tau_k\}$ with their continuum analogs $\{x_1, t\}$, and then performing a double Taylor series expansion to obtain a diffusion equation. The physical material parameters in this diffusion equation are defined by carefully applying the limits $\Delta\chi \rightarrow 0$ and $\Delta\tau \rightarrow 0$ to the series expansion coefficients.

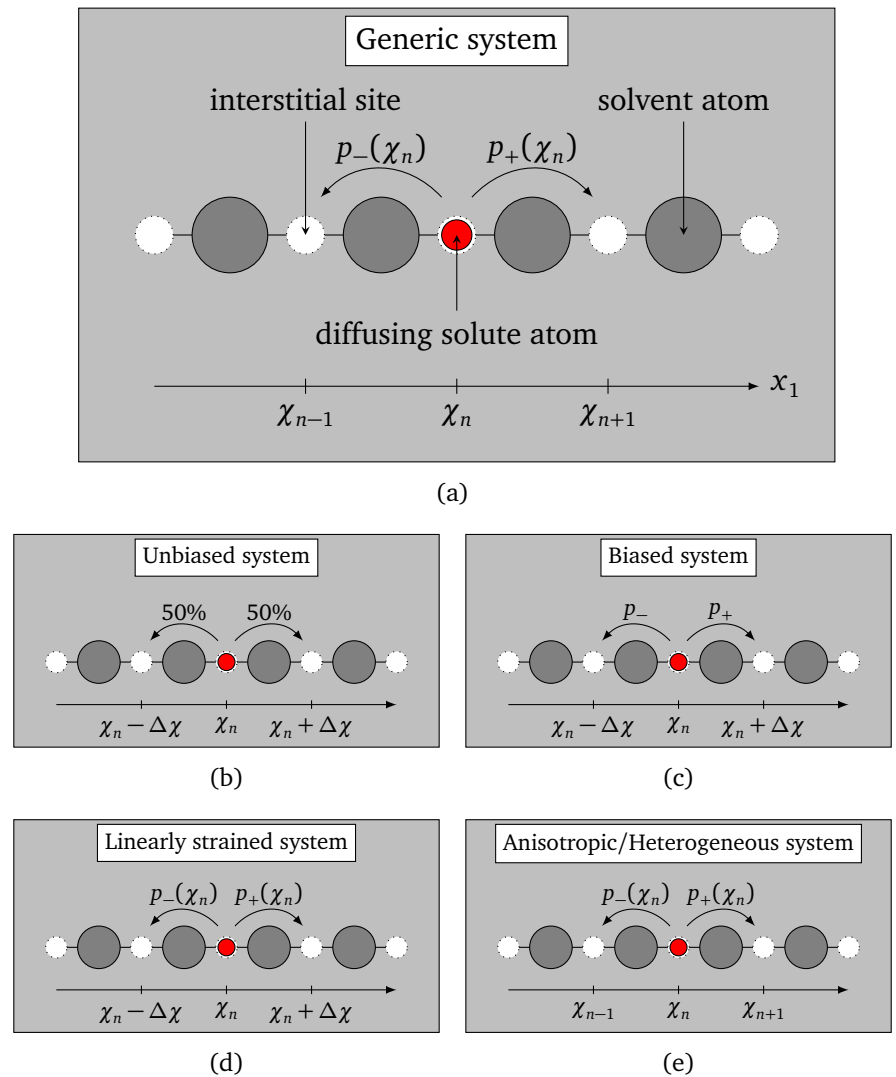
Unbiased System. In this case, the solute atom moves in either direction with equal probabilities, that is, the probability prefactors both equate to $1/2$ and so Eq. (5.1) takes on its simplest form

$$C(x_1, t) = \frac{1}{2}C(x_1 - \Delta\chi, t - \Delta\tau) + \frac{1}{2}C(x_1 + \Delta\chi, t - \Delta\tau). \quad (5.2)$$

FIG. 5.1

Biased random walk model

A one-dimensional representation of atomic scale interstitial diffusion as the transitions undertaken by a diffusing solute atom. (a) In the most generic case of a stressed, anisotropic, heterogeneous system, the interstitial sites are not uniformly distributed and the transition probabilities vary from site to site. (b) In the completely unbiased system, the interstitial sites are uniformly distributed and the diffusing solute atom can transition left or right with equal probabilities. (c) In the globally biased system, an external bias influences every transition in the same way even though the interstitial sites are uniformly distributed, and so the diffusing solute atom tends move in the direction of probabilistic favourability. (d) In the linearly strained system, the interstitial sites are approximated to be uniformly distributed but there is a local bias due to the stress profile. (e) In the heterogeneous system, the interstitial sites are generally not uniformly distributed and so there is also a local bias. In the anisotropic extension of this case, there is also directional bias.



Following the Taylor series expansion and the taking of limits, this recursion relation becomes the well known diffusion equation

$$\frac{\partial C(x_1, t)}{\partial t} = \left[\lim_{\substack{\Delta\chi \rightarrow 0 \\ \Delta\tau \rightarrow 0}} \left(\frac{\Delta\chi^2}{2\Delta\tau} \right) \right] \frac{\partial^2 C(x_1, t)}{\partial x_1^2}, \quad (5.3)$$

where the coefficient on the RHS is identified as the diffusivity. In Eq. (5.3), the only physical parameter is this diffusivity constant; it serves as an average or effective measure that can be fitted according to the microstructure as well as the temperature and the loading conditions. However, Eq. (5.3) is not adequate for the problem at hand because its solution will be independent of the stress profile.

Biased System. In this case, the solute atom moves preferentially in the direction of a global bias set by the unequal probabilities $p_+ \lessgtr p_-$, and so

Eq. (5.1) reduces to the form

$$C(x_1, t) = p_+ C(x_1 - \Delta\chi, t - \Delta\tau) + p_- C(x_1 + \Delta\chi, t - \Delta\tau). \quad (5.4)$$

Noting that $p_+ + p_- = 1$ and defining $\Delta p = p_+ - p_-$, this recursion relation becomes the biased diffusion equation

$$\begin{aligned} \frac{\partial C(x_1, t)}{\partial t} = & \left[\lim_{\substack{\Delta\chi \rightarrow 0 \\ \Delta\tau \rightarrow 0 \\ \Delta p \rightarrow 0}} \left(\frac{\Delta p \Delta\chi}{\Delta\tau} \right) \right] \frac{\partial C(x_1, t)}{\partial x_1} \\ & + \left[\lim_{\substack{\Delta\chi \rightarrow 0 \\ \Delta\tau \rightarrow 0}} \left(\frac{\Delta\chi^2}{2\Delta\tau} \right) \right] \frac{\partial^2 C(x_1, t)}{\partial x_1^2}, \end{aligned} \quad (5.5)$$

where the coefficient in the first term on the RHS corresponds to the small but constant drift velocity that influences the diffusion process. In Eq. (5.5), this additional drift parameter provides a very simplistic description of any global biases in the system. However, the absence of any spatial variation in this drift is a major limitation because it does not capture the effects of non-uniform stress gradients.

Linearly Strained System. In this case, the solute moves preferentially in the direction of the bias at a given interstitial site, that is, the inequality of the transition probabilities varies with the local environment. Now Eq. (5.1) reduces to the form

$$\begin{aligned} C(x_1, t) = & p_+(x_1 - \Delta\chi) C(x_1 - \Delta\chi, t - \Delta\tau) \\ & + p_-(x_1 + \Delta\chi) C(x_1 + \Delta\chi, t - \Delta\tau). \end{aligned} \quad (5.6)$$

Observing that $p_+(x_1) + p_-(x_1) \equiv 1$ and assuming that $\Delta p(x) = p_+(x_1) - p_-(x_1)$ is small everywhere in the small strain regime, this recursion relation becomes the gradient biased diffusion equation

$$\begin{aligned} \frac{\partial C(x_1, t)}{\partial t} = & \left[\lim_{\substack{\Delta\chi \rightarrow 0 \\ \Delta\tau \rightarrow 0 \\ \Delta p(x_1) \rightarrow 0}} \left(\frac{\Delta p(x_1) \Delta\chi}{\Delta\tau} \right) \right] \frac{\partial C(x_1, t)}{\partial x_1} \\ & + C(x_1, t) \left[\lim_{\substack{\Delta\chi \rightarrow 0 \\ \Delta\tau \rightarrow 0}} \left(\frac{\Delta\chi}{\Delta\tau} \right) \right] \left\{ \frac{\partial p_+(x_1)}{\partial x_1} - \frac{\partial p_-(x_1)}{\partial x_1} \right\} \\ & + \left[\lim_{\substack{\Delta\chi \rightarrow 0 \\ \Delta\tau \rightarrow 0}} \left(\frac{\Delta\chi^2}{2\Delta\tau} \right) \right] \frac{\partial^2 C(x_1, t)}{\partial x_1^2}, \end{aligned} \quad (5.7)$$

where the explicit spatial dependence in the coefficient of the first term on the RHS in conjunction with the second term on the RHS accounts for the

influence of a non-uniform bias. That is, Eq. (5.7) establishes a suitable template for incorporating the effects of a stress gradient due to a higher-dimensional defect. Therefore, Eq. (5.7) is the prototype of the stress-driven diffusion equation.

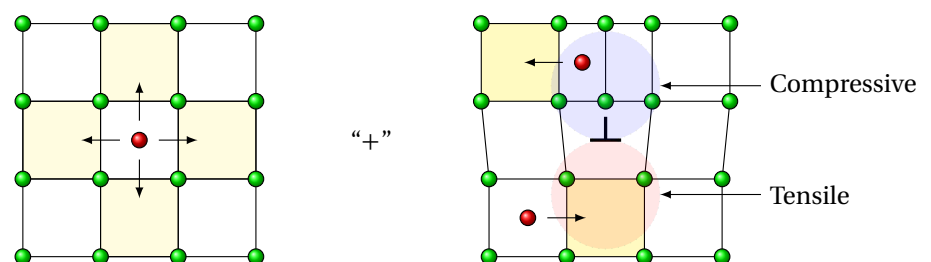
Anisotropic and Heterogeneous System. In order to actually apply Eq. (5.7) to the anisotropic diffusion of H in the heterogeneous microstructure of a Zr alloy specimen, the following aspects need to be considered. Firstly, it is necessary to extend this PDE to at least a two-dimensional framework so that the effects of anisotropy can be studied; this is a straightforward but tedious task. Secondly, the atomic scale heterogeneity that appears in the form of non-uniformly distributed interstitial sites in Eq. (5.1) must be appropriately averaged out by defining effective regular spatial and temporal intervals for the transitions; in this way, the analysis leading to the PDE in Eq. (5.7) remains valid. Thirdly, it is important to then relate the PDE coefficients, which have a clear physical meaning at the atomic scale, to their experimentally measured counterparts at the continuum scale; this includes the diffusivity and the stress state of the system.

The culmination of this analysis is a PDE in three variables, $\{x_1, x_2, t\}$, which describes the combined effects of the usual diffusion process as mediated by entropy through concentration gradients alongside the local influence of some bias that exhibits spatial variation through its gradients. For the purposes of this investigation, this bias is purely the consequence of the superposed stresses of all higher-dimensional defects in the system. Referring to illustration in FIG. 5.2, the aim is to translate the unknown atomistic quantities in Eq. (5.7) to their more recognisable thermodynamical format. In the two-dimensional extension of Eq. (5.7), the effects of anisotropy feature in three terms: (i) the diffusivity along the different crystallographic directions; (ii) the difference between the non-equal transition probabilities, which corresponds to the stress fields around defects in anisotropic continua; and (iii) the atomic-to-continuum scale coupling coefficient.

FIG. 5.2

Stress-driven diffusion

A visual representation of the stress-driven diffusion equation at the atomic scale as understood through the biased random walk model. The usual entropic diffusion competes with the influence of local stress-raisers such as dislocations.



5.2 Linear Irreversible Thermodynamics

In order to translate the atomic scale quantities in the biased random walk model into a macroscopic theory of stress-driven diffusion in an anisotropic polycrystalline material, it is essential to consider the general problem of diffusion in the framework of linear irreversible thermodynamics. In doing so, the relationship between the thermodynamic driving forces and respective fluxes can be determined as a function of the entropy production in a non-equilibrium state [Balluffi, Allen, and Carter (2005)].

Non-Equilibrium System. Consider such a non-equilibrium thermodynamic system with internal energy per unit volume u whose evolution towards equilibrium is governed by the state equation

$$du = Tds + \Psi_a d\psi_a, \quad (5.8)$$

where s is the entropy per unit volume and $\{\Psi_a\}$ are intensive state variables for whom $\{\psi_a\}$ are the corresponding extensive state variables per unit volume. Rearranging Eq. (5.8) and taking the time derivative implies that

$$\frac{\partial s}{\partial t} = -\nabla \cdot \mathbf{J}_{[s]} + \dot{s} \quad \text{with} \quad \mathbf{J}_{[s]} \equiv \frac{1}{T} [\mathbf{J}_{[u]} - \Psi_a \mathbf{J}_{[\psi_a]}]$$

$$\dot{s} \equiv \mathbf{J}_{[u]} \cdot \nabla \left(\frac{1}{T} \right) - \mathbf{J}_{[\psi_a]} \cdot \nabla \left(\frac{\Psi_a}{T} \right), \quad (5.9)$$

where $\mathbf{J}_{[\psi_a]}$ is the flux of extensive variable ψ_a and $\dot{s}$ is the entropy production per unit volume. The fundamental postulate of irreversible thermodynamics is that the local entropy production near equilibrium is semipositive-definite, that is,

$$\dot{s} \equiv \frac{\partial s}{\partial t} + \nabla \cdot \mathbf{J}_{[s]} \stackrel{!}{\geq} 0. \quad (5.10)$$

This statement is generally applicable for the evolution of any thermodynamic system that is close to equilibrium. However, its format is impractical for the purpose of efficient thermodynamic simulations because s must be computed explicitly as a function of the various fluxes. Instead, it is more useful to work exclusively with the fluxes, and relate these to the observables using simple constitutive relationships.

Force-Flux Relations. Now, in the framework of linear irreversible thermodynamics, the general force-flux relations can be determined by assuming that each flux depends on all of the possible driving forces in the system, that is, $\mathbf{J}_{[\psi_a]} = \mathbf{J}_{[\psi_a]}(\{\mathbf{F}_{[\psi_b]}\})$ and therefore, a first-order Taylor expansion about the equilibrium provides an approximation of the system in which fluxes

vary linearly with forces as

$$(J_{[\psi_a]})_i = L_{ab;ij} (F_{[\psi_b]})_j \quad \text{with} \quad L_{ab;ij} \equiv \frac{\partial (J_{[\psi_a]})_i}{\partial (F_{[\psi_b]})_j}, \quad (5.11)$$

where the Onsager direct coefficients $\{L_{aa;ij}\}$ connect each flux to its corresponding conjugate driving force and the Onsager coupling coefficients $\{L_{ab;ij} \mid a \neq b\}$ are responsible for the cross effects.

In this framework, it is straightforward to generalise the first law of Fickian diffusion for a concentration of interstitials, $C(\mathbf{x}, t)$, which relates the flux of the diffusing species to a gradient in the corresponding diffusing potential, Φ , through a total conjugate force given by

$$F_{[\Phi]} = -\nabla\Phi, \quad (5.12)$$

where Φ encapsulates the storage of energy due to a spectrum of driving forces experienced by the diffusing species. It is evident that Φ incorporates the sum of all such supplemental potentials, including the concentration chemical potential of the diffusing species. Consequently, the generalisation of the second law of Fickian diffusion leads to a PDE for thermodynamic force-driven diffusion,

$$\frac{\partial C(\mathbf{x}, t)}{\partial t} = -\nabla \cdot \mathbf{J}_{[\Phi]}, \quad (5.13)$$

where the indirect force-flux coefficients control the contribution of diffusion biases [Balluffi, Allen, and Carter (2005)]. In the one-dimensional setup, it is apparent that Φ must resemble

$$\Phi(x_1, t) \propto \left[C(x_1, t) \Delta p(x_1) + \left(\frac{\partial C(x_1, t)}{\partial x_1} \right) \right] \quad (5.14)$$

so that Eq. (5.13) can reproduce the three terms that describe diffusion in the linearly strained system. The aim is now to explicitly determine the exact form of the RHS of Eq. (5.13) and then deduce the equivalent coefficients in Eq. (5.7), which provides the bridge between atomic and continuum scale representations of stress-driven diffusion.

5.2.1 Generalised Diffusion Potentials

The choice of Φ completely specifies the simulated thermodynamics of the system. For the system of interest—interstitial diffusion of small solute atoms amongst the interstices of a distorted host crystal—the unbiased diffusive motion, which is mediated by entropy, can be described most simply by the Fickian diffusion potential. The flux of this Fickian diffusion potential is given in terms of the gradient of the usual chemical concentration

potential, $\phi(t, \mathbf{x})$, as

$$\begin{aligned} (J_{[\phi]})_i &= L_{[\phi][\phi];ij}(\mathbf{F}_{[\phi]})_j \\ &= -L_{[\phi][\phi];ij}(\nabla\phi)_j, \end{aligned} \quad (5.15)$$

where an approximate form of the direct coefficient $L_{[\phi][\phi]}$ is determined in the following for two cases: (i) the usual Fickian diffusion law for a non-ideal dilute solution; and (ii) an extension to stress-assisted Fickian diffusion for a distorted crystal. The former is well known and so it provides a springboard for the latter.

Fickian Diffusion. Consider a two-component solution in which component r consists of N_r particles; denoting the solvent as component 1 and the solute diffusing species as component 2, the Gibbs free energy of the two-component solution is given by

$$G_{\text{ISM}}(T, \{\Psi_a\}, \{N_r\}) = \sum_{r=1}^2 \left[N_r \phi_r(\{\Psi_a\}) + N_r k_B T \ln \left(\frac{N_r}{\sum_{s=1}^2 N_s} \right) \right], \quad (5.16)$$

under the assumption of an ideal solution model (ISM), that is, the entropy of mixing is that of a two-component ideal gas, and there is no change in the enthalpy upon mixing. The chemical potential of the solute is then given by

$$[\phi_{\text{ISM}}]_2(T, \{\Psi_a\}, C_2) \equiv \frac{\partial G_{\text{IS}}}{\partial N_1} = \phi_1^{(0)}(T, \{\Psi_a\}) + k_B T \ln(C_2) \quad (5.17)$$

$$C_2 \equiv \frac{N_2}{\sum_{r=1}^2 N_r}. \quad (5.18)$$

Now, the departure from ISM behaviour can be captured by the introduction of the activity of the solute dissolved in the solvent. Accordingly, Eq. (5.17) can be extended for a non-ideal solution model (NISM) as

$$[\phi_{\text{NISM}}]_2(T, \{\Psi_a\}, C_2) \simeq \phi_1^{(0)}(T, \{\Psi_a\}) + k_B T \ln(\gamma_2 C_2), \quad (5.19)$$

where γ_2 is the activity coefficient. Generally, γ_2 is a spatially-varying quantity. However, in the limit of dilute solution, it is known that

$$\lim_{C_2 \rightarrow 0} \gamma_2 \simeq \text{const.}, \quad (5.20)$$

which is the experimentally-verified Henry's law [Callen (1960)]. For this Henrian system, the chemical potential flux can be expressed in the desired form

$$(J_{[\phi]})_i \simeq -L_{[\phi][\phi];ij} \frac{k_B T}{C} (\nabla C)_j \quad \text{with} \quad (J_{[\phi]})_i = -D_{ij} (\nabla C)_j. \quad (5.21)$$

where the latter expression is the expected form for Fickian diffusion in which D_{ij} is the tensor of diffusivities. Observe that the crystallographic

symmetries are reflected in the transformations of D_{ij} in accordance with Neumann's principle; the component D_{ij} relates the concentration gradient in x_j -direction to the flux in the x_i -direction. Hence, the intrinsic diffusivity can be expressed in terms of the force-flux coefficient via the Nernst-Einstein equation,

$$D_{ij} = k_B T M_{ij} \quad \text{with} \quad L_{[\phi][\phi];ij} = C M_{ij}, \quad (5.22)$$

where M_{ij} is the interstitial mobility tensor whose components describe the average drift velocity gained by diffusing interstitials upon the application of a unit driving force [Balluffi, Allen, and Carter (2005)]. In the dilute limit, M_{ij} is expected to be independent of the interstitial concentration, and hence

$$\begin{aligned} \frac{\partial C(t, \mathbf{x})}{\partial t} &= (\nabla)_i [C(t, \mathbf{x}) M_{ij} (\nabla \phi)_j] \\ &= D_{ij} \frac{\partial^2 C(t, \mathbf{x})}{\partial x_i \partial x_j}, \end{aligned} \quad (5.23)$$

which is the Fickian diffusion equation with cross terms. (The usual linear diffusion equation is recovered if the diffusivity matrix is diagonal.) Now, these results can be extended straightforwardly for any diffusion potential Φ as

$$\frac{\partial C(t, \mathbf{x})}{\partial t} = (\nabla)_i [C(t, \mathbf{x}) M_{ij} (\nabla \Phi)_j], \quad (5.24)$$

which is an appropriate generalisation of the laws of the Fickian diffusion for this investigation.

Stress-Assisted Fickian Diffusion. The diffusion potential for stress-driven diffusion must incorporate contributions due to an appropriate elastic energy potential due to the stress field around a stress source, $[\sigma_{\text{SCF}}]$, as well as the usual concentration chemical potential. These contributions constitute a linear elastochemical (EC) potential of the form

$$\begin{aligned} \Phi_{\text{EC}}(T, \{\Psi_a\}, C, [\sigma_{\text{H}}](\mathbf{x}), [\sigma_{\text{SCF}}](\mathbf{x})) &= \phi_{\text{EI}}([\sigma_{\text{H}}](\mathbf{x}), [\sigma_{\text{SCF}}](\mathbf{x})) \\ &\quad + \phi_{\text{NISM}}(T, \{\Psi_a\}, C), \end{aligned} \quad (5.25)$$

where the elastic interaction potential ϕ_{EI} accounts for the elastic energy associated with the internal stress field $[\sigma_{\text{H}}]$ due to the elastic misfit caused by the solute atom in the crystal lattice of the solvent. Substituting Eq. (5.25) into Eq. (5.24) yields a differential equation which describes stress-driven

diffusion

$$\begin{aligned} \frac{\partial C(t, \mathbf{x})}{\partial t} = \frac{D_{ij}}{k_B T} & \left[\frac{\partial C(t, \mathbf{x})}{\partial x_i} \frac{\partial \phi_{\text{EI}}([\sigma_H](\mathbf{x}), [\sigma_{\text{SCF}}](\mathbf{x}))}{\partial x_j} \right. \\ & + C(t, \mathbf{x}) \frac{\partial^2 \phi_{\text{EI}}([\sigma_H](\mathbf{x}), [\sigma_{\text{SCF}}](\mathbf{x}))}{\partial x_i \partial x_j} \\ & \left. + k_B T \frac{\partial^2 C(t, \mathbf{x})}{\partial x_i \partial x_j} \right], \end{aligned} \quad (5.26)$$

which exhibits competing effects between the spatial gradients of the interaction energy against those of the usual chemical concentration potential. It is also straightforward to relate these continuum thermodynamical coefficients of the three terms to the unknown prefactors that appear in Eq. (5.7) as needed. For example, the diagonal components of the diffusivity tensor take the form

$$D_{ii} = \lim_{\substack{\Delta \chi_{(i)} \rightarrow 0 \\ \Delta \tau_{(i)} \rightarrow 0}} \left(\frac{\Delta \chi_{(i)}^2}{2 \Delta \tau_{(i)}} \right), \quad (5.27)$$

where the directionality of time step $\Delta \tau_{(i)}$ and spatial interval $\Delta \chi_{(i)}$ accounts for the crystalline anisotropy at the atomic scale. In addition, the other two coefficients can be formulated in terms of the elastic interaction energy, the form of which is discussed in due course.

A numerical approach is required to solve Eq. (5.26) because of the complicated expressions for the elastic fields of the system. Several options exist, including the explicit Euler algorithms and the implicit Crank-Nicolson algorithm [Crank (1979)]. However, the computational implementation of either method is compromised by the non-simple boundary conditions that result from overlaying a discretised grid to resolve the flaw geometry [Patel (2014)]. Therefore, a more convenient and computationally efficient scheme is required for simulating the equilibrium diffusion profile.

5.2.2 Equilibration

In the limit $t \rightarrow \infty$, it is reasonable to assume that the transient PDE solution of Eq. (5.26) approaches the steady state profile as defined in the limit that the elastochemical potential in Eq. (5.25) vanishes. These two limits correspond to a solute-solvent system in which the solute diffusivity is sufficiently large so that the solute concentration profile in the simulated region of the solvent, which can be chosen to be as small as appropriate, attains thermodynamic equilibrium almost instantaneously with respect to other (slower) time-dependent processes. Given H mobility in Zr, these limits are sensible for the purpose of this investigation. Therefore, solving Eq. (5.25)

in these limits establishes the equilibrium stress-diffusion concentration profile

$$C(\mathbf{x}; T) = c_0(T) \exp \left[-\frac{\phi_{\text{EI}}([\sigma_{\text{H}}](\mathbf{x}), [\sigma_{\text{SCF}}](\mathbf{x}))}{k_B T} \right], \quad (5.28)$$

where the temperature-dependent constant $c_0(T)$ is the uniform background concentration; this is assumed to be 150 ppm at $T = 673.15$ K in accordance with experimental work [Puls (2012) and Patel et al. (2018)].

Observe that Eq. (5.28) is an extension of the well-known Cottrell formula for a solute atmosphere around a Volterra edge dislocation [Cottrell and Bilby (1949)]. As previously discussed, in linear elasticity, the stress fields of a Volterra edge dislocation can be treated as Green tensor functions for higher-dimensional defects; a linear superposition of such dislocations can be used to model cracks and notches. Hence Eq. (5.28) is applicable for any simplified interaction between a point defect and any SCFs of higher dimensionality. Note again that Eq. (5.28) is only suitable in the dilute solution limit and, therefore, this analysis may not be valid at distances that are extremely close to the notch tip or near other lower-dimensional defects that act as hydride precipitation sites where the hydrogen-hydrogen interactions cannot be neglected.

As Eq. (5.28) is an analytical formula, it is straightforward to implement computationally provided that $\phi_{\text{EI}}([\sigma_{\text{H}}](\mathbf{x}), [\sigma_{\text{SCF}}](\mathbf{x}))$ can be obtained exactly using the knowledge of $[\sigma_{\text{H}}](\mathbf{x})$ and $[\sigma_{\text{SCF}}](\mathbf{x})$ through their respective closed-form expressions. This is now the only missing aspect of the stress-diffusion analysis, and it requires a unification of both the atomic and continuum scale representations of H point defects in the HCP α -Zr matrix.

5.2.3 Atomistic-to-Continuum Coupling

Recall that the main purpose of this study is to bridge the atomic scale elastic dipole model of H in Zr with the continuum scale treatment of higher-dimensional defects in the Zr alloy component whose tensile stresses drive the diffusion of H, and to pursue this avenue in a manner that is both accurate and efficient. Here, the notion of accuracy corresponds to the accounting of anisotropy of the interstitial system, whereas the notion of efficiency corresponds to the derivation of analytical or semi-analytical formulae which can readily be adapted into a computational framework without any of the time-consuming numerical bottlenecks that are typical of common grid-based diffusion solvers [Press et al. (2009)].

These requirements of accuracy and efficiency are met by Eq. (5.28) with the only remaining computation being that of the elastic interaction

energy, which involves the evaluation of an integral of the form

$$\phi_{\text{EI}}([\sigma_{\text{H}}](\mathbf{x}), [\sigma_{\text{SCF}}](\mathbf{x})) = - \iiint_{\mathcal{V}} d\mathcal{V}(\mathbf{x}') [\sigma_{\text{H}}]_{ij}(\mathbf{x}) [e_{\text{SCF}}]_{ij}(\mathbf{x}; \mathbf{x}'), \quad (5.29)$$

where the vector $\mathbf{x}'$ denotes the relative position between the site of the H atom and the origin of the coordinate system in which the stress state due to the higher-dimensional defects is expressed. The integral in Eq. (5.29) is simply an adaptation of the usual elastic interaction energy between two sources of distortion in a linear elastic continuum [Eshelby (1956) and Eshelby (1976)]. Observe that Eq. (5.29) features in the treatment of both the kinetics of stress-driven diffusion as well as the equilibrated limit of the diffusion profile around a stress-raiser. The former case constitutes the widely used isotropic theory of H diffusion in Zr, which underpins conventional models of the early stages of DHC failure. In these models, H interstitials are assumed to be misfitting spheres in an isotropic continuum, and accordingly Eq. (5.29) reduces to the form

$$\begin{aligned} \phi_{\text{EI}}([\sigma_{\text{H}}](\mathbf{x}), [\sigma_{\text{SCF}}](\mathbf{x})) &\simeq \Delta V_{\text{H}} P_{\text{SCF}}(\mathbf{x}) \\ &= -\Delta V_{\text{H}} \text{Trace}_{ij}[\sigma_{\text{SCF}}](\mathbf{x}), \end{aligned} \quad (5.30)$$

where $P_{\text{SCF}}(\mathbf{x})$ is the hydrostatic pressure, and ΔV_{H} is the spherical misfit volume of transport. Here $\phi_{\text{EI}}([\sigma_{\text{H}}](\mathbf{x}), [\sigma_{\text{SCF}}](\mathbf{x}))$ is the difference between the respective energies required to insert a spherical misfit at the position $\mathbf{x}$ in an isotropic continuum when it is subject to a uniform pressure of $P_{\text{SCF}}(\mathbf{x})$ and when it is subject to zero pressure. Observe that ΔV_{H} is a rotationally-invariant scalar and so it cannot capture the symmetry of interstitial site. Therefore the application of Eq. (5.30) within Eq. (5.28) is restricted to a homogeneous isotropic continuum. This shortcoming of the conventional DHC models was discussed qualitatively in the preceeding discussions, and so it is useful to be able to now see this mathematically within Eq. (5.30) for comparative purposes. Any stress-diffusion analysis conducted using $\phi_{\text{EI}}([\sigma_{\text{H}}](\mathbf{x}), [\sigma_{\text{SCF}}](\mathbf{x}))$ cannot truly account for crystalline anisotropy or microstructural heterogeneity.

Unlike the misfitting sphere model, it is possible to capture the interstitial symmetry using the more general elastic multipole model of point defects. In the multipole model, the distortion caused by a point defect in a crystal is represented by a multipolar expansion of defect forces. This approach involves discretising the volume integral in Eq. (5.29) into a summation over complete shells of neighbouring Zr atoms as

$$\phi_{\text{EI}}([\sigma_{\text{H}}](\mathbf{x}), [\sigma_{\text{SCF}}](\mathbf{x})) = - \sum_{\alpha} [f_{\text{H}}]_i(\mathbf{p}_{\alpha}) [u_{\text{SCF}}]_i(\mathbf{x} + \mathbf{p}_{\alpha}) \quad (5.31)$$

where the index α labels the neighbouring Zr atoms, $\mathbf{f}_H(\mathbf{p}_\beta)$ is the body force exerted by the H point defect on Zr atom β located at the position $\mathbf{p}_\beta$, and $\mathbf{u}_{SCF}(\mathbf{x})$ is the displacement vector field due to the SCF centred at the origin. In comparison to Eq. (5.29), observe that $[\sigma_H](\mathbf{x})$ has been re-expressed in terms of the defect forces and $[e_{SCF}](\mathbf{x})$ has then been replaced by the corresponding displacement field. As the variation of $\mathbf{u}_{SCF}(\mathbf{x})$ is small over the atomic scale distances, that is, $|\mathbf{p}_\alpha| \ll |\mathbf{x}|$, it is possible to perform a Taylor expansion about $\mathbf{x}$ to obtain

$$\begin{aligned} \phi_{EI}([\sigma_H](\mathbf{x}), [\sigma_{SCF}](\mathbf{x})) = & \left\{ \sum_{\alpha} [\mathbf{f}_H]_i(\mathbf{p}_\alpha) \right\} [\mathbf{u}_{SCF}]_i(\mathbf{x}) \\ & - \left\{ \sum_{\alpha} [\mathbf{f}_H]_i(\mathbf{p}_\alpha) p_{\alpha i} \right\} [\mathbf{u}_{SCF}]_{i,j}(\mathbf{x}) \\ & + \mathcal{O}(p_\alpha^2), \end{aligned} \quad (5.32)$$

where the first term on the RHS vanishes due to the condition of mechanical equilibrium, and the leading (non-zero) term in this multipolar expansion defines the elastic dipole tensor of H in Zr as

$$\rho_{ij} \equiv \sum_{\alpha} [\mathbf{f}_H]_i(\mathbf{p}_\alpha) p_{\alpha j}, \quad (5.33)$$

which agrees with the definition given earlier. Therefore, it is straightforward to evaluate Eq. (5.29) as a multiscale analytical formula that is sequentially parametrised by the first-principles DFT computation of $\rho_{[2]}$ through the expression

$$\phi_{EI}([\sigma_H](\mathbf{x}), [\sigma_{SCF}](\mathbf{x})) \simeq -\rho_{ij} [\mathbf{u}_{SCF}]_{i,j}(\mathbf{x}). \quad (5.34)$$

This is a central result in this investigation because it is now possible to convert analytically the closed-form expressions for the stress state around a defect in a hexagonal α -Zr crystal directly into an equilibrated H concentration diffusion profile as a function of crystalline anisotropy.

For the two hexagonal crystallographic planes that have been considered thusfar, namely the (0001) basal plane and the $(10\bar{1}0)$ prism plane, Eq. (5.34) simplifies in the plane strain framework to give two different expressions:

$$\phi_{EI}([\sigma_H](\mathbf{x}), [\sigma_{SCF}](\mathbf{x})) = \begin{cases} -\{ \varrho_{11}[e_{SCF}]_{11}(\mathbf{x}) + \varrho_{11}[e_{SCF}]_{22}(\mathbf{x}) \} & \text{on (0001)} \\ -\{ \varrho_{11}[e_{SCF}]_{11}(\mathbf{x}) + \varrho_{33}[e_{SCF}]_{22}(\mathbf{x}) \} & \text{on (10}\bar{1}0) \end{cases}, \quad (5.35)$$

which is the first clear demonstration of the effects of anisotropy.

5.3 Equilibrium Concentrations Profiles

The analytical conversion of stress contours in anisotropic continua to H atmospheres around defects is now straightforward to implement because it is both mathematically elegant and computationally efficient. As a demonstration of possibilities—and a gateway to later discussions on modelling the early stages of DHC failure—consider the equilibrium H profiles around dislocations, at the tips of slit cracks and near grain boundaries in a HCP α -Zr continuum. These profiles can be easily computed by substituting the previous results of the stress analysis into Eq. (5.35), which effectively constitutes the stress-diffusion analysis for this investigation.

Referring first to FIG. 5.3 and FIG. 5.4, which show H profiles around an edge dislocation, it is clear that the contours of H enhancement differ for the respective cases of prismatic and basal dislocations. In the case of the prismatic dislocation, the normal strains contribute equally in driving the H diffusion because their contribution is weighted by two identical components of the elastic dipole tensor. In contrast, the case of the basal dislocation shows how H diffusion may be biased along one particular crystallographic direction over another if the normal strain weightings, as specified by the elastic dipole tensor components, are not equal.

Extending this computation to a distribution of dislocations, FIG. 5.5 and FIG. 5.6 show the flaw-tip H concentration profile for two different classes of slit cracks in the hexagonal material. For the same reasons as before, it is evident that the region of H enhancement is seemingly greater for the crack opening on the prism plane as opposed to the basal plane. The trend in FIG. 5.7 supports this observation as the H concentration along the plane of the crack is always higher for the prism plane than the basal plane. Although such a trend may not be entirely consistent with experimental observations, this particular result does highlight the importance of incorporating the effects of anisotropy in predictive models of DHC failure. Note that standard FE or PF models, which omit the anisotropic elastic dipole tensor, would not capture such a result.

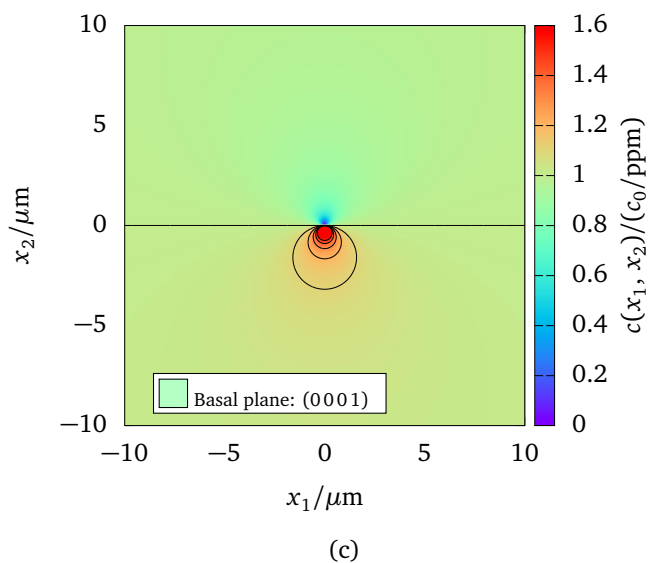
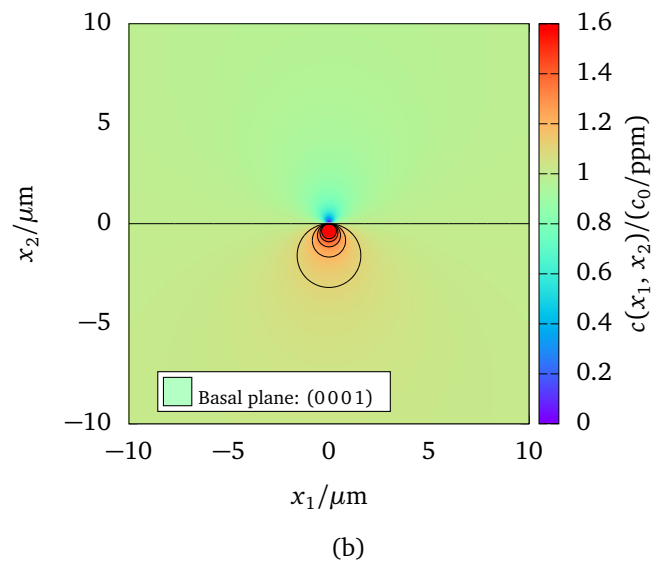
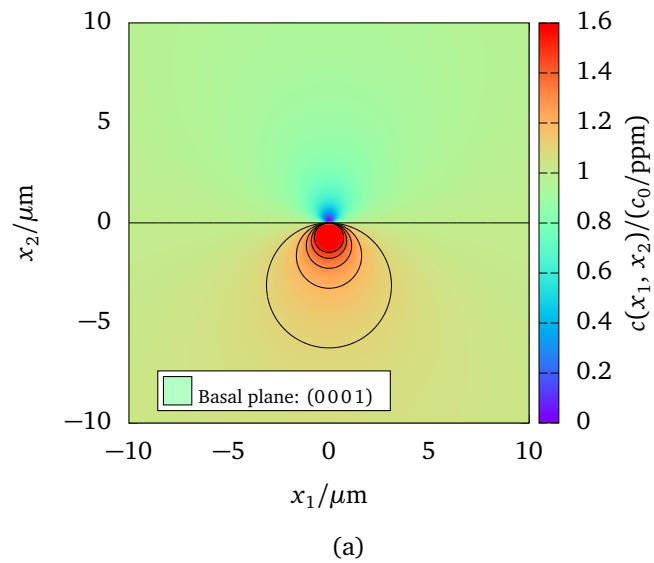
The effects of temperature are also shown here because the competition between stress and entropy as thermodynamic driving forces underpins the stress-diffusion analysis. At low temperatures, the stress dominates the H equilibration as the H interstitials occupy the most tensile regions around the defects. At high temperatures, entropy ensures that the H accumulation in the presence of stress is as dilute as possible.

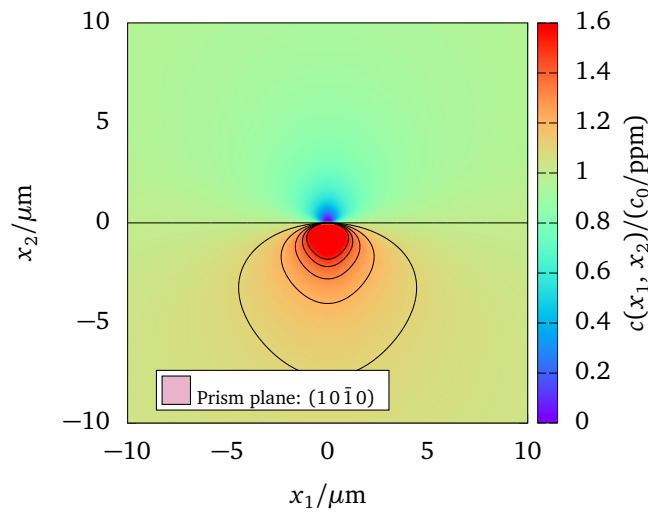
Finally, it is worth seeing the H profile around the symmetric tilt boundary in FIG. 5.8 as a simple example of an inter-granular nucleation site for hydride features.

FIG. 5.3

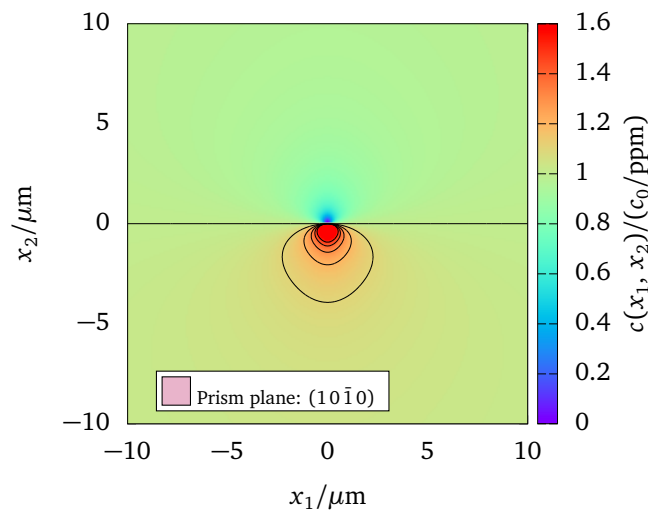
Hydrogen atmosphere around a prismatic dislocation

The equilibrium H concentration profile around a prismatic dislocation in Zr as a function of temperature. (a) Room temperature of $0.025 \text{ eV}/k_B$ which is the low-temperature regime. (b) A moderate temperature of 573 K which is characteristic of reactor operating conditions. (c) An elevated temperature of 673 K which is characteristic of dry storage. The H atoms have accumulated in the tensile region whereas the H atoms have been depleted from the compressive region. This effect is more pronounced at lower temperatures. These profiles are mathematically equivalent to those obtained from a fully a isotropic treatment of the stress and stress-diffusion analyses.

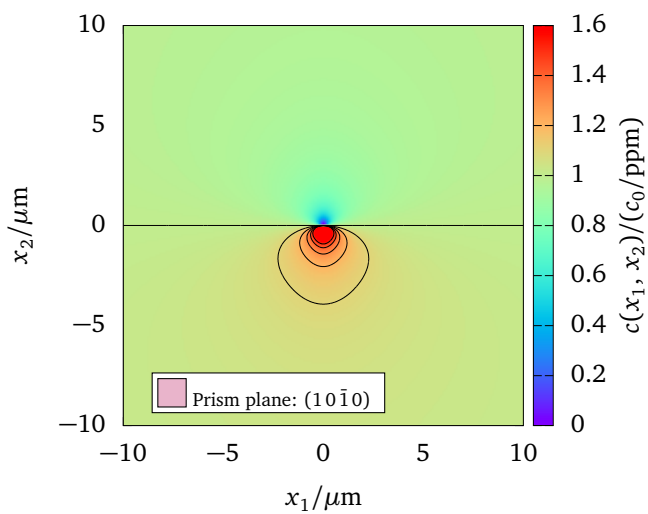




(a)



(b)



(c)

FIG. 5.4

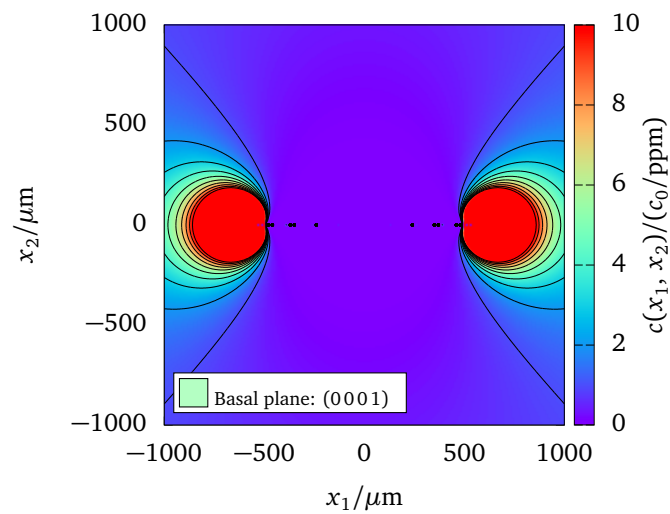
Hydrogen atmosphere around a basal dislocation

The equilibrium H concentration profile around a basal dislocation in Zr as a function of temperature. The same temperatures are used as before: (a) room temperature, (b) 573 K and (c) 673 K. The main difference here is the use of the anisotropic elasticity at the continuum scale and the anisotropic elastic dipole tensor at the atomic scale, which together produce a qualitatively and quantitatively different profile to the isotropic case.

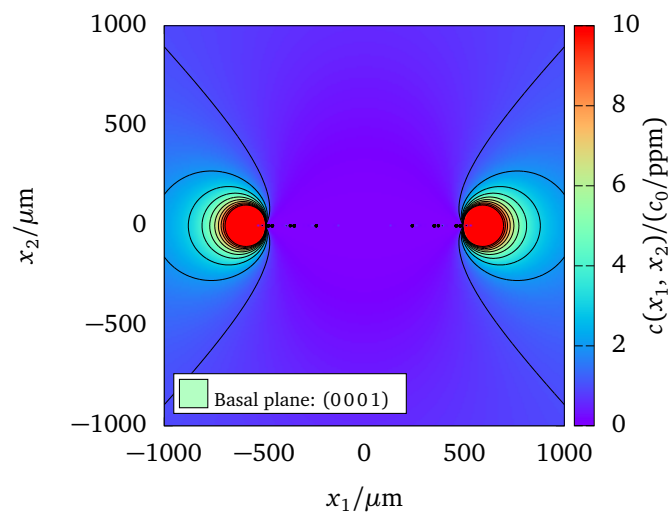
FIG. 5.5

Hydrogen atmosphere around a sharp tensile crack opening on the basal plane

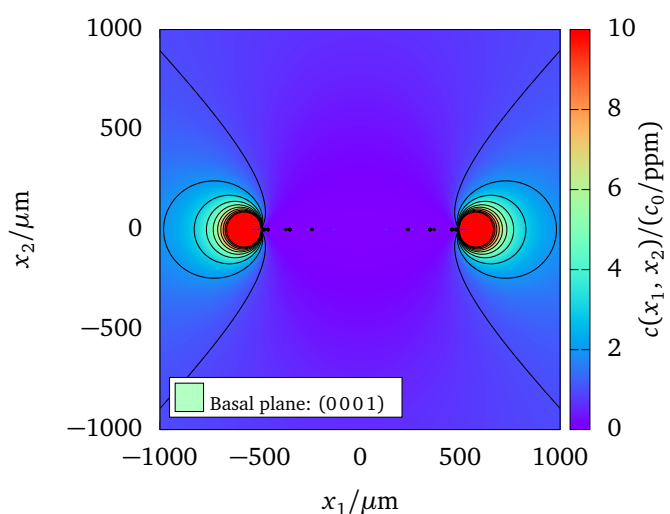
The equilibrium H concentration profile around a DBCS slit crack, constructed from a continuous coplanar distribution of prism dislocations in Zr, as a function of temperature. The same temperatures are used as before: (a) room temperature, (b) 573 K and (c) 673 K. Here it is possible to reap the rewards of mathematical effort in being able to efficiently compute crack-tip H profiles as a precursor to modelling the early stages of DHC failure.



(a)



(b)



(c)

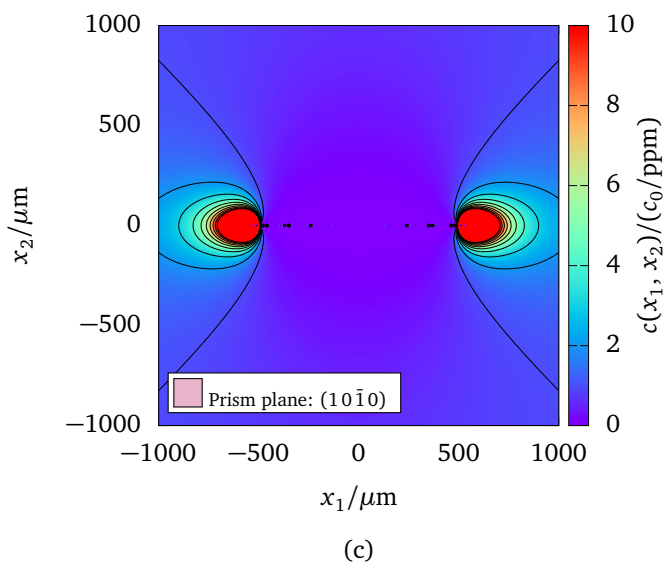
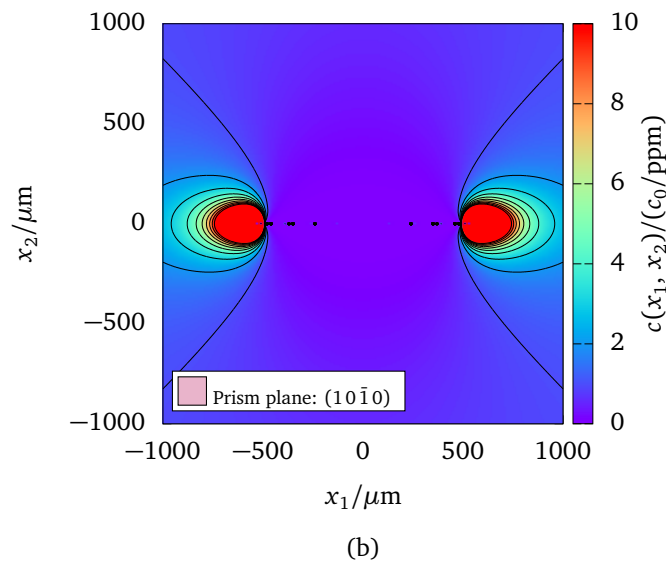
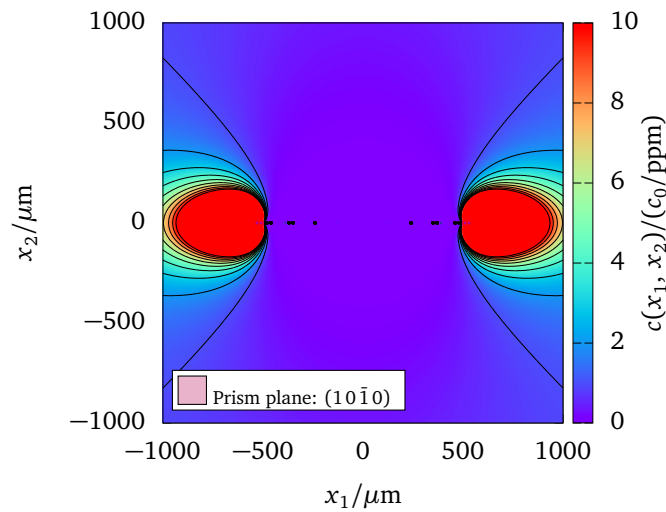


FIG. 5.6

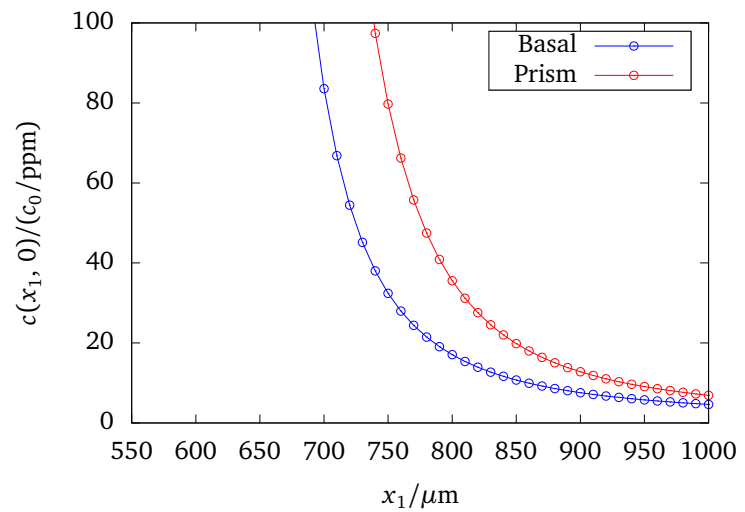
Hydrogen atmosphere around a sharp tensile crack opening on the prism plane

The equilibrium H concentration profile around a DBCS slit crack, constructed from a continuous coplanar distribution of basal dislocations in Zr, as a function of temperature. The same temperatures are used as before: (a) room temperature, (b) 573 K and (c) 673 K. The effects of anisotropy as observed for the case of a single edge dislocation are now reproduced for this dislocation model of a slit crack. The importance of this result cannot be overstated because it highlights the need for anisotropy in predictive models of DHC failure; worst case scenarios must be identified as a function of not only the flaw acuity but also the crystalline anisotropy.

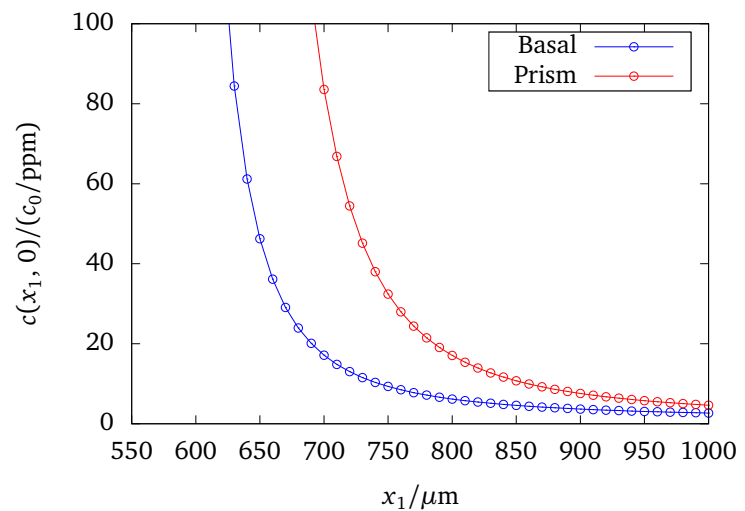
FIG. 5.7

Crack-tip hydrogen concentration as a function of anisotropy

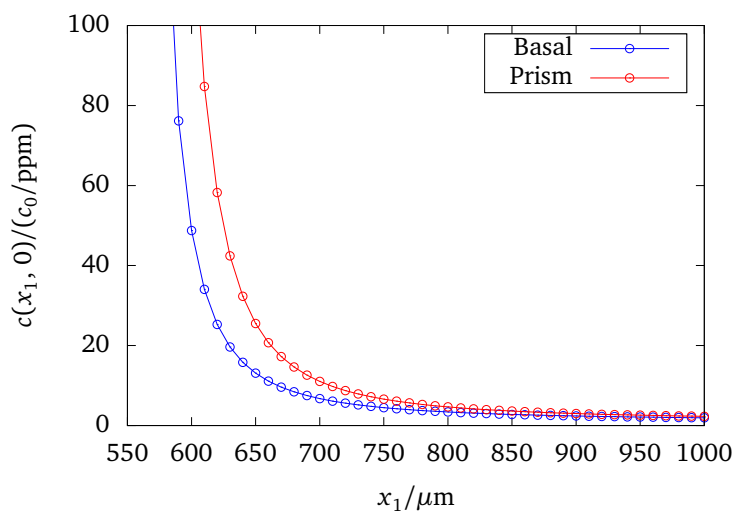
A comparison of the H concentration enhancement ahead of the crack tip along the plane of the crack for basal and prism cases. The same temperatures are used as before: (a) room temperature, (b) 573 K and (c) 673 K. Due to the inequality of the components of the elastic dipole tensor for H point defects in tetrahedral sites in HCP α -Zr crystal lattice, the crack opening on the prism plane is more potent at driving the H diffusion.



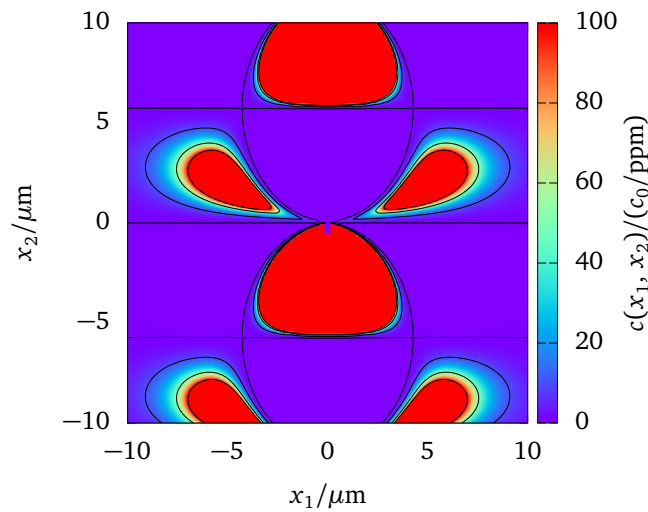
(a)



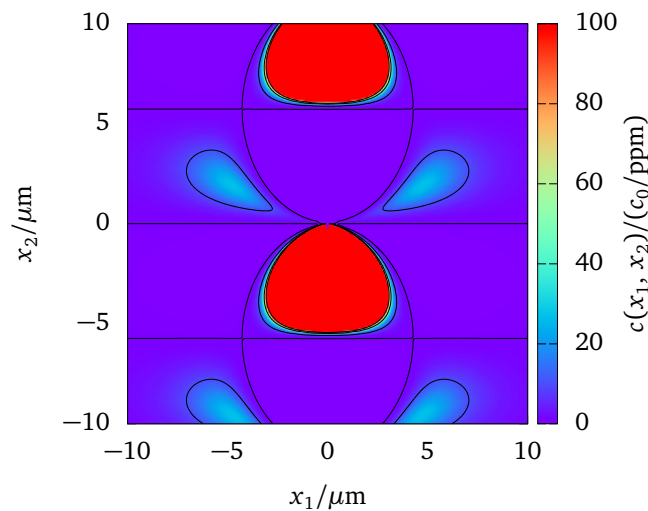
(b)



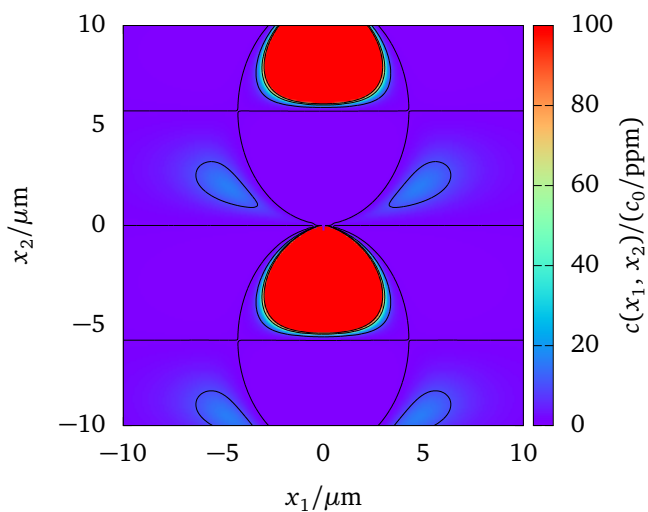
(c)



(a)



(b)



(c)

FIG. 5.8

Hydrogen atmosphere around a grain boundary

The equilibrium H concentration profile around a low-angle symmetric tilt boundary, constructed from a discrete array of prismatic dislocations in Zr, as a function of temperature. The same temperatures are used as before: (a) room temperature, (b) 573 K and (c) 673 K. This is mostly a visualisation exercise in the ensuing treatment of grain boundaries as inter-granular nucleation sites. But this result does highlight the capabilities of the proposed approach for conducting stress-diffusion analysis because such results are easy to obtain if closed-form expressions of the stress fields are known.

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6

Diffusion-Precipitation Analysis

Chapter Overview

The third module of this hybrid multiscale model of DHC is a phenomenologically accurate and algorithmic framework for simulating the mesoscale precipitation of the hydride features as controlled by the diffusion of H atoms. As opposed to the preceding stress and stress-diffusion analyses,—which involved well-established theoretical principles supported by rigorous mathematical formalisms—, the heuristic diffusion-precipitation analysis, as presented here, is far more ad hoc from the perspective of model development. That is, the diffusion-precipitation analysis will be driven primarily by the physical intuition offered by the aforementioned empirical observations as well as the speculative insight offered by very recent computational studies of the Zr-H system. Accordingly, this chapter aims to convey a candid account of the trial-and-error guesswork of this investigation along the pathway towards a multiscale model of DHC failure.

Before delving into these more advanced theoretical and computational concepts, it is essential to understand where mesoscale hydride precipitation in Zr exists—or rather, could exist,—within the broader field of phase transition modelling. The reason for this pedagogy here is because the present work does not strictly adhere to any of the common modelling methodologies that have been applied to almost every other phase transformation process, and so it is necessary to justify the choices made in this study that aims to construct a DHC model which is both accurate and efficient. Moreover, it will be particularly useful to relate the standard terminology of theoretical and experimental materials science to the unconventional language and approach used in this multiscale computational investigation.

Solid state phase transformations are central to physical metallurgy because almost every industrial alloy is subject to changes in temperature and pressure or, more generally, stress. This includes heat treatment and cold working during the pre-service manufacturing stages as well as thermomechanical cycling during the operation lifetime. Changes in temperature and pressure can induce changes in the microstructure of the alloy components in one of two ways: (i) deformation followed by recovery and recrystallisa-

tion; and (ii) phase transformation from a parent phase to a new daughter phase that is thermodynamically distinguishable with respect to its crystallographic structure and stoichiometric composition [Cahn and Haasen (1996), Callen (1960), and Khachaturyan (1983)]. The beginning of this chapter focuses on the theory of phase transformations in application to the Zr-H system. The theory presented here will then underpin the strategy for modelling the evolution of the hydrided microstructure of Zr alloys. It is worthwhile to begin this discussion by first introducing some basic principles behind the theory of phase transformations and then providing a comparison to the experimental observations of hydrides in Zr alloys.

Phase transformations are driven at critical temperatures and pressures by a reduction in the thermodynamic potential (or free energy) brought about by changes in the structural and compositional properties. The magnitude and extent of these changes characterise the mechanism by which the phase transformation occurs. There are two such mechanisms for multi-component systems such as alloys; the first is spinodal decomposition and the second is nucleation and growth. Spinodal decomposition involves changes that are small in magnitude but large in extent, whereas nucleation and growth involves changes that are large in magnitude but small in extent. In the case of spinodal decomposition, the parent phase is unstable to small fluctuations in the composition and hence there is no barrier to continuous transformation to a more stable daughter phase, a process which is entirely controlled by diffusion. This is in contrast to nucleation and growth during which the formation of the daughter phase necessitates the appearance of small complexes in the matrix of the parent phase; these small complexes are known as nuclei and they have the same properties as the corresponding bulk phase. A nucleation event can involve long-range thermally-activated diffusive transport and short-range clustering via quantum mechanical tunnelling as well as non-diffusive lattice reconfigurations. The nuclei grow to form microscopic islands of the daughter phase inside the parent phase matrix. Unlike spinodal decomposition, nucleation and growth requires a large free energy barrier to be surmounted. The fraction of this free energy barrier due to the interface between the parent and daughter phases is more appreciable because there is a large surface-to-volume ratio associated with the daughter phase islands. However, this free energy barrier is often much lower at existing interfaces that provide favourable conditions for heterogeneous nucleation. In crystalline materials, heterogeneous nucleation occurs at non-equilibrium defects such as grain boundaries, twin boundaries, dislocation networks and point defect clusters [Callen (1960), Khachaturyan (1983), Cahn and Haasen (1996), and Christian (2002)].

Considering the experimental studies of hydrides in Zr alloys, it is evi-

dent that the hydrided microstructures evolve according to a heterogeneous nucleation and growth mechanism. There are several reasons for why this is the case. Recall that there are stark differences in the crystallography and H stoichiometry between the (parent) dilute α -Zr-H solid solution phase in the high temperature regime and the (daughter) bulk γ -ZrH_{1.00} and δ -ZrH_{1.66} phases in the low temperature regime. This implies that there is an energy barrier for the phase transformation which is mediated by some H concentration solvus. Moreover, these two particular hydride phases typically appear as isolated islands in α -Zr matrix and these features are often found in the vicinity of grain boundaries, laths and intermetallic second-phase particles [Puls (2012) and Chamaa et al. (2018)]. Modelling the heterogeneous nucleation and growth of hydrides in Zr alloys falls within the realm of classical nucleation theory.

Classical nucleation theory encompasses a broad range of modelling strategies for different categories of phase transformations [Janssens et al. (2007)]. There are two main categories of phase transformations in metals, namely, polymorphous transitions and precipitation reactions. Polymorphous transitions involve a global change in the phase of the base metal, which affects all atoms in the alloy; an example is the transition from HCP α -Zr to BCC β -Zr at high temperatures. In contrast, precipitation reactions involve very local scale changes, where the spatial extent of the daughter phases is isolated around certain sites in the matrix, and usually the parent phase remains widely unaltered; an example is, of course, the formation of γ -ZrH_{1.00} and δ -ZrH_{1.66} phase features within the α -Zr-H solid solution at low temperatures. In a precipitation reaction, the single phase system becomes a multi-phase system that includes both parent and daughter precipitate phases. From the standpoint of nucleation and growth, precipitation reactions are just special cases of polymorphous transitions in which the daughter phase islands are restricted in size. Accordingly, some of the general ideas associated with global phase formation processes can be applied to their local counterparts [Cahn and Haasen (1996) and Callen (1960)]. However, working entirely within the framework of polymorphous transitions is often not the most accurate or efficient strategy for modelling the evolution of a precipitate-rich microstructure [Janssens et al. (2007)]. In order to then justify the strategy for modelling the hydrided microstructure of Zr alloys, it is important to determine what exactly is required for modelling such phase transformation processes.

Although there are many different types of phase transformation processes, there are several concepts that are common to most theoretical and computational models of phase transformations. The most general concept is that of the thermodynamical driving forces which govern structural and

compositional changes. The effect of these driving forces can be described in terms of an energy minimisation procedure at various length and time scales. At the atomistic scale, a phase transformation is most fundamentally the reorganisation of atoms into an assembly or packing that is more energetically favourable. At the microscopic scale, a phase transformation can be represented by the problem of a moving two-phase interface that reduces the free energy of the system. At the continuum scale, phase transformation can be quantified most simply by any changes in the macroscopic material properties, such as the elastic moduli and fracture toughness; here, the energy minimisation procedure is not treated explicitly and, therefore, empirical studies are often used to formulate relationships between material properties and the state variables of temperature and pressure as well as order parameters [[Janssens et al. \(2007\)](#)].

Moreover, there are also various time scales associated with phase transformations. These time scales are usually thought of as rates, such as the overall rate of progress of transformation or the rates of nucleation and growth. As previously stated, however, such time scales are more individualised to the specific process under consideration. Nevertheless, it is useful to use atomic time scales as a gauge because both polymorphous transitions and precipitation reactions involve the motion of atoms that correspond to the migration of interfaces between the parent and daughter phases. There are two modes by which the interface can migrate; these are respectively known as civilian (reconstructive) and military (displacive) transformations. In the case of civilian transformations, individual atoms make thermally activated jumps across the interface; therefore, the growth of daughter phase is controlled by the kinetics of diffusion. In the case of military transformations, atoms at the interface move in a coordinated shear-type motion; therefore, the daughter (martensite) phase grows into the parent (austenite) phase through a non-diffusive mechanism. Phase transformations that involve compositional changes are usually civilian whereas those that involve low-temperature crystallographic changes are usually military [[Cahn and Haasen \(1996\)](#)]. Diffusive transport is generally a much slower process than displacive motion. Hence, identifying the compositional and crystallographic differences between the parent and daughter phases is a crucial first step towards deducing the various time scales associated with a given phase transformation process.

A multiscale model of a phase transformation process should appropriately use information from the atomistic, microscopic and continuum scales. Without any allusions to the time scales, consider only the length scales for now. For a global polymorphous transition, the entire material undergoes a phase transformation and so it is straightforward to model the respective

parent and daughter phases unambiguously at all length scales. For example, it is relatively straightforward to depict the HCP α -Zr and BCC β -Zr phases in DFT, PF and FE simulations. However, multiscale modelling is more difficult for precipitation reactions because there are several intrinsic length scales associated with the precipitate features, including the sizes of precipitates, the thickness of matrix-precipitate interfaces and the inter-precipitate separation distances. For the case of micro-hydrides in Zr, the precipitate sizes range from ~ 1 nm to ~ 1 μ m, the interfaces are atomically sharp like grain boundaries, and the typical spacing between micro-hydride platelets of ~ 1 μ m depends on the autocatalytic (sympathetic) nucleation mechanism whereas the macro-hydride colonies could be ~ 100 μ m apart depending on the distribution of nucleation sites. Furthermore, as this is a heterogeneous nucleation process, there is a hierarchy of preferred nucleation sites, such as grain boundaries and SPPs, each of which has its own microstructural length scales. (In a homogeneous nucleation process, there would be only one length scale associated with the distribution of nucleation sites.) As previously discussed, the standard computational methods cannot convey all of these intrinsic length scales in one standalone simulation. The system size is the limiting factor for DFT and PF simulations, whereas the spatial resolution is the limiting factor for PF and FE simulations. Therefore, a multiscale model of DHC should carefully account for these length scales in a consistent manner.

A multiscale model of DHC should also account for the time scales associated with hydride precipitation. Recall that the parent α -Zr phase and the various daughter hydride phases differ in both stoichiometric composition and crystallographic structure. Given that H atoms are more mobile than Zr atoms, it is postulated that phase transformation process involves both civilian and military modes of growth. The hydride phases grow as H interstitials cluster in the α -Zr matrix, which enables Zr atoms to undergo a shear transformation from the hexagonal crystal structure to a cubic crystal structure [Puls (2012)]. This two-step mechanism is governed by the rate of H diffusion as well as the accumulation of H atoms into highly concentrated clusters. It is important to note that whilst the H clustering process also involves H diffusion, it is distinguished here from the linear diffusive transport of non-interacting H to the flaw tip. It is assumed that the clustering process is much faster than linear diffusion because of quantum mechanical nature of H-H interactions. Hence, precipitate growth is controlled by the rate of clustering, which is on the whole controlled by diffusion. In reactor conditions, the diffusion velocities of H in α -Zr are typically on the order of ~ 1 mm/hour, which defines the equilibration time scales for the flaw-tip H concentration profile and hydride microstructure. This can be further jus-

tified by noting that thermomechanical cycles span days. Hence, the time scales over which temperature and pressure change are much longer than the time taken for thermodynamic equilibration in the vicinity of the flaw tip. Therefore, for the purpose of this work, the time scales associated with precipitation will not be treated explicitly as the phase transformation process is on the most part governed by diffusion.

In the discussion thusfar, no attention has been given to the role of anisotropy during phase transformations. This is a tremendous oversight for modelling DHC because the crystalline anisotropy of HCP α -Zr has several important effects on hydride precipitation. Firstly, the intrinsic length scales associated with hydride features are not the same along all crystallographic directions. For example, it is misleading to state that the micro-hydride precipitate size is $\sim 1 \mu\text{m}$ because their morphology is more needle-like as opposed to spherical. This misrepresentation is likewise for the morphologies of macro-hydride colonies that form elongated assemblies because of the anisotropic orientation relationships that define the habit planes. Secondly, the combination of crystalline anisotropy and polycrystalline heterogeneity suggests that certain Zr alloy microstructures may be more susceptible to DHC failure than others. For example, certain grain boundaries could be more favourable as nucleation sites than others, which is, in part, a consequence of the compatibility stresses. If a particular microstructure contains many such highly favourable grain boundary nucleation sites, then hydride precipitation may be more pronounced and DHC failure more likely. Thirdly, the overall rate of the evolution of the hydride microstructure is affected by the stress-diffusion equilibration of the H concentration profile, which is in turn affected by the stresses in the anisotropic continuum as well as the anisotropic elastic dipole and mobility tensors. It is, therefore, clear that anisotropy is quite significant to the treatment of hydride precipitation in Zr alloys, and hence its effects cannot be excluded in the diffusion-precipitation analysis.

Unifying the themes of this discussion on phase transformations, the problem of hydrides in Zr may be summarised as follows. The evolution of the hydride microstructure is a precipitation reaction that involves both the civilian motion of H atoms and military motion of Zr atoms. The H atoms diffuse under the influence of the gradients of stress, temperature and chemical potential, and then cluster in the vicinity of heterogeneous nucleation sites. The process of H clustering is assumed to be much faster than diffusion and occurs simultaneously alongside the military motion of Zr atoms. Owing this displacive motion of Zr atoms, the matrix-hydride interfaces are atomically sharp. The matrix-hydride interface grows into the parent austenite until the micro-hydride precipitate attains a needle-like geometry of some criti-

cal size. This micro-hydride needle then provides a favourable environment for secondary micro-hydride nuclei to form in its vicinity. A macro-hydride colony is formed by the sequence of autocatalytic nucleation events and the merging of smaller colonies. The overall evolution of the hydride microstructure can be described by the minimisation of the free energy of the system.

In the following, each of these ideas is discussed in more detail in the context of multiscale modelling of the early stages of DHC failure. In particular, emphasis is given to the theoretical concepts that will underpin the computational methodology. Although the focus is on hydride precipitation in Zr in the context of DHC, many ideas presented here are general to other phase transformations processes, including polymorphous transitions. Owing to its multiscale complexity, DHC can be regarded as the quintessence of precipitation reactions in metal alloys. Therefore, the following concepts can easily be translated to other precipitation reactions that are equally (or less) complicated. Examples include hydride nucleation in Ti during SHC, the formation of carbides in steels during bainitic transformations and the growth of oxides in U fuel [[Bhadeshia \(2001\)](#)].

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6.1 Free Energy

In the early stages of DHC, thermodynamic driving forces encourage the precipitation of hydride phase particles in the parent α -Zr alloy containing H interstitials in solid solution. As explained previously, these thermodynamic driving forces also govern the long-range diffusion of H in the bulk matrix. In order to isolate the effects of the driving forces that pertain only to the phase transformation from the α -Zr-H solid solution to a hydride phase, it is assumed that the long-range diffusive transport of H interstitials has already taken place, that is, the α -Zr-H solid solution phase is in elasto-chemical equilibrium. The driving forces for precipitation correspond to the non-dilute clustering of H atoms and the martensitic reconfiguration of Zr atoms as well as the atomic reordering of H interstitials which transform the original HCP Zr lattice into the hydride crystal structure. In this sense, the processes of long-range diffusion and short-to-mid range precipitation are assumed to be causal but uncoupled.

Although hydride formation is indeed a precipitation reaction, it is more convenient to first consider a hypothetical polymorphous transition from the α -Zr-H solid solution phase to a pure hydride phase. (This is analogous to both experimental studies on the bulk hydride layers and DFT models of hydride crystals). The hydride phase may be either the metastable ζ -ZrH_{0.50} or γ -ZrH_{1.00} phases, or the stable δ -ZrH_{1.66} or ϵ -ZrH_{2.00} phases. However, for the sake of generality, the symbol $\hbar$ -ZrH _{κ} is used to denote a generic hydride phase. Understanding the α -Zr-H $\rightarrow$ $\hbar$ -ZrH _{κ} polymorphous transition will help introduce the concepts necessary for modelling hydride precipitation.

6.1.1 Driving Forces

The driving forces operate to minimise the total internal energy U of the thermodynamic system. The change in the internal energy during the polymorphous α -Zr-H $\rightarrow$ $\hbar$ -ZrH _{κ} transition is given by

$$\Delta U[\alpha\text{-Zr-H} \rightarrow \hbar\text{-ZrH}_{\kappa}] = U[\hbar\text{-ZrH}_{\kappa}] - U[\alpha\text{-Zr-H}] < 0, \quad (6.1)$$

where $U[\alpha\text{-Zr-H}]$ and $U[\hbar\text{-ZrH}_{\kappa}]$ are the respective internal energies of the system in the α -Zr-H phase and $\hbar$ -ZrH _{κ} phase as given by the integrated Gibbs-Duhem relations:

$$U[\alpha\text{-Zr-H}] = TS[\alpha\text{-Zr-H}] - PV[\alpha\text{-Zr-H}] + \sum_r \phi_r N_r[\alpha\text{-Zr-H}] \quad (6.2)$$

$$U[\hbar\text{-ZrH}_{\kappa}] = TS[\hbar\text{-ZrH}_{\kappa}] - PV[\hbar\text{-ZrH}_{\kappa}] + \sum_r \phi_r N_r[\hbar\text{-ZrH}_{\kappa}] \quad (6.3)$$

The energy change in Eq. (6.1) can be deconstructed by noting that U contains two contributions: (i) the free energy that amounts to the total work the system can perform; and (ii) the unusable energy that is lost to the surroundings when performing work, which is associated with the entropy. The driving forces then operate to minimise the free energy but this process may be accompanied by either a positive or negative change in the entropy of the system. The form of the free energy depends on the nature of the thermodynamic system [Callen (1960)].

Thermodynamic Potentials. The intellectual base for the thermodynamics of a metal alloy is the multi-component solid solution model [Cahn and Haasen (1996)]. Any structural change of a solid solution can be generally described by a reduction in the Gibbs free energy

$$G = H - TS \quad \text{with} \quad H = U + PV, \quad (6.4)$$

where H is the enthalpy. For transformations between phases of condensed matter, the changes in P and V are negligible in comparison to changes in U , and so the Gibbs free energy can be approximated by the Helmholtz free energy

$$F = U - TS. \quad (6.5)$$

It is the functional minimisation of F that governs the phase transformation. Recall that this is the premise of the PF method [Chen (2002)].

Critical Conditions. For a polymorphous $\alpha\text{-Zr-H} \rightarrow \beta\text{-ZrH}_\kappa$ transition at constant T , the driving force is given by the change in the free energy per unit volume as

$$\begin{aligned} \Delta F_{(V)}[\alpha\text{-Zr-H} \rightarrow \beta\text{-ZrH}_\kappa] &= \Delta U_{(V)}[\alpha\text{-Zr-H} \rightarrow \beta\text{-ZrH}_\kappa] \\ &\quad - T \Delta S_{(V)}[\alpha\text{-Zr-H} \rightarrow \beta\text{-ZrH}_\kappa], \end{aligned} \quad (6.6)$$

where $\Delta U_{(V)}$ and $\Delta S_{(V)}$ denote the respective changes in the internal energy and entropy per unit volume. At the critical temperature for phase transformation, T_c , the $\alpha\text{-Zr-H}$ phase and $\beta\text{-ZrH}_\kappa$ phase are in equilibrium and hence $\Delta F_{(V)}$ is zero, that is,

$$\Delta S_{(V)}[\alpha\text{-Zr-H} \rightarrow \beta\text{-ZrH}_\kappa] = \frac{\Delta U_{(V)}[\alpha\text{-Zr-H} \rightarrow \beta\text{-ZrH}_\kappa]}{T_c}. \quad (6.7)$$

For a small but finite undercooling, $(T_c - T)$, it is reasonable to assume that $\Delta U_{(V)}[\alpha\text{-Zr-H} \rightarrow \beta\text{-ZrH}_\kappa]$ and $\Delta S_{(V)}[\alpha\text{-Zr-H} \rightarrow \beta\text{-ZrH}_\kappa]$ are constant; then it is possible to express the driving force for phase transformation in Eq. (6.6)

as

$$\begin{aligned}\Delta F_{(V)}[\alpha\text{-Zr-H} \rightarrow \beta\text{-ZrH}_\kappa] &= \Delta U_{(V)}[\alpha\text{-Zr-H} \rightarrow \beta\text{-ZrH}_\kappa] \left(\frac{T_c - T}{T_c} \right) \\ &\simeq \Delta H_{(V)}[\alpha\text{-Zr-H} \rightarrow \beta\text{-ZrH}_\kappa] \left(\frac{T_c - T}{T_c} \right).\end{aligned}\quad (6.8)$$

Note that a correction must be applied for larger undercoolings. Considering the typical values of the latent heat changes, $\Delta H_{(V)}$, listed in **TAB. 6.1**, it is evident that the driving force for solid state transformations is much smaller than for solidification at similar undercoolings.

It might be reasonable to assume that $\Delta H_{(V)}$ for the hypothetical polymorphous $\alpha\text{-Zr-H} \rightarrow \beta\text{-ZrH}_\kappa$ transition would be similar to the $\beta \rightarrow \alpha$ transition in Zr at high temperatures. But such a global $\alpha\text{-Zr-H} \rightarrow \beta\text{-ZrH}_\kappa$ transition is not observed; hydride precipitates of distinct volumes form in the largely unchanged $\alpha\text{-Zr-H}$ matrix. One reason for this deviation pertains to an omission in Eq. (6.5) which at present does not account for matrix-precipitate interfaces.

6.1.2 Interfacial Energy

In both polymorphous transitions and precipitation reactions, the interfaces between the parent and daughter phases migrate during the evolution of the microstructure. There is an energy associated with these two-phase interfaces, which must be included in the computation of the total internal energy of the system at each stage of the phase transformation. This interfacial energy then contributes to the free energy and hence the driving force. In the case of precipitation reactions, the interfacial energy could restrict the size and geometry of the precipitate features, and it also governs

TAB. 6.1

Latent heat values

Examples of typical latent heat values for various bulk phase transformations of pure metals. Although these values are not directly comparable to the phase transformation from the $\alpha\text{-Zr-H}$ solid solution to the hydride phase, they provide some insight into the difficulties of directly relying upon experimental parameters for computational modelling.

Adapted from [Cahn and Haasen \(1996\)](#).

System	Polymorphous Transition	$\Delta H_{(V)}/(\text{kJ/g} \cdot \text{mol})$	T/K
CRYSTAL STRUCTURE CHANGE			
Fe	austenite to ferrite	−0.9	1183
Zr	BCC to HCP	—	—
Ti	BCC to HCP	−3.5	1155
MATTER STATE CHANGE			
Fe	liquid to solid	−15.5	1809
Zr	liquid to solid	−16.9	—
Ti	liquid to solid	−18.9	2133

the preferred crystallographic orientation relationships [Cahn and Haasen (1996)].

Planar Interface. In order to apply these ideas to hydride precipitation, Eq. (6.5) must then be modified to account for the α -Zr-H/ $\hbar$ -ZrH_k interfacial energy. Consider a virtual thermodynamic system consisting of an enclosed volume that contains a planar interface between the α -Zr-H solid solution and a pure $\hbar$ -ZrH_k phase. Suppose that this planar interface intersects the boundaries the enclosed volume, which is then embedded within a much larger thermodynamic system. The enclosed volume should be large enough to ensure that interface has no noticeable effect on the material along the boundary of intersection. (In practice, this volume could range from 1 nm × 1 nm × 1 nm to 1 μm × 1 μm × 1 μm for the case of α - $\hbar$ interfaces.) In comparison to the bulk treatment of an individual phase, there is now a surface area A that is common to each of the two phases. As the phase transformation progresses at a constant temperature and pressure, the microstructure evolves because changes in A reduce F , either directly or indirectly. The simplest way to see how changes in A affects F is to consider an infinitesimal change from A to $A + \delta A$ such that

$$\begin{aligned} U[A + \delta A] &\simeq U[A] + \delta U[\delta A] \\ &\simeq U[A] + \left[\lim_{\delta A \rightarrow 0} \left(\frac{\delta U}{\delta A} \right) \right]_{|A} \delta A \end{aligned} \quad (6.9)$$

Then it is possible to define the interfacial (or surface) energy as

$$\Gamma = \lim_{\delta A \rightarrow 0} \left(\frac{\delta U}{\delta A} \right)_{|A}, \quad (6.10)$$

which is an energy per unit area. It is now useful to derive an expression for Γ and see how it explicitly relates to the driving force.

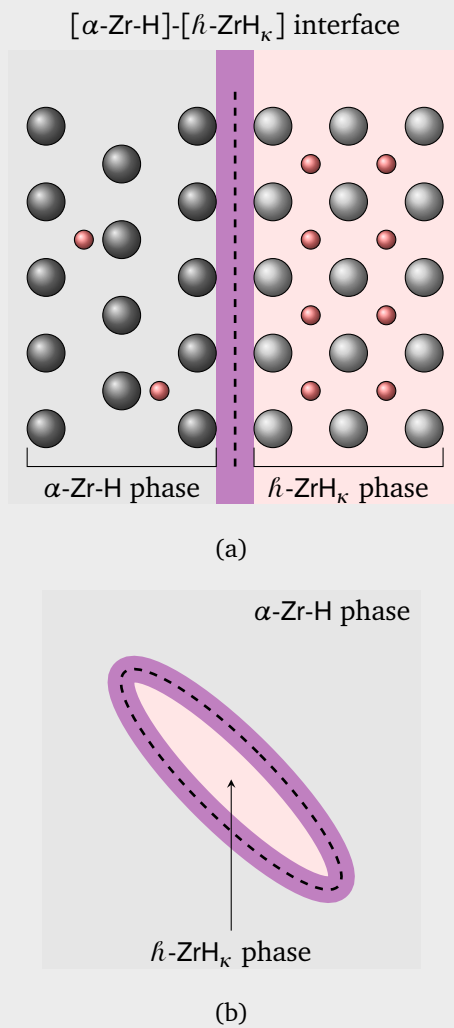
Suppose that the progress of phase transformation in the virtual thermodynamic system can be described by a variable ξ such that ξ is zero in the initial state when only the α -Zr-H-phase is present, and ξ is one in the final state that includes $\hbar$ -ZrH_k-phase precipitates in the α -Zr-H-matrix. For a given $\xi \in [0, 1]$, the two-phase system is at some stage along its evolution, denoted $(\alpha\text{-Zr-H}/\hbar)_{\xi}$, and let $A[(\alpha\text{-Zr-H}/\hbar)_{\xi}]$ be the total area of the two-phase interface at this stage. Then it is possible to write the total internal energy for this bounded system as

$$\begin{aligned} U[(\alpha\text{-Zr-H}/\hbar\text{-ZrH}_k)_{\xi}] &= TS[(\alpha\text{-Zr-H}/\hbar\text{-ZrH}_k)_{\xi}] - PV[(\alpha\text{-Zr-H}/\hbar\text{-ZrH}_k)_{\xi}] \\ &\quad + \sum_r \phi_r N_r[(\alpha\text{-Zr-H}/\hbar\text{-ZrH}_k)_{\xi}] \\ &\quad + \Gamma A[(\alpha\text{-Zr-H}/\hbar\text{-ZrH}_k)_{\xi}], \end{aligned} \quad (6.11)$$

FIG. 6.1

Matrix-hydride interface

A simplistic representation the energetic interface between the mismatching crystallographic lattices of the parent α -phase matrix and the daughter β -phase precipitate. (a) An atomic scale illustration of the sharp matrix-hydride interface. (b) A microscale illustration of a sharp interface that is a topological manifold that encloses the volume occupied by the hydride within the matrix.



that is, Γ may be interpreted as an excess Gibbs free energy of the interface per unit area. This is more apparent after rearranging Eq. (6.11) as

$$\Gamma = \frac{G[(\alpha\text{-Zr-H}/\beta\text{-ZrH}_x)_\xi] - \sum_r \phi_r N[(\alpha\text{-Zr-H}/\beta\text{-ZrH}_x)_\xi]}{A[(\alpha\text{-Zr-H}/\beta\text{-ZrH}_x)_\xi]}. \quad (6.12)$$

The Gibbs free energy would only account for compositional changes if the interfaces were ignored. In general, changes in the composition and in $A[(\alpha\text{-Zr-H}/\beta\text{-ZrH}_x)_\xi]$ are simultaneous. For example, as ξ increases, the amount of the $\beta\text{-ZrH}_x$ -phase component may change, which corresponds to a change in $A[(\alpha\text{-Zr-H}/\beta\text{-ZrH}_x)_\xi]$ accordingly. (These changes may be either positive or negative as ξ increases.) It is evident that a change in $A[(\alpha\text{-Zr-H}/\beta\text{-ZrH}_x)_\xi]$ could lower F if there is a reduction in the Gibbs free energy that is greater in magnitude than a change in the internal energy due to compositional changes, or vice versa.

Manifold Interface. The preceding theoretical treatment is far too simplistic considering FIG. 6.1 because the virtual thermodynamic system consisted of only one planar interface. In reality, however, the matrix-precipitate interface is a manifold that encloses the volume of a precipitate feature. In light of this shortcoming, two extensions are required for Γ to be a more useful physical quantity. Firstly, Γ must depend on the relative orientation between the parent matrix and daughter precipitate phases, which is particularly important for anisotropic crystals. Generally, Γ is then a spatially-varying field that changes along the manifold that encloses the precipitate. In the case of γ -hydride needles on the basal plane of the α -Zr-H matrix, there are at least three distinct interfaces to consider. Secondly, the enclosed volume, $V[(\alpha/\beta)_\xi]$, should refer to an entire precipitate feature embedded within a much larger thermodynamic system. A volume-to-area ratio then appears in Γ , implying that there is an optimal precipitate size and geometry for which the free energy is minimised.

So it is now clear why the interfacial energy, Γ , provides an essential contribution to the driving force for precipitation reactions. However, Γ is a very delicate parameter and, only in very rare systems, reliable values of Γ are known [Janssens et al. (2007)]. The main reason for this is that Γ cannot be measured directly by experimental methods. It is also difficult to compute Γ from first-principles because the state-of-the-art DFT simulation cannot yet model system sizes much larger than the precipitate features. Currently, it is only possible to obtain Γ through indirect means by comparing experimental results with suitable theoretical models that utilise Γ as a parameter.

In microstructural simulations, Γ is very sensitive to crystallographic misorientation and the thickness of the interface as well as elastic misfit

strains, degree of coherency and solute segregation. For the case of γ -hydrides in the α -Zr-H matrix, the values of Γ are not known. This is problematic for PF models where the interfacial energies must be treated explicitly in the computation of the driving force, F , and hence Γ is often treated as a fitting parameter to ensure that simulations coincide with experimental observations. However, as mentioned earlier, this is somewhat circular and, in turn, it may be both physically inaccurate and computationally inefficient.

For an accurate and efficient multiscale model of DHC, it is more useful to deduce the effects of Γ rather than work with Γ directly. It is then simpler to adopt the precipitate sizes, geometries and orientation relationships that have been determined through experimentation; the interfacial energy contribution to the free energy need not be considered explicitly in, say, a partial differential equation for the free energy, but its effects can instead be implemented through an algorithm for nucleation and growth. In any case, it can be argued that this is a sensible alternative because it is really not clear how Γ truly contributes to the mathematical form of F for the Zr-H system.

6.1.3 Strain Energy

The preceding analysis is useful for treating individual precipitates. However, the problem of DHC involves macro-hydride colonies that are composite assemblies of micro-hydride platelets. This is, in part, a consequence of Γ because it restricts the precipitate size, geometry and orientation relationships. As Γ is not known or treated explicitly, a completely novel approach is required to model the macro-hydride colonies. There is, in addition, another contribution to the driving force, F , that arises from the interaction between micro-hydrides platelets; this is the elastic strain energy [Khachaturyan (1983)].

From the standpoint of elastic field theory, as discussed previously, each precipitate is a three-dimensional defect that exerts its elastic distortion on the continuum. The earlier stress analysis introduced a planar model of a micro-hydride needle as represented by a Volterra edge dislocation dipole, whose stress state could be computed analytical using the principle of linear superposition [Patel et al. (2017)]. This is the ideal starting point for setting up an algorithmic framework for computing the energetics of a continuum that contains multiple micro-hydride needles in the vicinity of each other.

Multi-Hydride Systems. Given a system of N_H micro-hydride needles, $\{h_{\bar{\alpha}} | \bar{\alpha} = 1, 2, \dots, N_H\}$, in which the micro-hydride needle $h_{\bar{\beta}}$ is centred at the position $\mathbf{x}_{\bar{\beta}}$ with respect to some reference coordinate and at a relative orientation $\phi_{\bar{\alpha}}$, the total stress of the system can be expressed as linear superposi-

tion as

$$[\Sigma_{\text{sys}}]_{ij}(x_1, x_2; \{h_{\bar{\alpha}}\}) = \sum_{\bar{\alpha}} [\sigma_p]_{aij}(x_1 - x_{\bar{\alpha}1}, x_2 - x_{\bar{\alpha}2}; \ell_p, t_p, \phi_{\bar{\alpha}}) \quad (6.13)$$

which is a simple task for a computer to perform because the stress state of an individual precipitate, σ_p , has a known analytical expression. The geometrical parameters ℓ_p and t_p correspond to the needle length and thickness respectively. Note that there is an additional parameter for every micro-hydride needle embedded within σ_p , which are the relative orientation angles $\{\phi_{\bar{\alpha}}\}$ that are defined in a global reference of coordinates.

The total elastic energy contribution to the overall free energy of this planar system is then given by the standard expression for the strain energy per unit length, which, in terms of Eq. (6.13), can be written as

$$U_{\text{sys}}(\{h_{\bar{\alpha}}\}) = \frac{1}{2Y} \iiint_{\mathcal{C}} d\mathcal{C}(x_1, x_2) \delta U_{\text{sys}}$$

$$\delta U_{\text{sys}} = \left[(1 + \nu) [\Sigma_{\text{sys}}]_{ij}(x_1, x_2; \{h_{\bar{\alpha}}\}) [\Sigma_{\text{sys}}]_{ij}(x_1, x_2; \{h_{\bar{\alpha}}\}) \right. \\ \left. - \nu [\Sigma_{\text{sys}}]_{kk}(x_1, x_2; \{h_{\bar{\alpha}}\}) [\Sigma_{\text{sys}}]_{mm}(x_1, x_2; \{h_{\bar{\alpha}}\}) \right], \quad (6.14)$$

where the integration domain $\mathcal{C}$ is a simulation cell with appropriately chosen cell dimensions. [Note 6](#) The integrand, δU_{sys} , is a point-wise strain energy density that is positive definite as expected; its mathematical form is important in order to appreciate the underlying reasons for optimised (low energy) configurations of micro-hydride needle networks. The relative positions and orientations are then the free parameters for a multi-parameter optimisation problem; the steepest descent or conjugate gradients algorithms are amongst the options for such a multi-parameter space optimisation calculation. Again this optimisation is also a straightforward computational task, which, given a large value for N_H , is already far more efficient than the conventional PF modelling approach of optimising the free energy [[Bair, Zaeem, and Tonks \(2015\)](#) and [Chen \(2002\)](#)].

In order to showcase this effectiveness of the analytical expressions, the following two toy models of micro-hydride strain energetics are considered for demonstration purposes. The first of these two toy models, Toy Model A, is a precursor to more sophisticated simulations of notch-tip hydrides whereas the second of these two toy models, Toy Model B, emulates the stacking effect of two micro-hydride needles in a macro-hydride colony. These two toy models are visualised in [FIG. 6.2](#) from which it is clear that they serve to introduce the effects of stress.

Such a stress-precipitation analysis ignores the diffusion aspect of the multi-step phase transformation mechanism and instead assumes that there

Note 6

Numerical integration and simulation cells

The computations of the strain energetics require the implementation of numerical integration algorithms over the two-dimensional region of the simulation. The accuracy-efficiency trade-off can be investigated by considering an integrand sampling that is fine enough to meet a convergence criterion and coarse enough to retain the computational speed without mismanaging computer memory. Convergence tests have been performed given the nature of the singularities in the stress states of the dislocations, and the strain energy of an individual dislocation is one such test given that there is an analytical benchmark for comparison. For the sake of simplicity, the present work only uses the Newton-Cotes quadrature formulae that perform numerical integration over a rectangular simulation cell with uniform integrand sampling. Issues concerning the dislocation singularities are bypassed through the use of an appropriate core cutoff. Extensive convergence testing has not been undertaken in this investigation given the overarching aims of this project, and so further work is required to optimise the choice of numerical integration technique and simulation cell properties.

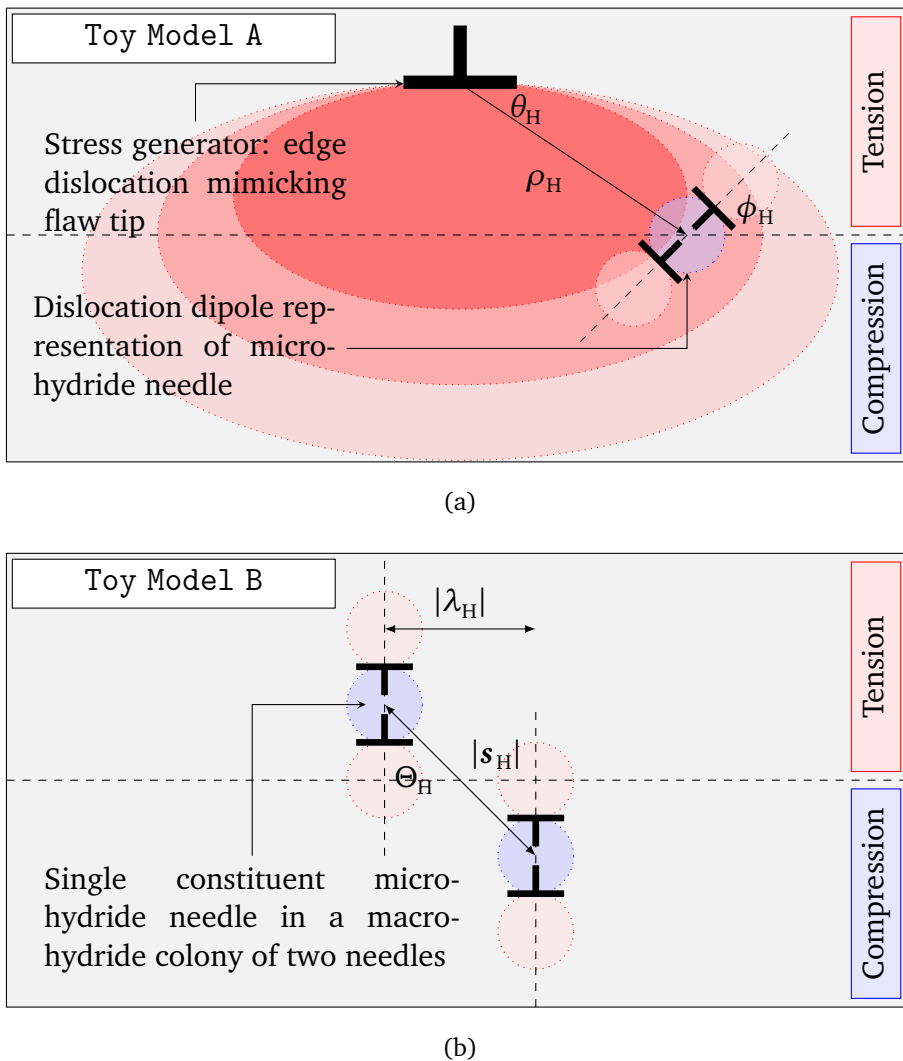


FIG. 6.2

Toy models of multi-hydrate systems

Two preliminary studies of the strain energetics of a continuum containing multiple micro-hydrate needles. The aim of these preliminary studies is to determine the parameters for which the strain energy is minimised, thus representing low free energy configurations. (a) A toy model of flaw-tip hydrides in which the orientation of the micro-hydrate needle relative to the flaw is the free parameter of interest. (b) A toy model of a macro-hydrate colony composed of two micro-hydrate needles in which the relative the angular configuration is the free parameter of interest.

already is sufficient H solute concentration available for micro-hydrate needles to form; it is then only necessary to determine the sequence in which the needles form and then optimise the strain energy sequentially to obtain the mechanical stable configurations of the micro-hydrate needle networks. These two toy models of multi-hydrate systems are discussed in more detail in the following passages; these preliminary results are important because later discussions effectively extend and combine these toy models to formulate a more comprehensive model of the early stages of DHC failure.

Toy Model of Flaw-Tip Hydrides. This first toy model, Toy Model A, is a preliminary check to see how a micro-hydrate needle aligns itself relative to a potent stress-raiser: a Volterra edge dislocation with a significantly larger slip vector that mimicks that tip of a crack or a notch. ^{Note 7}

The main purpose of this first preliminary study is to evaluate the strain

Note 7

Distributed dislocation representation of sharp cracks

Recall that the tips of sharp cracks in distributed dislocation models were marked by singularities that suggested the presence of a very large tensile field ahead of the flaw; so a lone but potent Volterra edge dislocation is a sensible choice as an initial gauge for simulating the effect of mechanical loading on hydrate orientation in the vicinity of a flaw.

energy variation for the setup of Toy Model A depicted in FIG. 6.2 as function of the relative orientation of the micro-hydride needle located in the vicinity of a fixed stress generator: the tensile region ahead of the Volterra edge dislocation that represents the stress profile ahead of a loaded flaw. A square simulation cell with the dimensions $20\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$ is chosen for convenience, and a spatial mesh resolution of $0.1\text{ }\mu\text{m}$ provides the necessary convergence without compromising the simulation runtime. The relative spacing between the stress generator and micro-hydride needle centre, ρ_H , is taken to be $10\text{ }\mu\text{m}$ in order to facilitate visualisation of physical fields given the choice of spatial resolution. The polar positioning of the micro-hydride is taken to be $(\pi/2)$ rad for simplicity so that the centres of both stress sources are vertically aligned in a symmetric simulation cell. All edge dislocations have the same Burgers vector of $1.0 \times 10^{-2}\text{ }\mu\text{m}$, noting that choice of the Burgers vector for the stress generator should not qualitatively change the outcome of this study.^{Note 8} In this toy model, the relative orientation of the micro-hydride needle, ϕ_H , is varied across the full angular range $[0, 2\pi]$ rad and strain energy is computed.

Note 8

Visualisation parameters

Although it would be ideal to select a larger Burgers vector for stress generator so as to reflect a more realistic flaw tip, such a choice interferes with visualisation of the results—and it is not necessary at this stage.

Before inspecting the single-valued strain energy, consider first the profiles of the strain energy density that are shown in FIG. 6.3, which are two-dimensional contour plots of the pointwise integrand in Eq. (6.14) obtained in the initialisation steps of the simulation. It is always worth remarking how rapidly such important simulation data can be generated with computational steps that adopt analytical formulae. This data can be efficiently processed and manipulated for important computations that require knowledge of the free energy, which is crucial for simulating thermodynamics at the mesoscale.

It is highly desirable that these thermodynamic simulations are indeed efficient because there is stochasticism in these two toy models, and stochastic randomness should ideally be averaged over statistical ensembles. Although Toy Model A is undeniably very simplistic, there are still about a dozen different parameters, including the physical microscopic details, such as the micro-hydride needle geometry and the relative positioning, as well as various computational artefacts such as the simulation cell dimension and the spatial mesh resolution. So, in order to really extract the useful information from such a toy model, that is, information needed to qualify trends and quantify errors, it is necessary to conduct a parametric study that would involve repeat simulations to compute the mean and standard deviations of the findings. Given that computing such statistical ensembles is a still quite a formidable task for even this simple analytical model, it would be impractical—or rather, virtually impossible—for PF simulations that bear a great computational expenditure to perform such a feat [Chen (2002)].

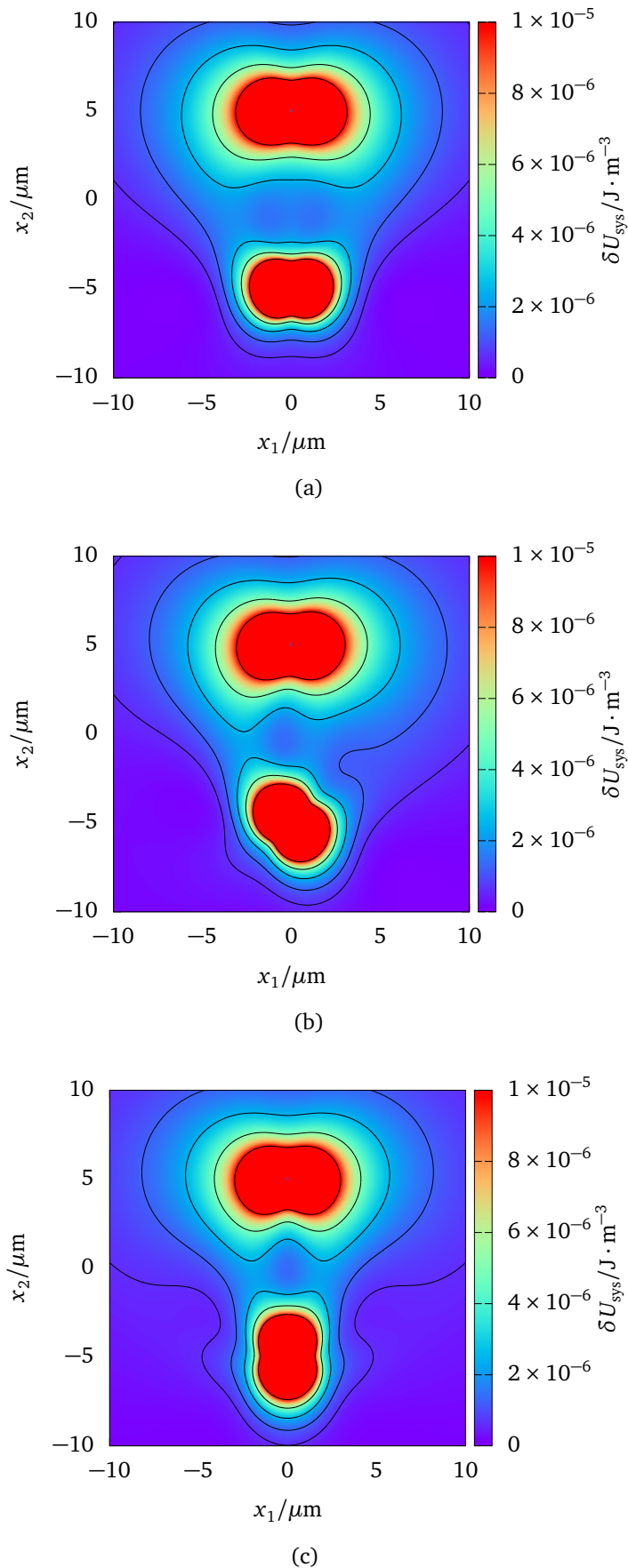


FIG. 6.3

Strain energy density for the toy model of a notch-tip hydride

The strain energy density profile for the instance of the toy model of a notch-tip hydride with the parameters described in the text. The upper lobe is due to the stress generator whereas the lower lobe is due to the dislocation dipole representation of a micro-hydride needle. The simulation cell is the integration domain so the configuration is more energetically stable or favourable if there are larger areal pockets in which the strain energy density assumes lower values. The size of such lower energy areal pockets is determined by the relative orientation of the micro-hydride needle ahead of the notch tip. (a) The minimum energy configuration for which $\phi_H = \pi/2$ rad. (b) A relatively high energy configuration for which $\phi_H = \pi/4$ rad. (c) A relative low energy configuration for which $\phi_H = 0$ rad

As for the profiles themselves in [FIG. 6.3](#), notice that the minimum energy configuration is when the micro-hydride is perfectly aligned along the radial direction away from the stress generator. The minimum energy configuration occurs when the tensile field of the stress generator is maximally diminished by the compressive field inside the micro-hydride needle. Referring to [FIG. 6.4](#), this clearly occurs when ϕ_H takes on the value $\pi/2$ rad in Toy Model A for the designated simulation parameters. Note that there are other values that also yield very low energy values such as 0 rad and π rad which can also be justified by the corresponding strain energy density profiles; in this case, the compressive region inside the micro-hydride needle is exposed to the tensile field of the stress generator, however, the tensile lobes emanating outwards from the dislocation dipole reinforce the tensile field of the stress generator, which then increases the overall strain energy for the simulation cell.

The micro-hydride needle prefers to align itself radially with the stress generator, which is a promising result for later simulations. It implies that individual needles would preferentially be orientated radially towards the loaded flaw if they had absolute freedom to reorientate (rigidly rotate) themselves. ^{Note 9} Intuitively, it is clear that a system with multiple micro-hydride needles would also exhibit the same minimum strain energy configurations if the stress generator provided the (sole) dominant elastic contribution to the overall free energy provided that the needle-needle interactions are negligible.

In this simplistic treatment of the free energy that includes only the strain energy contribution, the orientation of each micro-hydride needle is a full degree of freedom. That is, the orientation of a micro-hydride needle in its minimum energy configuration can effectively take any value in the range $[0, 2\pi)$ rads, barring any degenerate configurations due to symmetry. However, in reality, the micro-hydride needles have preferential orientations along, say, the basal plane, which is possibly attributed to the interfacial energy [[Carpenter \(1973\)](#), [Carpenter, Watters, and Gilbert \(1973\)](#), and [Puls \(2012\)](#)]. Therefore, in order to algorithmically include both the interfacial energy and strain energy contributions to the overall free energy, it is more appropriate to sample the preferential angles in the range $[0, 2\pi)$ rads that correspond to the minimum interfacial energy configurations and then determine the minimum strain energy out of these possibilities. This strategy is both accurate and efficient: it is reflective of the physical system at hand and it requires substantially less computational expenditure in comparison to the numerical optimisation of complex free energy expressions found in typical PF models [[Bair, Zaeem, and Tonks \(2015\)](#)].

Note 9

Reorientation

Observe that reorientation must involve the migration of H atoms and so this process would probably involve some surface diffusion.

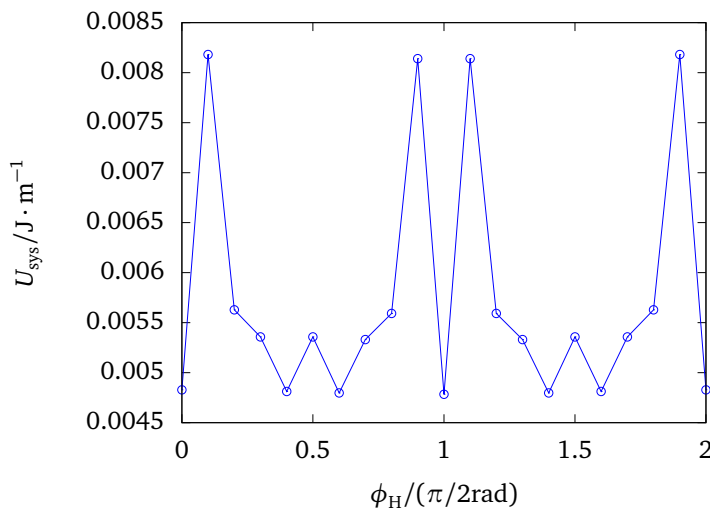


FIG. 6.4

Strain energy for the toy model of a notch-tip hydride

The variation of the strain energy with the relative orientation of the micro-hydride needle for the parameters described in the text. The minimum value for the strain energy occurs when ϕ_H is $\pi/2$ rad, and only slightly higher values are computed for the case when ϕ_H is either 0 rad or π rad as expected.

Toy Model of a Macro-Hydride Colony. This second toy model, Toy Model B, is a preliminary check to see how two adjacent micro-hydride needles may be favourably aligned in a segment of a macro-hydride colony. Recall how the substructure of a macro-hydride colony constitutes a network of micro-hydride needles, and it is hypothesised that these colonies form as a result of an autocatalytic nucleation mechanism [Puls (2012)]. The nucleation of one micro-hydride needle provides the environment for a subsequent nucleation event for another micro-hydride needle in its vicinity. Repetition leads to the formation of hydride features that span $\sim 100 \mu\text{m}$ in size. The substructure of such macro-hydride colonies involves the interaction between micro-hydride needles in close proximity.

The main purpose of this preliminary study is to determine the strain energetics of the macro-hydride colony substructure at a microscopic level. Noting that the superimposed stress fields of the dislocation dipole, which are used to represent the micro-hydride needle, decay rapidly with distance from the dislocation cores, it is worth restricting attention to the interaction of two adjacent micro-hydride needles within a larger macro-hydride colony. The staircase-like stacking of two micro-hydride needles forms the basis of Toy Model B, as shown in FIG. 6.2, which is one of the simplest possible substructural arrangements of the micro-hydride needle networks in the macro-hydride colonies. The simulation cell dimensions and dislocation dipole parameters for Toy Model B are the same as for Toy Model A but now the angle Θ_H determines the direction of the straight line that connects the respective centres of the micro-hydride needles. The angle Θ_H is the free parameter in this toy model, and it is essentially a measure of the slope of the macro-hydride colony with respect to a global coordinate sys-

tem; it is the angular component of the vector $\mathbf{s}_H$ that defines the separation between the centres of the two micro-hydride needles. Although it appears that $\mathbf{s}_H$ has two degrees of freedom in both its magnitude, $|\mathbf{s}_H|$, and its direction as specified by Θ_H with respect to the simulation cell vertical,—which is indeed true from a strictly mathematical standpoint,—it is worth keeping the horizontal separation between micro-hydride needles, λ_H , constant for physical reasons. The autocatalytic nucleation mechanism must hypothetically involve some predetermined range of separation between adjacent micro-hydride needles, and they are not typically observed in configurations where they lie head-to-head along the same crystallographic planes [Puls (2012), Perovic, Weatherly, and Simpson (1982), Perovic, Weatherly, and Simpson (1983), and Perovic and Weatherly (1984)]. Referring to the aforementioned micrographs of the micro-hydride needles at the TEM scales, it seems that fixing λ_H to be $1\ \mu\text{m}$ is a sensible choice for this simulation [Perovic and Weatherly (1984)].

Considering the strain energy profiles for Toy Model B in FIG. 6.5, it is evident that the highest energy configuration is one in which the two micro-hydride needles are perfectly aligned. This is because the tensile and compressive stresses of the respective dislocation dipoles superimpose constructively and reinforce each other; the resultant stress field is effectively representative of a single dislocation dipole with a larger slip vector. Therefore, as shown in FIG. 6.6, such a perfectly aligned configuration is the least energetically favourable one. As Θ_H increases alongside the corresponding increase in the vertical separation between the micro-hydride needles, defined by $|\mathbf{s}_H| \cos(\Theta_H)$, it is evident that the overall strain energy decreases as expected. The obvious explanation for this lies in Eq. (6.14), from which it is clear that the point-wise integrand assumes lower values if the tensile and compressive stresses from respective dislocation dipoles are able to negate each other more as the two oppositely signed edge dislocations approach each other.

The curve in FIG. 6.6 suggests that there are a range of relatively low energy configurations beyond Θ_H values of $\sim \pi/4$ for the fixed λ_H value of $1\ \mu\text{m}$, which agrees with the previous explanation. This implies that there would be minimum energy configurations in the presence of a non-uniform background stress, such as the stress around a loaded flaw. However, it is important to restrict the lower range of Θ_H in order to ensure that the micro-hydride needles are not too far apart. Note that there is also a numerical integration effect which needs to be considered because of the finiteness of the simulation cell and the integration domain.

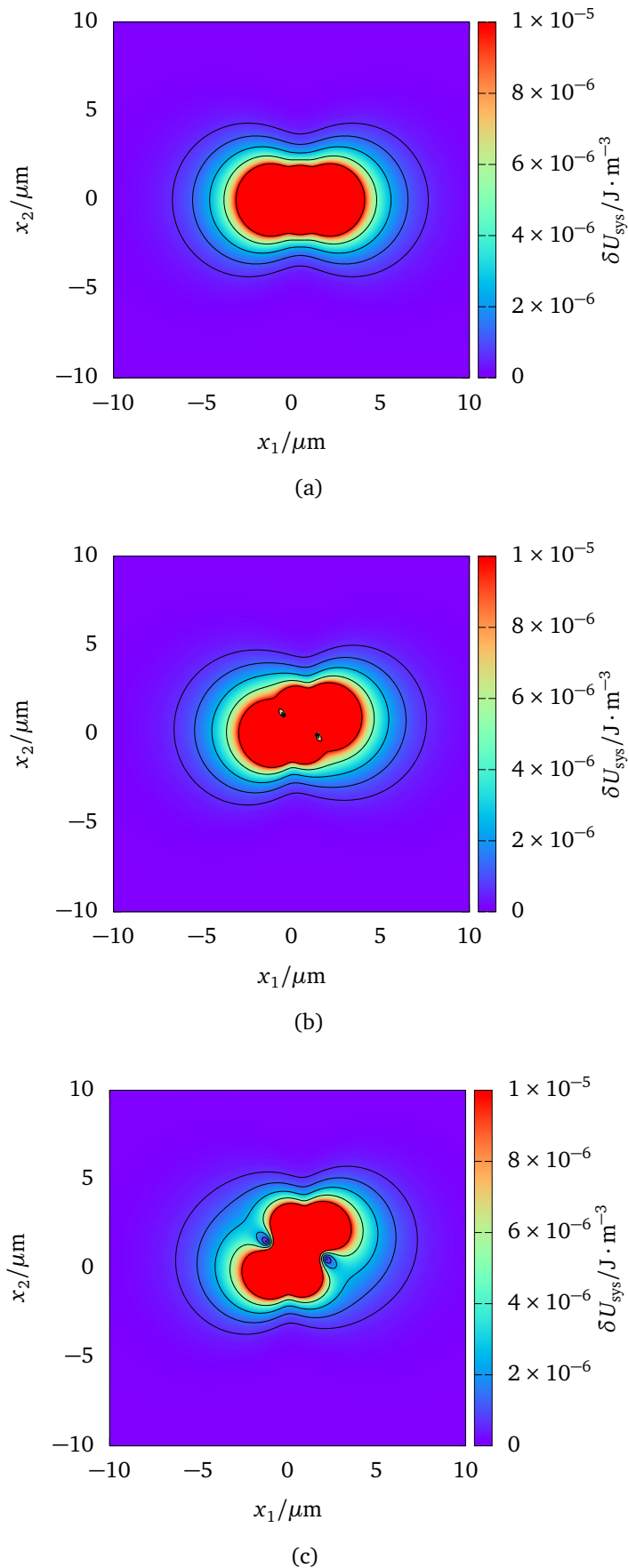


FIG. 6.5

Strain energy density for the toy model of the macro-hydride colony

The strain energy density profile for the instance of the toy model of a (microscopic segment of a) macro-hydride colony with the parameters described in the text. The slope is measured by the relative vertical separation of the centres of the two micro-hydride needles. The central lobe is the result elastic energy of the overlap of the two dislocation dipoles, and the appearance of small diminished regions therein is indicative of the destructive interference of the compressive and tensile contributions from the individual sources. (a) The highest energy configuration with a relative vertical separation of $0\mu\text{m}$. (b) The starting point for a series of very low energy configurations marked by the relative separation of $1\mu\text{m}$. (c) An extremely low energy configuration at a relative separation of $2\mu\text{m}$.

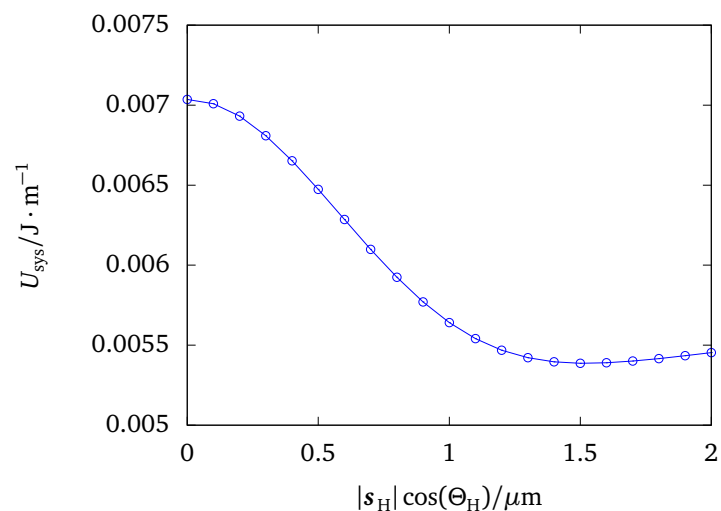
The results of both toy models are promising from the perspective the free energy optimisation, especially given that they accurately reflect the observed physical details of the micrographs and they are computationally efficient to implement. The latter strength is particularly valuable in moving forward for a more comprehensive multiscale model of the first stages of DHC failure. Such a model would require several modifications of Toy Model A with a more realistic notch geometry as well as the effects of the interfacial energy, which would then be combined an extended version Toy Model B in which multiple micro-hydride needles would be treated within larger macro-hydride colonies. Of course, one of the main challenges of such multiscale modelling is the unification of the different length scales; however the conformal symmetries of elastic fields implies that these two preliminary studies would be applicable for more realistic parameters.

The diffusion-precipitation analysis at hand has thusfar focused entirely on the free energy optimisation following precipitation whilst neglecting the underlying diffusion-controlled mechanism. To that end, it is now essential to translate these simplistic simulations of micro-hydride needle precipitate networks into a more complete algorithmic framework that accounts for nucleation and growth of the hydride features alongside the evolution of the H concentration profile. This algorithmic framework for nucleation and growth of hydrides in Zr will be draw upon general ideas in the theory of phase transformations, but it will be specific to the DHC phenomena in order to retain the physical accuracy and computational efficiency bestowed by the treatment of the free energy so far.

FIG. 6.6

Strain energy for the toy model of a macro-hydride colony

The variation of the strain energy with the relative slope between the two micro-hydride needles with a fixed horizontal separation for the parameters described in the text. The configurations become more energetically favourable as the vertical separation increases.



6.2 Nucleation and Growth

Understanding the main contributions to the free energy provides the basic insight into modelling an equilibrated hydrided microstructure, but it is far from a complete strategy for an accurate and efficient multiscale model of diffusion-controlled nucleation and growth of hydride precipitate features in the Zr matrix. In reference to the standard methodologies for simulating phase transitions and, in particular, classical nucleation models of diffusion-controlled precipitation,—which include details such as the progress rate for the overall transformation as well as the diffusion of the mobile species in the parent matrix and daughter precipitate phases corresponding to the migrating matrix-precipitate interface boundaries—, it is important to contextualise the present work so that it is clear how the conventional concepts can be adopted or omitted [Janssens et al. (2007)].

It is worth highlighting from the outset that the multiscale modelling of the evolving hydrided microstructure in the present work begins to diverge considerably from the typical PF models in two ways. Firstly, the interface between the α -phase Zr-H solid solution and β -phase hydride is assumed to be atomically sharp in accordance with experimental micrographs. ^{Note 10} Secondly, the free energy optimisation procedure does not involve solving PDEs on a spatial grid but rather an algorithmic workflow is implemented to account for the observations of the experimental studies of micro-hydride needles and macro-hydride colonies in the anisotropic polycrystalline Zr alloy material. Both of these distinctions should ensure greater accuracy, but given these drastic differences in comparison with the legacy-bounded PF modelling in the name of efficiency, it is then worthwhile to draw parallels with the more general modelling concepts in phase transformation modelling [Chen (2002)].

There are two standard concepts that are particularly relevant to models of sharp-interface phase transitions and diffusion-controlled precipitation; these concepts are (i) the progress rate for the overall transformation towards completion and (ii) the kinetics that accounts for the impingement between two or more growing nuclei. These two concepts are formalised concurrently within the statistical geometric theory of the extended volume [Janssens et al. (2007)]. Application of statistical geometry to the early stages of DHC will provide a rigorous foreground to the more unconventional ideas that are put forward in this heuristic diffusion-precipitation analysis and, in turn, this foreground will justify the novel features of a bespoke multiscale model of DHC failure.

Note 10

Modelling precipitate-matrix interfaces

The computational representation of the interface requires a preset spatial resolution, whether it involves an explicit treatment that can be readily visualised or an implicit treatment used in geometrical tracking. This preset effectively places a constraint on the minimal thickness of the boundary that can be captured by the simulation. Given that microstructural models do rarely, if ever, describe atomic scale resolutions, any physical interface, even if it is known or assumed to be atomically sharp, is diffuse by default; the spatial resolution cannot convey such a relatively thin interface. Such a diffuse representation of the hydride-matrix interface is clearly inaccurate if the spatial resolution of the simulated micrograph is comparable to the corresponding experimental TEM scales.

6.2.1 Progress Rate

One of the greater difficulties with multiscale modelling is the unification of the vastly different time scales, a computational challenge that is immediately apparent for the atomic scale H diffusion-controlled nucleation and growth of microscopic and macroscopic hydride precipitate features. The previous discussions provide reasonable grounds for the efficient treatment of the distinct length scales of micro-hydride needles and macro-hydride colonies in a single simulation cell, that is, it is straightforward to describe lengths in the excess of $\sim 100\ \mu\text{m}$ whilst retaining the spatial resolution below $\sim 1\ \mu\text{m}$ for the elastic fields. However, there is no mention of the time scales because the computational strategy for coupling the H diffusion and hydride precipitation has not been established.

The main concern is the rate of progress for the evolution of the hydride microstructure as a function of the stress-driven diffusion of H atoms to the loaded flaw which causally (or chronologically) enables the nucleation and growth of the micro-hydride needles; this is the essence of a multiscale model of the first stages of DHC failure. It is necessary to consider the temporal aspects of stress-diffusion analysis alongside the temporal aspects of the diffusion-precipitation analysis, and investigate whether it is feasible—or even pragmatic—to explicitly capture both sets of time scales simultaneously in a computational model.

Temporality. As a counterpart to the length scales, the generic paradigm of time scales in computational modelling refers to both the overall temporal interval during which a process occurs as well as the regular or irregular temporal graduations therein that describe the kinetics of the process. The time scales are also an artefact of the intersection between computational science and computer science in the sense that they can connect the real physical temporality of the phenomena to the simulation runtime of the computational model. Longer intervals and finer graduations often translate into a greater number of calculation steps over a simulated time loop, and hence the simulation runtime would be slower for the same computing power. Time scales accordingly factor into the accuracy-efficiency trade-off, which is a vital consideration to the present work. And even if the physical temporality is excluded partly or entirely from the computational model,—that is, the model is, for example, quasi-static, time invariant or non-kinetic, and so the simulation runtime is independent of physical temporality,—this temporality must somehow be extractible because real (physical) material phenomena cannot be instantaneous but rather they involve finite time domains and steps.

Therefore, it would be gross oversight to not devote any attention to

time scales, especially in a multiscale model in which the length scales are bridged. For the multiscale modelling problem at hand, there is a restriction to the early stages of DHC failure, and so it is worth defining the physical temporality of these early stages through an appropriate selection of time scales, and estimating how the time scales would affect the simulation runtime. Given that the stress analysis is time invariant whilst the stress-diffusion analysis is non-kinetic, it is the diffusion-precipitation analysis that must address the paradigm of time scales.

Consider first the various time scales for hydride precipitation in the Zr matrix, which include: (i) the time for the long-range transport of the H atoms to the stress-raiser as defined, in part, by the material-dependent diffusivity that is also sensitive to the thermal and mechanical conditions; (ii) the time for mid-range clustering of H atoms to the nucleation site which would typically involve some quantum mechanical effects in the form of H-H interactions; (iii) the times for the martensitic militaristic reconfiguration of Zr atoms alongside any short-range reordering of the H into preferential tetrahedral sites in the new Zr crystal lattice leading to the formation of a sub-microscopic hydride phase feature; (iv) the time for the morphological growth of individual micro-hydride needles as dictated by migration of sharp matrix-hydride interfaces; and (v) the time for the formation of macro-hydride colonies through a sequence of autocatalytic nucleation steps. Of course, these five time scales constitute a very simplistic hierarchy, and it is perhaps not so straightforward to clearly distinguish these processes or their corresponding time scales in reality. However, it is crucial to make such an assumption here for the purpose of the multiscale modelling in order to identify which time scales can be treated explicitly during the simulation runtime and how the implicit time scales can be used to determine the overall progress rate.

The overall progress rate can be simply evaluated by a time derivative of the progress of the phase transformation. As previously stated, the progress itself can be represented by the variable $\xi \in [0, 1]$, where ξ is zero when there are no β -ZrH_κ-phase features in the Zr matrix, and ξ tends to one as the Zr microstructure is completely hydrided. Here, the challenge is specifying these initial and final values of ξ through the aforementioned hierarchy of time scales. Physically, it can be argued that ξ is zero before any long-range transport of H atoms because it is essentially the elevated H concentration that is needed for hydride precipitation in accordance with the diffusion-first model. But it can also be reasoned that ξ remains zero until the simulation cell (micrograph) can resolve the smallest hydride feature, and so a sufficient amount of H concentration build-up is required through long-range transport before the ξ clock begins ticking. The latter choice for

ξ is particularly striking because it demonstrates the interdependence of the length and time scales in a computational model of hydride precipitation. The ambiguity persists for the theoretical limit in which ξ approaches one because this terminal state could be interpreted as a global $\alpha\text{-Zr-H} \rightarrow \beta\text{-ZrH}_x$ transition, that is, a polymorphous transition, a hypothetical state which is not observed in experiments. So it is more appropriate to let ξ increase proportionally to the fraction of the Zr microstructure that has transformed into a hydride phase, which is suitable for this precipitation reaction. However, as previously stated for PF and FE models, it is somewhat circular to set the terminal point of ξ beforehand to a predefined value of choice because it is counterproductive to the required predictive capabilities. Therefore, the diffusion-precipitation analysis in the present work will employ an alternative measure for ξ using the available experimental data as well as the physical information from the preceding analyses of the computational model.

Bottlenecks. In order to proceed here and qualify the progress rate through ξ , it is important to rank the aforementioned time scales for hydride precipitation, and identify the temporal bottlenecks, that is, any time-dependent precursors to the evolution of the hydrided microstructure which are either exceptionally slow in relation to other requirements or necessitate completion before the other steps can themselves proceed. As previously stated, it is a tremendous simplification to reduce the complexities of hydride precipitation to the five or so distinct time scales, and there is still considerable uncertainty as to sub-microscopic mechanisms that constitute the $\alpha\text{-Zr-H} \rightarrow \beta\text{-ZrH}_x$ precipitation reaction. In reference to [TAB. 6.2](#), there are range of factors that affect these time scales, and so it is not obvious which time-dependent precursor could be the main temporal bottleneck from the standpoint of theory or experiment alone.

There is nonetheless a computational criterion that must be met in order for hydrides to precipitate, which provides a gauge for the progress variable, ξ , and it provides one temporal bottleneck that is physically important for the remainder of this investigation. This computational criterion is based on the infallible principle of mass conservation, and it refers to the toy models of the micro-hydride needles formulated in the previous discussion. Both toy models are grounded in the free energy optimisation that is central to the thermodynamics of phase transformations. And even though this free energy optimisation is clearly a non-kinetic procedure, that is, it has no real semblance of physical temporality, neither toy model can be implemented in a computational diffusion-precipitation analysis without implicitly alluding to the time scales that couple H diffusion to the hydride precipitation for

TAB. 6.2

Ranking of the physical temporality of hydride precipitation

A multiscale breakdown of the approximate steps that mediate the H diffusion-controlled precipitation of hydrides in Zr matrix as well as the estimates of the time scales in terms of the simulation time interval and gradation alongside the relevant length scale. The long-range transport of the H atoms is the assumed bottleneck because the H atoms are needed in any regard to form Zr hydride phase features. The mid-range clustering of H atoms is non-linear stress-driven diffusion in the vicinity of nucleation sites at lower length scales which cannot be described by linear thermodynamics. The militaristic motion of Zr atoms is comparable to the speed of sound in the metal, and H atom reordering is also presumed to be just as fast. The time scales for the nucleation and growth of micro-hydride needles and the formation of macro-hydride colonies are the main unknowns; but it is assumed that the migration of the hydride-matrix interface and the generation of autocatalytic nucleation sites can be subsumed into the overall time scales pertaining to H diffusion but slightly slower because other requirements for phase transformation must be satisfied.

Time Scale	Simulation Scope	Dependencies
LONG-RANGE TRANSPORT OF H ATOMS		
τ [transport] Interval: $\sim 10^3$ s Graduation: $\sim 10^0$ s	ℓ [component] Length: $\sim 10^{-3}$ m Rank: $\sim 10^{-6}$ ms $^{-1}$	Diffusivity (isotope, microstructure, temperature), notch acuity, component size, thermomechanical cycling
MID-RANGE CLUSTERING OF H ATOMS		
τ [clustering] Interval: $\lesssim 10^0$ s Graduation: $\lesssim 10^{-3}$ s	ℓ [microstructure] Length: $\sim 10^{-6}$ m Rank: $\gtrsim 10^{-6}$ ms $^{-1}$	Diffusivity, nucleation site potency (defect topology, energetics), quantum effects
MILITARISTIC RECONFIGURATION OF Zr ATOMS		
τ [reconfiguration] Interval: $\sim 10^{-10}$ s Graduation: $\lesssim 10^{-10}$ s	ℓ [lattice] Length: $\sim 10^{-10}$ m Rank: $> 10^{-6}$ ms $^{-1}$	Mobility, quantum effects
SHORT-RANGE REORDERING OF H ATOMS		
τ [reordering] Interval: $\lesssim 10^{-10}$ s Graduation: $\lesssim 10^{-10}$ s	ℓ [lattice] Length: $\sim 10^{-10}$ m Rank: $> 10^{-6}$ ms $^{-1}$	Interstitialcy, transition state, quantum effects
MORPHOLOGICAL GROWTH OF MICRO-HYDRIDE NEEDLE		
τ [microprecipitate] Interval: $\sim 10^3$ s Graduation: $\lesssim 10^0$ s	ℓ [microprecipitate] Length: $\sim 10^{-6}$ m Rank: $\lesssim 10^{-6}$ ms $^{-1}$	Interface migration, surface diffusion
FORMATION OF MACRO-HYDRIDE COLONY		
τ [macroprecipitate] Interval: $\sim 10^5$ s Graduation: $\lesssim 10^3$ s	ℓ [macroprecipitate] Length: $\sim 10^{-4}$ m Rank: $\lesssim 10^{-6}$ ms $^{-1}$	Autocatalytic nucleation rate, growth rate

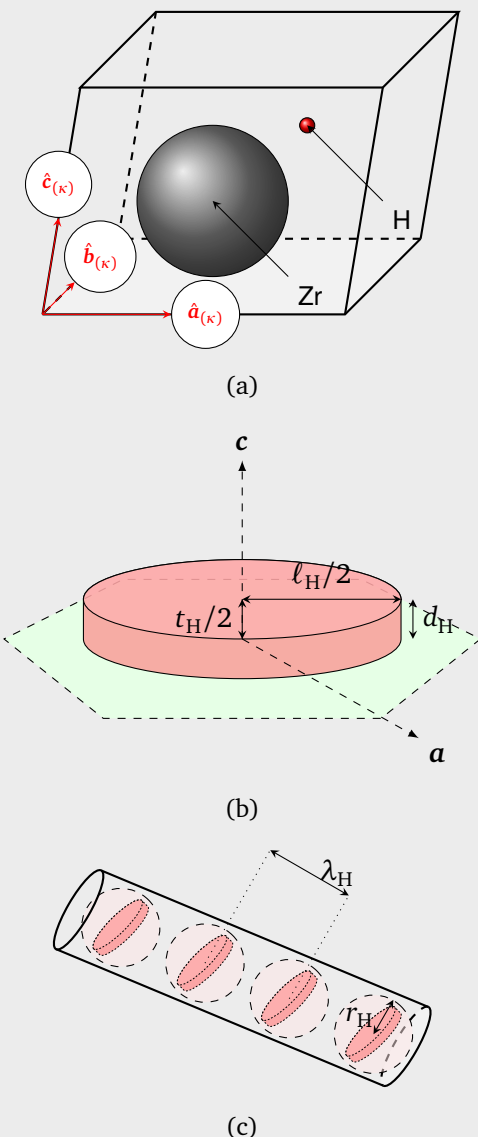
self-consistency. Most simply, both toy models portray the elastic fields of a micro-hydride needle that is essentially a $\bar{h}$ -ZrH $_{\kappa}$ -phase region of a fixed volume, which provides a direct relationship to the amount of H mass content required inside of this volume.

This H mass balance is a crucial self-consistency criterion that intertwines chemical scales—or rather, the representation of the chemistry at specific length and time scales—in the computational model, and it unifies the stress, stress-diffusion and diffusion-precipitation analyses because it provides a temporal measure of the overall progress. This mass conservation principle dictates that there must be a minimum quantifiable number of

FIG. 6.7

Coupling chemical scales

Hydrogen mass conservation in the diffusion-precipitation analysis. (a) An example of a Wigner-Seitz unit cell of a zirconium hydride phase. (b) A model of a pure-phase micro-hydride platelet approximated as elliptical cylinder on the basal plane; the curved surface of the cylinder coincides with the two-fold symmetry of the prism plane. (c) A representation of a segment of a macro-hydride feature as an array of stacked micro-hydride platelets.



mobile H atoms, which have accumulated in the vicinity of the precipitates through a combination of the long-range transport and mid-range clustering. Supposing that all such classical motion pertaining to the H atoms can be subsumed into the macroscopic stress-driven diffusion of the H concentration profile whilst assuming that the short-range reordering of the H atoms and militaristic reconfiguration of the Zr atoms is significantly faster, then the temporal bottleneck is the time scale that satisfies the H mass conservation principle.

Mass Conservation. In contrast to the aforementioned PF and FE models that couple H diffusion and hydride precipitation, which rely on the empirical Zr-H phase diagrams as an input, it is crucial to emphasise that the present work adopts a more fundamental criterion for the existence of any hydride feature, namely, the availability of a sufficient concentration of H atoms in the region within the Zr matrix that is defined to be nucleation site. This unified diffusion-precipitation criterion invokes a mass balance principle: there is a conservation of H atoms when the Zr-H solid solution containing diffusible mobile H concentration in nucleation site undergoes a transformation into the hydride phase precipitate feature with some specified geometry and uniform stoichiometry. It is clear that the overall number of H atoms must remain unchanged before and after the phase transformation. Verifying the physical equivalence of H atoms in the untransformed and transformed Zr matrices is arguably more accurate in theory and simulation than simply reading off the solvus from the phase diagram; the reasoning behind this argument is clarified in due course, but consider first a practical demonstration of the mass conservation principle.

Referring to the previous discussions on the idealisation of a macro-hydride colony as a stack of micro-hydride needles, the H mass balance criterion can be applied in the diffusion-precipitation analysis as follows. Using the multiscale perspective of the hydride features as depicted in FIG. 6.7, consider the generic $\bar{h}$ -ZrH $_{\kappa}$ hydride phase, where the parameter κ defines its chemical composition and labels its crystallographic lattice parameters $a_{(\kappa)}$, $b_{(\kappa)}$ and $c_{(\kappa)}$, which define its Wigner-Seitz unit cell. It will later become clear why κ has been introduced as a simulation artefact for multiscale modelling of $\bar{h}$ -ZrH $_{\kappa}$ -phase features in this diffusion-precipitation analysis, but it can assume the known values for the γ -ZrH $_{1.00}$ -phase and δ -ZrH $_{1.66}$ -phase stoichiometries according to experiment.

Now suppose that there exists a (ZrH $_{\kappa}$)-phase micro-hydride platelet whose simplified geometry can be approximately described by, say, an elliptical cylinder of major and minor semi-axes, $\ell_H/2$ and $t_H/2$ respectively, as well as a non-zero axial depth d_H , as depicted in FIG. 6.7(b). Therefore,

supposing that each unit cell contains $n[\text{Zr}]$ atoms of Zr, then the number of hydrogen atoms, $N[\text{H}]$, required to form such a platelet is straightforward to compute using the formula:

$$N[\text{H}] = \kappa \left(\frac{v_{\text{H}}}{\Omega_{(\kappa)}} \right) \quad \text{with} \quad v_{\text{H}} = \left(\frac{\pi \ell_{\text{H}} t_{\text{H}} d_{\text{H}}}{4} \right), \quad (6.15)$$

where v_{H} is the volume of a micro-hydride platelet, and $\Omega_{(\kappa)}$ is the Wigner-Seitz atomic cell volume as given by

$$\Omega_{(\kappa)} = \frac{|\mathbf{a}_{(\kappa)} \cdot (\mathbf{b}_{(\kappa)} \times \mathbf{c}_{(\kappa)})|}{n[\text{Zr}]}. \quad (6.16)$$

Therefore, if such a hydride platelet forms within a spherical nucleation site of radius r_{H} , the average point-wise density of hydrogen atoms required for phase transformation within this region is given by the formula:

$$\rho_{\text{H}} = \frac{N[\text{H}]}{V_{\text{H}}} \quad \text{with} \quad V_{\text{H}} = \frac{4\pi r_{\text{H}}^3}{3}, \quad (6.17)$$

where V_{H} is the volume of a (spherical) nucleation site. These formulae for $N[\text{H}]$ and ρ_{H} can now be used to estimate computational parameters necessary for coupling the length and time scales for the computational implementation of stress-driven diffusion-controlled precipitation. Note also that the expressions for $N[\text{H}]$ and ρ_{H} apply more generally than the particular choices of micro-hydride platelet and nucleation site geometries used in this work. ^{Note 11} Therefore, sensible values for v_{H} and V_{H} should enforce a cross-scale consistency for the diffusible hydrogen concentration upon hydride precipitation or dissolution. In addition, it is straightforward to extend these ideas from the scale of an individual micro-hydride needle to the scale of larger macro-hydride colony whose substructure is some network of the platelets. The substructural distribution density of micro-hydride needles within the macro-hydride colony can be quantified by additional geometrical parameters, which can be used to determine the number of H atoms required. In the case of an ideal stacking as shown in FIG. 6.7(c), this substructural density could be represented by the inter-platelet spacing, λ_{H} , based on experimental observations.

This H mass balance criterion is not only physically accurate but it is also computationally efficient because it requires only one algorithmic step: a numerical integration of the diffusible H concentration inside every nucleation site. However, it must be stated again that the stoichiometric parameter κ is a simulation artefact that must be chosen in accordance with the main assumptions of the multiscale model: the planar mechanical setting in the stress analysis as well as the linear thermodynamic regime in the stress-diffusion analysis. It is often cited in experimental work that, in reference to

Note 11

Heterogeneous nucleation sites

It is important to highlight the versatility of this approach because it facilitates the treatment of the hierarchy of heterogeneous nucleation sites, and the differences in the thermodynamic favourability can be incorporated without much effort. For example, the nucleation site volume could be large for nucleation sites such as grain boundaries which are more favourable. In addition, the nucleation sites need not be spherical; their geometry can be more reflective of the microstructural features that they represent.

Note 12

Coupling chemical scales of hydrogen diffusion and hydride precipitation

For simulating hydrides within this background H concentration limit, it reinforces the need to replace the usual spatial field treatment of hydrides found in PF and multi-field FE models with a discretised and localised nucleation framework. Moreover the explicit treatment of macro-hydride structures, as composites of repeating units of micro-hydrides platelets and parent metal phases, shows that even a macro-hydride itself cannot be treated as a pure hydride phase. This assumption is further justified by the very notion of precipitation being a special case of phase transformation in which only a small fraction of the material actually undergoes the phase transformation process at highly localised sites.

TAB. 6.3

Mass conservation criterion for hydride phases

Possible simulation parameters for the mass balance criterion in application to the TCP γ -ZrH_{1.00}-phase and FCC δ -ZrH_{1.66}-phase platelets. The bulk stoichiometric values must be adjusted in the simulation according to the background diffusible H concentrations. Then it is possible to compute the number of H atoms contained in a single mono-phase microscopic hydride feature. The nucleation sites radii are estimates based on the typical length scales over which the elastic fields of localised stress-raisers decay. Larger radii can be chosen for δ -ZrH_{1.66}-phase features as they require more H atoms.

the Zr-H partial eutectoid phase diagram, hydride precipitation is observed for bulk H concentrations in the excess of 100 ppm, that is, there is a 100 mg worth of H atoms in a dilute solution per 1 kg worth of Zr atoms [Puls (2012)]. Given that a Zr atom is heavier than a H atom by a factor of ~ 100 , this bulk H concentration corresponds to a ratio of 1 : 100 for hydrogen-to-zirconium atoms. However, the most commonly observed hydride phases, namely the γ -ZrH_{1.00}-hydride and δ -ZrH_{1.66}-hydride needles, are known to have $\kappa \geq 1$, which means that hydrogen-to-zirconium atom ratio is closer to 1 : 1, and hence the H concentration is $\sim 10,000$ ppm within such pure hydride phases. Therefore, should an entire Zr specimen be charged uniformly with a bulk H concentration of 100 ppm, then it would appear that less than 1% of the material should have undergone a phase transition into the aforementioned pure hydride phases. ^{Note 12} The initial background H concentration profile can essentially be used to calculate the final hydride volume fraction; the choice of κ provides a crucial connection between the mass balance criterion at the atomic scale and the overall progress rate at the microscale. In turn, this multiscale connection can be used to calibrate unknown parameters, such as V_H and v_H , which must be adjusted to the linear two-dimensional system. An example of the mass balance criterion is presented in TAB. 6.3 for the hydride phases under consideration, which is applied in FIG. 6.8 to evolve the H profile during a nucleation and growth of a single micro-hydride needle.

Simulation Parameters	γ -ZrH _{1.00} -Hydride	δ -ZrH _{1.66} -Hydride
BULK PROPERTIES		
Stoichiometry	$\kappa \simeq 1.00$	$\kappa \simeq 1.50$
Lattice parameters	$ a_{(1.00)} = 4.596 \text{ \AA}$ $ b_{(1.00)} = 4.596 \text{ \AA}$ $ c_{(1.00)} = 4.969 \text{ \AA}$	$ a_{(1.50)} = 4.788 \text{ \AA}$ $ b_{(1.50)} = 4.788 \text{ \AA}$ $ c_{(1.50)} = 4.788 \text{ \AA}$
MICRO-HYDRIDE PROPERTIES		
Platelet geometry	$\ell_H \simeq 1 \mu\text{m}$ $t_H \simeq 100 \text{ nm}$ $d_H \simeq 100 \text{ nm}$	$\ell_H \simeq 1 \mu\text{m}$ $t_H \simeq 100 \text{ nm}$ $d_H \simeq 100 \text{ nm}$
Hydrogen atoms	3.028×10^7	4.321×10^7
MACRO-HYDRIDE PROPERTIES		
Nucleation site geometry	$r_H \simeq 5 \mu\text{m}$	$r_H \gtrsim 5 \mu\text{m}$
Substructure geometry	$\lambda_H \simeq 10 \mu\text{m}$	$\lambda_H \simeq 10 \mu\text{m}$

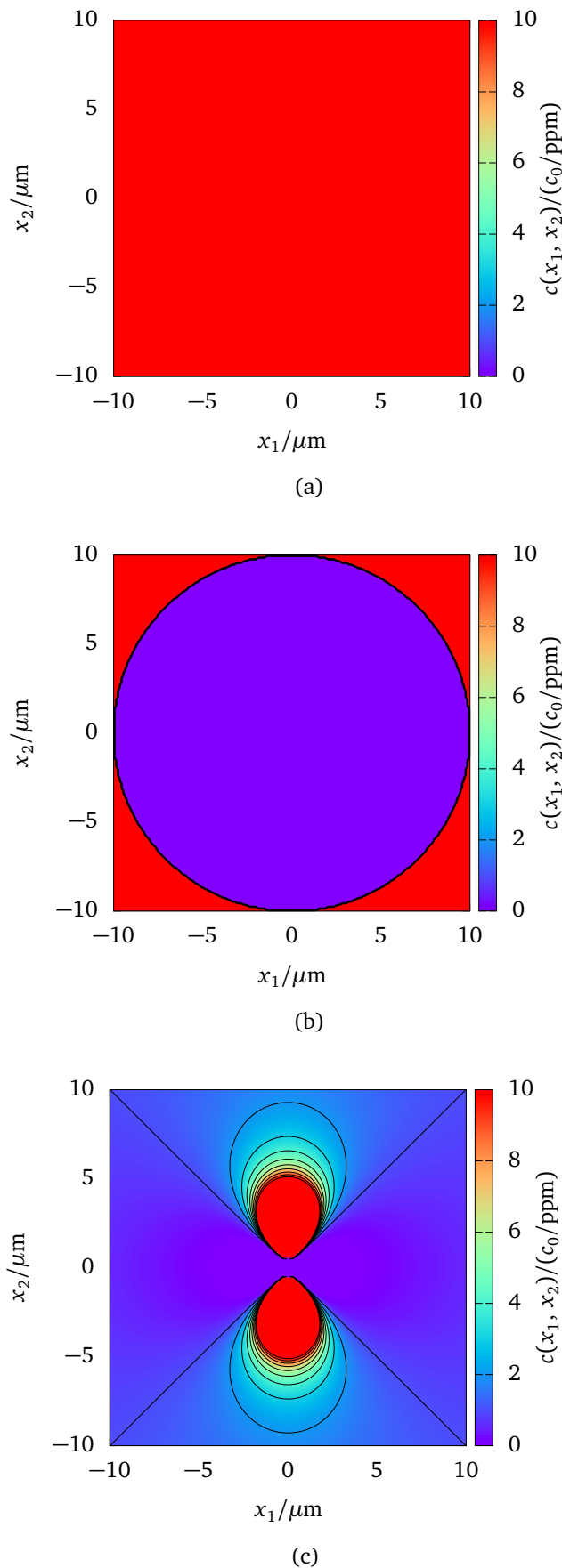


FIG. 6.8

Mass conservation criterion for a micro-hydrate needle

A two-dimensional demonstration of the evolution of the H concentration profile upon the nucleation of a micro-hydrate needle in this multiscale diffusion-precipitation analysis. The evolution is demarcated in three distinct algorithmic steps over which the passage of time is assumed to be much shorter than the temporal interval associated with the long-range stress-driven transport of H into the circular nucleation site. The simulation uses the lower room temperature 0.025 eV as opposed to the standard reacting operating temperature in order to facilitate visualisation; however the three algorithmic steps would yield similar concentration profiles at all temperatures in this mathematical framework. (a) The initial diffusible H concentration profile around a nucleation site, which is 10 times the value of the uniform background concentration. (b) The discontinuous depletion of the diffusible concentration in the circle nucleation site upon a nucleation event during which a specified number of H atoms in the diffusible concentration profile must be integrated into the microscopic precipitate feature as atomic constituents. (c) The mid-range stress-driven diffusion of the diffusible H atoms due to the elastic distortion caused by the microscopic precipitate feature.

6.2.2 Kinetics

The progress rate of the H diffusion-controlled hydride precipitation in the α -Zr matrix can be determined by the multiscale mass balance criterion, but this alone does not clarify the role of various time scales in a multiscale model of the early stages of DHC failure. To this end, it is necessary to consider the kinetics of the phase transformation, and derive a direct relationship between the progress parameter, ξ , and the time, τ , or more specifically, the temporal interval and gradations. The following discussion begins by applying the general statistical geometric theory of the extended volume to the nucleation and growth of daughter $\hbar$ -phase precipitate features in the parent α -phase material [Janssens et al. (2007)]. These theoretical concepts are then reviewed from the perspective of computational mechanics and thermodynamics, which concludes with a preview of the simulation strategy that underpins this diffusion-precipitation analysis.

Extended Volume. Consider the general $\alpha \rightarrow \hbar$ phase transformation at some initial time τ_0 when ξ is just above zero, that is, there is initially a small but non-zero number of $\hbar$ -ZrH_k-phase nuclei in the HCP α -Zr matrix. And let Π_H denote the density of nuclei at some given time. Assuming that the micro-hydride needles are really pure hydride phase features,—which is a reasonable simplification according to the aforementioned TEM scale observations that define the necessary spatial resolution in the present work—, these nuclei correspond to the micro-hydride needles whose geometries resemble anisotropic platelets as represented by the axially flat elliptical cylinders in the preceding discussion. Suppose that these micro-hydride platelets grow at some uniform rate; each geometrical parameter is now function of time with a constant time derivative. Suppose also that the macro-hydride colonies grow at some uniform rate, and the autocatalytic nucleation mechanism can be subsumed into the rate of formation of new nuclei. The new nuclei are located randomly and so there are two specific corrections that need to be made in the calculation of the transformed volume upon a continuation of nucleation and growth steps: (i) the transformed volume must account for the possible impingement when growing precipitates overlap; and (ii) the transformed volume must also account for the prospect of new nuclei being seeded within the transformed volume.

The uncorrected volume is denoted the extended volume, $v_H[\text{extended}]$, and it can be related to the actual transformed volume, $v_H[\text{transformed}]$, using a probabilistic approach. In turn, the actual transformed volume provides the temporal bridge connecting the atomic scale diffusion of the H atoms to the nucleation and the microscale measure of the progress of the phase transformation; this connection will provide a mathematical for-

mula: a function $\xi(\tau)$ that incorporates the key aspects of the diffusion-precipitation analysis through which it will be possible to extract the time scales of the phase transformation.

In classical nucleation theory, the overall progress of a general phase transformation process is given by a characteristic sigmoidal curve of the form

$$\xi(\tau) = 1 - \exp(-K(T)\tau^\eta) \quad \text{with } K > 0 \quad \text{and } \eta \in [1, 4] \quad (6.18)$$

where the temperature-dependent coefficient, K , contains the nucleation and growth rates, and exponent, η , is related to the underlying mechanism that governs the phase transformation [Janssens et al. (2007)]. There is often some ambiguity when quantifiable expressions for K and η are not available; this ambiguity is particularly prominent in η because it assumes the same value for different nucleation and growth mechanisms [Christian (2002)]. Nevertheless, the simplicity of this handbook formula is very useful in computational models of phase transformation where the physical temporality is not explicitly captured. In principle, $v_H[\text{precipitate}]$ can be evaluated once the equilibrium microstructure is simulated, and then Eq. (6.18) could be inverted to estimate the time that the thermodynamic system requires to attain this point of progress. Such elegant progress formulae would undeniably be very convenient in simulations of the early stages of DHC failure which do not feature any temporality as such. But the formalism that precedes Eq. (6.18) has not been rigorously applied to microstructural models of hydrided microstructure of Zr alloys [Puls (2012) and Bair, Zaeem, and Tonks (2015)]. Therefore, a brief attempt is made here in this diffusion-precipitation analysis for two reasons: (i) some notion of time is needed in this multiscale model at this stage given that it is absent in the stress and stress-diffusion analyses; and (ii) there is inherent value in this original, albeit rudimentary, derivation that aims to distill the complexity of H diffusion-controlled hydride precipitation in Zr alloys into a handbook formula, which can be readily deployed in preliminary engineering assessments.

In this application of the extended volume approach, statistical geometry is used to describe nucleation and growth of micro-hydride needles as well as the formation of macro-hydride colonies. Obtaining such a handbook formula is paramount, and so certain aspects of the complexity of this phase transformation phenomenon will be streamlined whilst other details will be appropriately omitted. The hydride nucleation and growth rates are assumed to be loosely intertwined with the former depending on the latter in the following capacity. An initial fixed density of heterogeneous nucleation sites, $\Pi_H(\tau_0)$, undergoes stepwise changes after some critical time intervals, $\tau[\text{microprecipitate}]$, over which the infinitesimally small nuclei grow to a

critical size large enough generate additional nucleation sites in their neighbourhood, which imitates the autocatalytic nucleation mechanism. Each nucleus grows anisotropically at constant rates into a microscopic platelet that resembles a flattened elliptical cylinder as previously described. Assuming a sufficient concentration of H atoms clustered inside of the nucleation site as well as relatively fast militaristic reconfiguration of Zr atoms and short-range reordering of the H atoms, the formation of macro-hydride colonies is dependent entirely on the nucleation and growth of micro-hydride needles; the extended hydride phase volume can be determined exclusively in terms of the nucleation and growth rates. The rates of nucleation and growth are intertwined with the former depending on the latter. So it is easier to begin with the problem of a single nucleation event at time τ_0 for which the growth in the extended volume at time τ can be written as

$$\Delta v_H[\text{extended}] \propto \left[\frac{d\ell_H}{d\tau} \frac{dt_H}{d\tau} \frac{dd_H}{d\tau} \right] (\tau - \tau_0)^3, \quad (6.19)$$

where the constant growth rate is indicated by the absence of time dependence in the time derivatives; the proportionality factor is ignored for the sake of clarity but it would depend only the chosen geometry of the platelet. After a critical time interval, $\tau[\text{microprecipitate}]$, additional nuclei are generated such that

$$\begin{aligned} \Pi_H(\tau_0 + \tau[\text{microprecipitate}]) &= \Pi_H(\tau_0) \\ &+ \tau[\text{microprecipitate}] \cdot \dot{\Pi}_H, \end{aligned} \quad (6.20)$$

where $\dot{\Pi}_H$ is the constant rate of nucleation which subsumes the autocatalysis once individual nuclei attain their critical size. Note that this discretised equation is a precursor for a recursion relationship provided that there is sufficient H concentration and the nuclei are very small relative to the total specimen volume and hence non-interacting. (In this case, Π_H can be described by a floor function or a ceiling function.) Assuming that the overall time when ξ reaches one is much larger than the temporal graduation marked by interval $\tau[\text{microprecipitate}]$, it is possible to take the limit where $\Pi_H\tau$ is continuous function, and accordingly state that the total number of nuclei generated over a time interval $\Delta\tau_0$ since the beginning is proportional to $\dot{\Pi}_H\Delta\tau_0$ and so Eq. (6.19) can be extended to multiple precipitates as

$$\Delta v_H[\text{extended}] \propto \dot{\Pi}_H \left[\frac{d\ell_H}{d\tau} \frac{dt_H}{d\tau} \frac{dd_H}{d\tau} \right] (\tau - \tau_0)^3 \Delta\tau_0, \quad (6.21)$$

where the proportionality constant is modified to include the total volume of the specimen as well. The total extended volume is an integration of Eq. (6.21) with respect to the variable τ_0 that now represents the time of

nucleation rather the start of the phase transformation; the upper and lower integration limits are then τ and 0 respectively. Before evaluating the integral, however, further details about hydride precipitation can be incorporated into Eq. (6.21) to account for the micro-hydride geometries and the formation of macro-hydrides via autocatalysis. Firstly, it is easier to ignore the precipitate growth in two of the three dimensions given that the micro-hydride needles are understood to be lenticular misfits [Puls (2012), Carpenter (1973), and Carpenter, Watters, and Gilbert (1973)]. Secondly, macro-hydride colonies can be decomposed into a sequential network of micro-hydride needle in which the growth of one leads to the nucleation of another; this sequence prevents further growth beyond the critical size so there is some inverse or reciprocal time dependence in the growth rate in the remaining one of the three dimensions. Proceeding in this manner leads to the integral of the form

$$\begin{aligned} v_H[\text{extended}] &\propto \dot{\Pi}_H \dot{\ell}_H \int_0^\tau \Delta \tau_0 \\ &\propto \dot{\Pi}_H \dot{\ell}_H \tau, \end{aligned} \quad (6.22)$$

where $\dot{\ell}_H$ is some constant growth rate prefactor, and the proportionality constant is again modified to include details of the growth restriction during the autocatalysis sequence as well as the properties of the macro-hydride colonies. Note that there is only growth along the direction corresponding to ℓ_H and this dimension has been chosen for obvious reasons.

Now that the extended volume has been expressed in terms of the time, it is now straightforward to compute the actual transformed volume and, hence, the overall progress rate using statistical geometry. Denoting the total volume of the specimen as $v_H[\text{total}]$ and then writing the probability that the change in the extended volume pertains to the untransformed regions so that

$$\Delta v_H[\text{transformed}] = \left(1 - \frac{\Delta v_H[\text{transformed}]}{\Delta v_H[\text{total}]} \right) \Delta v_H[\text{extended}]. \quad (6.23)$$

Upon separation of variables and integration, it can be shown that the overall progress rate can be approximated as

$$\begin{aligned} \xi(\tau) &= \frac{v_H[\text{transformed}]}{v_H[\text{total}]} = 1 - \exp\left(-\frac{v_H[\text{extended}]}{v_H[\text{total}]}\right) \\ &= 1 - \exp\left[-\left(\frac{K_H \dot{\Pi}_H \dot{\ell}_H}{v_H[\text{total}]}\right) \tau\right] \end{aligned} \quad (6.24)$$

where the proportionality constant K_H includes the aforementioned details about the hydride precipitation: (i) the geometry of the micro-hydride needles; (ii) the total volume of the Zr alloy specimen that is capable of undergoing a phase transformation; and (iii) the restricted growth due to autocatalysis and properties of the macro-hydride colonies.

Dynamics. The overall progress rate is now available in the convenient format of a handbook formula. The explicit time dependence has been derived in which η is roughly one, which agrees with known interpretations of the exponent; this particular value is broadly associated with the diffusion-controlled growth of needles and plates that have a large separation [Janssens et al. (2007) and Christian (2002)]. There are also several unknowns in the explicit expression for $K(T)$ such as K_H , $\dot{\Pi}_H$ and $\dot{\ell}_H$, which must be inferred through statistical sampling of experimental data. These unknowns embody the various intermediate time scales related to the H diffusion-controlled precipitation of hydrides in Zr alloys, and so reasonable theoretically estimates can also be made, but these calculations are beyond the scope of this work.

The value of the handbook formula is not only its ease of use but also the originality in its derivation which attempts to incorporate some of the complexity of the evolution of the hydride microstructure. Although this primitive derivation is still in its infancy, the preliminary result in Eq. (6.24) is nonetheless immediately applicable to the problem of temporality in the multiscale diffusion-precipitation analysis. For instance, it is possible to deduce the unknown prefactor to the time variable using the knowledge of the initial H concentration in the specimen alongside the H mass balance criterion; experimental findings or analogous PF and FE studies can be referenced to extrapolate the limit in which ξ approaches one [Puls (2012), Bair, Zaeem, and Tonks (2015), Jernkvist and Massih (2014), and Jernkvist (2014)]. In turn, the physical temporality can be extracted by simply counting the number of micro-hydride needles in the simulation cell. So the importance of Eq. (6.24) cannot be overstated because it now means that physical temporality or dynamics need not be explicitly featured in the simulation scope of the diffusion-precipitation analysis.

Ensemble averages of $K(T)$ can be devised to fine-tune the aspects of physical temporality in the multiscale model. However, this fine-tuning is only feasible if the simulation strategy is efficient. The simulation runtime must be fast in the unified stress, stress-diffusion and diffusion-precipitation analyses. Prior to the inception of Eq. (6.24), the diffusion-precipitation analysis was the main crux to the simulation runtime. However, it is now clear that a quasi-static or non-kinetic diffusion-precipitation analysis is more than viable. That is, such a simulation strategy is not only more efficient in comparison to PF and FE models but the multiscale mass balance criterion and extended volume formula together constitute a far more accurate account of hydrides in Zr alloys. Now it is possible to put forward a complete simulation strategy for the evolution of the hydride microstructure that optimises the multiscale diffusion-precipitation analysis.

6.3 Microstructural Evolution

Many of the general concepts in phase transition modelling have now been explored and adapted to the case of hydride precipitation in Zr alloys, which is the gateway into developing a novel multiscale diffusion-precipitation analysis. The backbone of the multiscale model can be constructed by establishing a unified algorithmic workflow that incorporates the main findings of the preceding discussions: (i) the free energy optimisation procedure should involve the separate but interconnected minimisation of the interfacial energy of individual micro-hydride needles and the strain energy of the networks of micro-hydride needles residing in close proximity as constituents of macro-hydride colonies; (ii) the H mass balance criterion governs precipitation of micro-hydride needles of specified geometries in regions of elevated H concentration accumulated due to diffusion; and (iii) the free energetics are treated quasi-statically whilst the diffusion-controlled precipitation criterion is implemented in a non-kinetic manner, although the physical temporality is obtainable as needed through the progress rate. Several avenues into algorithmic unification can be pursued but the priority is the accuracy-efficiency trade-off, and so the present work outlines one simple two-dimensional simulation strategy.

6.3.1 Precipitate Lifecycle

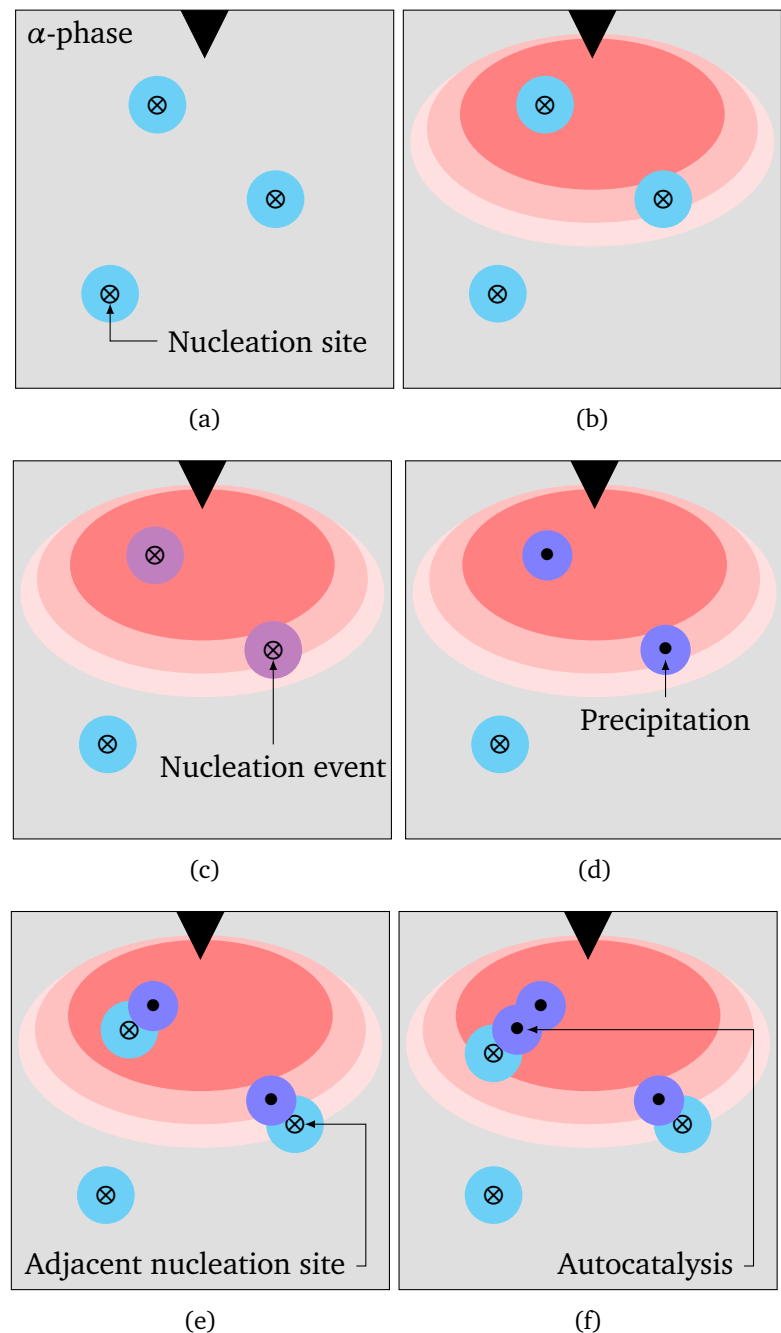
The quasi-static mechanical and non-kinetic thermodynamic assumptions can be translated into a compact algorithm that simulates the lifecycle of micro-hydride needles leading to the formation of macro-hydride colonies in the Zr alloy microstructure. The sequence of algorithmic steps is illustrated in **FIG. 6.9**, which summarises how the contents of a simulated microstructure evolve over iterations of nucleation and growth. There is an initial population of nucleation sites that are randomly distributed in the microstructure ahead of the volumetric flaw. Stress and stress-diffusion analyses provide the enhanced H profile ahead of the flaw. The activation of individual nucleation site is then checked, and nucleation events are triggered if the H mass balance criterion is satisfied. Nucleation events lead to the precipitation of micro-hydride needles as well as the generation of secondary autocatalytic nucleation sites in their vicinity. Adjacent activation of secondary nucleation sites mimics the autocatalysis and the eventual repetition results in the emergence of macro-hydride colonies.

It is clear that **FIG. 6.9** is a versatile template because it can readily accommodate additional layers of complexity, such as the exact number and relative placement of secondary nucleation sites, and these microstructural details can be informed by experimental micrographs as well as comple-

FIG. 6.9

Algorithmic breakdown of the diffusion-controlled lifecycles of precipitates

An illustrated representation of the microstructure evolution in terms of the multiscale algorithmic steps that capture the nucleation and growth micro-hydride needles in the Zr-H solid solution whose repetition mimics the autocatalytic formation of macro-hydride colonies. The physical temporality is not treated explicitly but it can be extracted based on the initial background H concentration and the countable number of the precipitates in the matrix at a given algorithmic step. (a) The untransformed and uncontaminated α -Zr alloy microstructure with a random distribution of heterogeneous nucleation sites. (b) The equilibrated flaw-tip H concentration profile following the ingress of H atoms and their long-range stress-driven transport. (c) Nucleation site activation checks that inspect the diffusible H concentration within the bounds of the individual nucleation sites. (d) Nucleation events enforce the H mass balance criterion that correct the H concentration inside activated sites where a micro-hydride needle is precipitated whilst dormant sites remain unaffected. (e) Nucleation events generate adjacent nucleation sites as per the autocatalysis. (f) The substructure of the macro-hydride colonies takes form when adjacent nucleation sites are repeatedly triggered.



mentary DFT, PF and FE simulations when necessary. But the real benefit is the unprecedented accuracy-efficiency trade-off. That is, the simulation cells can be SEM sizes but with TEM resolutions, whilst the algorithmic steps scale favourably with the only physical features of interest, namely, the precipitates.

It is worth noting that the treatment of the diffusion-controlled precipitate lifecycle so far has neglected the dissolution kinetics. The reversed phase transformation from β -phase to the α -Zr-H solid solution is, however, just as important from the standpoint of DHC failure because the thermal

ratchetting is attributed to the hysteresis caused by the repetition of precipitation and dissolution [Eadie, Metzger, and Léger (1993), Shek (1998), Darby, Martin, and Scarth (2013), and Puls (2012)]. It is possible to describe some aspects of the dissolution process by simply inverting the mass balance criterion, but simulating the reverse phase transformation is more complicated than just traversing the progress backwards in the time variable whilst backpedalling the algorithm for nucleation and growth [Janssens et al. (2007)]. That is, there are additional theoretical and computational challenges that must be surmounted in order to formulate a more complete treatment of the hydride precipitate lifecycle in the context of DHC failure. For example, the mechanism that underpins the memory effect involves sub-microscopic dislocation networks around micro-hydride needles which hypothetically contribute to a macroscopic residual stress build-up upon the dissolution of entire macro-hydride colonies. This memory effect is a truly multiscale phenomenon which can only be conveyed in a mesoscale model of the hydride microstructure where the hysteretic relationship between precipitation and dissolution can be mechanistically predicted.

Such a comprehensive mesoscale simulation strategy is typically beyond the capabilities of the standard monoscale PF and FE models because these methodologies lack the versatility needed to incorporate the multiscale complexity into one accurate and efficient computational framework [Bair, Zaeem, and Tonks (2015), Jernkvist and Massih (2014), and Jernkvist (2014)]. So here is a fortunate opportunity to trial the multiscale diffusion-precipitation analysis conceived in this investigation and compare it against some of the benchmarks of accuracy, efficiency and versatility. This preliminary test and skeletal comparison uses thermal ratchetting as the quintessence of the multiscale complexity of the precipitate lifecycle. The preliminary test aims to outline the computational mesoscale mechanics that constitute the general simulation strategy for the evolution of the hydride microstructure and demonstrate that it can indeed be applied to the case of thermal ratchetting. The skeletal comparison against PF and FE models of DHC failure intends to provide a broad-brush picture of the relative accuracy, efficiency and versatility of this multiscale DHC simulation strategy at first glance.

The computational mesoscale mechanics should emulate the evolution of the hydride microstructure through an extension of the precipitate lifecycle sequence in FIG. 6.9 that incorporates the efficient elastomechanical free energy optimisation as conveyed by the combination of Toy Model A and Toy Model B in FIG. 6.2 as well as the mass balance criterion in FIG. 6.7 which offers an accurate and efficient multiscale chemomechanical bridge, which can be used to predict ratchetting.

6.3.2 Mesoscale Mechanics

The multiscale complexity of the early stages of DHC failure can be deconstructed into a single phenomenological description: fracture stress-driven H diffusion-controlled nucleation, growth and dissolution of hydride phase precipitate features in the anisotropic heterogeneous microstructure of Zr alloys. This self-contained description is not complete but it does establish the remit of the mesoscale mechanics as some multiscale integration of the stress, stress-diffusion and diffusion-precipitation analyses alongside the specific nuances of the Zr-H system. It is more appropriate to focus on the role of the diffusion-precipitation analysis in the schema and set aside the effects of the hexagonal crystallography of Zr and the polycrystallinity of the Zr alloy microstructure for now. So it is only necessary to brainstorm some amalgam that combines the stress, stress-diffusion and diffusion-precipitation analyses in which the generic precipitate lifecycle sequence can be easily customised using supplementary experimental data and then readily translated into the mesoscale mechanics that replicate the observed evolution of the hydride microstructure.

This stress-diffusion-precipitation amalgam is conceptualised in [FIG. 6.10](#) as a diagrammatic algorithm which indicates the prospective connections between the stress, stress-diffusion and diffusion-precipitation analyses alongside a checklist of the particularities of the Zr-H system. The amalgam is understandably vague in comparison to the legacy-bounded PF and FE methodologies even though there appears to be some logical reasoning to the algorithmic workflow. This ambiguity does raise some doubts about the viability of the amalgam in practice but these reservations can be momentarily overlooked given the rigorous functionality of the individual algorithmic steps on the whole. So a walkthrough should suffice in conducting the aforementioned preliminary test and skeletal comparison.

The preliminary test concerns the multiscale complexity of thermal ratchetting. The memory effect is perhaps the mechanistic precursor to the ratchetting thermal phenomenon: the gradual build-up of localised residual stresses upon repeated nucleation, growth and dissolution of precipitates over a series of thermomechanical cycles. The memory effect can be predicted using a variant of the proposed amalgam in [FIG. 6.10](#) that incorporates the microscale evolution of the dislocation microstructure around individual micro-hydride needles into the macroscale evolution of the hydride microstructure through the Zr-H system nuances which are embedded in mesoscale mechanics and multiscale complexity. Such an amalgam variant could include the plastic relaxation around micro-hydride needles which is observed in TEM studies; this dislocation plasticity can be encoded within

the relevant computational steps that are listed under the headings of the precipitate lifecycle sequence and the chemomechanical bridge in FIG. 6.10, namely, the respective algorithmic parallel sub-steps pertaining to the nucleation, growth and dissolution of micro-hydride needles, and the elastic fields of the system. For example, nucleation and growth could be accompanied by the superposition of the stresses due to micro-hydride needle and the plastic relaxation whilst the dissolution could result in non-vanishing residual stresses due to the remaining dislocation network; and the algorithmic loop would invariably capture the ratchetting behaviour as each loop iteration increases the density of the residual dislocation network. It can be reasoned that the residual stress ratchet would lead to the ratchetting of the H concentration and hence the hydride population in turn; this argument is based solely on the proposed algorithm but it will later be justified through a minimal working example of the stress-diffusion-precipitation amalgam.

The skeletal comparison is now an instructive exercise because the preliminary test has justified the multiscale complexity of thermal ratchetting to be a tractable phenomenon that is within the predictive capabilities of the mesoscale mechanics whose phenomenological accuracy exceeds the existing PF and FE studies. The majority of the individual steps involve the closed-form formulae as part of the stress and stress-diffusion analyses whereas the remaining other steps require only simple numerical computations such as the spatial integration of multi-dimensional fields that is needed for the stress energy minimisation and the mass balance criterion in the diffusion-precipitation analysis. The mesoscale mechanics is accordingly more efficient in contrast to the traditional PF and FE methodologies which rely on solving coupled PDEs with multiple variables and non-trivial boundary conditions. This simulation efficiency enables the amalgam to surpass the combined capabilities of PF and FE methodologies: the simulation cell resolution can be finer than the discretisation in PF models but the simulation cell size can match the FE models.^{Note 13} Intuition suggests that the amalgam is versatile, that is, it can be easily adapted to other multiscale DHC sub-phenomena such as the flaw-tip hydride reorientation or embrittlement. So the proposed strategy seemingly appears to outclass the standard PF and FE methodologies in terms of accuracy, efficiency and versatility.

The diffusion-precipitation analysis concludes with the stress-diffusion-precipitation amalgam as the intellectual basis to the multiscale model of the early stages of DHC failure. The amalgam embodies a transcendental simulation strategy to describe the evolution of the hydride microstructure through mesoscale mechanics that capture the multiscale complexity of the Zr-H system. This promising outcome precedes the development of a bespoke model of DHC in which the amalgam is advanced and realised.

Note 13

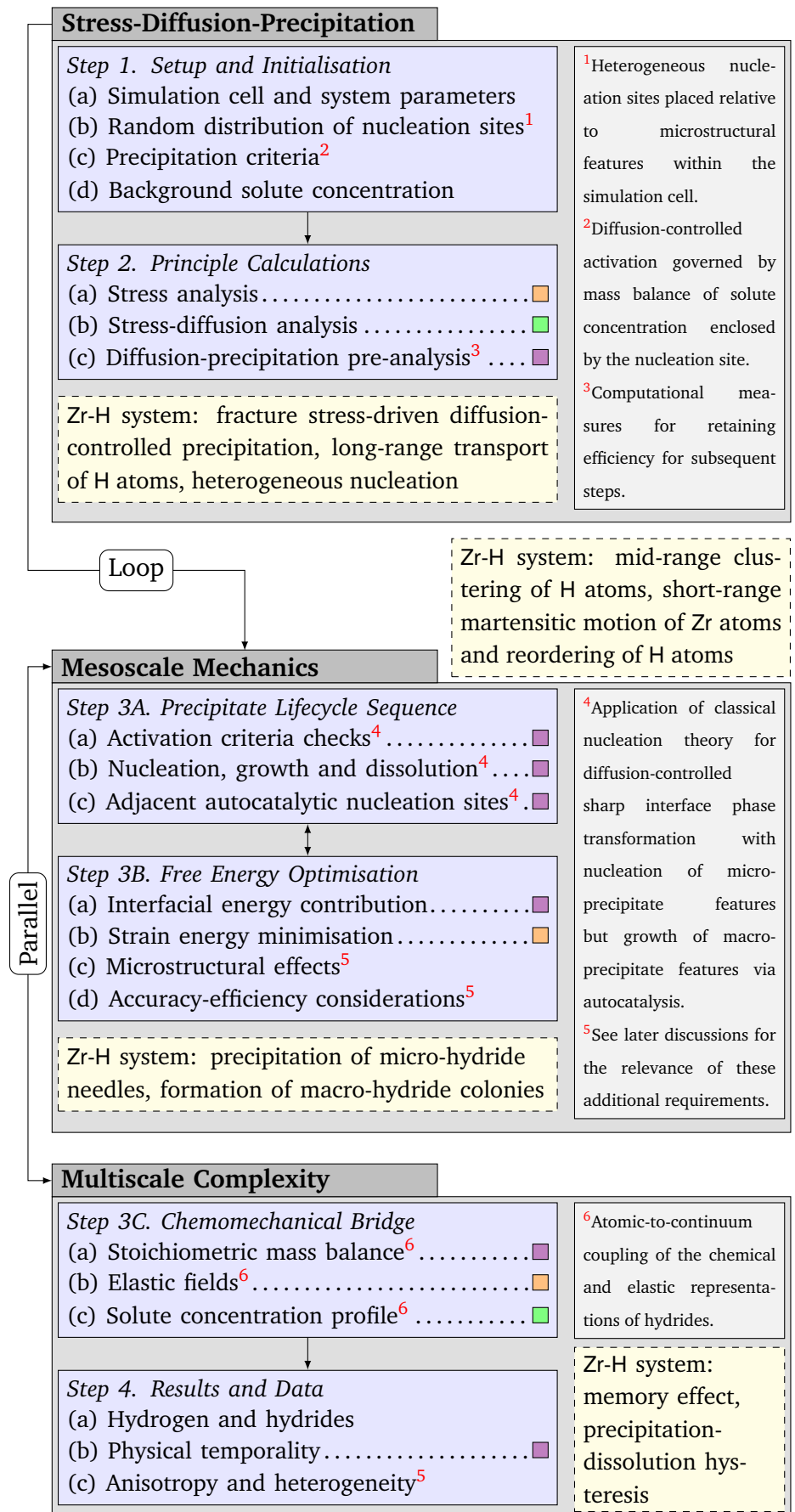
Prospective evaluation of the accuracy-efficiency trade-off

The stress-diffusion-precipitation amalgam presents a rather unique scenario in somewhat defying the trade-off that is common to the accuracy-efficiency relationship of the standard modelling methodologies. This is a formidable claim but it can be supported given that simulation accuracy has multiple definitions in the realm of models that are classified to be phenomenologically accurate. The simulation accuracy can be measured in terms of the numerical precision to which the mathematical equations are being solved or it can be quantified relative to the experimental data when available. But these two definitions do not align with each other in the case of PF studies; increased numerical precision restricts the simulation cell size and so it is not possible to simulate the realistic micro-hydride needle networks and macro-hydride colonies which are seen in TEM and SEM experiments. That is, the standard PF models succumb to accuracy-efficiency trade-off as numerical precision must be sacrificed to obtain the efficiency required to replicate experimental observations. There is, however, alignment in the two definitions of simulation accuracy when it comes to amalgam whose simulation runtime scales with the total number of micro-hydride needles. The numerical precision is not an issue given the availability of closed-form expressions and so the computations are highly efficient. The simulation efficiency bestows unexpected benefits that allow a greater number of micro-hydride needles to be simulated and hence achieve a greater phenomenological accuracy relative to experimental observations.

FIG. 6.10

Stress-diffusion-precipitation amalgam

An algorithmic amalgamation of the stress, stress-diffusion and diffusion-precipitation analyses that serves as the intellectual basis to the multiscale model of the early stages of DHC failure. The amalgam is partitioned into three separate but interconnected algorithmic schemata: (i) the stress-diffusion-precipitation analysis that encompasses the interplay between stress-driven diffusion and diffusion-controlled precipitation; (ii) the mesoscale mechanics that emulates the lifecycle of the individual micro-hydride needles and the interactions between networks of micro-hydride needles that constitute the macro-hydride colonies; and (iii) the multiscale complexity that couples the atomic scale mobile solute content, microscale precipitate morphology and continuum scale elastic distortion. The specific nuances of the Zr-H system are highlighted where such details can be incorporated. The vast majority of the individual steps and sub-steps have been extensively explored in the diffusion-precipitation analysis. Only the exact nature of the multi-step interconnectivity remains unclear but prospective connections are shown. It must be noted that this approach is so far removed from the traditional PF and FE methodologies but it does lead to a favourable simulation runtime that hypothetically scales with the total number of micro-hydrides in the simulation cell. The simulation scaling can be deduced upon inspection of the parallel steps within the loop.



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Part III

Multiscale Theory and Simulation

7

Model Formulation

Chapter Overview

After introducing the three separate analyses and a high-level amalgam, the next step is to truly piece together these modules into a hybrid model that describes stress-driven diffusion-controlled precipitation. As previously discussed, a very rudimentary combination of these analyses is common to standard PF and FE models. But the application of such generic diffusion-precipitation models to DHC failure has so far proven to be inadequate for nuclear fuel performance codes because such models are neither physically accurate nor computationally efficient [Motta (2017)]. So the aim of the present work is to put forward a more purpose-built model that can satisfy the requirements of industrial safety assessments in terms of the desired accuracy and efficiency. This can be achieved by incorporating into the hybrid model specific details of the Zr-H system as understood through SEM and TEM experiments as well as adapting concepts from existing DFT, PF and FE methodologies. This purpose-driven approach should then result in a bespoke multiscale framework for simulating flaw-tip H profiles and hydrided microstructures in anisotropic heterogeneous Zr alloys. The formulation of this bespoke model of DHC is the focus of this chapter.

The model setup and simulation strategy can be summarised as follows. Consider first a two-dimensional simulation cell that depicts the vicinity of the notch tip in the Zr alloy component. The simulation cell resembles a micrograph, that is, it provides a visualisation of key metallographic features. This simulated micrograph should be able to portray: (i) the geometries of the notch, plastic zones, grains, and intra-granular and inter-granular nucleation sites; (ii) the contours of H enhancement and depletion as well as hydrided and denuded regions; and (iii) the morphologies of micro-hydride needles and macro-hydride colonies. Although such geometries, contours and morphologies can be represented to an arbitrarily high degree of accuracy, the extensive use of nonsimple shapes increases the computational complexity and often not much physical insight is gained by doing so. Therefore, the present work proposes a more compact representation of metallographic features by using line segments, convex polygons, ellipses and

smooth curves as appropriate. Here, grains are represented by a space-filling tessellation of convex polygons, intra-granular nucleation sites are represented by circles, and micro-hydride needles are represented by finite line segments. The benefit of using these simpler geometrical constructs is considerable in all aspects of the simulation.

The primary input to this model is the set of variables that describe the notch acuity, component microstructure and thermomechanical conditions. The microstructural input is particularly important as it distinguishes the different Zr alloys in terms of the average grain size, texture and intra-granular nucleation site density. In addition, the model also requires the input of physical quantities pertaining to the Zr-H system as well as the computational artefacts that are inherent to programming language choices and code development environments, which ensure successful implementation of the theoretical underpinnings and simulation strategy into a software capable of realising the model. Some physical quantities can be obtained or inferred from TEM or SEM findings; this includes the typical size of micro-hydride needles and their configurational positioning within macro-hydride colonies. Other physical quantities can be chosen according to DFT and PF studies; the relevant examples concern the anisotropic interstitialcy of H in α -Zr and the energetics of the hydride-matrix interfaces. Most computational artefacts can be calibrated using sensitivity studies as usual; this includes spatial mesh resolutions and singularity cut-offs. The input can then be used to initialise the simulation by assuming a uniform background H concentration with no hydrides. The initialisation procedure generates one possible realisation of the physical system with a particular set of input; each realisation exhibits some stochastic variation because grain morphologies and intra-granular nucleation site locations are random.

The notched Zr alloy specimen is subject to a remote uniform tensile load. The elastic fields ahead of the notch can be computed using standard FE-based techniques for stress analysis but it is more computationally efficient to employ the closed-form expression derived using the mathematical theory of planar elasticity. For this reason, this model assumes an infinite linear elastic continuum for defect micromechanics, which serves as a sensible starting point for testing this framework. The elastic fields of the multi-defect system can then be obtained by a superposition of the corresponding elastic fields of individual defects.

These elastic fields drive the long-range transport of H interstitials occupying tetrahedral sites in HCP α -Zr, a process which is described within the framework of linear irreversible thermodynamics using an elastochemical diffusion potential. The elastochemical potential includes the elastic interaction energy between the point defect forces exerted by the H intersti-

tials on the neighbouring Zr atoms and the distortion generated by higher-dimensional defects in the Zr continuum. The coupling between atomic and continuum length scales is provided by the leading term in the elastic multipole model of point defects, namely, the elastic dipole tensor. The elastic interaction energy can be determined by using the elastic dipole tensor for H in α -Zr as obtained from DFT calculations [Nazarov et al. (2016)]. The elastochemical potential drives H diffusion to tensile regions ahead of the notch. In turn, the overall rate of H diffusion controls the precipitation of hydrides.

As the H concentration profile evolves over time, nucleation sites are periodically checked for the prospect of precipitation. A nucleation site is activated if the precipitation criterion is satisfied, and a micro-hydride needle is added to the simulation cell. The stress state of each micro-hydride needle is approximated by a dipole of edge dislocations. The configuration of the micro-hydride needle is computed by sampling possible orientations and selecting the minimum strain energy state. The characteristic autocatalytic nucleation mechanism can be mimicked by imposing constitutive rules for placing additional nucleation sites adjacent to an activated nucleation site. These steps are repeated to replicate the formation of macro-hydride colonies as composites of micro-hydride needles in the parent Zr metal. Computational geometry checks can be performed at each step to ensure that the microstructural arrangements agree with experimental findings. For example, these geometrical checks can be used to distinguish the assemblies of micro-hydride needle in macro-hydride colonies at intra-granular and inter-granular nucleation sites [Patel et al. (2018)]. This procedure emulates the free energy minimisation at a local scale but it also bypasses the computational complexity of a global multi-parameter space optimisation that is required for analogous PF models.

This hybrid model makes effective use of geometrical simplifications, analytical formulae and algorithmic optimisations. It is, therefore, anticipated that this hybrid model surpasses the individual capabilities of DFT, PF and FE models. This advanced capability is expected not only in terms of system size and resolution, but also the accuracy and efficiency with which the multiscale physics can be simulated. A part of this statement will be more conclusively verified at a later stage once the model is formalised. Nonetheless it is straightforward to deduce by inspection that several stages of the simulation will be much faster than, say, existing PF models with FE overheads, the main examples being the stress-diffusion analysis and the free energy minimisation procedure.

So far, the only bottleneck that is apparent is the use of computational geometry for each nucleation event. Although these geometrical checks can

be performed by eye, such manual checks can be tedious, time-consuming and prone to human error. In this model, the need for automation is clear because the overarching aim of this work is to develop a statistical framework, and manual checking would be impractical for a large data set of simulated micrographs. As it stands, these geometrical checks scale with the number of hydrides in the simulation cell. This seems undesirable but it can be argued that in the later stages of the model development such checks need not be exhaustive following careful sensitivity studies. If this indeed proves to be the case, the model is capable of eliminating any stochastic variation by performing statistical averages over ensembles of simulated micrographs. This is, however, beyond the the scope the present work and the focus for now is addressing the nuanced technical challenges that come with developing the new model.

As the proposed model is novel to this field of research, there are several important considerations that must be explored before undertaking any further theoretical development or computational implementation. Firstly, it is necessary to justify the various assumptions and, if possible, quantify their effect on the simulated physics. This is crucial because of the complicated nature of the hybrid model. Secondly, it is useful to translate the various aspects of the model—including the methods for representing physical entities, solving physical equations and describing physical processes—into an algorithmic workflow. The algorithmic workflow should be as general as possible so that it is easier to identify a programming strategy. Thirdly, it is sensible to plan beforehand the program architecture through, say, a breakdown of the program modules and interfaces. The significance of such planning cannot be overstated because it ensures that the software is sustainable, that is, it retains flexibility for future changes and improvements. Finally, it is good practice to perform simple verification checks to ensure the modules and interfaces work as intended.

The remainder of this chapter explores in more depth these aspects of the model formulation. This is the code specification of this bespoke model, which is a documentation that serves as the interface between computational science and computer science. That is, the code specification is the intellectual basis for both the modelling methodology and its implementation within a custom software. This is particularly important for a bespoke model that requires sizeable code development, which is the case here. In addition, nuclear fuel performance codes must be robust and sustainable; these requirements can be addressed through the code specification because it is an invaluable resource for testing, maintaining and improving such advanced codes. Accordingly, this chapter is, in part, a code specification for this hybrid model, and it is the main result of this investigation.

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7.1 Schematic Overview

Due to the intricate nature of this hybrid model, it is worthwhile to first introduce the overarching aspects of the computational framework. This includes the scope of the simulation, the layout of the building blocks that constitute the model, and the relevant elements of computational geometry.

7.1.1 Scope

The simulation scope shown in **FIG. 7.1** is defined as follows. The simulation cell is a rectangular area of dimensions $L_1 \times L_2$ where both L_1 and L_2 are much smaller than dimensions of the Zr alloy specimen or component. It is possible to choose macroscopic L_1 and L_2 values that are much larger than typical PF simulations and comparable to certain FE simulations. However, unlike standard FE models, it is assumed that the simulation cell represents some region within a (semi-)infinite continuum. The main advantage of this assumption is the applicability of the conformally invariant aspects of the elastic field theory.

The analytical formulae derived using the mathematical theory of planar elasticity generally hold for continua that are either (i) isotropic and heterogeneous or (ii) anisotropic and homogeneous. The first case describes a Zr microstructure in which all basal poles are aligned in the direction orthogonal to the plane of the simulation. The second case provides a suitable first approximation for highly textured Zr alloys.

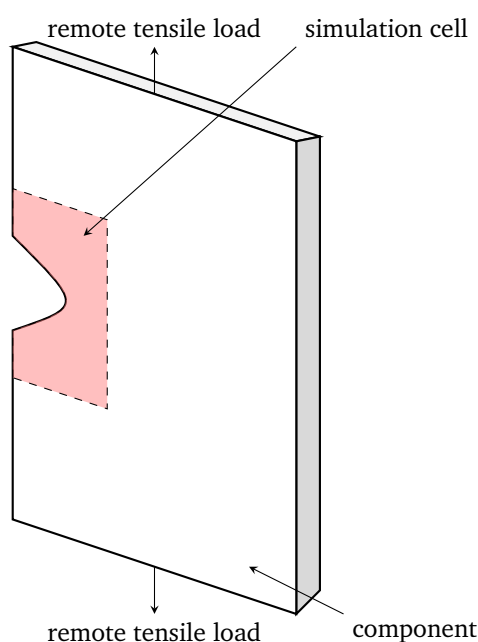


FIG. 7.1

Simulation scope

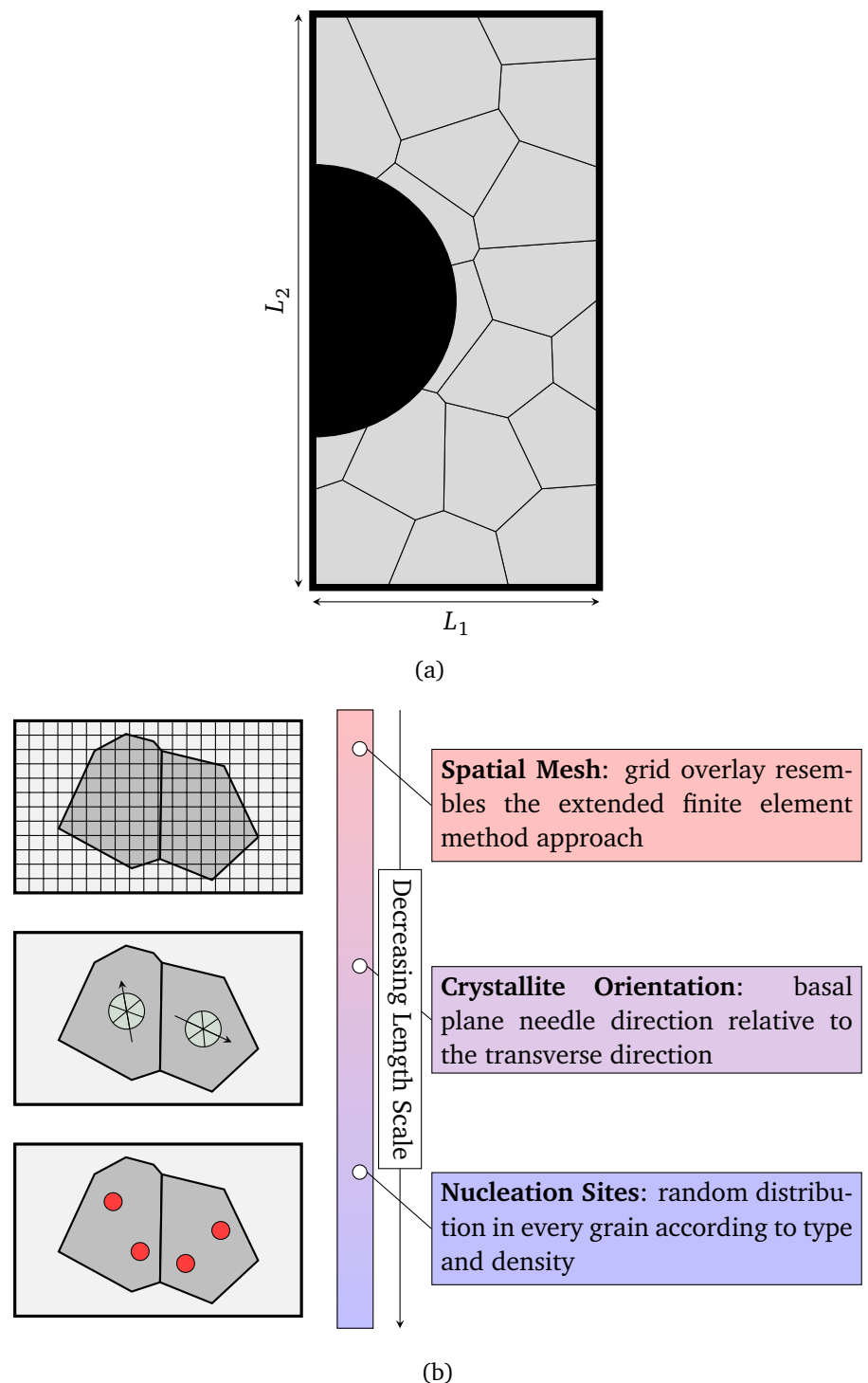
The simulation cell depicts a comparatively small area relative to the component as a whole. Considering the size of standard Zr alloy clad components, it is sensible to assume that this simulation cell is part of a (semi-)infinite continuum and that the tensile load is applied remotely. Note that the traction-free surface condition applies for the boundary of the notch and the half-space where applicable. These surface corrections are more difficult to compute for non-trivial notch geometries.

For an isotropic heterogeneous medium, the simulation cell is divided into several computational layers of the physical description of the component. As illustrated in FIG. 7.2, the collective treatment of different metallographic features requires a computational overhead for performing various geometrical checks.

FIG. 7.2

Simulation cell setup

A high-level outline of the computational implementation of the multiscale model. (a) An example of the simulation cell depicting the flaw geometry and the morphology of the grains. Most of the foregoing simulations will use an elliptical hole because analytical closed-form expressions are well known for the corresponding elastic fields. By varying the minor semi-axes, it is straightforward to approximate the geometries of both slit cracks and blunt notch. (b) A hierarchy of the levels of physical description. The spatial mesh is used to convey spatially-varying fields. The grains are represented by convex polygons and their sub-structure contains randomly positioned intra-granular nucleation sites. For the case of the isotropic heterogeneous system, the basal plane of each crystallite has a specific orientation around the basal pole. This is particularly important in incorporating the effects of the hydride-matrix interfacial energy because there are three preferred directions along which the micro-hydrides grow on the preferred (0001) habit planes. Observe that computational techniques are required to merge the spatial mesh and the geometries of metallographic features as they do not generally coincide with each other; this paradigm is quite similar to the extended FE framework.



Spatial Mesh. The simulation cell is discretised into a spatial mesh, denoted $\mathbf{S}$, whose resolution is defined by uniform horizontal and vertical mesh spacings, Δl_1 and Δl_2 so that

$$\mathbf{S} = \left\{ (m\Delta l_1, n\Delta l_2) \mid m, n \in \mathbb{N} \text{ with } m\Delta l_1 \leq L_1, n\Delta l_2 \leq L_2 \right\}. \quad (7.1)$$

Although the simulation methodology uses analytical formulae for both stress analyses and stress-diffusion analyses, this discretisation still has several important physical implications. Firstly, all spatially varying fields are represented on the grid points of the discretised mesh. This includes the elastic fields of the system as well as the diffusible H concentration. But this also includes a pointwise texture map that encodes crystallite orientation at every point so that it is possible to perform tensor analysis with material tensors in the heterogeneous medium. Secondly, the grid points are used to position microstructural features such as the intra-granular nucleation sites and micro-hydride needles, which bypasses the need for numerical interpolation where possible. Therefore, the choice of Δl_1 and Δl_2 enforces a limit on what is the smallest possible metallographic feature that can be explicitly visualised in the simulated micrograph. [Note 14](#)

Microstructure. The polycrystalline microstructure of the Zr alloy specimen can be represented by a two-dimensional space-filling tessellation that is composed of (non-overlapping) convex polygons. In this geometrical tessellation, each polygon represents a crystallite; an intersecting edge between adjacent polygons represents a grain boundary. There are many different triangulation methods for establishing such a tessellation, the simplest being a standard Poisson-Voronoi diagram [[Press et al. \(2009\)](#)]. In the present work, the microstructure is represented by a homogeneous Poisson-Voronoi diagram, $\mathcal{V}$, which can be constructed as follows.

Suppose that the $L_1 \times L_2$ simulation cell is populated by Voronoi cell seeds, $\mathbb{V} = \{\mathbf{p}_\alpha \mid \alpha = 1, 2, \dots, N_g\}$, which act as the nuclei for N_g grains. The seeds are randomly distributed according to a Poisson distribution. The Voronoi cell $\mathcal{V}_\alpha \subset \mathcal{V}[\mathbb{V}]$ associated with $\mathbf{s}_\alpha$ can be defined as the set of points in the two-dimensional Euclidean space, $\mathbb{E}^2$, which are closer to $\mathbf{s}_\alpha$ than any other element of $\mathbb{S}$, that is,

$$\mathcal{V}_\alpha \equiv \left\{ \mathbf{x}_\alpha \mid \mathbf{x}_\alpha \in \mathbb{E}^2 \text{ with } \mathfrak{D}(\mathbf{x}_\alpha, \mathbf{p}_\alpha) < \mathfrak{D}(\mathbf{x}_\alpha, \mathbf{p}_\beta) \forall \beta \neq \alpha \right\}, \quad (7.2)$$

where the map $\mathfrak{D}(\mathbf{q}, \mathbf{p}_\alpha)$ determines the normal Euclidean distance between $\mathbf{q} \in \mathbb{E}^2$ and $\mathbf{p}_\alpha \in \mathbb{V}$ in the usual way:

$$\mathfrak{D}(\mathbf{q}, \mathbf{p}_\alpha) = \sqrt{(q_1 - p_{\alpha 1})^2 + (q_2 - p_{\alpha 2})^2}. \quad (7.3)$$

The initial seed lattice, $\mathbb{V}$, completely determines the morphology and size distribution of the Voronoi cells. There are various computational methods

Note 14

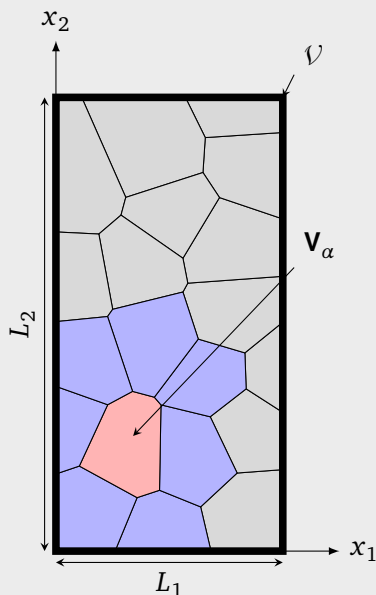
Interpolation

In principle, different (non-coinciding) spatial meshes can be used for the stress analyses and stress-diffusion analyses, and microstructural features can be positioned arbitrarily on non-grid points because it is still possible to determine the elastic field using the analytical closed-form expressions. From the computational standpoint, this framework would, of course, be much more general but it would require interpolation methods to be implemented. Interpolative computations, such as cubic spline fitting, would be an inconvenient addition to a computational methodology that is already quite complicated. Moreover, interpolation would constitute additional numerical steps that contribute to the overall computational expenditure. For example, the crystallite orientation would have to be assigned to every off-grid point after the initialisation, which can be difficult to implement efficiently. For these reasons, interpolation is avoided but it is again worth noting that this leads to a slight loss of accuracy in the physical description of the system.

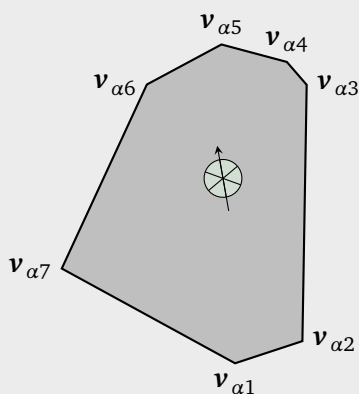
FIG. 7.3

Computational representation of the polycrystalline microstructure

(a) A random Voronoi tessellation induced by a homogeneous Poisson process. A nearest neighbour search is required to determine the set of neighbouring Voronoi cells that share an edge. (b) A single Voronoi cell as an ordered node list of vertices. All mesh points that are enclosed by this set of vertices are allocated a crystallite orientation.



(a)



(b)

for implementing Eq. (7.2) in practice, most notably the Fortune sweep line algorithm which is used for this model [de Berg et al. (2008)].

Considering the tessellation depicted in FIG. 7.3, the Poisson-Voronoi diagram does indeed resemble—at least qualitatively—the typical polycrystalline microstructures of the Zr alloy specimens with smaller grain sizes [Patel et al. (2018)]. Due to the properties of the $\mathcal{V}[\mathbb{V}]$, the density of the seeds, $\rho_g = N_g/(L_1 L_2)$, can then be chosen according to the average grain size, l_g , and this approximation is suitable for a homogeneous crystallisation process in which all grains nucleate randomly and simultaneously and grow at the same rate [Janssens et al. (2007)]. Therefore, ρ_g is a sensible standalone microstructural parameter for the as-received and possibly enhanced grain Zr alloy specimens, and it can be deduced from experiment. However, ρ_g would not a complete measure for microstructures in which there is a large or non-uniform variation in the grain sizes; this includes, for example, the blocky- α specimens which exhibit a bimodal distribution of grain sizes [Patel et al. (2018)].

In addition to the grains and grain boundaries that are specified by $\mathcal{V}$, the substructure of individual grains must also be incorporated through the hierarchical levels of physical description. This substructure includes any inter-granular and intra-granular defects, such as nucleation sites and hydride features, and, in later discussions, the crystallographic slip planes as specified by the crystallite orientation. Referring to FIG. 7.2, the challenge of constructing such a simulated micrograph, which is embedded with this multiscale description of the microstructure, extends to the broad field of computer vision [de Berg et al. (2008) and Press et al. (2009)]. That is, the computer must be able recognise, store and manipulate the spatial relationships between grains and their respective substructures. For example, suppose that a micro-hydride needle is added to the simulation cell at a random position; then it is crucial that the computer can quickly and precisely identify the grain(s) in which this hydride feature would exist, and whether it would traverse any grain boundaries. These computational checks can then be used to distinguish between allowed and forbidden microstructural configurations within the realm of simulated or hypothetical possibilities. In turn, these computational checks can be used to enforce microstructural rules that govern the simulated physics, and these rules can be adapted from experimental observations. In the given example of the micro-hydride needle, microstructural rules could account for the coherency of the hydride-matrix interfaces and the known orientation relationships [Carpenter (1973) and Carpenter (1978)].

The concept of microstructural rules—imposed using computer vision—is inherent to this hybrid model, and this is a paradigm of the overlap be-

tween computational science and computer science. For the purpose of this work, computer vision of the microstructure can, in part, be achieved at a very simplistic level by implementing the geometrical algorithms that are commonly encountered in computer graphics [de Berg et al. (2008) and Press et al. (2009)]. More specifically, computer vision of $\mathcal{V}$, or rather the extent to which it is needed in this work, can be automated using only three families of algorithms that are widely used for the computational geometry of convex polygons.^{Note 15} These three algorithmic families will be introduced in due course, but the focus for now is using $\mathcal{V}$ as a computational basis for the microstructure. As it stands, $\mathcal{V}$ is simply an abstract mathematical construct defined by Eq. (7.2) and, in its current form, it is neither sufficient nor convenient for the efficient use of computational geometry. This is because $\mathcal{V}$ is generated and stored independently of the other levels of the physical description depicted in FIG. 7.2, and there is an apparent disconnect between the various data structures that are needed to encapsulate different details of the microstructure. This disconnect would be reflected in the program architecture, leading to the following problems: (i) a data structure for $\mathcal{V}$ would typically not contain a list of the nearest neighbours to any given Voronoi cell; (ii) a function that returns a random Euclidean vector point within the $L_1 \times L_2$ cell would typically not distinguish the corresponding Voronoi cell; and (iii) an initialisation step that utilises the spatial mesh in conjunction with $\mathcal{V}$ would typically not exclude the spatial domain of the notch. These are but a few of the computational (geometrical) problems that emerge in this microstructural solver.

For the purpose of computer vision, it is, therefore, more suitable to treat $\mathcal{V}$ in terms of the more general class of mathematical structures known as graphs or complex networks. A graph or a complex network is most simply a collection of nodes and a corresponding collection of edges that connect the nodes [Steen (2010) and Evans (2004)]. Applying the principles of graph theory, each Voronoi cell $\mathcal{V}_\alpha \subset \mathcal{V}[\mathbb{V}]$ is a N_α -sided convex polygon object $\mathbf{V}_\alpha \in \mathbf{V}[\mathbb{V}]$ that can be stored as an ordered list of its constituent nodes and edges:

$$\begin{aligned} \mathcal{V}_\alpha &\mapsto \mathbf{V}_\alpha \quad \text{with} \quad \mathbf{V}_\alpha \equiv (\mathbf{V}_\alpha[\text{node}], \mathbf{V}_\alpha[\text{edge}]) \\ \mathbf{V}_\alpha[\text{node}] &\equiv \{\mathbf{v}_{\alpha n} | n = 1, 2, \dots, N_\alpha\} \\ \mathbf{V}_\alpha[\text{edge}] &\equiv \{\langle \mathbf{v}_{\alpha n}, \mathbf{v}_{\alpha(n+1)\%N_\alpha} \rangle | n = 1, 2, \dots, N_\alpha\}, \end{aligned} \quad (7.4)$$

where $\mathbf{v}_{\alpha n}$ is the n th vertex of $\mathbf{V}_\alpha$ and $\langle \mathbf{v}_{\alpha n}, \mathbf{v}_{\alpha(n+1)\%N_\alpha} \rangle$ is a bi-directional edge between the enclosed nodes. In later discussions, it will become clear why these lists must be ordered so that the geometrical algorithms can be implemented in their most optimised formats. It is then important to emphasise that $\mathbf{V}[\mathbb{V}]$ denotes an organised data structure that is somewhat distinct

Note 15

Automated computer vision

It is entirely possible to perform manual geometrical checks by inspecting the simulated micrographs and then applying the microstructural rules. However, this is not feasible for various reasons. In particular, manual checks become increasingly difficult as the spatial resolution becomes finer, and so human error is more likely. But even if human error was not an issue, manual geometrical checks would be impractical for any realistic choices of the microstructural parameters because of the enormous number of checks that would be required for both individual simulations and statistical ensembles of simulated micrographs. For example, a realistic simulation cell could contain hundreds or thousands of grains. The long-term need for automation is clear in this investigation.

from its abstract mathematical counterpart, $\mathcal{V}[\mathbb{V}]$, and that the computational construction of $\mathbf{V}[\mathbb{V}]$ from $\mathcal{V}[\mathbb{V}]$ is not a trivial task. As shown in FIG. 7.3, there are two reasons why this is the case: (i) a nearest neighbour search is required to list all neighbouring Voronoi cells to every $\mathbf{V}_\alpha \in \mathbf{V}[\mathbb{V}]$, which becomes increasingly complicated as N_g takes on larger and more realistic values; and (ii) the node list $\mathbf{V}_\alpha[\text{node}]$ for every $\mathbf{V}_\alpha \in \mathbf{V}$ must be ordered so the corresponding edge list, $\mathbf{V}_\alpha[\text{edge}]$, can also be appropriately be ordered. Therefore, the construction of $\mathcal{V}[\mathbb{V}]$ requires more computations than Eq. (7.2) in which $\mathcal{V}[\mathbb{V}]$ is simply a list of the known nodes and edges of the Voronoi diagram. This construction procedure involves finding the dual graph of $\mathcal{V}[\mathbb{V}]$ using Delauney triangulation, but the laborious details are not presented here [de Berg et al. (2008) and Press et al. (2009)].

Texture. The computational description of the polycrystalline microstructure requires, in addition to the grain morphologies, a texture map that allocates a crystallite orientation to every grain. This texture map, $\mathbf{T}$, is defined on $\mathbf{S}$ by a pointwise matrix field, $\mathfrak{Q}(\mathbf{x})$, that encodes a discretised representation of $\mathcal{V}$ and the Euler rotational angles that are required for a coordinate transformation from the natural coordinate system of the domain of each hexagonal crystallite, $\mathcal{V}_\alpha \subset \mathcal{V}$, to the global coordinate system of the simulation cell. In general, $\mathfrak{Q}(\mathbf{x})$ would be the multiple of three rotational matrices at every mesh point, but $\mathbf{T}$ is a much simpler data structure for the problem at hand.

In the planar setting, $\mathbf{T}$ can be constructed using a distribution of crystallite orientations specified by microstructural input of the Kearns parameters. Recall that there are several different commercial Zr alloy materials fabricated with distinct textures. For the case of weld components, the texture is random, that is, $f_n = f_r = f_t = \frac{1}{3}$, and so the simulation cell should convey an isotropic heterogeneous medium in which each Zr crystallite is allocated a random angular orientation about the basal pole. For the case of the highly textured CANDU pressure tubes, the basal poles are orientated towards the radial direction, that is, $f_r \simeq 1.0$, and so the simulation cell should convey an anisotropic homogeneous medium that is essentially the prism plane of a large Zr crystallite. Stress analysis is facilitated by the respective approximations of isotropy in the former case and homogeneity in the latter case. That is, in both cases, stress analysis assumes a homogeneous continuum from the standpoint of elastic field theory. Nevertheless, $\mathbf{V}[\mathbb{V}]$ and $\mathbf{T}$ are still essential to the treatment of anisotropy and polycrystallinity, and the corresponding effects on H diffusion and hydride precipitation. And the construction of $\mathbf{V}[\mathbb{V}]$ and $\mathbf{T}$ within this hybrid model paves the way for more sophisticated models of the Zr alloy microstructures in the context of DHC

research.

In order to construct $\mathbf{T}$, computer vision is required to discretise $\mathcal{V}$ onto $\mathbf{S}$ so that each mesh site can be allocated the correct crystallite orientation. For the purpose of this investigation, this discretisation involves translating $\mathcal{Q}(\mathbf{x})$ into a list of matrices for each grain so that

$$\mathbf{T}[\{f_n, f_r, f_t\}] = \{\mathcal{Q}_\alpha(\mathbf{x}) \mid \mathbf{x} \in \mathbf{V}_\alpha \text{ for } \alpha = 1, 2, \dots, N_g\}, \quad (7.5)$$

noting how $\mathbf{T}$ is parametrised by the microstructural input $\{f_n, f_r, f_t\}$ as appropriate. The application of Eq. (7.5) is, of course, trivial for a homogeneous system because all mesh points are allocated the same orientation. For the case of the highly textured CANDU pressure tubes, every transformation matrix produces a rotation about the x_1 -axis by $\pi/2$ rad, that is,

$$\mathbf{T}[\{f_n = 0, f_r = 1, f_t = 0\}] \longrightarrow \mathcal{Q}_\alpha(\mathbf{x}) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix} \forall \alpha, \quad (7.6)$$

and Eq. (7.5) can be implemented without the need for computer vision. But the application of Eq. (7.5) is in general not trivial for a heterogeneous system in which the grains are misorientated. For the case of weld components, a two-dimensional random texture can be generated using a list of random angles $\{\theta_\alpha \mid \alpha = 1, 2, \dots, N_g\}$ and supposing that each Voronoi cell represents the basal plane of a Zr crystallite with a relative crystallographic misorientation, that is,

$$\mathbf{T}[\{f_n = 1, f_r = 0, f_t = 0\}] \longrightarrow \mathcal{Q}_\alpha(\mathbf{x}) = \begin{bmatrix} \cos \theta_\alpha & \sin \theta_\alpha & 0 \\ -\sin \theta_\alpha & \cos \theta_\alpha & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad (7.7)$$

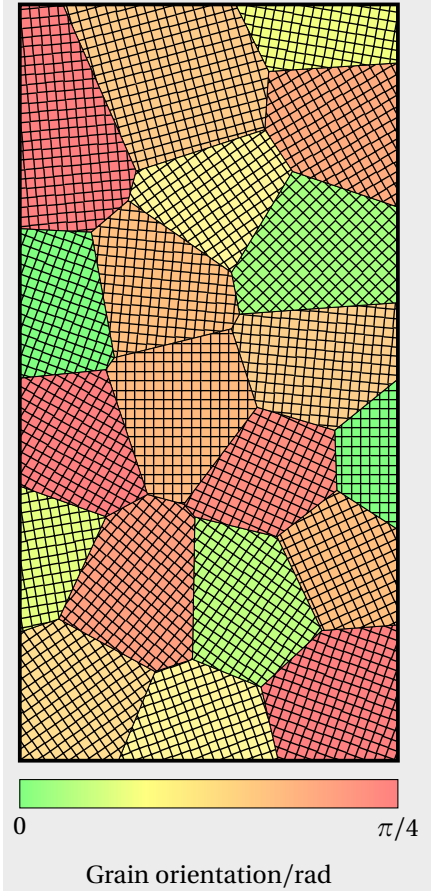
where $\theta_\alpha \in [0, \pi/3)$ specifies the unique orientation of the $[1\bar{2}10]$ direction in crystallite $\mathbf{V}_\alpha$ relative to the fixed x_1 -axis of the simulation cell. As shown in FIG. 7.4, the random texture is reflected in the substructure of each grain.

The computer vision of $\mathbf{T}[\{f_n, f_r, f_t\}]$ in conjunction with $\mathbf{V}[\mathbf{V}]$ helps build a simulation environment in which the stress-diffusion and diffusion-precipitation analyses can account for the polycrystalline microstructure of Zr alloy. It is now possible to incorporate the role of the texture in the treatment of H diffusion as well as the microstructural rules that dictate the local microscale (and even sub-microscale) energetics of hydride precipitation as a function of the crystal orientation.

FIG. 7.4

Computational representation of the texture map

The weld texture of a Zr alloy consisting of randomly orientated grains. The orientations are defined by a single angle around the basal pole, and the basal pole of every crystallite is directed along the normal to the simulation cell. The parallel lines within each Voronoi cell represent crystallographic planes; for the purpose of clarity, only two sets of orthogonal crystallographic planes are shown in each grain.



Nucleation Sites. The explicit computational treatment of hydride precipitation at distinct heterogeneous nucleation sites requires the computer vision of the various categories of intra-granular and inter-granular nucleation sites as well as micro-hydride needles and macro-hydride colonies. The geometrical representation of these microstructural features is perhaps the most intriguing aspect of this hybrid model because this governs the accuracy-efficiency trade-off of the simulated physics. On the one hand, these computational geometries should reflect experimental observations where possible. But on the other hand, these computational geometries must be simple enough to not compromise the speed at which geometrical checks are performed. So the aim now is to select carefully minimalistic geometries of these microstructural features and then employ the computer vision of $\mathbf{V}[\mathbb{V}]$ and $\mathbf{T}[\{f_n, f_r, f_t\}]$ to design a set of microstructural rules.

Consider first a nucleation site, $\mathbf{N}$, which is, in essence, some bounded region of the simulation cell over which the diffusible H concentration on $\mathbf{S}$ can be integrated to some value $N_H[\mathbf{N}]$ that can be used to check some precipitation criterion. The nucleation site is said to be activated (or dormant) if the precipitation criterion is met (or not met) at a given stage of the simulation. If the precipitation criterion is satisfied, there is a nucleation event in which a hydride feature, denoted $\mathbf{H}[\mathbf{N}]$, is added to simulation cell. This approach is sensible if the geometries of $\mathbf{N}$ and $\mathbf{H}[\mathbf{N}]$ are aptly chosen so that the precipitation criterion can invoke mass balance self-consistency: $N_H[\mathbf{N}]$ must equal or exceed the H stoichiometric composition of $\mathbf{H}[\mathbf{N}]$, that is, there must be a sufficient amount of diffusible H within $\mathbf{N}$ which can then cluster to form $\mathbf{H}[\mathbf{N}]$ of some fixed geometry. This mass balance approach is motivated by the need to model the diffusion-precipitation coupling in a self-consistent manner at the microscale.

The practical questions concerning the computational geometries of $\mathbf{N}$ and $\mathbf{H}[\mathbf{N}]$ still remain to be answered. The answers depend on the choice of the length and time scale at which precipitation is treated. At the length scales of SEM observations, the nucleation sites and macro-hydride colonies can primarily be categorised, in the broad sense, as either intra-granular and inter-granular features [Patel et al. (2018)]. Operating exclusively at these coarse length scales, approximate geometries of $\mathbf{N}$ and $\mathbf{H}[\mathbf{N}]$ can be chosen accordingly to the SEM observations. For example, recall that certain inter-granular macro-hydride colonies whose morphologies coincide with grain boundaries; the morphology of these hydride features can be modelled by configuring $\mathbf{N}$ and $\mathbf{H}[\mathbf{N}]$ to be specific edges within $\mathbf{V}[\mathbb{V}]$, which is simplistic but nonetheless effective. However, there is no need to settle for such a coarse geometrical description. The real benefit of this hybrid model is that spatial resolution of $\mathbf{S}$ can be fine enough to capture the substructure of

the macro-hydride colonies as thermodynamically favourable assemblies of micro-hydride needles. That is, the simulated micrograph can portray a system size that is comparable to SEM studies whilst also maintaining a (digital) resolution that is characteristic of TEM studies. At the length scales of TEM observations, the nucleation sites are understood to be highly localised microstructural defects, and micro-hydride needles resemble lenticular platelets in staircase-like stacks [Puls (2012), Perovic, Weatherly, and Simpson (1983), and Patel and Stopher (2017)]. Then the computational geometries of $\mathbf{N}$ and $\mathbf{H}[\mathbf{N}]$ should be based on this microscopic understanding.

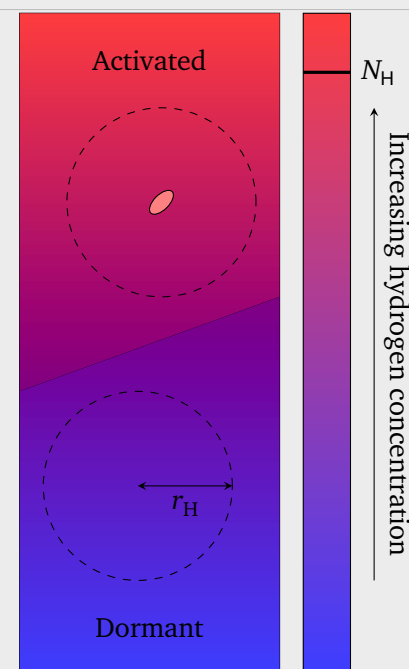
At the microscale, $\mathbf{N}$ could correspond to any class of crystallographic defect that act as heterogeneous nucleation sites. This includes: (i) intra-granular sites near SPPs, dislocation networks, point defect clusters, and other hydride features; and (ii) inter-granular sites such as grain boundaries or other defects near grain boundaries. As the mid-range clustering process of $\mathbf{H}$ is not treated explicitly in this work, there is no need to describe the exact geometries of any of these nucleation sites. Instead it is better to devise minimalistic geometries that facilitate computer vision, and then use the precipitation criterion as a gauge to rank the potency or favourability of different nucleation sites. In this way, different nucleation sites can be treated with the same set of geometrical checks. At this stage, the choice of nucleation site geometry is, in some sense, arbitrary. For the sole purpose of proceeding with the model formulation, a circle of radius r_H is chosen to represent a microscopic nucleation site. A circle is a convenient choice because its centre point is well defined so the nucleation site can be easily located using computer vision, and there is only one variable sensitivity parameter, namely, r_H , which can be used to calibrate the precipitation criterion. As shown in FIG. 7.5, it is then straightforward to implement the mass-balance approach by varying r_H according to the potency of a given class of nucleation sites.

Nucleation sites can be distributed randomly on $\mathbf{S}$ according to the microstructural properties of the Zr alloy under investigation. One possible measure would be the ratio of intra-granular and inter-granular nucleation sites, which can be used to distinguish the commercially pure Zr specimens from the Zircaloy specimens that contain more intra-granular SPP nucleation sites [Patel et al. (2018)]. As grain boundaries are only represented by the edges of Voronoi cells, it is sensible to decompose each Voronoi cell into two sub-domains for inter-granular and intra-granular features respectively; this is discussed further in due course.

FIG. 7.5

Computational representation of intra-granular nucleation sites

The computational implementation of microscale precipitate of hydrides using the proposed mass balance approach. Each nucleation site is represented by a circle. The diffusible $\mathbf{H}$ concentration is integrated within the circle. If there is enough $\mathbf{H}$ to form a micro-hydride needle of a pre-determined geometry and size, then the nucleation site is activated and the micro-hydride needle is added to the simulation cell. The diffusible $\mathbf{H}$ concentration is also corrected following a successful nucleation event.



Hydrides. Following a similar line of reasoning, it is convenient to represent the computational geometry of micro-hydride needle, $\mathbf{H}[\mathbf{N}]$, as either a line segment, rectangle or ellipse. These are all relatively simple shapes from the standpoint of computer vision, and choice really depends the accuracy-efficiency trade-off. In terms of accuracy, an elliptical geometry agrees with the aforementioned TEM observations that depict the lenticular morphology of micro-hydride needles [Carpenter (1973) and Puls (2012)]. In terms of efficiency, computer vision of the spatial relationship between line segments on $\mathbf{S}$ and $\mathbf{V}[\mathbf{V}]$ is much simpler to implement and much more rapid during the simulation runtime [de Berg et al. (2008)]. The present work opts for a line segment (or a thin rectangular) representation because this is consistent with the dislocation dipole model of the elastic fields around a micro-hydride needle.

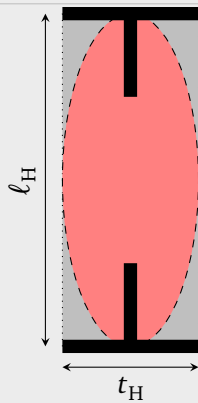
Referring to FIG. 7.5, the precipitation criterion for a given $\mathbf{N}$ can then be based on the size of $\mathbf{H}[\mathbf{N}]$ as follows. Suppose that $\mathbf{N}$ is checked periodically for its H concentration, and that the time interval for these periodic checks, τ_H , is sufficiently long to allow the mid-range clustering of H atoms—and subsequent short-range martensitic motion of Zr atoms and short-range re-ordering of H atoms—that would typically lead to the nucleation and growth of a micro-hydride needle of some fixed size. As shown in FIG. 7.6, this needle size is given in terms of the length ℓ_H and the thickness t_H , both of which can be deduced from TEM experiments [Carpenter (1973)]. For this micro-hydride needle with a uniform stoichiometric composition, it is possible to compute the number of H atoms, c_{solvus} , that occupy the precipitate phase by considering the volume of the relevant Wigner-Seitz unit cell. The precipitation criterion is satisfied if this number is exceeded by the amount of diffusible H atoms in the nucleation site at the time of the check. The H mass balance check then establishes an adjusted solvus, c_{solvus} , that models diffusion-precipitation in a self-consistent manner at the microscale.

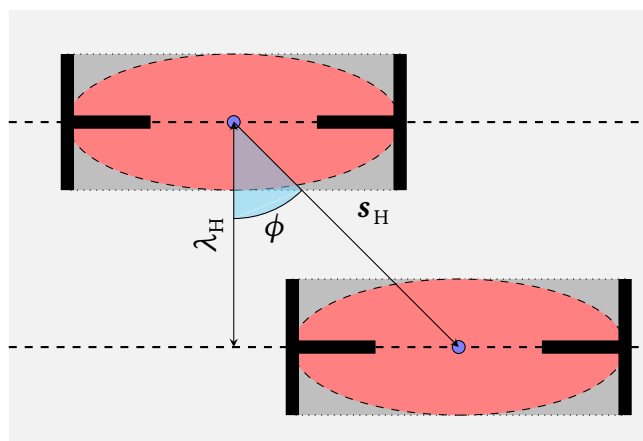
If the nucleation site $\mathbf{N}$ is activated, the micro-hydride needle $\mathbf{H}[\mathbf{N}]$ is added to the simulation cell. The precipitation criterion can also be extended to impose local microstructural rules using the computer vision of $\mathbf{H}[\mathbf{N}]$ in relation to $\mathbf{T}[\{f_n, f_r, f_t\}]$ as well as other micro-hydride features and grain boundaries. These microstructural rules can account for the habit planes and preferred orientations as well as the strain energetics and relative configurations within the substructure of macro-hydride colonies. In order to mimick the characteristic autocatalytic (sympathetic) nucleation mechanism, additional nucleation sites can be placed in the vicinity of an activated nucleation site. As depicted in FIG. 7.7, the staircase-like stacking can be replicated by placing a second nucleation site at a relative position, s_H , to an activated one.

FIG. 7.6

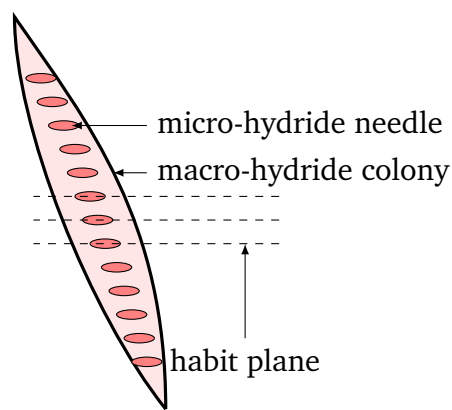
Computational representation of a micro-hydride needle

The computational geometry of a micro-hydride needle as either a line segment, rectangle or an ellipse.

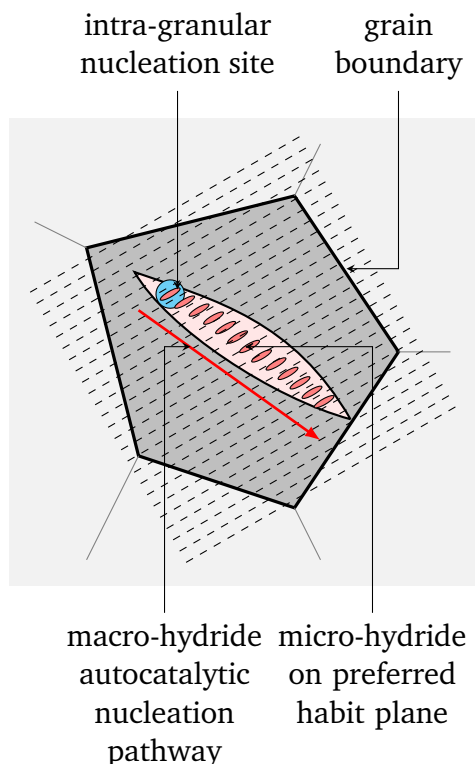




(a)



(b)



(c)

FIG. 7.7

Computational representation of micro-hydride needles and macro-hydride colonies

The autocatalytic nucleation mechanism that leads to formation of staircase-like stack substructures of macro-hydride colonies can be mimicked by placing one additional nucleation site in the vicinity of an activated nucleation site. The exact relative positioning, s_H , can be adapted from TEM studies that show this effect. (a) The stacking of two micro-hydride needles as represented using the dislocation dipole model. The strain energetics of this system can be used to determine stable or unstable configurations by sampling over the variable angle ϕ whilst keeping the spacing λ_H constant. The sampling rate should respect the spatial resolution of the simulation cell, and the sampling range should be confined to the domain of the nucleation site. (b) An illustration of a macro-hydride colony as a staircase-like stack of micro-hydride needles residing on preferred habit planes. Computer vision of the micro-hydride needles and the texture can be used to ensure that they reside on the preferred habit planes and maintain the preferred orientation relationships. (c) A two-dimensional computational geometric representation of a grain containing a macro-hydride feature. The intra-granular nucleation site initiates the formation of the principal micro-hydride in the autocatalytic nucleation pathway, which depicts the growth of the macro-hydride. Note also that the micro-hydride needles lie on the crystallographic planes which specify the orientation of the grain. In reality, the substructure of macro-hydride colonies can be much more complicated but this setup establishes the foundation for more sophisticated models.

7.1.2 Layout

The main building blocks of the hybrid model are organised in order as follows:

- ▶ *Input.* The primary input to this model are the set of variables that describe the notch acuity, component microstructure and thermomechanical conditions. This allows the model to predict H concentration profiles and hydrided microstructures for different notched specimens, commercial alloys and reactor settings. The input also includes other physical parameters as well as computational parameters, which are chosen based on either experimental findings, other models or sensitivity studies. ^{Note 16}
- ▶ *Initialisation.* The different layers of the simulation cell are built using the given input. This begins with building the discretised spatial meshes on which the elastic fields and H concentration profile are represented. This is followed by an overlay of the geometry of key metallographic features, namely, the notch, grains and nucleation sites.
- ▶ *Simulation Methodology.* For the most part, the algorithmic workflow is built around the simulation methodology, which is one of the innovative aspects of the present work. This involves unifying stress analysis, stress-diffusion analysis, diffusion-precipitation analysis, and elements of computational geometry. The current framework allows for different variations of the algorithmic workflow depending on the type of assumptions made about the system. The present work focuses on one particular variant.
- ▶ *Post-Processing.* Once the simulation has converged and self-consistency verification checks are made, the data is processed for visualisation. These results can then be compared with their TEM or SEM counterparts. Again, it is necessary to acknowledge the modelling assumptions made at this stage.
- ▶ *Output.* The main output of the present work is a set of simulated micrographs that depict the key metallographic features. Further research is required to translate these images into an alternate fracture criterion to the K_{IH} standard in industry.

The particular variant of the proposed framework is outlined in **FIG. 7.8**, which incorporates various notch geometries that are particularly relevant to industry and assumes that macro-hydride colonies consist of a staircase stack of micro-hydride needles that have precipitated at intra-granular nucleation sites.

Other variations may require different parameters. For example, problems which feature inter-granular nucleations sites or a hierarchy of hetero-

Note 16

Parametrisation

Most physical parameters relevant to this model can theoretically be determined from first-principles calculations of the Zr-H system, that is, their physical origin is well understood in terms of the system energetics. This includes the elastic constants and the diffusivity. If electronic structure simulations could model larger systems, it would be possible to obtain parameters pertaining to the morphologies of the micro-hydride needles and macro-hydride colonies. However, this is currently not possible in practice because of the system size limitations of DFT, and hence the required parameters are adapted from TEM and SEM findings as well as other computational or experimental studies.

geneous intra-granular nucleation sites would need additional geometrical parameters. Due to the diverse capabilities, this framework can be tailored to different instances of the DHC mechanisms as well as similar processes such as hydride precipitation in Ti in the context of SHC failure.

FIG. 7.8

Simulation layout

A possible breakdown of the main building blocks of the hybrid model. This particular variant of the proposed framework describes elastoplastic slit cracks, elliptical holes and V-notches through the mathematical theory of planar elasticity. The main assumptions of this particular variant concern the macro-hydride morphology, that is, each macro-hydride colony is a staircase-like stack of individual micro-hydrides which precipitate sequentially. In this case, only two additional parameters are required for replicating the autocatalytic nucleation process; these parameters correspond to the relative separation between each micro-hydride needle in the stack. In reality, however, the macro-hydride substructure is more complex and the network of constituent micro-hydride needles is more complicated. Moreover, this particular variant only assumes the existence of inter-granular nucleation, which again is a shortcoming given the potency of grain boundaries as nucleation sites. However, both assumptions are sensible at this stage for setting up and testing the model. And, of course, the generality of the framework readily allows for more complex microstructural details to be incorporated. Therefore, this framework is broadly applicable and it can be easily extended to case of, say, hydrides in Ti or carbides in steel.

Input			
	Parameter	Symbol	Description
Material Properties	Elastic constants	$\{C_{ijkl}, S_{ijkl}\}$	Elastic moduli for anisotropic stress analysis
	Lattice constants	$\{a, c\}$	Slip parameters for crystallographic dislocations
Microstructure	Texture	$\langle \ell_g \rangle$	Average grain size for Voronoi tessellations
	Directionality	$\{f_R, f_T, f_N\}$	Kearns parameters for grain orientations
	Nucleation sites	$\{\rho^{(a)}\}$	Densities of nucleation sites of type $\{a\}$
Notch Geometry	Slit crack	c_1	Crack length in DBCS model
	Elliptical notch	$\{c_1, c_2\}$	Major and minor semi-axes in Vitek-DBCS model
	V-Notch		Root-radius and opening angle in Tovo model
	Plastic zone	p_1	Length of a fixed coplanar zone
Hydrogen Diffusion	Diffusivity	D_{ij}	Material-dependent diffusion constant matrix
	Elastic interaction	ρ_{ij}	Elastic dipole tensor for elastochemical potential
	Solvus	$c_{\text{solvus}}(T)$	Adjusted solvus concentration
	Time step	Δt	Time step for Euler and Crank-Nicholson algorithms
	Initial conditions	c_0^H	Initial uniform background hydrogen concentration
	Boundary values	c_{pq}^H	Hydrogen concentration at simulation boundaries
	Flux conditions	$\dot{c}_{pq}^H$	Hydrogen flux at simulation boundaries
	Equilibration	$\langle \Delta c_{ij}^H \rangle, \tau_{\text{eq}}$	Sensitivity criterion for successive time intervals
Hydride Precipitation	Needle size	$\{\ell_H, t_H\}$	Length and thickness of micro-hydride needles
	Needle stress	B_H	Burgers vector for dislocation dipole model
	Needle misfit	e_H	Micro-hydride misfit strain the slip vector direction
	Phase content	N_H	Stoichiometric composition of pure hydride phase
	Stack separation	$\{s_H, \lambda_H\}$	Inter-hydride distance in macro-hydride structure
System Conditions	Thermal cycle	$T(\tau)$	Temperature as a function of time
	Loading cycle	$\sigma_L(\tau)$	Uniform remote loading stress as a function of time
Computational	Simulation cell	$\{L_1, L_2\}$	Dimensions of the two-dimensional simulation cell
	Spatial mesh	$\{\Delta l_1, \Delta l_2\}$	Spatial grid resolution for stress-driven diffusion
	Nucleation setup	$r_H^{(a)}$	Radius of circular intra-granular nucleation sites
	Nucleation check	$\tau_H^{(a)}$	Time interval for checking nucleation site activation
	Stress cut-offs	$\{\sigma_N^*, \sigma_D^*\}$	Cut-offs for notch and dislocation stress singularities
	Gaussian values	$\{\mu, \sigma\}$	Normal distribution means and standard deviations
	Random numbers	$\{v\}$	Seeds for uniform random number generators

I : Initialisation	II : Simulation Methodology	III : Post-Processing																											
<table><tr><th>Setup</th></tr><tr><td>1 Simulation cell build</td></tr><tr><td>2 Spatial mesh build</td></tr><tr><td>3 Notch geometry input</td></tr><tr><td>4 Microstructure input</td></tr><tr><td>5 Nucleation site distribution</td></tr><tr><th>Principal Calculations</th></tr><tr><td>6 Loaded notch stress state</td></tr><tr><td>7 Equilibrium hydrogen profile</td></tr></table>	Setup	1 Simulation cell build	2 Spatial mesh build	3 Notch geometry input	4 Microstructure input	5 Nucleation site distribution	Principal Calculations	6 Loaded notch stress state	7 Equilibrium hydrogen profile	<table><tr><th>Stress-Driven Diffusion</th></tr><tr><td>1A Concentration mesh iteration</td></tr><tr><td>2C Solute mass balance correction</td></tr><tr><th>Diffusion-Controlled Precipitation</th></tr><tr><td>1B Nucleation activation criterion</td></tr><tr><td>2A Computational geometry check</td></tr><tr><td>2B Addition of precipitate classes</td></tr><tr><td>3A Needle configuration evaluation</td></tr><tr><td>3B Stress state update</td></tr></table>	Stress-Driven Diffusion	1A Concentration mesh iteration	2C Solute mass balance correction	Diffusion-Controlled Precipitation	1B Nucleation activation criterion	2A Computational geometry check	2B Addition of precipitate classes	3A Needle configuration evaluation	3B Stress state update	<table><tr><th>Verification and Validation</th></tr><tr><td>1 Numerical checks</td></tr><tr><td>2 Sensitivity analysis</td></tr><tr><td>2 Experimental comparison</td></tr><tr><td>3 Modelling comparison</td></tr><tr><th>Result Preparation</th></tr><tr><td>1 Simulated micrographs</td></tr><tr><td>2 Statistical ensembles</td></tr><tr><td>3 Interface with other models</td></tr></table>	Verification and Validation	1 Numerical checks	2 Sensitivity analysis	2 Experimental comparison	3 Modelling comparison	Result Preparation	1 Simulated micrographs	2 Statistical ensembles	3 Interface with other models
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Output			
	Visualisation	Parametric Study	Sensitivity Study
Hydrogen Concentration	Notch-tip hydrogen profiles	$\{c_1, c_2\}, c_0^H, c_{pq}^H, \dot{c}_{pq}^H$	$\{\sigma_N^*, \sigma_D^*\}, \langle \Delta c_{ij}^H \rangle, \tau_{\text{eq}}$
Hydride Microstructure	Notch-tip hydride networks	$\langle \ell_g \rangle, \{f_R, f_T, f_N\}, \{\rho^{(a)}\}$	$\{\ell_H, t_H\}, s_H$
Fracture Criterion	Notch-tip crack pathways	$T(\tau), \sigma_L(\tau)$	$\{\mu, \sigma\}, \{v\}$

7.1.3 Geometry

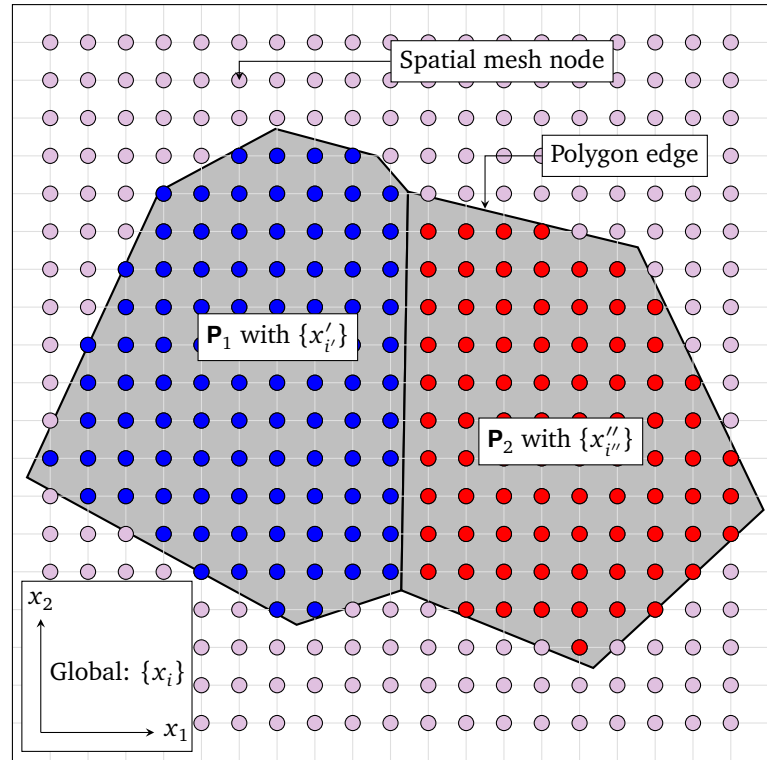
Computational geometry plays a substantial role in this hybrid model. There are three specific families of algorithms of interest to the proposed variant of the multiscale framework:

- ▶ *Point-in-a-polygon*. The point-in-a-polygon (PIP) problem posits whether a point in the plane of a polygon lies inside, outside or on the boundary of a polygon. There are many standard PIP algorithms for arbitrarily complex polygons but more efficient algorithms exist for convex polygons.
- ▶ *Polygon-line segment intersection*. The polygon-line segment intersection (PLSI) problem posits whether a finite line segment coincides with any edges of a polygon. There are many powerful PLSI algorithms that are used in line clipping methods.
- ▶ *Line segment intersection*. The line segment intersection (LSI) problem posits whether there are any crossings between a list of line segments. The LSI algorithms can become increasingly inefficient for a large list of line segments if the pairs of crossing segments in the input sequence are not adjacent elements in the list.

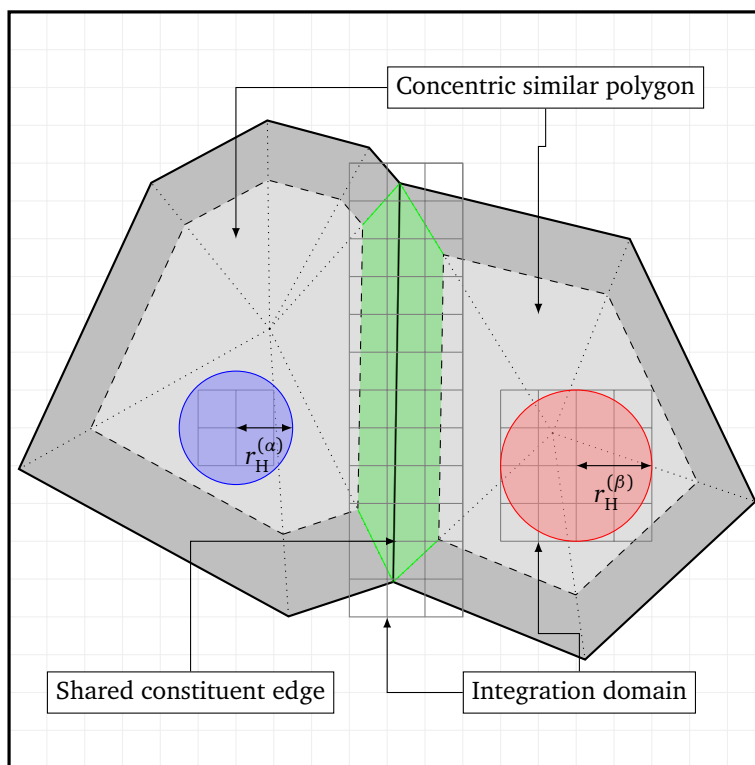
FIG. 7.9

Point-in-a-polygon problems

The significance of a PIP algorithm in assigning grain orientations to the spatial mesh nodes. Material tensors such as the elastic stiffness or elastic dipole tensors are defined in the natural coordinate system of the crystal. In a heterogeneous system, pointwise tensor calculations that couple such material tensors with global tensors involve transforming the material tensors into the global coordinate system. This paradigm applies to the case of both isotropic and anisotropic heterogeneous systems for describing the effects of texture.



- Point in polygon P_1 : $T'_{i'j'} = \Omega_{i'i} \Omega_{j'j} T_{ij}$
- Point in polygon P_2 : $T''_{i''j''} = \Omega_{i''i} \Omega_{j''j} T_{ij}$



-  Region of intra-granular macro-hydride colonies
-  Region of inter-granular macro-hydride colonies
-  Intra-granular nucleation site of type α
-  Intra-granular nucleation site of type β
-  Inter-granular nucleation site or precipitate-free zone

FIG. 7.10

Concentric similar polygon setup

The significance of establishing a secondary layer composed of small concentric similar polygons for distinguishing regions of intra-granular and inter-granular nucleation sites. This setup is constructed using a combination of the PLSI and PIP algorithms. Here the intra-granular nucleation sites are represented using circles. The size of the circle essentially represents the catchment area of a given nucleation site over which the H concentration can be integrated. The circle size can be used in conjunction with the established hierarchy of heterogeneous nucleation sites; a larger circle can be used to represent a more potent nucleation site. In this example, the larger circle may be an energetic SPP-matrix interface whereas the smaller nucleation site may be a point defect cluster. For an isotropic heterogeneous system, the effects of anisotropy can be indirectly incorporated by ensuring that the precipitation criterion is not equal at all grain boundary nucleation sites.

All three families of algorithms feature prominently in the processing of computer graphics [de Berg et al. (2008) and Press et al. (2009)]. Simple versions of the algorithms are uniquely adapted into this hybrid model. The exact applications of these algorithms to the problem at hand is explained through FIG. 7.9, FIG. 7.10 and FIG. 7.11, from which it is clear that the overall initialisation procedure is not trivial.

It is important to highlight that certain aspects of free energy minimisation have been replaced entirely with computational geometry checks. Referring to FIG. 7.11 in particular, forbidden configurations of micro-hydride needles are determined entirely using the PLSI and LSI algorithms. A PLSI check is used to prevent scenarios in which micro-hydride needles traverse a grain boundary; this rule is based on the assumption that a micro-hydride needle cannot maintain coherency across the interface between two misorientated grains. A LSI check is used to prevent scenarios in which micro-

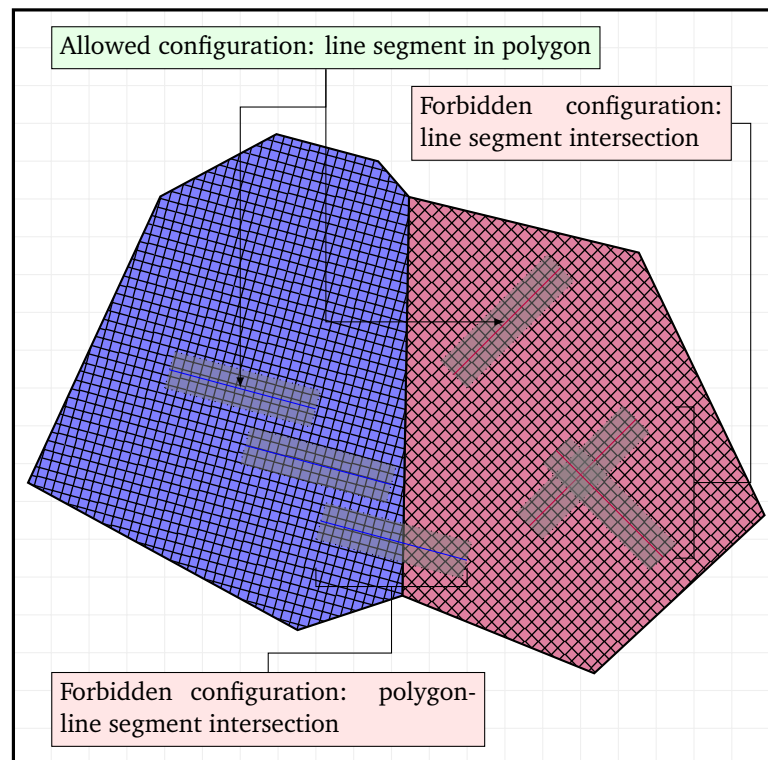
hydride needles crisscross over each other; this rule applies to the low H concentration regime. In the high H concentration regime, micro-hydrides needles may overlap with other and so the LSI checks can be omitted. These geometrical checks can be further modified in accordance with TEM and SEM observations. Moreover, unlike PF models, there is no need to translate experimental findings into complicated free energy terms [Bair, Zaeem, and Tonks (2015)]. Therefore, computational geometry serves as a powerful tool for efficiently replicating the microstructural physics observed in TEM and SEM studies.

Note that as the geometrical representation of the key metallographic features becomes more accurate, the application of such algorithms becomes more difficult. For example, if the micro-hydride needles were described as rectangles—rather than line segments—the number of computational geometrical checks would be quadrupled per micro-hydride needle. Therefore, it is best to continue to operate with the simplest possible description of the metallographic features. For this reason, the program architecture must be designed carefully in order to truly reap the benefits of computational geometry. As a corollary, an inefficient implementation of the computational geometrical checks could be a major bottleneck in the simulation runtime. In order to further contextualise the role of computational geometry, it is necessary to reflect upon the assumptions that are incorporated in the model.

FIG. 7.11

Polygon-line segment intersection and line segment intersection problems

The significance of PLSI and LSI algorithms for determining allowed and forbidden configurations of micro-hydride needles within the polycrystalline microstructure. These configurational rules are determined using TEM and SEM findings. For example, PLSI algorithm is used to check if a hydride crosses a grain boundary; this is not likely (or not possible) as the precipitate cannot maintain coherency on either side of the grain boundary if there is large relative misorientation between the grains. Similarly, micro-hydride needles may not crisscross due to restricted micro-hydride morphologies; this can be accounted for using a LSI algorithm.



7.2 Modelling Considerations

This section details the main assumptions, input parameters and sources of stochastic variation.

7.2.1 Assumptions

Due to the complexity of the problem at hand, numerous theoretical assumptions have been made so far about the nature of the DHC mechanism, and more computational assumptions will have to be made so that the model is tractable. In the following, an extensive list of assumptions is given. Each assumption is grouped into one of the four categories as defined in **TAB. 7.1**, and it is justified using the information presented in the previous discussions, including the experimental evidence in the literature as well as DFT, PF and FE models. Possible limitations are also provided for each assumption.

Assumption	Description	Examples
Framework	These overarching assumptions pertain to the overall model; such assumptions affect almost every aspect of the model, including the theoretical and computational input, methods and output.	▶ The model is developed in a planar framework. ▶ The simulation cell represents an area of an infinite continuum.
Theoretical	The assumptions pertain to the physical theories used to describe the phenomena at hand; such assumptions are made before any computational implementation.	▶ Stress analysis is undertaken using linear elasticity. ▶ Diffusive phase transformations are described using linear irreversible thermodynamics.
Computational	These assumptions pertain to the computational implementation of the physical theory; such assumptions are made to reduce the computational complexity of representing physical features and solving physical equations.	▶ The geometry of grains is represented by simple convex polygons. ▶ The singularities of the stress fields around dislocations are normalised with a radial cut-off condition.
Phenomological	These assumptions are more specific to the DHC mechanism itself and are usually a mixture of both theoretical and computational aspects.	▶ The dynamics of H diffusion and hydride precipitation are uncoupled in terms of rates. ▶ The model only includes intra-granular nucleation sites for now.

TAB. 7.1

Types of assumptions

Definitions and examples of the four types of assumptions that are used in the formulation of the hybrid model. All of these assumptions contribute to the overall tractability of model and help facilitate the computational implementation. The framework assumptions are the most important. The theoretical assumptions can usually be improved at a later stage based on additional experimental evidence; but any improvement risks adding to the overall computational expenditure. The computational assumptions generally require further testing, which will be conducted as part of the verification checks. The phenomenological assumptions are very specific to the DHC mechanism as well as the variant of the proposed framework.

Framework Assumptions

ASSUMPTION F1

The model describes a planar medium that represents a cross-sectional area of the Zr alloy component.

Justification:

- ▶ The component of interest is a cylindrical shell whose axial depth of ~ 4 m is much greater than its cross-sectional dimensionality.
- ▶ It is common practice to use a 2D representation of the component through its cross-section as this provides a straightforward comparison with 2D micrographs [Puls (2012)].
- ▶ Several validated DHC safety cases use 2D models that couple diffusion and precipitation [Martin (2013)].

Limitations:

- ▶ It is not possible to depict the realistic three-dimensional geometries of important metallographic features such as the notches, grains and micro- and macro-hydride morphologies.
- ▶ Certain aspects of the two-dimensional model do not translate straightforwardly to the three-dimensional formulation. For example, the computational geometry checks become much more complicated if the grain morphology is described by polyhedra.
- ▶ The texture is entirely two-dimensional. In the isotropic heterogeneous medium, each grain can only be allocated an orientation relative to the basal pole. In anisotropic heterogeneous medium, all grains must be aligned, and so the medium is essentially homogeneous from the standpoint of elastic field theory. It is, therefore, not possible to fully model processes such as hydride re-orientation or the shape change associated with the martensitic transformation.

ASSUMPTION F2

The simulation cell which represents Zr alloy microstructure is a (small) area of an infinite continuum.

Justification:

- ▶ The simulation cell of this model represents an area of $1 \text{ mm} \times 1 \text{ mm}$ which is a small relative to the cross-sectional area of a typical Zr alloy components.
- ▶ A simulation cell dimension of $500 \mu\text{m}$ is smaller than the component thickness; the fuel-side surface effects can be ignored and so it is sensible to work with a (semi-)infinite continuum.
- ▶ There is good agreement between analytical results obtained using the infinite continuum approximation and FE-based process zone models of finite geometry components [Martin (2013) and Vitek (1975)].

Limitations:

- Most boundary conditions are ignored at all stages of the simulation so there are no corrections of the stresses and diffusion fluxes at the free surface of the specimens.
- This is not a commonly used simplification in industrial models because of the use of FE solvers [[Martin \(2013\)](#), [Jernkvist and Massih \(2014\)](#), and [Jernkvist \(2014\)](#)].

ASSUMPTION F3

In this model, the DHC mechanism is treated as a standalone failure mechanism caused by H pick-up and the reactor operating conditions.

Justification:

- The overarching aim of this work is to transition beyond dated burn-up calculations in nuclear fuel performance codes and help improve safety cases based on H pick-up. This requires a mechanistic treatment of every possible mode of failure in the Zr alloy component that is either a direct or indirect consequence of the presence of H in the Zr matrix. This is incredibly complicated because DHC constitutes only one of the many possibilities. But DHC is a complicated failure mechanism in its own right, and so, as a starting point, it is necessary to isolate DHC from other possible failure mechanisms that may occur alongside DHC initiation.
- As Zr is a hydride-forming metal, the dominant H embrittlement mechanism is DHC, and there is limited experimental evidence for HELP or HED failure [[Puls \(2012\)](#)].
- The mechanistic understanding behind this multiscale model is based on the extensive experimental work on H and hydrides in Zr alloys at various length scales; such multiscale experimental work on other failure mechanisms in Zr alloys is limited.
- The proposed model goes beyond existing microstructural models of DHC failure and its generality lays the groundwork for similar models that describe other phenomena which involve diffusion and precipitation.

Limitations:

- Industrial safety cases must account for other failure mechanisms that occur in tandem with DHC such as fatigue, creep and irradiation damage.
- Modern nuclear fuel performance codes aim to unify DHC, fatigue and creep failure mechanisms into a holistic component scale model, and the individual treatment of DHC is not common [[Tonks et al. \(2017\)](#)].

ASSUMPTION F4

This model subscribes to the diffusion-first hypothesis of the early stages of DHC as opposed to the precipitation-first hypothesis.

Justification:

- ▶ The diffusion-first hypothesis is well supported by experimental evidence [McRae, Coleman, and Leitch (2010)].
- ▶ The groundwork for developing a theoretical and computational framework based on the diffusion-first hypothesis is well established, and so existing PF and FE models can be used as a guide.

Limitations:

- ▶ This model is not adaptable to the precipitation-first hypothesis should the (limited) experimental evidence supporting precipitation-first hypothesis prove to be conclusive.

ASSUMPTION F5

This is a model of the early stages of the DHC mechanism, that is, there is no DHC initiation in the scope of the simulation.

Justification:

- ▶ This considerably simplifies the stress-diffusion and diffusion-precipitation as the system stress state is virtually static throughout the simulation.
- ▶ This is common assumption in PF models as well as the earlier FE models.

Limitations:

- ▶ It is not clear how this model can be extended to incorporate crack dynamics.
- ▶ Standard validation methods focus exclusively on DHC initiation.
- ▶ This falls short of the most advanced FE models which also include the fracture process using a cohesive (process) zone approach.

ASSUMPTION F6

The Zr alloy specimen microstructure is represented by either an isotropic heterogeneous medium or an anisotropic homogeneous medium.

Justification:

- ▶ This adds overall simplicity of the model in terms of eliminating the numerical micromechanical computations of anisotropic heterogeneous continua.
- ▶ The use of either anisotropy or heterogeneity is beyond existing PF and FE models that feature both H and hydrides.

Limitations:

- ▶ The combined effects of both the crystalline anisotropy and polycrystalline heterogeneity are very important to the micromechanics of Zr alloys. Such effects can only be inferred or incorporated indirectly into the current model.

ASSUMPTION F7

The system temperature and the remote loading are kept constant over time. The conditions are chosen to reflect the period of cooling during the thermomechanical cycling, and hence only precipitation is treated.

Justification:

- ▶ This simplifies the overall simulation methodology because there is no need to re-calculate the system stress fields at every time step.
- ▶ Certain aspects of the framework can easily be adapted to include such temporal variations; this includes the stress-diffusion analysis where the time dependence can be included in the system stress state and temperature.

Limitations:

- ▶ This is not a common assumption in FE models because DHC initiation is usually quantified in terms of thermomechanical cycles.
 - ▶ Further research is required to understand how the temperature cycles affect the hydride dissolution and re-precipitation processes.
-

Theoretical Assumptions

ASSUMPTION T1

All stress analysis is undertaken within the framework of linear elasticity.

Justification:

- ▶ The reactor loading conditions should not cause any noticeable plastic deformation of the Zr alloy component.
- ▶ The mathematical theory of linear elasticity, in a planar setting, exhibits some conformal symmetry; owing to this symmetry, it is straightforward to compute the stress fields around many classes of defects regardless of their relative sizes.
- ▶ Analytical and semi-analytical formulae for stress fields around defects can be used alongside the principle of superposition to improve the computational speed and efficiency.
- ▶ The effects of plasticity can still be described by modelling the evolution of the dislocation microstructure using constitutive rules. This would, however, drastically increase the computational effort and simulation runtime.

Limitations:

- ▶ Analytical formulae are usually restricted to defects with very simple geometries.
 - ▶ This linear regime is not entirely valid considering that the Zr alloy may undergo plastic deformation in the vicinity of the notch tip. Local scale plasticity is thought to play an important role in the formation of denuded zones and around small defects, which cannot be fully described here.
 - ▶ This is not a common assumption in industry practice where the cohesive (process) zone analysis is preferred because the FE framework facilitates the application of non-linear elastoplastic modelling through constitutive relationships. Strain gradient plasticity is also possible.
-

ASSUMPTION T2

The elastic interaction energy between the H point defect forces and elastic fields of all other stress-raisers can be computed using the elastic dipole tensor.

Justification:

- ▶ The elastic dipole tensor captures the trigonal symmetry of the atomic environment of the H point defect.
- ▶ It becomes possible to model the H diffusion as function of the polycrystalline texture.
- ▶ This surpasses existing PF and FE models which assume the standard isotropic misfitting sphere model for H interstitials.

Limitations:

- ▶ The correct use of this multiscale elastic interaction energy for a anisotropic heterogeneous system requires the use of the PIP algorithm, which can be computationally expensive.
- ▶ The DFT computations of the elastic dipole tensor are at 0K and so it is unclear how temperature affects the elastic dipole tensor is only the leading term and additional terms may be necessary for a more accurate description of the point defect symmetry; this requires more first-principles calculations.

ASSUMPTION T3

The long-range transport of H in Zr under the influence of the gradients of chemical potential and stress can be described within the framework of linear irreversible thermodynamics. The temperature gradients are not considered here.

Justification:

- ▶ This is a standard assumption in industry practice and there are various experimentally validated FE models which operate within this framework.
- ▶ This assumption allows for a relatively large simulation cell with sufficient resolution to describe micro-hydride precipitation; this is in stark contrast to the microscopic PF model system sizes.
- ▶ It is straightforward to incorporate the effects of temperature gradients at a later stage if necessary.

Limitations:

- ▶ The main drawback of this approach is that it does not describe non-linear H diffusion in the vicinity of defects in which H-H interactions may play a role. Therefore, it is not possible to model accurately the mid-range H clustering and short-range H re-ordering which would occur very close to the notch-tip or within nucleation sites.
- ▶ This falls short of PF models in which the free energy formalism readily allows for the treatment of non-linear diffusion and hence the coupling between diffusion and precipitation. Most FE models also incorporate the effects of temperature gradients.
- ▶ The use of this purely macroscopic theory of diffusion ignores other possible transport mechanisms such as grain boundary diffusion and transport along fast diffusion paths as well as low temperature quantum tunnelling. In addition, this model does not account for the effects of sources and sinks that are standard to models of H diffusion in other metals [Barrera et al. (2018)].

ASSUMPTION T4

The evolution of hydrided microstructure is a free energy optimisation problem in which the free energy includes the elastic strain energy and the hydride-matrix interfacial energy.

Justification:

- ▶ This is standard assumption in the general theory of structural transformations in metals.
- ▶ This is an adaptation of the PF modelling strategy but using more simpler expressions of the free energy.

Limitations:

- ▶ This relies on the PF modelling approach being correct; however there are no experimentally validated PF models to date.

Computational Assumptions

ASSUMPTION C1

The shapes of certain metallographic features can be represented by simple geometrical structures.

Justification:

- ▶ It is common practice in microstructural models to use convex polygons to represent grains.
- ▶ Modelling micro-hydrides as either lines or rectangles simplifies any geometrical checks that must be performed by the computer; this is in contrast to the nonsimple topologies of micro-hydrides in PF models with adds to the computational expenditure without providing any useful information.
- ▶ The choice of convex polygons (over other classes of polygons) further facilitates geometrical checks as the computational algorithms for describing intersections between convex polygons are more optimised.

Limitations:

- ▶ The morphologies of grains in, say, the blocky- α specimens may be more complicated than convex polygons.
- ▶ Micro-hydride morphologies are significantly more complex than line segments; it is not clear how the choice of line segments over, say, ellipses affects the end results.

ASSUMPTION C2

Singularities in the stress fields around defects are normalised with an appropriately chosen cut-off.

Justification:

- ▶ This is standard practice in models that the stress fields of Volterra dislocations; a core cut-off radius is chosen to avoid the singularity.
- ▶ The computational implementation of a simple cut-off is easier and more efficient than other normalisation methods that aim preserve the nature of the singularities around crack tips.

Limitations:

- The end results are very sensitive to these cut-offs and so more research is required in order to appropriately calibrate the model. This includes, in particular, the notch-tip H profiles.

ASSUMPTION C3

The use interpolation is avoided by the appropriate placement of the nucleation sites on the spatial mesh nodes.

Justification:

- This is purely for the computational convenience of implementing two-dimensional quadrature algorithms without additional numerical computations.
- This is straightforward to correct at a later stage if it drastically affects the physical results.

Limitations:

- In general, metallographic features need not coincide with the spatial mesh nodes.
- Under this assumption, the resolution of the spatial mesh must be able capture the dimensions of the smallest metallographic features.

Phenomological Assumptions

ASSUMPTION P1

The evolution of the hydrided microstructure can be modelled as a function of an equilibrated notch-tip H concentration profile.

Justification:

- The long-range thermally activated transport of H is much slower than the additional steps required to complete the phase transformation process, namely, the mid-range clustering and short-range reordering of H as well as the reconfiguration of the Zr atoms. That is, the rate of hydride nucleation is much faster than the stress-driven transport of H to the notch tip.
- It is computationally efficient to separate the stress-diffusion analysis and the diffusion-precipitation analysis because the rates do not generally match.
- This approach is sensible given the macroscopic dimensions of the simulation cell.

Limitations:

- This is a major assumption and it is not made in any existing PF and FE model to date.

ASSUMPTION P2

Intra-granular nucleation sites can be represented by circles. Inter-granular nucleation sites are not treated.

Justification:

- These two assumptions are only made to test the model. The choice of circle is arbitrary at this stage and other shapes can be chosen after further testing.
- The radius of the circle can be used to distinguish the various classes of intra-granular nucleation sites with respect to the precipitation criterion.

Limitations:

- ▶ Grain boundaries are very potent nucleation sites and so their absence as potential nucleation sites is not realistic.
 - ▶ The nucleation site geometry (or size) is another sensitivity parameter which requires further investigation for appropriate calibration.
-

ASSUMPTION P3

The evolution of the hydride microstructure can be described by the quasi-static stepwise nucleation of individual micro-hydrides and addition of adjacent secondary nucleation sites in order to mimic the autocatalytic nucleation mechanism.

Justification:

- ▶ This bypasses the complexity of a multi-parameter optimisation of the system free energy that is common to all PF models. This is valid for the hydrided microstructures in the low H concentration regime that is of interest.
- ▶ Computational geometry can be used to reproduce the observations of TEM and SEM studies without the explicit need to perform any minimisation.
- ▶ This simplification allows larger system sizes to be simulated rapidly.

Limitations:

- ▶ This is major assumption that requires further testing. It is quite likely that standalone simulations will equilibrate to local minima in the free energy landscape as opposed to global minima.
-

ASSUMPTION P4

All micro-hydride configurational rules are based on the knowledge of γ -ZrH_{1.00}-phase and δ -ZrH_{1.66}-phase needles.

Justification:

- ▶ The γ -ZrH_{1.00}-phase and δ -ZrH_{1.66}-phase needles are the most commonly encountered
- ▶ The configurational rules are based on experimental evidence, and there are many TEM and SEM studies of these two phases.

Limitations:

- ▶ Due to the high H stoichiometric composition of these two phases, it is difficult to justify the use of a linear diffusion theory.
-

ASSUMPTION P5

The precipitation criterion is a mass-balance problem, that is, the H concentration that is enclosed by the nucleation site must integrate to match the stoichiometry and the areal size of the micro-hydride needle.

Justification:

- ▶ This provides a direct and explicit physical connection between the diffusion profile and the precipitation events, which is not evident in PF and FE models.

Limitations:

- ▶ Linear irreversible thermodynamics does not predict very large H concentrations so the model must further assume a very large initial H concentration in order to ensure that the sizes of nucleation sites are physically relevant.
-

7.2.2 Parameters

In reference to FIG. 7.8, the assumptions can now be used to configure the test input parameters for verification checks as well as provide estimates for suitable input parameters that can be used in more realistic simulations. These input parameter choices are summarised here.

Parameters	Values and Comments
Material Properties	
Elastic constants	<u>Test Case:</u> $C_{11} = 130.1 \text{ GPa}$, $C_{12} = 78.6 \text{ GPa}$, $C_{13} = 65.7 \text{ GPa}$, $C_{33} = 155.9 \text{ GPa}$, $C_{44} = 28.2 \text{ GPa}$ <u>Realistic Case:</u> $C_{11} = 130.1 \text{ GPa}$, $C_{12} = 78.6 \text{ GPa}$, $C_{13} = 65.7 \text{ GPa}$, $C_{33} = 155.9 \text{ GPa}$, $C_{44} = 28.2 \text{ GPa}$ <u>Comments:</u> These values can be adapted from either experimental studies of Zr alloys at various temperatures or DFT simulations of a pure α-Zr crystal at absolute zero temperature [Akhtar (1973) and Burr (2014)].
Lattice constants	<u>Test Case:</u> $a = 3.2331 \text{ \AA}$, $c = 5.1491 \text{ \AA}$ <u>Realistic Case:</u> $a = 3.2331 \text{ \AA}$, $c = 5.1491 \text{ \AA}$ <u>Comments:</u> The values are not used directly in the present work; but these values are needed for implementing dislocation core cut-offs. These values would also be needed in any self-consistency checks that involve computing the Wigner-Seitz unit cell volume. Note that it would be sensible to choose these values according to the temperature where possible.
Microstructure	
Average grain size	<u>Test Case:</u> $l_g = \{10, 50, 100, 200\} \mu\text{m}$ <u>Realistic Case:</u> $l_g = 50 \mu\text{m}$ <u>Comments:</u> The test case values are used to demonstrate the model as clearly as possible. Here these values are simply approximated from the scaled Voronoi tessellation, which is purely for the sake of convenience at this stage. For the realistic cases, they must be specified beforehand for the given Zr alloy microstructures of interest [Chamaa et al. (2018)].
Texture	<u>Test Case:</u> $f_t = 1$ <u>Realistic Case:</u> $f_{n,r,t} = \frac{1}{3}$ <u>Comments:</u> These values for the Kearns parameters apply for random weld textures [Puls (2012) and Strasser, Adamson, and Garzarolli (2008)]. See ASSUMPTION F1.

Nucleation site density	<u>Test Case:</u> $\rho^{(\text{SPP})} = 1$ or 2 per grain. <u>Realistic Case:</u> N/A <u>Comments:</u> The values for the intra-granular SPP nucleation site density are chosen in order to demonstrate the model. Further experimental work is required to quantify these microstructural parameters for heterogeneous nucleation sites in various commercial Zr alloys [Chamaa et al. (2018)]. See ASSUMPTION P2.
-------------------------	--

Flaw Acuity

Elliptical hole	<u>Test Case:</u> $c_1 = 5.00 \mu\text{m}$, $c_2 \in [0.1, 4.99] \mu\text{m}$ <u>Realistic Case:</u> $c_1 = 500.00 \mu\text{m}$, $c_2 \in \{50, 495\} \mu\text{m}$ <u>Comments:</u> The test cases are chosen for demonstration purposes. The realistic values are based on sensible approximations for sharp cracks and blunt notches that are considered in experimental studies [Cui et al. (2009)].
-----------------	--

Hydrogen Diffusion

Diffusivity	<u>Test Case:</u> N/A <u>Realistic Case:</u> N/A <u>Comments:</u> The diffusion kinetics are not considered as the focus is on hydride precipitation. Further work is required to quantify the anisotropic mobility tensor or diffusivity matrix.
Elastic dipole tensor	<u>Test Case:</u> $\rho_{11} = 1.68 \text{ eV}$, $\rho_{33} = 1.74 \text{ eV}$ <u>Realistic Case:</u> $\rho_{11} = 1.74 \text{ eV}$, $\rho_{33} = 2.36 \text{ eV}$ <u>Comments:</u> The test values are based on earlier DFT studies [Majevadia (2014)]. The realistic values are based on more recent first-principles calculations that use a combination of DFT and experimental findings [Nazarov et al. (2016)]. See ASSUMPTION T3.
Critical solvus	<u>Test Case:</u> $c_{\text{solvus}}(T = 573 \text{ K}) \sim 10^5 \text{ ppm}$ <u>Realistic Case:</u> N/A <u>Comments:</u> The test value for the adjusted solvus based on the stoichiometric composition of $\gamma\text{-ZrH}_{1.00}$- and $\delta\text{-ZrH}_{1.66}$-phase hydride features [Puls (2012)]. See ASSUMPTION P2 and ASSUMPTION P5.

Background concentration	<u>Test Case:</u> $c_0^H \sim [10^2, 10^4]$ ppm <u>Realistic Case:</u> N/A <u>Comments:</u> The test values are higher than the values used in similar FE models [Jernkvist and Massih (2014) and Jernkvist (2014)]. See ASSUMPTION P2 and ASSUMPTION P5.
Hydride Precipitation	
Needle size	<u>Test Case:</u> $\ell_H \sim [5, 10]$ μm <u>Realistic Case:</u> $\ell_H \sim [1, 2]$ μm <u>Comments:</u> The test values are chosen to show a clear demonstration of the PLSI checks in practice. The realistic values have been deduced from TEM studies of $\gamma\text{-ZrH}_{1.00}$-phase needles [Carpenter, Watters, and Gilbert (1973) and Perovic, Weatherly, and Simpson (1983)]. See ASSUMPTION T1 and ASSUMPTION C1.
Needle stress	<u>Test Case:</u> $B_H \sim 100\text{\AA}$ <u>Realistic Case:</u> N/A <u>Comments:</u> The test values are based on experimental studies of the misfit strains around $\gamma\text{-ZrH}_{1.00}$-phase needles [Carpenter, Watters, and Gilbert (1973) and Perovic, Weatherly, and Simpson (1983)]. See ASSUMPTION T1 and ASSUMPTION C1.
Needle misfit	<u>Test Case:</u> $e_H \sim 20\%$ <u>Realistic Case:</u> $e_H \sim 5\%$ <u>Comments:</u> The test values are for demonstration purposes. The realistic values have been adapted from TEM studies [Carpenter, Watters, and Gilbert (1973) and Carpenter (1973)]. See ASSUMPTION T1 and ASSUMPTION C1.
Hydrogen content	<u>Test Case:</u> $N_H \sim 10^7$ H atoms <u>Realistic Case:</u> N/A <u>Comments:</u> The test value is assumed for demonstration purposes but chosen based on the approximate number of H atoms in a $\gamma\text{-ZrH}_{1.00}$-phase micro-hydride needle of the specified geometry. See ASSUMPTION P1.
Stack separation	<u>Test Case:</u> $s_H \in [5, 10]$ μm, $\lambda_H \in [0, 5]$ μm <u>Realistic Case:</u> $s_H \in 5$ μm, $\lambda_H \in 1$ μm <u>Comments:</u> The test values are chosen for a clear demonstration of the PLSI checks. The realistic values are based on TEM observations of $\gamma\text{-ZrH}_{1.00}$-phase needles in a staircase-like stack configuration. See ASSUMPTION P4.

System Conditions

Temperature

Test Case: $T = 0.025 \text{ eV}/k_B$

Realistic Case: $T = \{0.049, 0.058\} \text{ eV}/k_B$

Comments: The test value of room temperature is chosen for demonstration purposes. The realistic values should be informed by the thermomechanical cycles used in industry; the elastic constants, lattice constants and critical solvus should be chosen to reflect the system temperature at a given time for self-consistency [Puls (2012) and Strasser, Adamson, and Garzarolli (2008)].

Loading

Test Case: $\sigma_L = 100 \text{ MPa}/\sqrt{\text{m}}$

Realistic Case: $\sigma_L = [10, 20] \text{ MPa}/\sqrt{\text{m}}$

Comments: The test value for a remote uniform tensile load is chosen for demonstration purposes. The realistic values should be informed by the thermomechanical cycles used in industry [Puls (2012) and Strasser, Adamson, and Garzarolli (2008)].

Computational

Simulation cell

Test Case: $L_1 = 20 \mu\text{m}$, $L_2 = 40 \mu\text{m}$

Realistic Case: $L_1 = 1000 \mu\text{m}$, $L_2 = 2000 \mu\text{m}$

Comments: The test (realistic) values here correspond to the test (realistic) values for the elliptical notch geometry. The realistic values are based on SEM observations of the hydrided process zones [Cui et al. (2009) and Puls (2012)].

Spatial mesh

Test Case: $\Delta l_1 = 0.2 \mu\text{m}$, $\Delta l_2 = 0.2 \mu\text{m}$

Realistic Case: $\Delta l_1 = 0.1 \mu\text{m}$, $\Delta l_2 = 0.1 \mu\text{m}$

Comments: Both sets of values for the spatial mesh resolution are based on the need to resolve individual micro-hydride needles and their relative positions.

Nucleation setup

Test Case: $r^{\text{SPP}} \in [5, 25] \mu\text{m}$

Realistic Case: N/A

Comments: The range of test values for the radius of the intra-granular nucleation site is simply an educated guess based on the background H concentration and the adjusted solvus. Further sensitivity studies and experimental studies are required to determine this crucial parameter [Chamaa et al. (2018)].

7.2.3 Stochastics

The input parameters do not completely specify the system due to several sources of randomness. That is, each simulated realisation with a given set of input parameters exhibits the following stochastic variations:

- ▶ *Grain Morphology*. The grain morphology is determined by the random distribution of Voronoi seeds whose density is related to the average grain size. Therefore, the grain morphology that is generated is random. This randomness features in every PIP and PLSI check for a given realisation of the input.
- ▶ *Texture*. The weld texture involves randomly allocating a basal plane orientation to each grain. This randomness features in every PIP check for a given realisation of the input.
- ▶ *Nucleation Site Distribution*. The intra-granular nucleation sites are positioned randomly within each grain. This randomness governs the output of the diffusion-precipitation analysis.
- ▶ *Computational Ordering*. The order in which quasi-static steps are performed can also introduce randomness. For example, the order in which nucleation sites are checked and activated governs the output of the diffusion-precipitation analysis; this variation becomes more sensitive as the density of nucleation sites increases, and so the computational ordering becomes increasingly important.

Each simulated micrograph must then be taken in the context of this stochastic variation. This randomness can be averaged out by considering a statistical ensemble of simulated micrographs. It is worth emphasising again that statistical modelling in this capacity is a real possibility with the proposed model because of the computational efficiency, and this claim will be supported with examples in due course.

This stochastic variation is characteristic of most other microstructural solvers, including PF models, but their simulation runtimes are far too high to facilitate any meaningful statistical averaging [Janssens et al. (2007) and Chen (2002)]. The multi-field FE models are, however, entirely deterministic and so the paradigm of statistical averaging does not feature in such models [Jernkvist and Massih (2014) and Jernkvist (2014)]. So the computational efficiency is then the real benefit of the present work from the standpoint of nuclear fuel performance codes [Tonks et al. (2017) and Aybar and Ortega (2005)].

7.3 Simulation Strategy

In the previous discussions, the different computational elements of the model were introduced and the main assumptions were explained. Based on this understanding, it is now possible to put forward one strategy for formulating one complete variant of the proposed framework. This variant is then implemented into a working code that will subsequently be used to generate simulated micrographs.

Developing upon [FIG. 7.8](#), the following set of discussions focus on the individual steps required to initialise the simulation and devise the algorithmic workflow that describes the simulation methodology. The framework assumptions underpin the input whereas the phenomenological assumptions are central to the simulation methodology.

7.3.1 Initialisation

In reference to [FIG. 7.8](#), the sample set of input parameters can be used to initialise the simulation as follows. The simulation cell setup requires the parsing of the computational parameters, including the simulation cell dimensions and spatial mesh resolutions, as well as the physical parameters pertaining to the notch geometry, microstructural properties of the Zr alloy, and the temperature and loading conditions.

Due to the extensive use of computational geometry checks, the efficiency of the setup procedure is reduced with increasing complexity of the notch geometry, a smaller average grain size and a greater density of intragranular nucleation sites. At this point, the organisation and storage of the geometrical data structures would be crucial for an efficient implementation of the code. [Note 17](#)

Once the setup of the simulation cell is complete, two principal calculations need to be performed prior to the main simulation methodology. First, the elastic fields around the loaded notch are computed. These elastic fields are then used to evaluate the equilibrium H profile.

A detailed breakdown of these initialisation steps is shown in [FIG. 7.12](#) which provides more information about the computational aspects of this procedure. Note that although the setup is a one-off computation in the present work, it must be redesigned for the case of statistical ensembles in order to avoid repeat computations.

Note 17

Sorting of geometrical information

One example of the importance of sorting concerns the LSI checks that forbid two micro-hydrides crossing each other. The standard LSI algorithms check for intersections in order of the sequence in which the line segments are stored; this order affects the efficiency of the checking process. If two nucleation sites are close together within the same grain, it is essential to store the corresponding micro-hydride geometrical data as adjacent entries in the sequence. Otherwise computational time will be wasted for LSI checks between micro-hydrides that are far apart. Such problems become increasingly time-consuming as the hydride density evolves over the course of the simulation.

FIG. 7.12

Simulation initialisation

An example of the simulation initialisation steps as implemented in the present work. The simulation cell dimensions are kept large enough to visualise the morphology of the macroscopic macro-hydride colonies. But the spatial mesh resolution is chosen so that the substructure of the colonies can also be visualised. This multiscale nature is unique to this hybrid model. An elliptical notch geometry is chosen mainly for convenience as previously stated. The grain boundaries are the partitions defined by a standard Voronoi tessellation generator; the average grain size is used to distribute Voronoi seeds as usual. Circular intra-granular nucleation sites are then positioned in the grains. For the case of the elliptical notch geometry, closed-form analytical expressions can be derived for the system stress state as well as the equilibrium H concentration. Observe that there is considerable degree of flexibility to this initialisation process; the framework can easily be adapted to, say, a system with inter-granular nucleation sites or different classes of intra-granular nucleation sites. In essence, the framework is able to distinguish the microstructures of the different commercial Zr alloys.

I : Initialisation		
	Setup	
1	Simulation cell build	Establish a Cartesian coordinate system (x_1, x_2) and define a rectangular cell of dimensions $L_1 \times L_2$ which marks the boundaries of the planar simulation. <i>Note: considering micrographs of notch-tip hydrides, a sensible choice for this work is to set $L_1 = L_2/2 = 1000\mu\text{m}$ as this is the typical size of the region in the vicinity of the notch that contains a high density of hydride features.</i>
2	Spatial mesh build	Set the numerical resolution of the simulation cell by dividing into n_1 units along the x_1 -direction and n_2 units along the x_2 -direction, define the grid spacing as $\Delta l_1 = L_1/n_1$ and $\Delta l_2 = L_2/n_2$. The simulation cell mesh is used for defining spatial grids for elastic fields and diffusion concentration profiles. <i>Note: for simplicity, it is useful to set $n_1 = n_2$ to be some power of 10 and, given the smallest necessary physical unit in these simulations is the dimension of a micro-hydride needle of length $1\mu\text{m}$, it is sensible to set $n_1 = n_2 = 10^5$.</i>
3	Notch geometry input	Place the notch such that half-space boundary lies between the coordinates $(0, -L_2/2)$ and $(0, +L_2/2)$ centralised at the origin. Identify the spatial grid points that lie within the notch and distinguish the points that mark out the surface of the notch as closely as possible. <i>Note: for the elliptical notch with major and minor semi-axes, c_1 and c_2, it is straightforward to determine the surface points by the considering the equation of an ellipse: $(x_1/c_1)^2 + (x_2/c_2)^2 = 1$.</i>
4	Microstructure input	Generate the texture using a two-dimensional Voronoi tessellation of convex polygons using a random seed distribution within the simulation cell. The density of the random seed distribution should be chosen to produce grain boundaries that define an average grain size $\langle \ell_g \rangle$. For every grain, define an orientation with respect to the transverse direction according to $\{f_R, f_T, f_N\}$, which have to be appropriately translated to the planar system. Use a point-in-a-polygon algorithm attribute the grain orientation to every grid point. <i>Note: for the random (in-plane) texture $f_R = f_T = f_N = 1/3$, each grain should be specified with an orientation randomly chosen within the range $[0, \pi/3]\text{rad}$. For testing purposes, $\langle \ell_g \rangle$ is taken to be within the range $[50, 100]\mu\text{m}$.</i>
5	Nucleation site distribution	According to $\rho^{(a)}$, distribute randomly intra-granular nucleation sites of type a within each grain using a point-in-a-polygon algorithm. Each intra-granular nucleation site is a circle of a radius of $r_H^{(a)}$ and hence must be positioned within the relevant grain such that its circular boundary does not cross any grain boundaries. Once set, all grids points that fall within a nucleation site need to be identified. <i>Note: for testing purposes, only one type of intra-granular nucleation site is chosen and each grain contains only one nucleation site; however, in reality, there should be multiple types of nucleation sites and a larger density in every grain. For test purposes, $r^{(a)}$ is taken to fall within the range $[5, 25]\mu\text{m}$.</i>
Principal Calculations		
6	Loaded notch stress state	The stress fields of the notch are determined at every grid point according to the appropriate analytical or semi-analytical expressions. <i>Note: expressions for the stress fields of slit cracks, elliptical voids and V-notches are well known in planar elasticity. Cut-offs must be enforced to overcome any singularities in the formulae.</i>
7	Equilibrium hydrogen profile	Set the uniform background concentration at every grid point. Compute the equilibrium concentration profile either via solving the stress-driven equation with zero-flux conditions or approximating it by setting the elastochemical potential to zero. Determine which nucleation sites are activated by checking their hydrogen content.

7.3.2 Simulation Methodology

Following the initialisation, the simulation methodology consists of a sequence of steps which are repeated to describe the evolution of the H concentration profile and hydrided microstructure. In reference to FIG. 7.8, the steps can be ordered:

- ▶ Step 1A. *Concentration Mesh Iteration*. The H profile is evolved according to the stress-diffusion analysis.
- ▶ Step 1B. *Nucleation Activation Criterion*. The H content enclosed by the nucleation site is integrated; the nucleation site is activated if the precipitation criterion is met.
- ▶ Step 2A. *Computational Geometry Check*. Both PSLI and LSI algorithms are applied to determine allowed micro-hydride configurations.
- ▶ Step 2B. *Addition of Precipitate Classes*. If there are allowed micro-hydride configurations, a precipitate object is added to the simulation cell. Adjacent nucleation sites are also added to the simulation cell.
- ▶ Step 2C. *Solute Mass-Balance Correction*. Diffusible H concentration is removed in accordance with the micro-hydride size and stoichiometric composition.
- ▶ Step 3A. *Needle Configuration Evaluation*. The possible configurations are sampled for the minimum strain energy state.
- ▶ Step 3B. *Stress State Update*. The global system stress state is updated to account for the new micro-hydride feature.

This sequence of steps can be translated into the general algorithmic workflow presented in FIG. 7.13, which is essentially a nest of three loops.

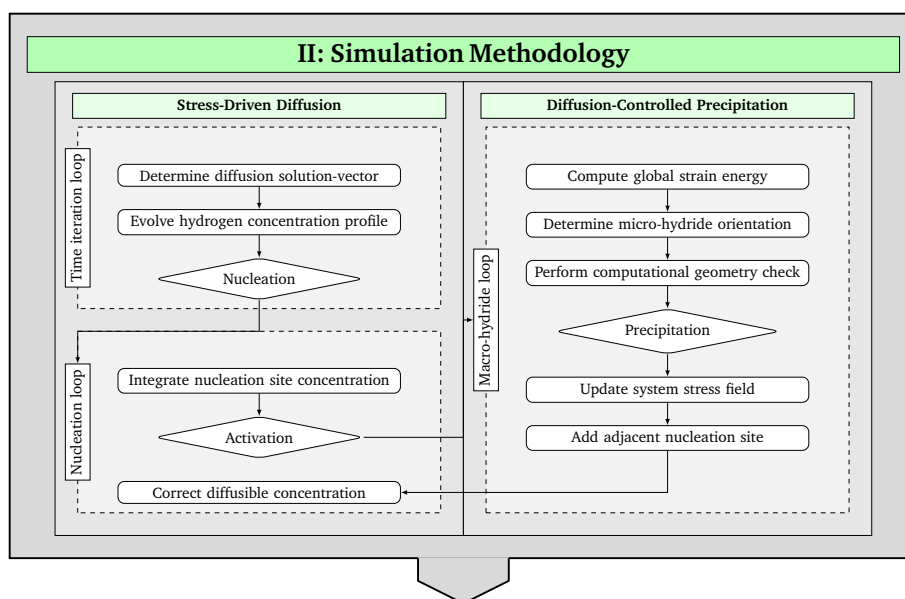


FIG. 7.13

Algorithmic workflow for the simulation methodology

A flowchart of the main simulation methodology for connecting the stress-diffusion and diffusion-precipitation analyses. The primary loop over time concerns the stress-diffusion analysis. The secondary loop over the nucleation sites and tertiary loop over the autocatalytic mechanism connect the stress-diffusion and diffusion-precipitation analyses. This three-loop nesting is only made possible because of the phenomenological assumptions made earlier.

7.4 Code Specification

Having established the theoretical and computational framework, the actual code can be designed, developed and tested. The present work introduces an object-orientated multi-modular program that implements the proposed hybrid model. This custom software is expected to perform as an advanced microstructural solver that uses multiscale physics in conjunction with optimised algorithms. This software is built for the purpose of modelling DHC but its generality is retained so that it can be used to simulate other similar phenomena. This section serves as a basic code specification for this custom software.

7.4.1 Modules

Alongside the pre-processor and the post-processor, there are four main modules of this software:

- ▶ *Simulation Cell Builder*. This module contains the functionality for initialising the system. Routines invoke the algorithms of computational geometry to set up the metallographic features present in the simulation cell.
- ▶ *Stress Calculator*. This module contains the functionality for stress analysis. Routines invoke the mathematical theory of planar elasticity which is used for defect micromechanics.
- ▶ *Diffusion Solver*. This module contains the functionality for stress-diffusion analysis. Routines use the standard numerical methods for solving partial differential equations.
- ▶ *Precipitation Iterator*. This module contains the functionality for the diffusion-precipitation analysis. Routines are customised and tailored to the specific variant of the proposed framework.

Each of these modules consists of classes and functions, some which call upon established methods in standard computational programming libraries.

7.4.2 Program Architecture

The overall assembly of these modules, classes, functions and libraries into one self-contained software package is a considerable challenge. Designing the program architecture is perhaps the most important stage of the model development. In [FIG. 7.14](#), the computational schematic of this hybrid model is showcased. In essence, the complexity of the DHC mechanism has now been reduced and transformed into a built-for-purpose multiscale modelling software, which is one of the central results of this investigation.

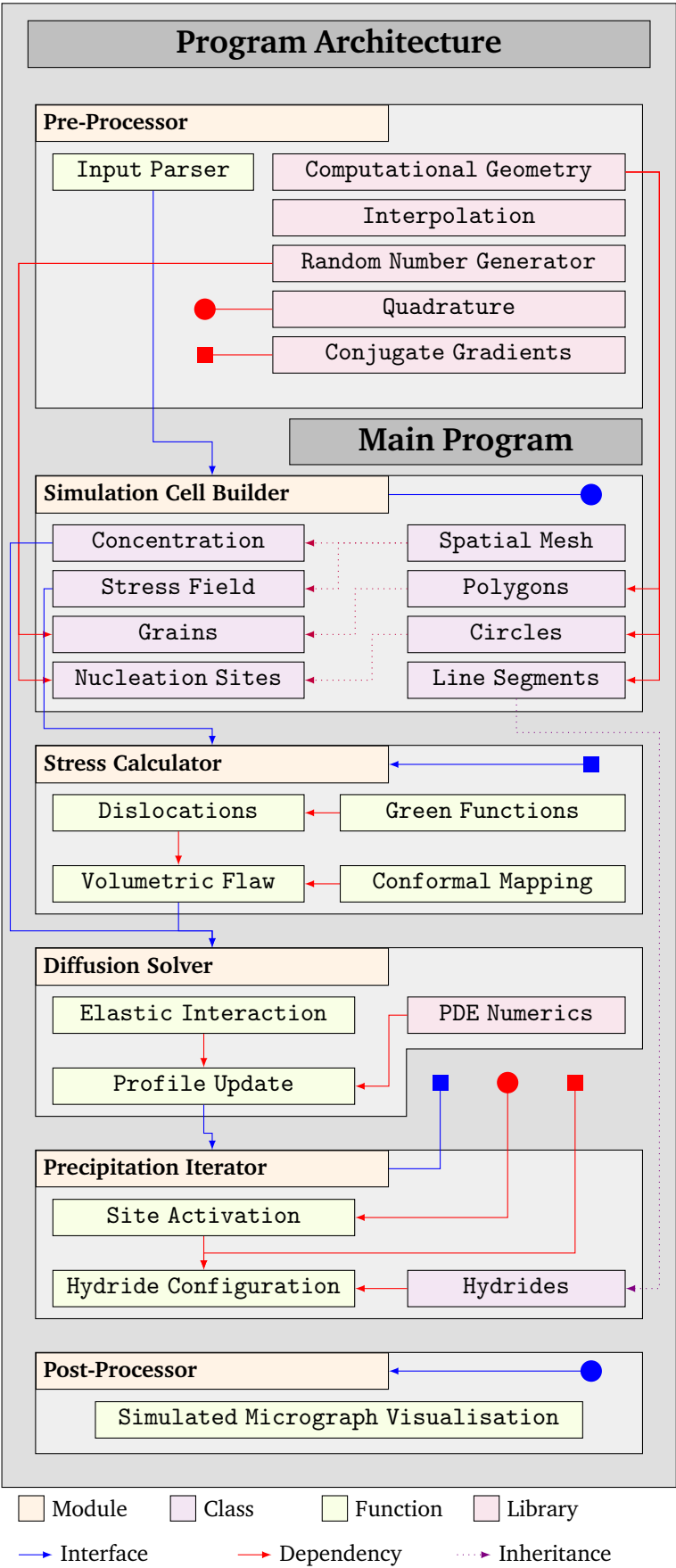


FIG. 7.14

Program architecture

A schematic of the object-orientated program which implements the proposed model of the DHC mechanism. The main modules, functions, classes and libraries are shown as well as the most important connections between these architectural elements. The simulation cell builder contains a hierarchy of classes and inheritances based on the library of computational geometry; these classes are used to represent the key metallographic features. The stress calculator is able to use both analytical and semi-analytical techniques for evaluating the elastic fields around dislocation networks in either isotropic heterogeneous media or anisotropic homogeneous media. The diffusion solver adapts the standard numerical methods for solving partial differential equations for diffusion to case of a heterogeneous continuum that is non-uniformly stressed. The precipitation iterator is most customisable module because its functionality depends the exact phenomenological assumptions about the microstructural physics. Optimising the interfaces between the different modules underpins the efficiency of the computational model. Note that there are no current dependencies on the library for interpolation; but as the model is developed further, interpolation routines will become necessary for the generality of the framework. Note also that this program architecture does not show other libraries that are needed for random number generation, linear algebra and tensor transformations.

7.4.3 Implementation

The actual implementation of the program architecture into a working code requires some consideration because the choice of programming language has an effect on the overall efficiency. This is because the efficiency of the implementation of algorithmic computational geometry depends heavily on the internal code optimisation of a given programming language; and certain programming languages have more optimised data structures for storing and manipulating geometrical information [de Berg et al. (2008)].

The proposed model relies on its ability to out-perform standard PDE solvers through its extensive use of computer vision, and so then the choice of programming language is of paramount importance. For this reason, this custom software is developed primarily in C++ because it offers a natural backdrop for computational geometry. As shown in FIG. 7.15, it is straightforward to implement an efficient PIP check within a single `for` loop within a C++ code. The same is also true for PLSI and LSI algorithms due to the availability of sorted containers as data structures.

FIG. 7.15

Implementation of a point-in-a-convex polygon algorithm

An efficient implementation of a PIP algorithm within a C++ that is specific for a convex polygon. The convex polygon is defined as an ordered list of nodes and edges in either clockwise or anticlockwise order. This is convenient because of the availability of sorted containers as data structures. Then the point-in-a-polygon algorithm involves a highly simplified application of the Jordan curve theorem to case of a convex polygon. This results in a very fast computational method involving a single `for` loop containing a lone `if` statement. Note that a PIP algorithm would be far more difficult to implement for non-convex polygons.

```

1 // Point-in-a-Polygon Algorithm: Convex Polygons
2 template<class T>
3 int polygon<T>::ALGORITHM_point_in_polygon (vector3d<T>
4     point)
5 {
6     // Integer return value: 1/0 = FALSE/TRUE
7     int CHECK = 0; // Initially FALSE
8
9     // Counters over polygon nodes
10    int i, j;
11
12    // Single loop over all nodes and edges
13    for (i=0, j=(sides-1); i<sides; j=i++)
14    {
15        // If statement to check point coordinates relative to
16        // all nodes
17        if ( ( (node[i].y > point.y ) != (node[j].y >
18            point.y) ) &&
19            point.x < (node[j].x - node[i].x ) ( point.y - node[
20            i ].y) / (node[j].y-node[i].y) + node[i].x )
21        {
22            CHECK = 1; // TRUE if statement is satisfied
23        }
24    }
25
26    return CHECK;
27 }

```

7.5 Verification

This investigation has required sizeable code development. It is, therefore, not possible to provide an exhaustive breakdown of every verification check at this stage. It is instead more useful to see the functionality of the bespoke model in its entirety for the first time, and verify the successful implementation of computer vision, which is the novel aspect of this work. The PIP algorithm was showcased earlier so consider here the PLSI algorithm.

The role of the PLSI algorithm is to enforce certain microstructural rules in the solver that are based on experimental observations of the orientation relationships and the coherency of the matrix-hydride interface. In the algorithmic workflow depicted in FIG. 7.13, nucleation events of micro-hydride needles are accompanied by the addition of adjacent nucleation sites; this is the so called macro-hydride loop. As shown in FIG. 7.16, when the macro-hydride loop encounters a grain boundary, a PLSI check prevents forbidden configurations in which the orientation relationships are not maintained.

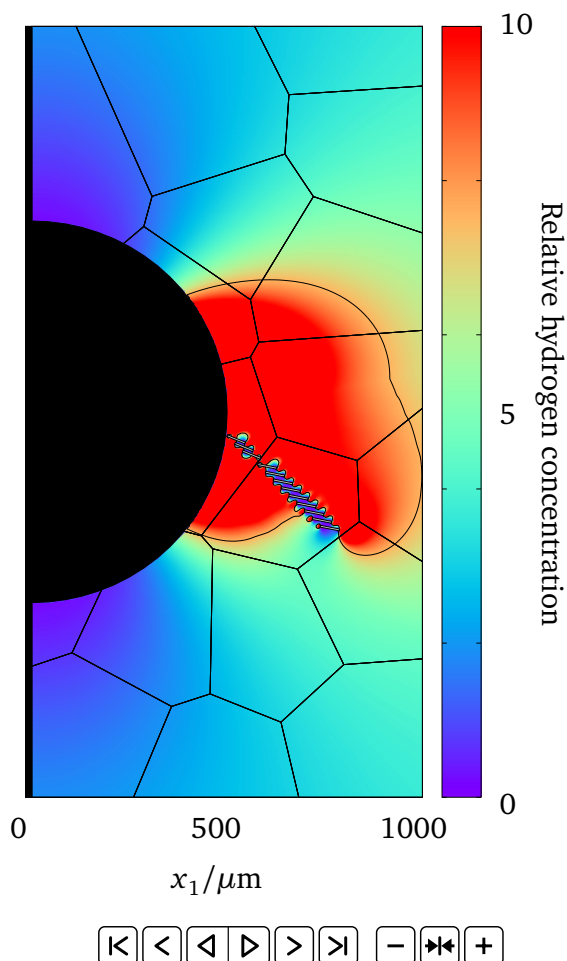


FIG. 7.16

An example of a simulated micrograph. The formation of a trans-granular macro-hydride colony emanating from the notch-tip over the iteration of the macro-hydride loop in the algorithmic workflow. This verification check is a demonstration of a working PLSI algorithm for modelling autocatalytic nucleation in the heterogeneous microstructure. The PLSI check is triggered when a micro-hydride needle within a macro-hydride colony intersects with a grain boundary; this is one of the hypothesised forbidden configurations that is implemented within this particular variant of the proposed methodology. This simulation is generated using the test parameters but with the realistic simulation cell dimensions and notch geometries. The metallographic details of this simulated micrograph are explored in due course.

[Animation available in the digital format.](#)

Note 18**Test parameters and conformal symmetry**

The use of the aforementioned test parameters to verify the model involves exploiting the conformal (or angle-preserving) symmetries of elastic field theory. That is, any physical parameter which is a constituent prefactor in the analytical closed-form expressions of the elastic fields of the system can be appropriately rescaled to facilitate the computation and visualisation, and this rescaling does not drastically alter the phenomenological accuracy of the simulated physics. This assumption can be justified as follows. First observe that rescaling a prefactor only changes the magnitude of the elastic field whilst preserving the general shape of its contours. For example, this mathematical symmetry is apparent for the case of dislocations in isotropic continua; the elastic field contours around a dislocation retain their shape regardless of the Burgers vector or the isotropic elastic constants. Several other prefactors also exhibit this conformal symmetry, including the aspect ratio of the elliptical notch, the remote tensile loading and the hydride thickness. As computations within this framework only involve simple manipulations of the superposed elastic fields, the overall energetics of the system are more or less identical if alternative prefactors are chosen.

It is clear that the barebones version of the software works as intended in **FIG. 7.16**, but it is still necessary to demonstrate some preliminary parametric studies to flesh out the software verification. In the first set of parametric studies, only the stress-diffusion analysis is utilised, and notch-tip H concentration profiles are simulated. In reference to the recent shifts in the industry standards for nuclear fuel performance, a H pickup approach has been suggested for evaluating the expected operation lifetime of Zr alloy components [Strasser, Adamson, and Garzarolli (2008) and Coleman (2003)]. As H pickup ultimately governs DHC failure, it is possible to construct a fracture initiation threshold based entirely in terms of the H enhancement. In turn, the H enhancement can be parametrised by the flaw acuity, microstructural properties and thermomechanical cycling. The proposed model is in a unique position to conduct these parametric studies in one unified framework. In the second set of parametric studies, the full capabilities of the model are utilised, and notch-tip hydrided microstructures are simulated. These simulated micrographs are directly compared with their experimental TEM and SEM counterparts. It is important to highlight that such comparisons are only possible because this framework enables sufficiently large system sizes to be simulated with a relatively high numerical resolution.

Before proceeding, it is worth noting these simulated micrographs are prepared so that the computational mechanics can be easily explained, and that the metallographic features can be easily visualised. Due to multiscale nature of this problem, visualisation can be problematic if realistic parameters are chosen because, for example, the relative geometries of the notch and the micro-hydride needles differ by many orders of magnitude. For this reason, the model uses the test parameters listed earlier rather than realistic parameters for demonstration purposes. ^{Note 18}

As the choice of the prefactors does not drastically alter the simulated physics, it is sensible to use certain test parameters appropriately alongside realistic parameters that are justified in the previous discussions. Accordingly, the preliminary results must be interpreted in an almost dimensionless sense in which only relative geometries matter. This is nonetheless useful because it is clear to see the relative sizes of the notch, grains and micro-hydride needles, as well as the effects they have on each other. And, of course, at a later stage in the development of this model, more realistic parameters can be incorporated. For now, the preliminary studies can provide a good demonstration of the capabilities of this hybrid multiscale model as well as an opportunity to understand how to interpret its main output: the simulated micrographs.

7.5.1 Contour Tests

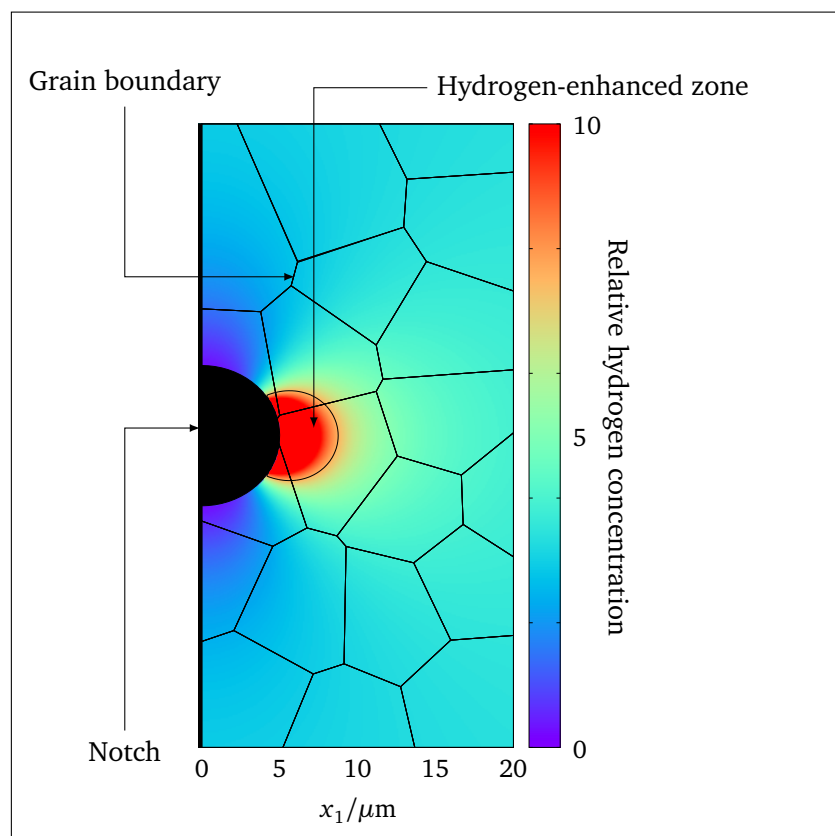
In this first set of parametric studies, the contours of the equilibrium flaw-tip H concentration profiles are computed. An example of a simulated micrograph depicting the notch-tip H enhancement is shown in FIG. 7.17, which will be used as a template for interpreting these results. It is evident the elevated H profile is localised entirely within the vicinity of the tensile state of the notch. Note that the implicit time required to attain this steady state can be estimated using the H diffusivity at the system temperature.

The important metallographic feature of interest here is the contour that marks out the H-enhanced zone. Hydride nucleation is expected to be particularly pronounced in this zone. In terms of this model, this phenomenon would be reflected by the activation of nucleation sites that reside within this region bounded by the contour. For a given Zr alloy with particular microstructural characteristics, this contour could be calibrated by inspecting SEM findings, which can then be used to predict the H-enhanced zones around various flaw acuties in specimens of the same Zr alloy. Whilst similar to existing PF and FE models, this framework also sets up the capability to predict the H enhancement for different Zr alloy microstructures with greater efficiency.

FIG. 7.17

Interpretation of a simulated notch-tip hydrogen profile

A contour plot of the notch-tip H enhancement overlayed with the notch geometry and grain morphologies. The H concentration is given relative to the uniform background concentration. The hydrogen-enhanced zone marks out the region which is expected to become densely populated with hydrides, and so this zone may be compared with experiments. Note that intra-granular nucleation sites are not shown here for the sake of clarity, but there is a density of one intra-granular nucleation site per grain, each of which is randomly placed in the system. This simulation uses the test parameters.



Effects Flaw Acuity. It is clear from experimental studies that the distribution of macro-hydride colonies ahead of a flaw varies drastically with its acuity. That is, certain notch geometries are more prone to DHC failure [Puls (2012) and Cui et al. (2009)]. This implies that such notch geometries are, in part, more potent drivers of the long-range H transport.

In particular, dense hydride process zones are observed at the tips of sharp cracks; this suggests that a pronounced H enhancement is highly localised in the vicinity of the notch tip. This is in contrast to blunt notches which have a much sparser distribution of radially orientated macro-hydrides [Cui et al. (2009) and Schofield (2002)].

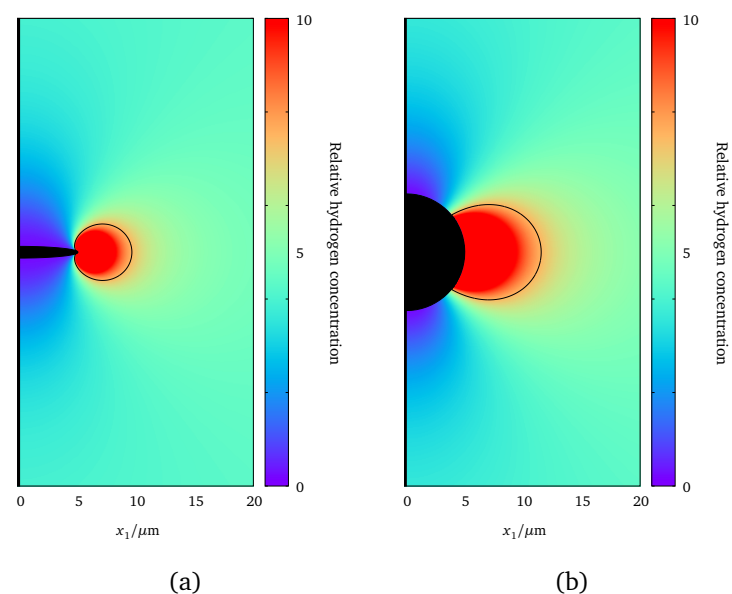
This stress effect is very straightforward to demonstrate using the proposed model by varying the notch geometry. As shown in FIG. 7.18, the sharper notch does indeed have a more pronounced and more localised H enhanced zone. The blunter notch, however, has a larger H enhanced zone and so a broader set of nucleation sites may be activated. This process is discussed later in the context of hydride precipitation.

Tests of other notch geometries, such the V-notch, suggest that there may be an optimal geometry in terms of the notch size and sharpness for which the H enhanced zone is the smallest and least concentrated. In addition, there is also the role of notch tip plasticity to consider; the local dislocation microstructure may actually reduce the stress state for the case of the sharp cracks, which leads to denuded zones [Patel (2014)].

FIG. 7.18

Notch-tip hydrogen profiles as function of notch acuity

The H enhancement profiles ahead of two elliptical holes. (a) Sharp crack as represented by a small minor semi-axis. (b) Blunt notch as represented by a large minor semi-axis. As the notch becomes blunter, it becomes a larger defect that generates stresses much farther across the continuum. As the notch becomes sharper, the effects of the crack tip singularity become more prominent. The H concentration profile equilibrates according to the respective stress contours. This simulation uses the test parameters.



Effects of Texture. The current framework only considers either isotropic heterogeneous media or anisotropic homogeneous media. As the stress-diffusion analysis is undertaken using only the elastic fields around the notch without any input of the intrinsic grain boundary stresses, neither of these two systems can adequately describe the effects of texture on the hydrogen-enhanced zone. The effects of texture only become apparent for anisotropic heterogeneous continua. In this case, the elastic interaction energy must be computed by considering compatibility stresses due to the misoriented grains.

It is, however, possible to approximate—or simply demonstrate—how the texture may influence H diffusion in polycrystalline Zr alloys using a toy model in which isotropic elasticity is assumed at the continuum scale but the two otherwise equal components of elastic dipole tensor are chosen to differ by a small ratio. To a certain extent, this toy model describes a near isotropic heterogeneous system, that is, a texture composed of slightly mis-oriented basal poles. In this case, the compatibility stresses may be small enough for the assumption of continuum isotropy to be valid.

The elastic interaction may then be computed but the pointwise tensor calculation must account now for the grain orientation because there is no longer any rotational symmetry of the elastic dipole tensor about the basal pole. As shown in **FIG. 7.19**, the notch-tip H enhancement zones vary noticeably even within the scope of this simple toy model.

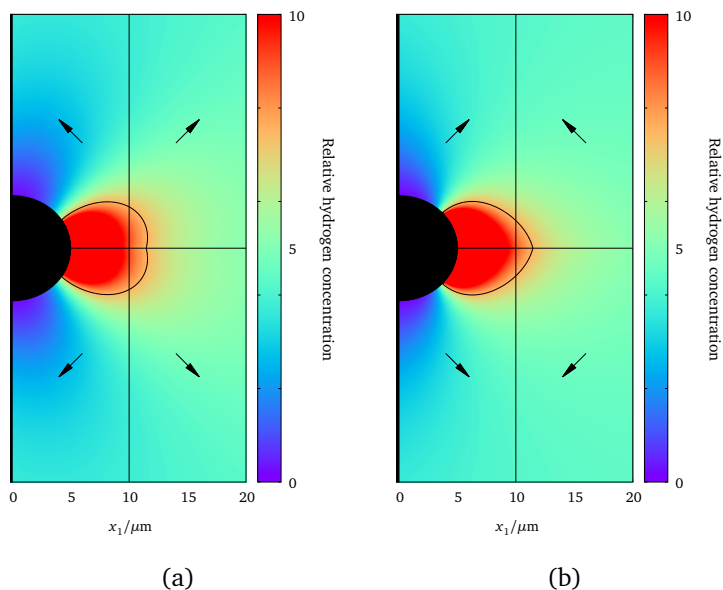


FIG. 7.19

Notch-tip hydrogen profiles for a toy model of anisotropic polycrystalline specimen

A simple four-grain system in which the arrows in each grain indicate the orientation relative to the basal pole. The effects of texture are very apparent. This is not surprising because of the differences in the stress state of the isotropic and anisotropic heterogeneous media can be considerable. A more accurate strategy for exploring the role of texture would be to use a crystal plasticity model for stress analysis. This simulation is generated using the test parameters but assuming that $\rho_{11} = 1.68 \text{ eV}$ and $\rho_{22} = 1.69 \text{ eV}$, which is a small ($\sim 1\%$) deviation.

7.5.2 Morphology Checks

The flaw-tip H enhancement only provides a very conservative estimate for the likelihood of DHC initiation. Due to the complexity of the local microstructure, similar flaw acuities may lead to almost identical H enhanced zones but very different macro-hydride colony morphologies. Predicting these microstructural deviations requires the full scope of this hybrid model, that is, utilising both stress-diffusion and diffusion-precipitation analyses.

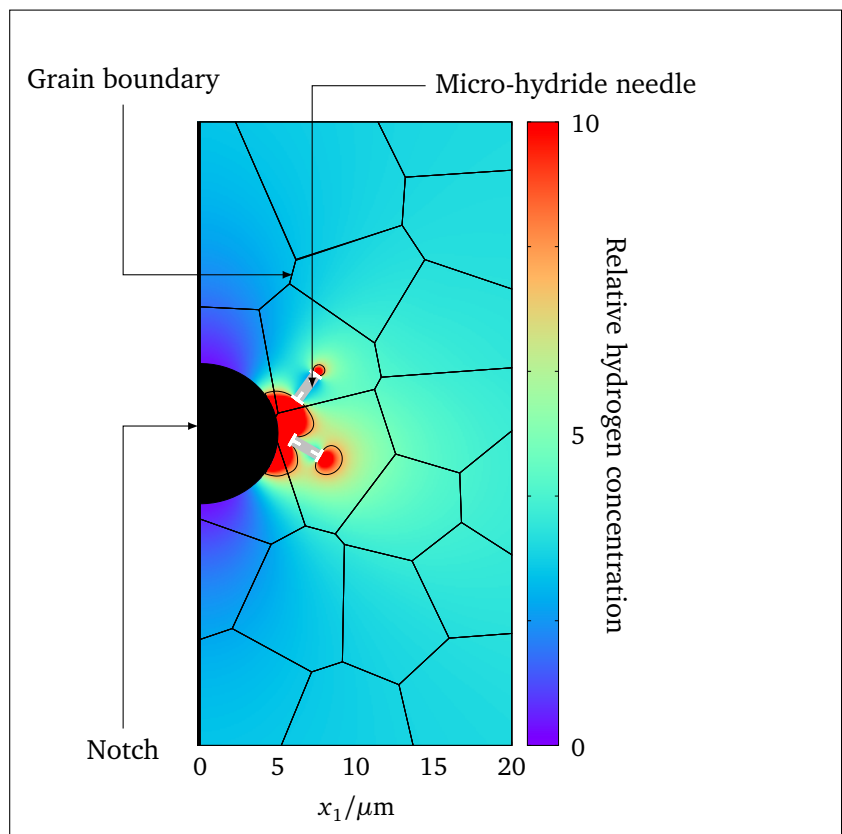
The initialisation procedure and the simulation methodology proposed earlier is now implemented to simulate hydrided microstructures. An example of a simulated micrograph is depicted in **FIG. 7.20** which is an iteration of the concentration profile in **FIG. 7.17** over the macro-hydride loops.

As shown in **FIG. 7.21**, repeating the computational steps over the nucleation and macro-hydride loops inevitably leads to formation of the micro-hydride networks that constitute the macro-hydride colonies. In this framework, the effects of notch acuity, texture and average grain size can be directly related to the hydride network configuration. This a very simple demonstration of the capabilities of the model, but these simulated micrographs are also the first of their kind in this field of research.

FIG. 7.20

Interpretation of a simulated notch-tip hydrided microstructure

A contour plot of the notch-tip H enhancement overlayed with the notch geometry and grain morphologies as well as individual micro-hydride needles that are represented by edge dislocation dipoles. Two intra-granular nucleation sites have been activated and the respective micro-hydride needle orientations have been evaluated, following which the H profile is then updated. Observe the depletion of the diffusible H at the nucleation site. In addition, H is redistributed in the tensile stress fields at either end of the micro-hydride needle; this is suggestive of the prospect of subsequent nucleation events. This simulation uses the test parameters.



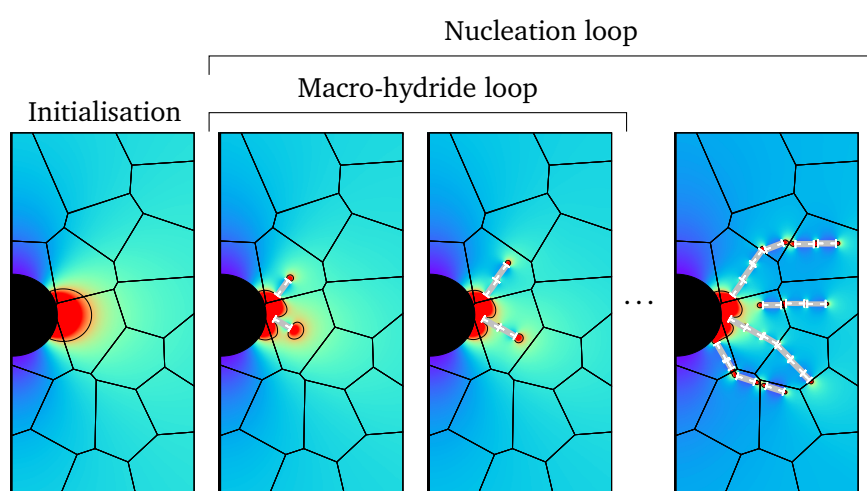


FIG. 7.21

Morphological growth of macro-hydride colonies

A demonstration of the autocatalytic nucleation mechanism during which macro-hydride colonies are formed from a sequence of nucleation events. The relative dimensions of the notch and the micro-hydride needles are not representative of the actual system for this particular example but the general approach remains the same. This simulation uses test parameters.

Morphological Evolution. It is now clear how the subsequent iterations over the nucleation and macro-hydride loops lead to the morphological growth of macro-hydride colonies. Within this framework, the governing factor that controls the macro-hydride morphology is the number and relative positions of secondary nucleation sites. For example, the end-to-end chains of micro-hydride needles depicted in FIG. 7.21 are not observed in experimental studies. However, TEM studies show the staircase stacking of micro-hydride needles that is reproduced in FIG. 7.22, and so this is a possible configuration for larger macroscopic assemblies [Perovic, Weatherly, and Simpson (1983)].

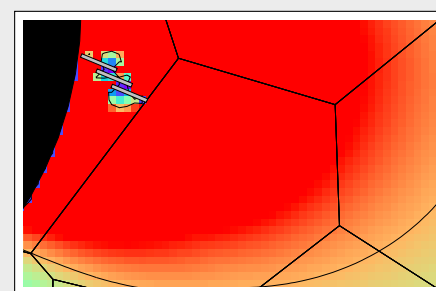
In general, the substructure of the macro-hydride colonies may be much more complex. As shown in FIG. 7.23, this complexity may be captured to an arbitrarily high level of accuracy within the scope of this framework. There are, however, far too many degrees of freedom for conducting an exhaustive sensitivity study. So the challenge is to identify the different possible realistic macro-hydride substructures that ensure the simulation is tractable with respect to the computational geometry checks and the free energy minimisation procedure. This is necessary in order to produce simulated micrographs that use realistic notch geometries, grain morphologies and micro-hydride sizes.

Further model development in this capacity relies primarily on gaining more experimental insight through TEM and SEM studies in particular. For now, it is sensible to proceed with the assumption that each macro-hydride colony is composed of a staircase stacking of micro-hydride needles. This assumption completes the setup of the computational framework, and now more realistic micrographs can be simulated.

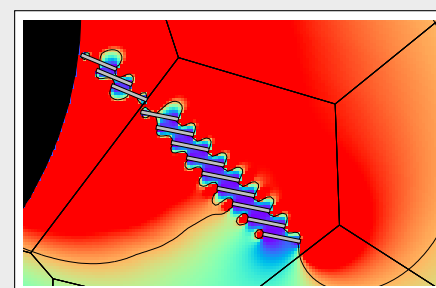
FIG. 7.22

Stacking of micro-hydride needles

The substructure of a trans-granular macro-hydride colony. (a) The initial sequence of nucleation events in one grain before a grain boundary forces the morphological growth into a different grain. (b) The completion of the final sequence of nucleation events which ends with a depleted local H content.



(a)

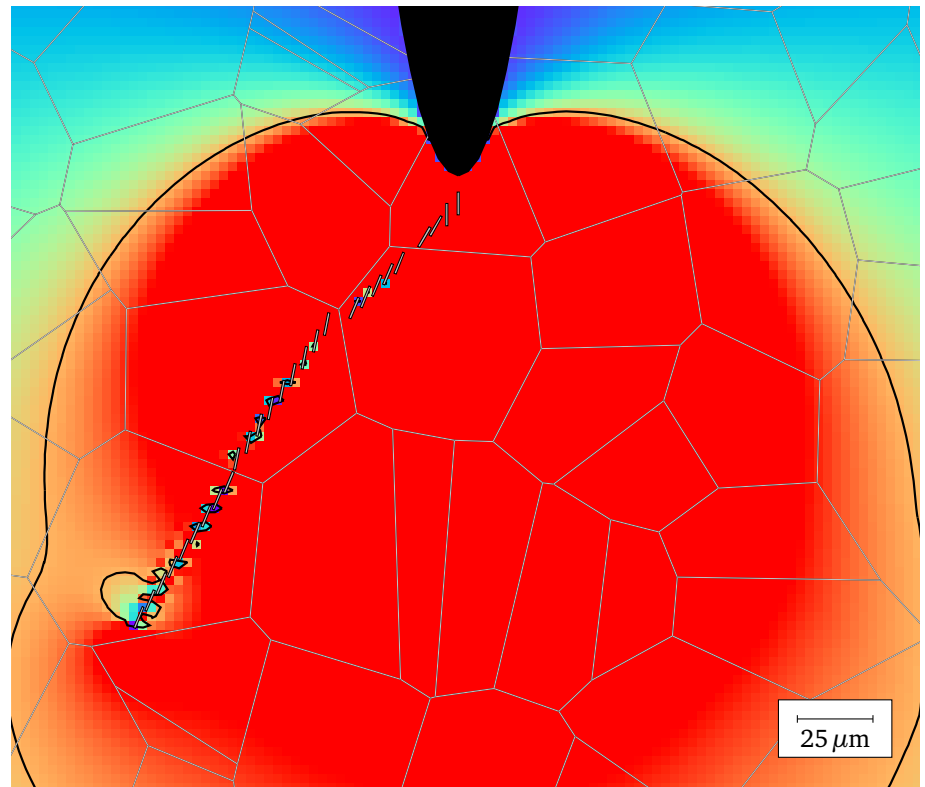


(b)

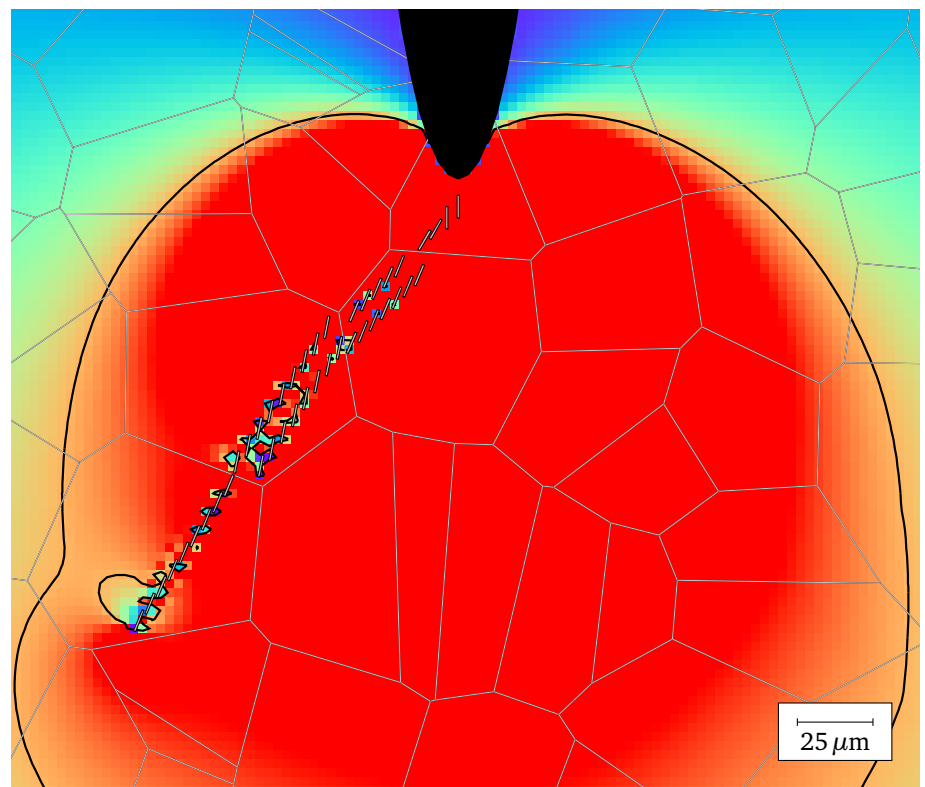
FIG. 7.23

The complex substructure of a macro-hydride colony

The effect of modifying the microstructural rules that govern the morphological evolution of a trans-granular macro-hydride colony. (a) A trans-granular macro-hydride whose composite substructure consists of a single staircase-like stack of micro-hydride needles. The microstructural rule involves the addition of a single nucleation site in an adjacent grain when the macro-hydride loop encounters a grain boundary. This leads to the formation of a long but thin macro-hydride colony. (b) The same setup as before but now either one or two additional nucleation sites are placed in the adjacent grain when the macro-hydride loop encounters a grain boundary. As the PLSI check forbids a nucleation event in this case, the addition of two nucleation sites in the adjacent grains describes the scenario in which the unused H concentration is then redistributed into a second nucleation event. This leads to formation of a more dense or thicker macro-hydride feature. The main purpose of this demonstration is the versatility of the model in describing the complexities of realistic macro-hydride colonies to a sensible degree of accuracy. Note that the two additional nucleation loops are not treated concurrently for simplicity, that is, these are non-interacting constituent macro-hydride colonies. Using experimental evidence, more complicated microstructural rules can then be applied as needed whilst ensuring that the simulation speed is then not compromised by the need for many LSI checks. A similar effect would be observed for greater nucleation site densities. This simulation uses realistic parameters.



(a)



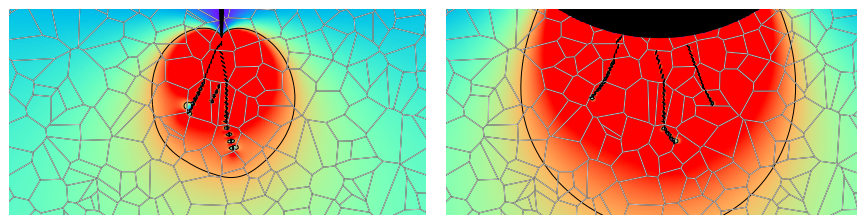
(b)

7.5.3 Parameter Setting

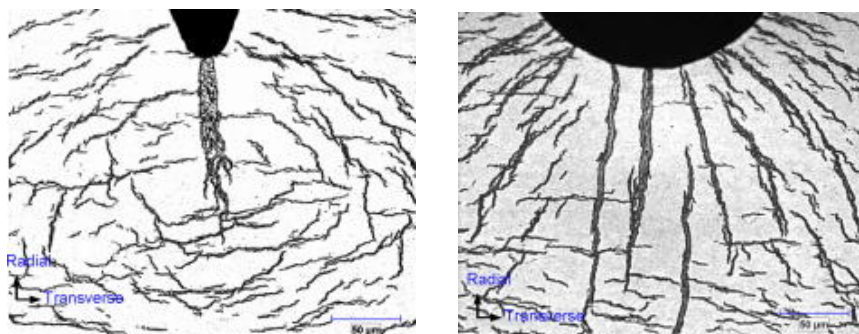
Having showcased the broad capabilities of this hybrid model, it is now worth applying the framework to a more realistic system using parameters that are more physically representative. In this model system, the size of simulation cell is comparable of optical micrographs and its resolution is sufficient to describe micro-hydride needles. Therefore, it is possible to portray with greater accuracy the relative sizes of the notch, grains and macro-hydride colonies. The simulated micrographs can then be directly compared to experimental micrographs.

As shown in **FIG. 7.24**, the simulated micrographs resemble their experimental counterparts. For the case of a sharp crack, the evolution of a narrow process zone that is densely populated with hydrides forms can now be mechanistically predicted. These hydrided microstructures are more prone to DHC failure and the ability to predict such worst case scenarios is immensely useful from the standpoint of industry.

For the case of the blunt notch, the simulated micrographs depicts the characteristic radial patterns of macro-hydride colonies. In the model, this is a minimum free energy configuration of the hydrides. In practice, however, such hydrided microstructures are observed after a series of thermomechanical cycles over which the hydride features repeatedly precipitate and dissolve; this modelling extension is formalised in due course.



(a)



(b) Cui et al., 2009

FIG. 7.24

A comparison of the simulated and experimental hydrided microstructures for different notch geometries

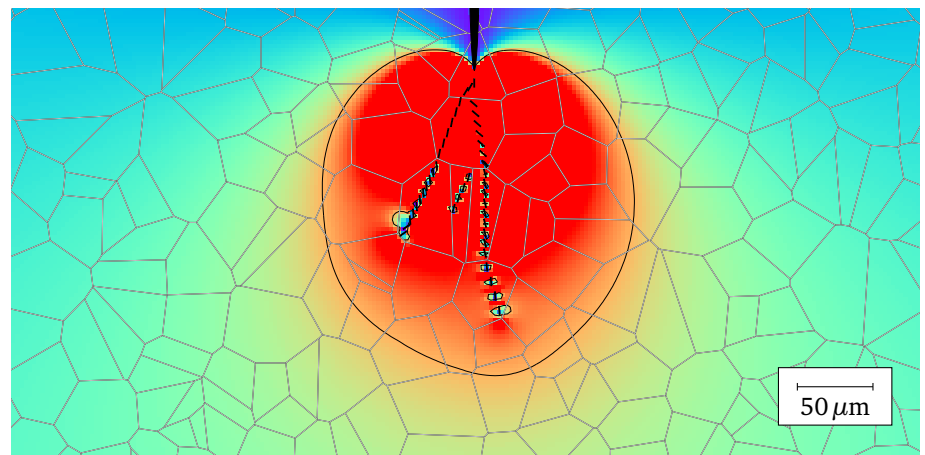
(a) In this simulation, the intra-granular nucleation site density is assumed to be very low; this is for the purpose of computational simplicity because it ensures that macro-hydride colonies do not interact, and therefore any additional computational geometry checks do not need to be performed. Note that in this simulation the micro-hydrides are chosen to be larger by a factor of ~ 5 for the purpose of visualisation; however the overall simulation is not drastically affected. This simulation uses the realistic parameters. (b) Experimental micrographs for similar flaw acuities.

For the case of the sharp crack, FIG. 7.25 depicts the same flaw-tip hydride process zone at a greater resolution. There is good quantitative agreement between the size of the simulated H-enhanced zone and the length of the hydride process zone. That is, the trans-granular macro-hydride colonies emanating from the flaw tip are predicted to grow to lengths in the range of $\sim [100, 200] \mu\text{m}$ for these notch geometries. There is still a considerable amount of diffusible H in this region; therefore, the modified rule suggested in FIG. 7.23 can be used to predict denser hydride process zones.

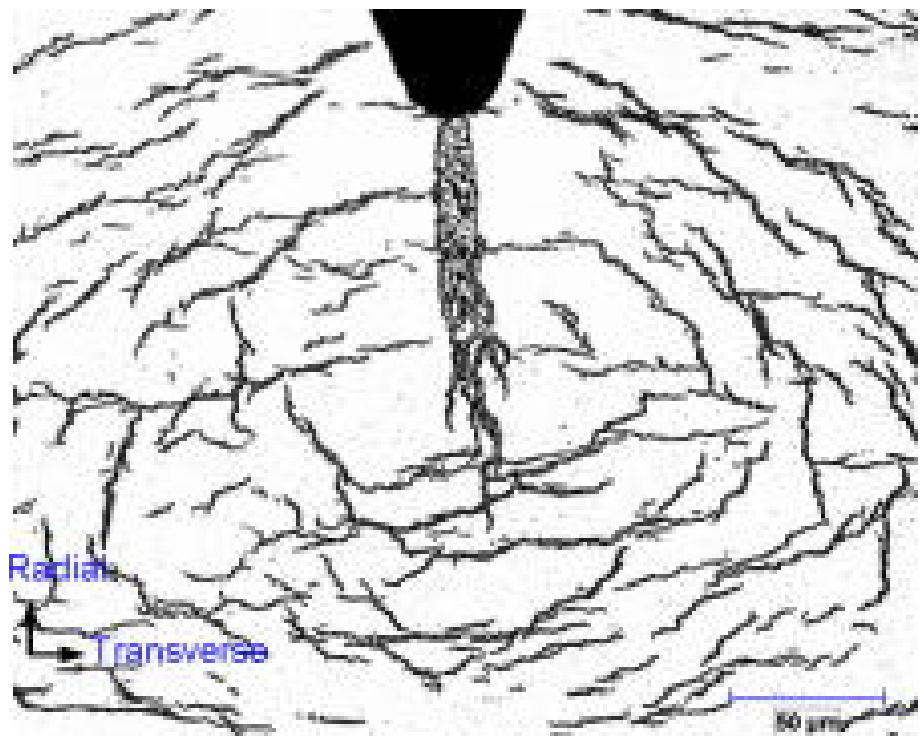
FIG. 7.25

The formation of dense hydride process zones ahead of sharp cracks

(a) The sequential evolution of three trans-granular macro-hydride colonies that constitute a dense hydride process zone emanating from a sharp crack. Observe how the micro-hydride needles are tightly aligned to reduce the long-range stresses in the system. Notice also how the H depletion becomes more apparent at distances further away from the crack tip and thereby restricting the continuation of the nucleation and macro-hydride loops. The geometry of the crack governs the size of the process zone because it controls the global H accumulation. (b) The experimental micrograph shows the existence of a swirl region around the hydrided process zone. In this swirl region, the macro-hydride colonies appear to form circular networks over a series of thermomechanical cycles. The exact cause of this effect is not clear from a physical standpoint so further studies are required to develop and incorporate the necessary microstructural rules that convey this phenomenon.

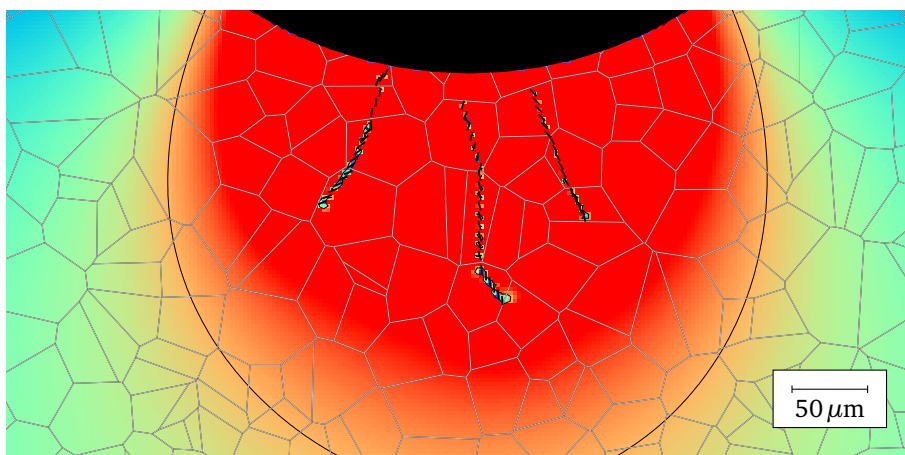


(a)

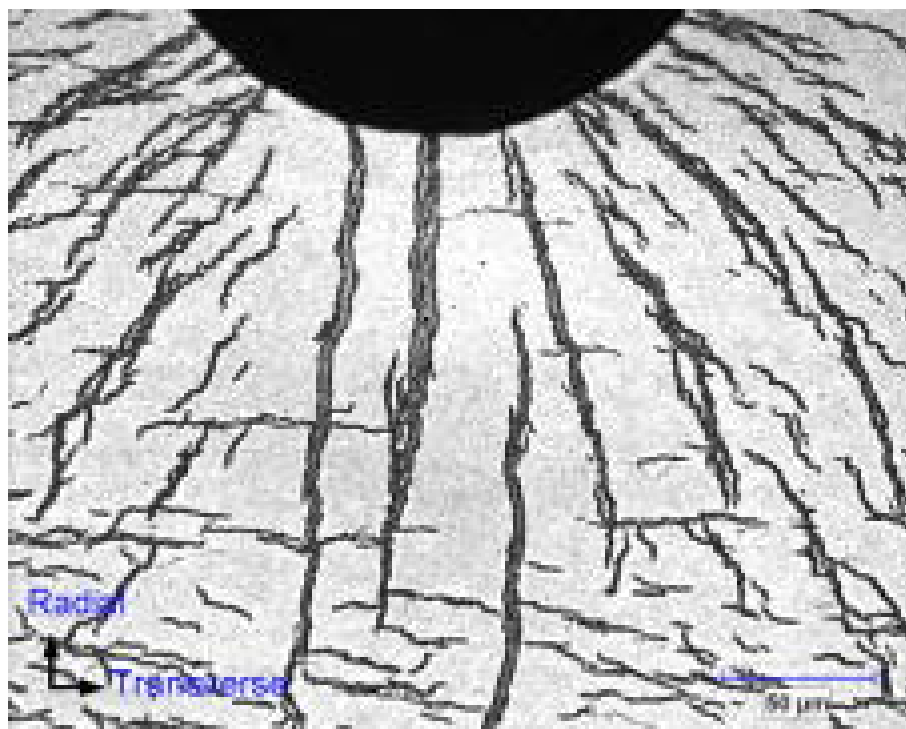


(b) Cui et al., 2009

For the case of the blunt notch, FIG. 7.26 depicts the same flaw-tip radial hydride patterns at a greater resolution. Again, there is good quantitative agreement in the typical lengths of the simulated macro-hydride colonies. Note that the nucleation and macro-hydride loops may be iterated further here, which would lead to either longer or thicker features depending on the choice of microstructural rules. These results may be used to extract quantities related to DHC susceptibility; this includes the volume fraction of radially orientated hydrides and the hydride network connectivity.



(a)



(b) Cui et al., 2009

FIG. 7.26

The formation of radial hydride patterns around blunt notches

(a) The sequential evolution of three trans-granular macro-hydride colonies that constitute a sparsely distributed pattern of radially orientated hydrides around a blunt notch. As opposed to the case of the sharp crack, the H enhanced zone is much larger here due to the size of the notch. Over the same number of iterations over the nucleation and macro-hydride loops, there is not a noticeable depletion of H around the micro-hydrides needles that are situated further away from the notch tip. This suggests that these macro-hydride colonies are likely to grow longer over the subsequent iterations. (b) The experimental micrograph shows the present of circumferential hydrides as well as radial hydrides, and it appears that the number of these features increases at distances that are further away from the notch. It is quite possible that these are inter-granular macro-hydride colonies that coincide with the grain boundaries. In a more realistic simulation, it is then necessary to account for this phenomenon by incorporating inter-granular nucleation sites as well as the local stress effects due to the grain boundaries between highly misorientated crystallites.

It must also be noted that the circumferential macro-hydride colonies observed at distances further away from the notch cannot be captured in this particular variant of the proposed framework. The reason for this shortcoming is the fact that the present model only considers the global elastic energetics of the system, which are dominated by the notch. In reality, the morphological growth of the macro-hydride colonies is also governed by the local elastic energetics. In particular, grain boundaries generate local stresses which can influence the configurational arrangement of the micro-hydride needles; such stress effects may be more influential further away from the notch [Chamaa et al. (2018)]. In order to then incorporate the effects of grain boundaries, it is necessary to extend the framework to describe anisotropic polycrystalline systems, which is also a topic of the ensuing discussion.

As it stands, however, the current framework is still very powerful in its own right. Due to use of analytical formulae, this multiscale model effortlessly achieves system sizes that are comparable to SEM studies whilst maintaining the resolution of TEM studies. The main advantage of this framework over similar PF and FE models is then its simulation speed. [Note 19](#)

Note 19

Comparison of modelling speeds

The computational runtime for individual simulations presented here typically range from the order of seconds to minutes using basic computing resources. In contrast, the computational runtime is much slower for existing PF models which are then typically restricted to TEM scales. The same can be said for FE models at the component scale.

As the simulation runtime is fast, the stochasticism of the framework can be averaged out over a statistical ensemble of simulated micrographs. In a statistical ensemble, each simulated micrograph is a possible realisation of the system given a particular set of input parameters. There many possible realisations in the configurational space of hydrided microstructures that are physically allowed. By sampling as many realisations as possible, statistically averages can be extracted from the model. These averages can quantify the metallography of hydrided microstructures in a manner that has been inaccessible to experimental studies as well as other modelling methodologies. For example, in this framework, it would be straightforward to quantify the average macro-hydride morphology and orientation as a function of, say, grain size distribution. Such statistical averages can be used to construct and parametrise more sophisticated criteria for DHC initiation. This statistical prowess contributes to the overall predictive capabilities of this hybrid model.

Evidently, the statistical prowess of this multiscale framework is very important for industrial safety cases. But this is only possible because the current form of the framework is both more phenomenologically accurate and computationally efficient than its contemporaries. In the next steps towards validation, however, the framework will need to be developed further to incorporate the aforementioned extensions; the accuracy is expected to increase but at the cost of efficiency. This accuracy-efficiency trade-off must be handled carefully so that the statistical prowess is not compromised.

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8

Simulated Micrographs

Chapter Overview

The principal result of this investigation is the inception of a theoretical and computational framework for modelling the early stages of DHC failure. This hybrid multiscale model has led to the development of a state-of-the-art microstructural solver that couples H diffusion and hydride precipitation in Zr alloys whilst accounting for crystalline anisotropy and polycrystalline heterogeneity. The main output of this model is a set of simulated micrographs which depict the mesoscale networks of defects through the geometries, morphologies and contours of key metallographic features in the vicinity of the flaw tip. It must be emphasised that this multiscale model is in its infancy; a considerable amount of further development is required to verify and validate all of the novel aspects of the new framework. Nevertheless, this microstructural solver could be the forerunner of advanced fuel performance codes in which the multiscale complexity of the DHC phenomenon can be simulated with accuracy and efficiency. In order to better support this claim, this chapter intends to demonstrate the diverse capabilities of this bespoke model by showcasing a series of simulated micrographs which can be directly compared with experimental findings.

In the context of nuclear safety assessments for Zr alloy components, it is standard engineering practice to use handbook formulae that quantify the DHC initiation threshold through a critical stress intensity factor. As stated earlier, this DHC initiation threshold can be parametrised by the flaw acuity, microstructural properties and thermomechanical cycles [Puls (2012), Martin (2013), Schofield (2002), and Coleman (2003)]. Systematically varying these parameters and then organising their effects on the initiation threshold in the format of look-up tables ensures that the handbook approach is convenient in the industrial setting. But it is clear that experimentation alone cannot explore the full parameter space at hand. And it is also beyond the scope of the existing fuel performance codes that rely on conventional DFT, PF and FE simulation strategies whose intensive computations often require high performance computing. Such advanced computing resources would be warranted if the results of DFT, PF and FE were meaningful to the spe-

cific problem of DHC failure. But the associated computational expenditure is difficult to wholly justify when DFT methodologies are limited to atomic scale systems at absolute zero temperature, PF methodologies struggle to produce qualitative images even at the scale of individual micro-hydride needles, and FE methodologies grapple exclusively with deterministic PDEs that cannot capture the stochastic mesoscale evolution of the hydrided Zr alloy microstructure. Even the combination of DFT, PF and FE methodologies appears inadequate because their extensive simulation runtimes do not readily cater to parametric studies which involve statistical averaging [Tonks et al. (2017)]. A complete handbook containing simulated DHC initiation criteria requires an altogether different multiscale modelling strategy—one that prioritises the simulation accuracy-efficiency paradigm.

Therefore, this investigation has placed a very deliberate emphasis on the notion of the accuracy-efficiency trade-off. And it has culminated in the conception of a phenomenologically accurate model of the early stages of DHC failure which has been transmuted into an efficient software. Having verified this custom software using simple studies with test parameters, it can now be utilised as intended with more realistic parameters. The simulated micrographs depict the flaw-tip H enhanced and hydride-rich zones alongside other metallographic features such as intergranular and intragranular nucleation sites and events. Several parametric relationships will be quantified and compared to experimental findings as appropriate. It will become clear that these simulated micrographs can be directly superimposed with their experimental counterparts at the SEM or TEM scales, a notable feat that has so far eluded traditional PF and FE simulations [Motta and Chen (2012), Motta (2017), Jernkvist and Massih (2014), Jernkvist (2014), Martin (2013), Shek and Xu (2015), and Bair, Zaeem, and Tonks (2015)].

The main strength of this multiscale simulation strategy is not only its phenomenological accuracy but also its unprecedented efficiency. A time stamp is used to highlight the speed at which each simulation ran to completion after the initial software setup and compilation; it is even more impressive that these fast simulation runtimes—some of which fall below a third of a second—have been achieved on an ordinary workstation running a 2.9 GHz processor with an unremarkable graphics card. It is a true testament to the analytical closed-form expressions that were derived in the stress and stress-diffusion analyses as well as an optimised geometrical algorithm underpinning the diffusion-precipitation analysis. It really cannot be overstated that high performance computing is not needed where a modest computer suffices because the bespoke software can then be easily adopted in an industrial setting for further research.

Towards the end of this chapter, three such further extensions to this

hybrid model are briefly introduced as a pathway leading to future research. The first extension seeks to incorporate the kinetics of precipitation and dissolution over a series of thermal cycles, which provides the mechanistic basis needed to predict the ratchetting phenomenon; this involves supplying the dislocation dipole model of a micro-hydride needle to a DDP framework in order to generate the plastic memory around hydrides during their lifecycle [Patel et al. (2017)]. The second extension proposes a means to include a crucial oversight in the model as it stands, namely, the intrinsic and compatibility stresses at grain boundaries in heterogeneous polycrystalline Zr matrix constituting anisotropic HCP crystallites; the stress state correction to anisotropic heterogeneous media involves repackaging and adopting constitutive CPFE output using computational geometry [Wilson and Patel (2017) and Dunne and Petrinic (2005)]. The third extension covers artificial intelligence because machine learning could become a fashionable approach to computational materials science and so it is worth speculating how pattern recognition can be retrofitted into the computer vision techniques that are used in this hybrid modelling strategy. In all three of these extensions, the accuracy-efficiency metric is discussed.

As a final piece of commentary on the accuracy-efficiency balance before proceeding, it goes without saying that the simulation speed is a ubiquitous theme across computational materials science and, in particular, multiscale modelling, even if the simulation runtimes are seldom documented at execution let alone the primary concern during the model inception. Most certainly, considerable attention is usually devoted to the simulation realism: its quantitative, qualitative, phenomenological or topological accuracy with respect to existing data. In general, modelling methodologies can always improve their accuracy through various extensions including the addition of higher-order effects, the selection of finer spatial resolutions and temporal graduations, the reduction of algorithmic errors, and the augmentation of the computational mechanics [Janssens et al. (2007)]. Such gains in the simulation accuracy are almost always taxed by the losses in the simulation efficiency. There are usually diminishing returns when increasing simulation accuracy does not lead to much new scientific insight. It may be a controversial point to raise but introspection based on the present work suggests that the trade-off leans more towards the side of the simulation efficiency rather than the simulation accuracy, especially when the problem is shrouded in multiscale complexity, and this certainly is the case with DHC failure.

Ultimately, simulations can feature as one of the many tools in the overall material design process, and it is undeniable that the verisimilitude of the computational mechanics can never emulate the actual physical phenomena

due to the myriad approximations. So it can be argued that there is often not much value in a lone simulated datum irrespective of its accuracy, especially when vast computing power has been dedicated to its creation. It is more instructive when a collection of simulated data can be generated in real time—even though the simulation accuracy is only moderate—as long as this data can be appropriately contextualised whilst acknowledging its limitations. That is not to say that simulation accuracy is unimportant, but in the case of nuclear safety assessments of Zr alloy components where there is a historical track record of experimental literature, there is a convincing reason why DHC simulation strategies should opt towards simulation efficiency: statistical ensembles can provide error margins and confidence intervals in the simulated data where each datum corresponds an entire simulated micrograph. A minimalistic multiscale modelling strategy could quantify the uncertainty in its simulated microstructures using multiple realisation of the same system with the same parameters; simulation efficiency bestows this statistical prowess. It is this ideal which has served as the motivation to the present work and so ensemble averages are evaluated over 5–10 realisations with the same simulation parameters. Each realisation is labelled with three ordered initialisation seeds: (i) texture; (ii) intergranular nucleation sites; and (iii) intragranular nucleation sites. The initialisation seeds act as a microstructural identity in some sense, and these are supplied to the corresponding random number generators.

Even if the existing fuel performance codes abstain from delving into the intricacies of simulation efficiency, it will eventually—and possibly very soon—become a major concern given the multiscale complexity of DHC failure. The risk of DHC initiation could persist for centuries to come as dry storage casks continue to store the radiotoxic nuclear waste but the computing power may be capped in the upcoming decade in accordance with Moore's Law [Moore (1965)]. Therefore, models of DHC failure would undoubtedly need to become faster if the simulations intend to convey an increasingly accurate picture of this complex multiscale phenomenon. To this end, this investigation has pursued this formidable challenge with diligence, and the fruits of its labour will be evident in the simulated micrographs of the flaw-tip H profiles and hydride microstructures.

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8.1 Hydrogen Profiles

The first series of simulated micrographs displays the contours of the H enhancement ahead of the loaded flaw in the Zr alloy microstructure. The stress and stress-diffusion analyses are respectively used to compute the elastic fields around an elliptical notch and the equilibrated H concentration profile. The diffusion-precipitation analysis is employed alongside computer vision to enforce the stoichiometric mass conservation principle at intergranular and intragranular nucleation sites. Hydride features do not appear in these particular micrographs but the ratio of the intragranular-to-intergranular nucleation events provides the necessary quantitative connection to experimental SEM images. There are three subsets of parametric studies which respectively explore the effects of the flaw acuity, microstructural properties and thermomechanical conditions.

8.1.1 Effects of Flaw Acuity

This first subset of simulated micrographs presents flaw-tip H profiles as a function of the sharpness or bluntness of the elliptical notch under a constant remote loading; the flaw acuity corresponds to the ratio of the minor and major semi-axes in the case of the elliptical hole.

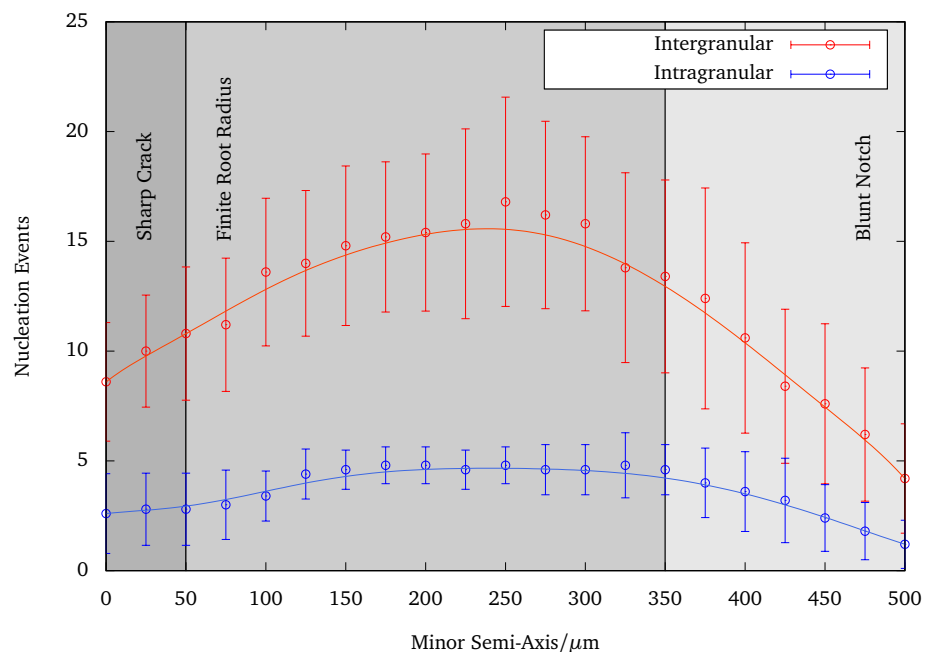
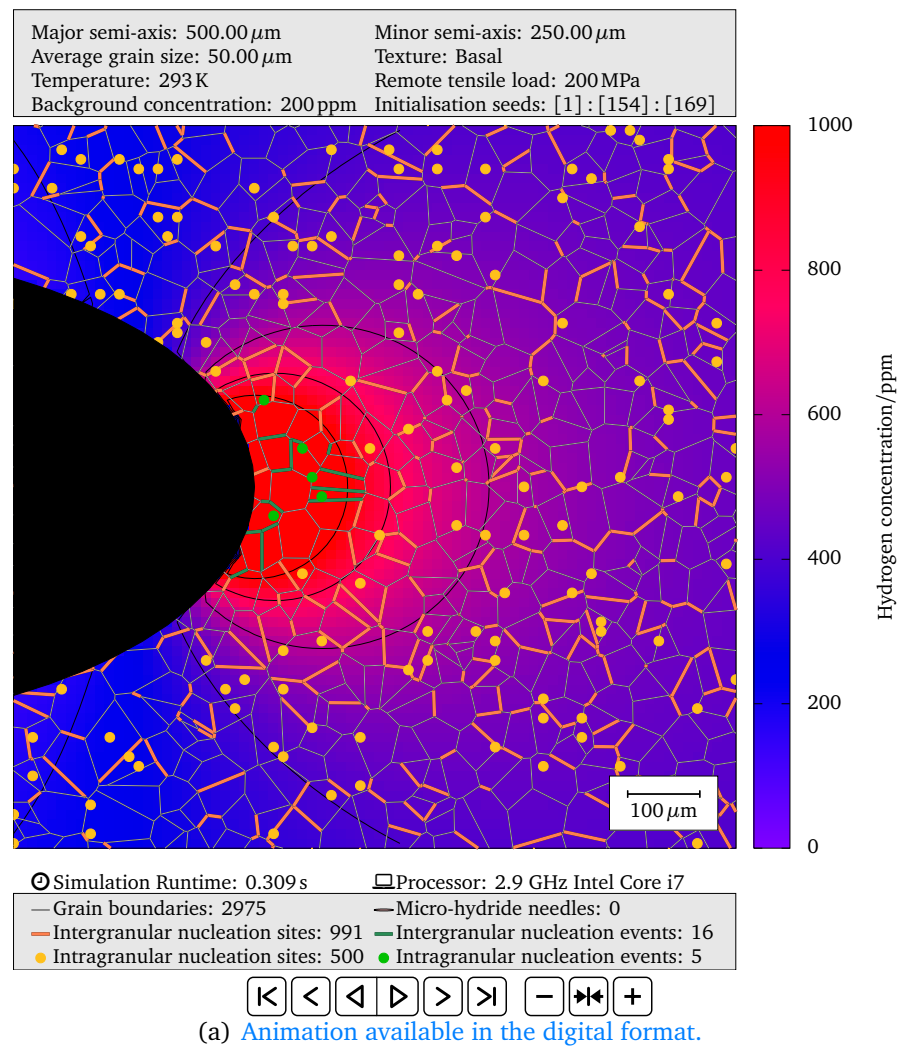
Notch Geometry. Many experimental and computational studies survey various flaw acuities and aim to identify worst-case scenarios for DHC failure [Shek and Xu (2015) and Cui et al. (2009)]. Such critical flaw acuities are understood to be intermediate geometries that reside between two extrema: the sharp crack regime and the blunt notch regime. Certain V-notch geometries fall within this high-risk category but no theory or simulation has been able to conclusively justify this experimental observation, especially given that standard cohesive (process) zone models predict the worst-case scenario to be the sharp crack [Puls (2012)].

However, the simulated micrographs generated by the multiscale model, which are animated in FIG. 8.1, lend some quantitative support to this experimental observation. The worst-case flaw acuity corresponds to the situation in which the flaw-tip hydride population is at its densest, which results from the maximal number of intergranular and intragranular nucleation events. It is clear from the data trend in FIG. 8.1 that neither the sharp crack nor the blunt notch regimes generate the stress profiles needed to enhance the H concentration over a sufficiently large region that contains many nucleation sites. As H diffusion drivers, sharp cracks are strong but small stress-raisers whereas blunt notches are large but weak stress-raisers. In contrast, finite root-radii seem to be Goldilocks flaw acuities as seen in experiments.

FIG. 8.1

Simulated micrographs of the flaw-tip hydrogen profile as a function of the flaw acuity

The regions of H enhancement and prospective nucleation events ahead of the elliptical notch with a fixed major semi-axis and a variable minor semi-axis in the high solvus limit. The simulation assumes an isotropic heterogeneous medium in which roughly one-third of the grain boundaries are randomly allocated as potential intergranular nucleation sites. On average, there is roughly one intragranular nucleation site per grain. Note that the remote loading is about tenfold typical values but the loading must be large to satisfy the H mass conservation principle dictating the precipitation criteria. Room temperature is chosen because it is low enough to ensure that trend in the nucleation events remains clear; higher temperatures result in a more diffuse concentration profile and hence very few nucleation events. (a) The contours of the H concentration profile in increments of 200 ppm with the highest value of 1000 ppm chosen as the mass balance criterion. Observe that most nucleation events occur when the minor semi-axis is near $250\mu\text{m}$ in the V-notch regime, which is true for both intergranular and intragranular nucleation sites. The simulation runtime is also noteworthy as all simulations take roughly a third of a second on a rudimentary processor. (b) The statistical trend in the nucleation events computed through ensemble averages over different microstructural realisations with the same simulation parameters. Each realisation has a different group of intergranular nucleation sites from the list of available grain boundaries whilst the intragranular nucleation sites have different positions. The mean values are plotted with the errors defined by the standard deviation, a feat made possible by the simulation efficiency.



(b)

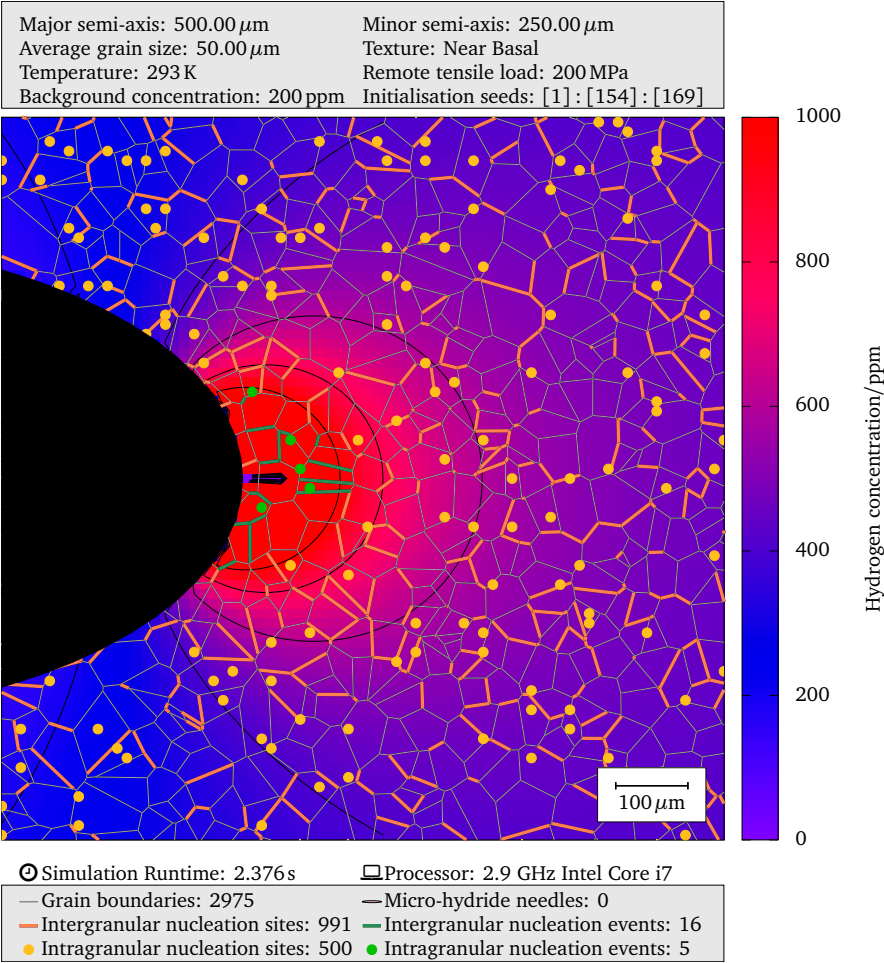


FIG. 8.2

A simulated micrograph of the denuded flaw-tip hydrogen profile in the presence of a plastic zone

A narrow coplanar plastic zone is introduced to justify an experimental postulate which suggests that plastic yielding shields the flaw tip and thereby reduces the H enhancement. Here the plastic zone is chosen to be 50 μm in which is 10% of the major semi-axis of the elliptical notch. It is evident that the plastic shielding does indeed lead to a denuded region which is the same size and geometry as the plastic zone. It is reasonable to assume that more realistic plastic zones would also provide a shielding effect. Hence it implies that sharp flaw acuities may not constitute the worst-case scenario if the high flaw-tip stresses lead to a small plastic yielding that shields the flaw against H enhancement and hence hydride precipitation. Observe that this simulation runtime is an order of magnitude greater due to the computation of the image-corrected dislocation stresses that constitute the plastic zone.

Plastic Zones. Flaw-tip stresses can be large enough to cause plastic yielding, which results in a plastic zone localised ahead of the flaw. The exact size and shape of the plastic zone depends on various factors, such as the flaw acuity, grain size, texture, and loading. As a highly simplified example, consider a narrow coplanar plastic zone that emanates 50 μm out from the notch tip. This is not unlike the DBCS elastoplastic slit crack model, or rather its finite root-radii counterpart, which has been successfully verified with industrial FE models [Martin (2013) and Vitek (1975)]. As shown in FIG. 8.2, the flaw-tip plastic shielding leads to the formation of a denuded region, which agrees very well with an experimental postulate that implicates plastic zones in the preventing hydride precipitation very close to the notch [Schofield (2002)]. It is straightforward to extend this concept to more realistic plastic zone geometries, but this example should suffice in demonstrating the H reduction in the presence of plastic yielding.

8.1.2 Effects of Microstructure

The second subset of simulated micrographs presents flaw-tip H profiles as a function of the microstructural properties, including grain size, crystalline anisotropy and polycrystalline texture, and alloying additions. These particular simulations are the first of their kind in this field of research and boast considerable industrial relevance.

Grain Size. The microstructures of commercial Zr alloys are carefully manufactured to have a fine grain size distribution that is normalised around a mean value within the range $[50, 100]\mu\text{m}$, but heat treatments during operation can cause grain growth leading to coarse grain sizes in the range $[100, 200]\mu\text{m}$ and even beyond into the dangerous blocky- α territory [Tong (2016) and Tong and Britton (2017)]. Although the correlation between fine grain size and mechanical toughness is understood, there is still much speculation about the relationship between the grain size and DHC initiation [Chamaa et al. (2018)]. It would be enlightening to produce a detailed comparative study of the hydride features across Zr specimens with varying grain sizes, but such a study would be a painstaking experimental task and it is not feasible with current PF and FE models.

But such a comparative study falls comfortably within the remit of the multiscale model conceived in this investigation. The simulated micrographs in FIG. 8.3 show how nucleation events vary with the average grain size: coarser grain microstructures exhibit a lower percentage of intergranular nucleation events. This trend is also reflected in the ensemble averages in FIG. 8.3 which chart the increases in the ratio of intragranular-to-intergranular nucleation events; intragranular nucleation remains roughly constant as expected because these sites represent intragranular defects, such as SPPs, whose density would be the same in a specific Zr alloy regardless of the grain size. As the grain size increases, grain boundaries become larger and so fewer intergranular sites are enclosed inside the H enhanced contour.

There is reasonable quantitative agreement with SEM experiments in which macro-hydride colonies have been counted in pure Zircadyne-702 specimens; the ratios of the intragranular-to-intergranular macro-hydride colonies were determined to lie between ~ 0.2 at fine grain sizes of $50\mu\text{m}$ and ~ 1.7 at coarse grain sizes of $200\mu\text{m}$ in these experiments [Chamaa et al. (2018)]. Assuming that every nucleation event in FIG. 8.3 results in a single macro-hydride colony, then there is a close resemblance in the simulated ratios: ~ 0.55 at $50\mu\text{m}$ and ~ 1.45 at $200\mu\text{m}$ when there is an average of only one intragranular nucleation site in every grain.

FIG. 8.3

Simulated micrographs of the flaw-tip hydrogen profile as a function of the grain size

The regions of H enhancement and prospective nucleation events ahead of the elliptical notch in various Zr alloy microstructures with different average grain sizes within the range $[50, 200] \mu\text{m}$. The simulation assumes an isotropic heterogeneous medium in which roughly one-third of the grain boundaries are randomly allocated as potential intergranular nucleation sites. On average, there is roughly one intragranular nucleation site per grain, which represents a Zr specimen with very few alloying additions, such as the commercially pure Zircadyne-702 material. Room temperature is assumed in order to maximize the number of the nucleation events, and a lower H mass conservation criterion of 600 ppm is chosen for the same reason. (a) The contours of the H concentration profile in increments of 200 ppm which remain in a fixed position as they depend only on the flaw acuity. Observe that the intragranular site density decreases as the average grain size increases in an almost proportionate manner, though it is not one-to-one due to the use of modified computer vision checks. Again it is important to note the sheer speed of the simulation given that there is no equivalent in the PF and FE modelling strategies. (b) The ensemble averages showing the trends in the percentage of intergranular and intragranular nucleation events as well as the ratio. There is a fairly sharp crossover point around an average grain size of $100 \mu\text{m}$, which demarcates the fine grain and course grain microstructures, and this abrupt demarcation agrees with SEM experiments that count the intergranular and intragranular macro-hydride colonies. The simulated means and standard deviation error bars agree quantitatively with these SEM findings.

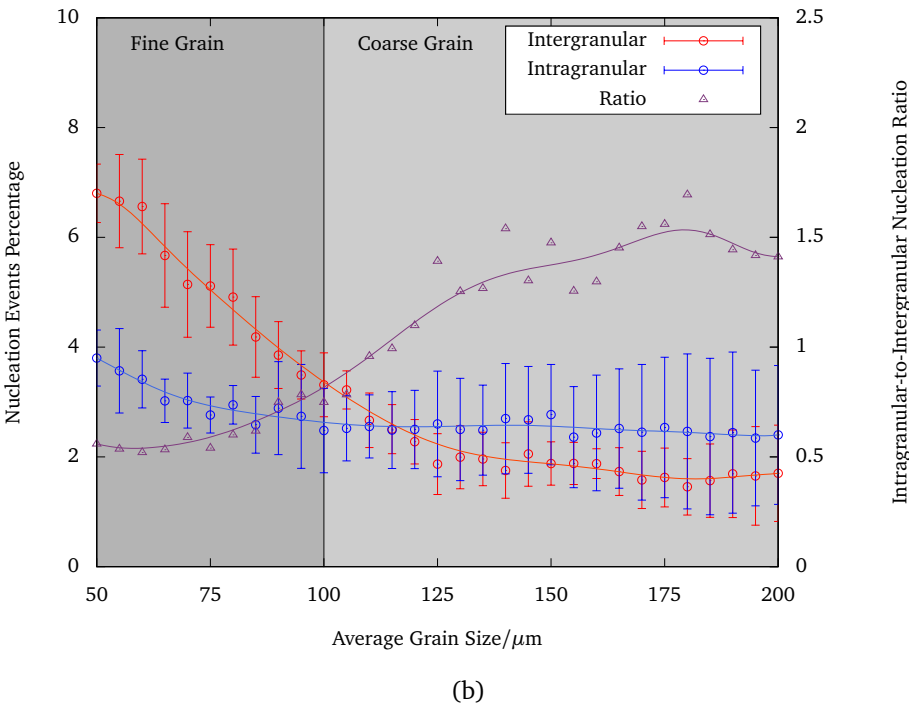
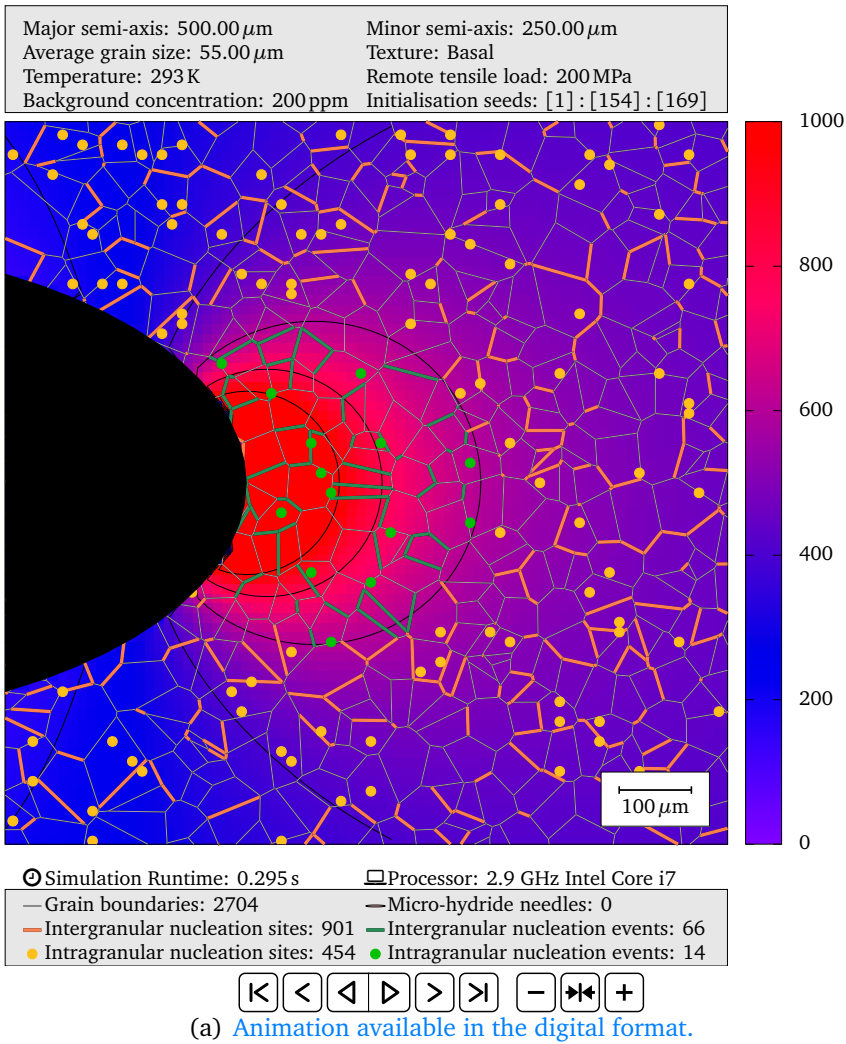
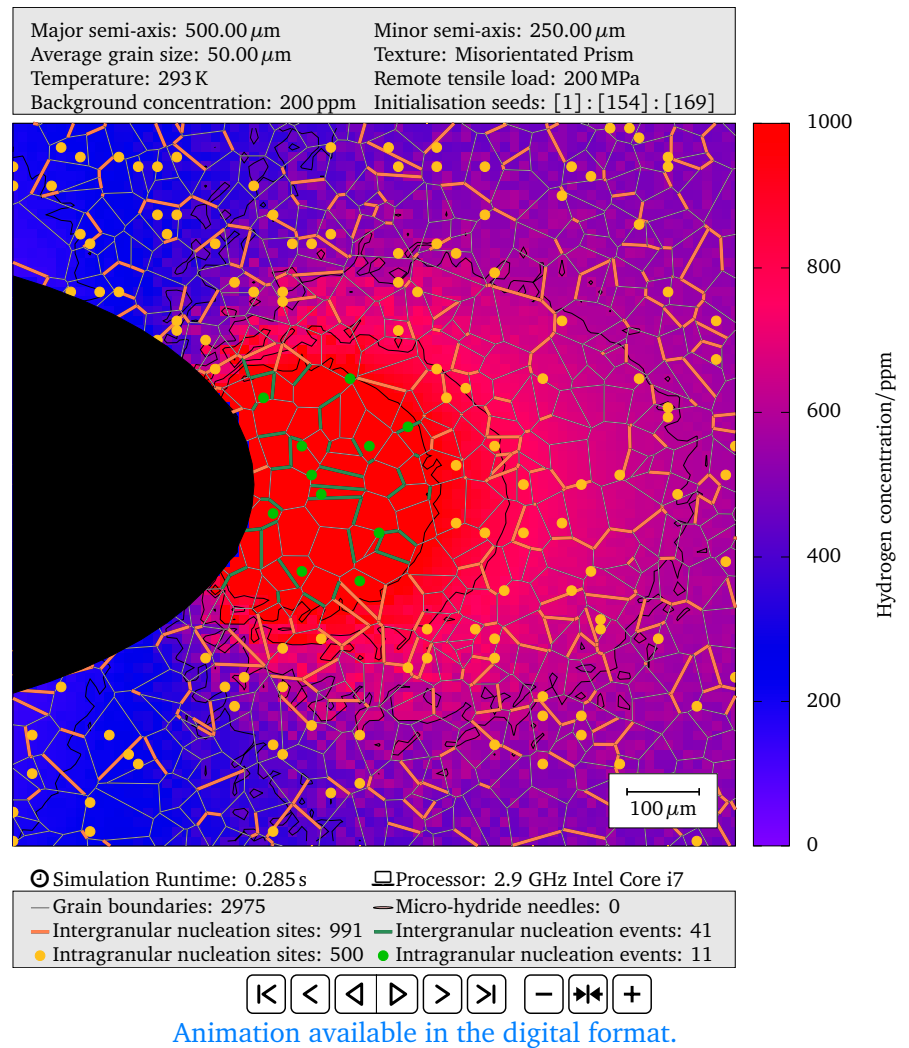


FIG. 8.4

Simulated micrographs of the flaw-tip hydrogen profile as a function of the crystalline anisotropy at the atomic scale

The regions of H enhancement and prospective nucleation events ahead of the elliptical notch in a CANDU reactor Zr alloy component with a near radial texture, that is, the basal pole is directed towards the elliptical foci with individual misorientation up to $\pi/3$ rad with respect to the horizontal. Each realisation begins with a uniquely generated texture. A crude 10% stress state correction is applied to adapt the isotropic formulae into this anisotropic homogeneous medium. The two non-equal components of the elastic dipole tensor couple with the three plane strain tensor components, and the coupling is weighted by the angle of misorientation in each grain. The weighted coupling leads to the irregular and discontinuous contours. The realisations do not have identical nucleation events but there are ~ 2.6 times more intergranular nucleation events and ~ 2.2 times more intragranular nucleation events in comparison to the basal texture.



Crystalline Anisotropy. The HCP crystallography of Zr is an important consideration in DHC failure as texture is carefully controlled during the manufacturing process in order to optimise the component lifetime, but the exact role of anisotropy has not been fully deciphered. Of course, the continuum scale effects of anisotropy have been explored using CPFE models in which the stresses at grain boundaries are determined using the notion of strain compatibility [Dunne and Petrinic (2005)]. But the atomic scale effects of the anisotropic HCP crystallography on H diffusion in Zr have eluded standard PF and FE models which need an atomic-to-continuum scale representation of the anisotropic Zr-H system. The proposed multiscale framework is designed precisely to meet this need through the use of the elastic dipole tensor [Nazarov et al. (2016)]. The simulated micrographs in FIG. 8.4 depict the isolated effects of the anisotropic trigonal interstitialcy due to H diffusion along the prism plane, which results in $\sim [2.2, 2.6]$ times more nucleation events.

Alloying. Commercial Zr alloys contain various constituent solute additions that improve the mechanical strength and corrosion resistance. The principal alloying species include Cr, Fe, Ni and Sn, which can harden into small intermetallic SPP inclusions that reside within the grains, as well as Nb, which lowers H pick-up, and O, which stabilises the α -phase in Zr microstructure. These alloying additions can be duplicitous in some sense: they can inhibit the overall likelihood the DHC initiation in one way whilst simultaneously exacerbating the conditions that lead to hydride precipitation. For example, H ingress is reduced due to Cr, Fe and Nb, all three of which improve waterside corrosion resistance; but these three alloying additions destabilise the α -phase (or stabilise the β -phase) and thereby facilitate the formation of the γ -ZrH_{1.00}-hydride and δ -ZrH_{1.66}-hydride features [Puls (2012)]. In addition, these SPP inclusions can operate as intragranular nucleation sites [Chamaa et al. (2018)]. So accounting for the effects of alloying species is not as simple as tampering the background H concentration or the elastic stiffness constants. Such subtleties associated with alloying have not been studied using PF and FE models, and so it is worth explaining how the hybrid multiscale model can suitably convey the differences between various Zr alloy designs.

Consider again the main alloying effects and how they can be incorporated within the input to the multiscale model. If alloying improves corrosion resistance, the reduced H pick-up would manifest as a lowered background H concentration, which would reduce the raw number of nucleation events as long as the H mass-conserving precipitation criterion remains unchanged. As demonstrated in FIG. 8.5, if alloying contributes inclusions to the matrix, the SPP density can be a part of the intragranular nucleation site count, which could lead to greater number of nucleation events. Both alloying effects can be adapted into the multiscale model, and the described consequences do not add further complexity to the simulation. That is, the effects of such alloying additions have an obvious connection with the simulation parameters and the simulated micrographs.

It is not immediately apparent how the α -phase destabilisation can be modelled because the atomic scale precipitation energetics have not been considered. Despite this shortcoming, there is a simpler alternative within the remit of the multiscale model, namely, recalibrating the nucleation criterion solvus. This particular alloying effect is implicit within the preset H enhancement threshold that is specified by the H mass conservation criterion. As shown in FIG. 8.6, the α -phase destabilisation alloying effect can be subsumed into the choice of the H enhancement contours. Increasing α -phase destabilisation effects correspond to a lower contour intervals and hence a greater percentage of nucleation sites lead to nucleation events.

FIG. 8.5

Simulated micrographs of the flaw-tip hydrogen profile as a function of the alloying additions that operate as nucleation sites

The regions of H enhancement and prospective nucleation events ahead of the elliptical notch in different Zr alloys with variable amounts of the alloying elements Cr, Fe, Ni and Sn, which can form SPP inclusions. The SPP inclusions reside within grains where they may operate as intragranular nucleation sites; the local defect stresses around these inclusions may drive H diffusion and hence encourage hydride precipitation. (a) The contours of the H concentration profile, which is constant as it depends solely on the flaw acuity as well as the temperature and loading. A higher number of intragranular nucleation site corresponds to a greater number of SPPs which are assumed to be the main defects that enable hydride precipitation within the grains themselves. Within the range of [1, 5] intragranular nucleation sites per grain, a sufficiently large background H reservoir ensures that all intragranular nucleation sites enclosed by the contour marked at 600 ppm will lead to nucleation events. Note that this result is valid even after the intergranular nucleation sites have depleted the H concentration; it is only procedurally sensible to first check the intergranular nucleation sites because grain boundaries rank higher as thermodynamically favourable nucleation sites. (b) The ensemble averages showing the trend in the total number of nucleation events and the ratio of intragranular-to-intergranular nucleation events, which is almost linear with increasing intragranular nucleation site density. In the commercially pure Zr specimens, grain boundaries dominate as nucleation sites, but there is an expected increase in the precipitates within the grains in Zr alloys that contain more SPP inclusions.

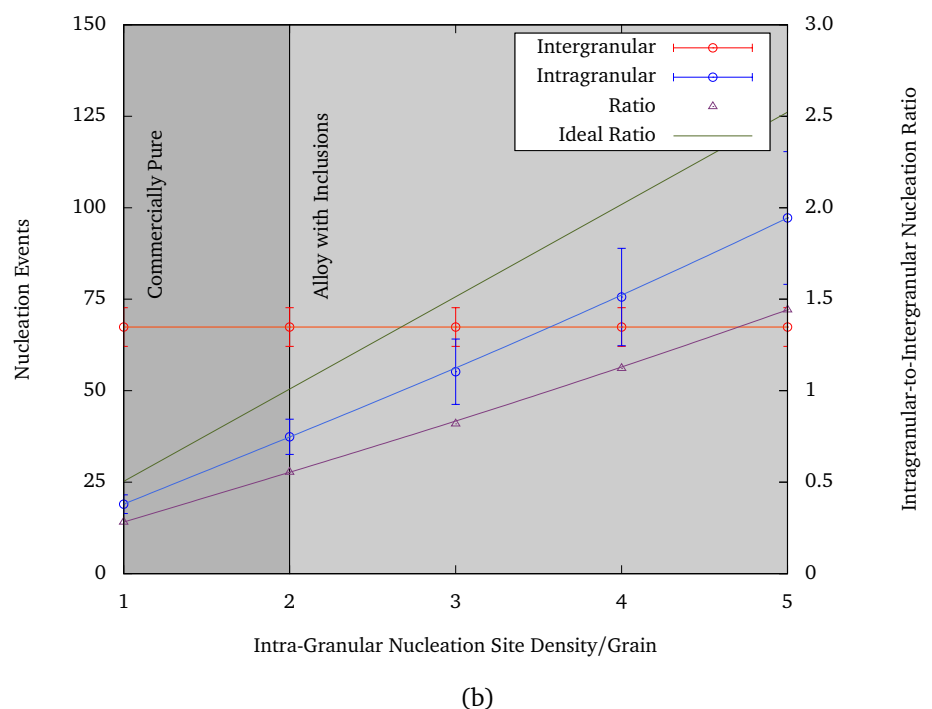
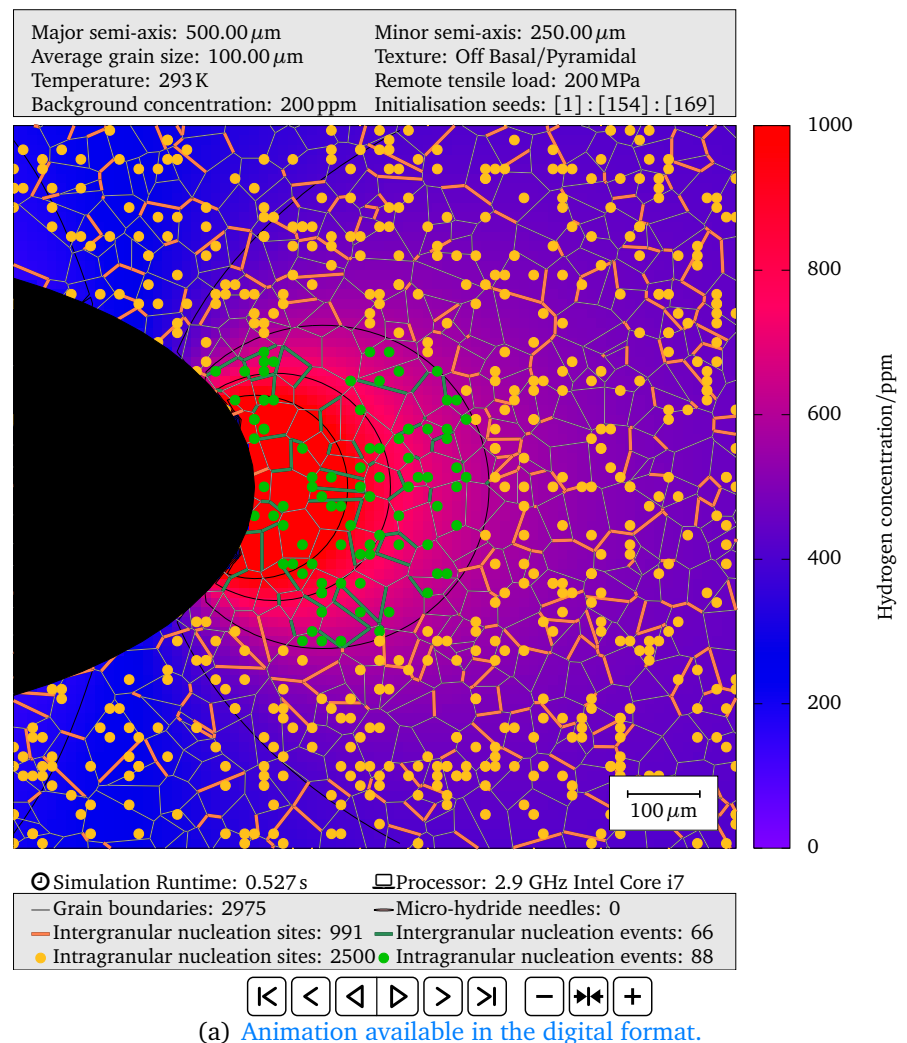
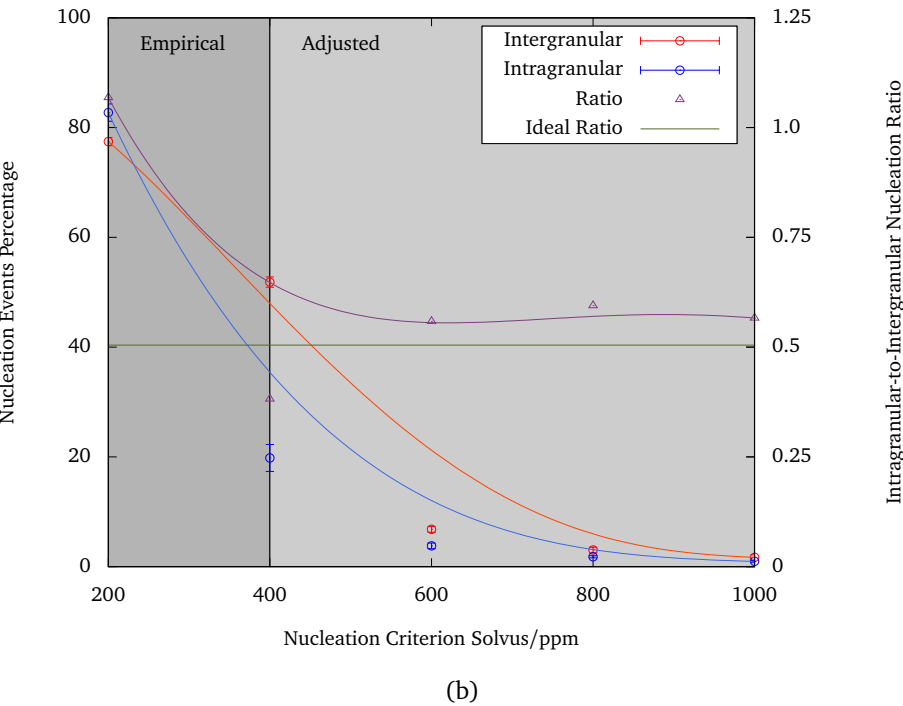
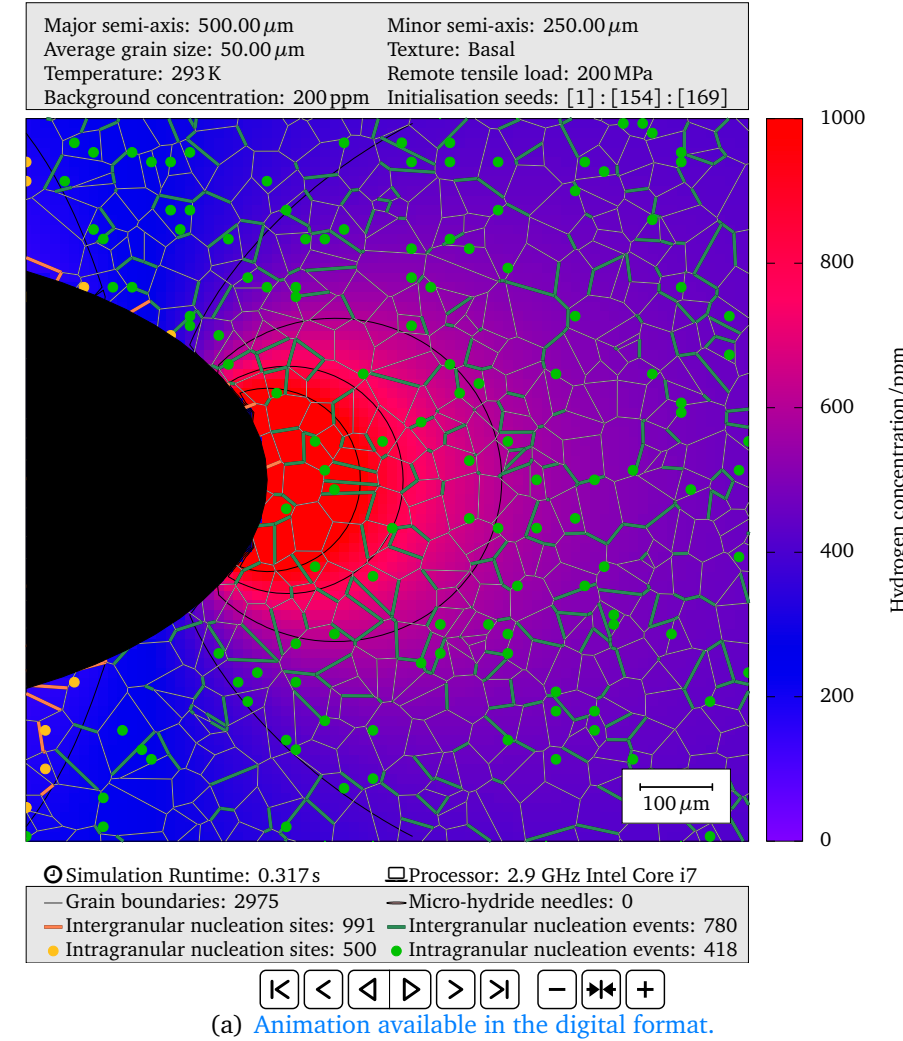


FIG. 8.6

Simulated micrographs of the flaw-tip hydrogen profile as a function of the alloy additions that reduce the hydride precipitation transus

The regions of H enhancement and prospective nucleation events ahead of the elliptical notch in different Zr alloys with variable amounts of the alloying elements Cr, Fe and Nb, which destabilise the α -phase and therefore lower the energy required to transform the α -Zr-H solid solution into the γ -ZrH_{1.00}- or δ -ZrH_{1.66}-hydride phases. The variable H enhancement contour that conveys the alloying effect of α -phase destabilisation and hence a lower thermodynamic energy barrier for hydride precipitation. The contour encloses the intergranular and intragranular nucleation sites that have satisfied the H mass conservation criterion, that is, the prospective nucleation events. The H mass balance principle is a novel aspect and it is based on logical reasoning as well as causality in the diffusion-first hypothesis. Further details are given in the text. (a) Increasing amount of an alloying addition which destabilises the α phase and lowers the transus to encourage hydride precipitation, which is represented by the changing the stoichiometric coefficient which is used as a free simulation parameter to define the chemomechanical bridge in the computational application of the H mass-conserving principle. It is simpler to adjust the solvus through this computational artefact without any detailed physical premise. (b) A comparison of the experimental solvus values and the adjusted values needed in this model. Note that the ideal ratio of intra-to-intergranular nucleation sites is matched closely by the corresponding ratio for events at higher solvus values. The ideal ratio is preset by the simulation parameters.



8.1.3 Effects of Thermomechanical Cycling

The third subset of simulated micrographs presents flaw-tip H profiles as a function of the temperature and loading, and these simulations will provide an insight into the service lifetime of Zr alloy component and the impact of thermomechanical cycles on DHC initiation. It must be stated from the outset that temperature and loading do not feature so prominently in this multiscale model; the former appears only in the stress-diffusion analysis as a thermodynamic measure of the entropy whereas the latter can only be seen in the stress analysis as a mere prefactor to the analytical closed-form expressions to the stress state around flaws with simple geometries. A more rigorous formalism is required to embed temperature and loading effects in the stress, stress-diffusion and diffusion-precipitation analyses. Nevertheless it is still useful to visualise the individual relationships between H enhancement and these system parameters as they exist in the current version of the model.

Temperature. It is clear that the stress gradients become less influential in directing the H interstitial diffusive hops towards tensile regions as the temperature increases and entropy becomes a more powerful agent acting against localised H enhancement. This observation is indeed reproduced in the simulated micrographs in **FIG. 8.7** that depict the H enhancement at three industrial temperatures, namely, room temperature, reactor operating temperature and dry storage temperature [Billone, Burtseva, and Einziger (2012) and Billone, Burtseva, and Liu (2013)]. The reactor operating and dry storage temperatures are hundreds of degrees higher than room temperature, and the diffuse H profiles at these higher temperatures are immediately noticeable. At these high temperatures, the H enhancement is so low that that intergranular and intragranular nucleation events have fallen by a factor of 10, notwithstanding the unaccountable changes in the hydride precipitation kinetics.

In order to improve the self-consistency of this multiscale model with regards to the temperature effects, it is necessary to include the temperature dependencies in the elastic constants as part of the stress analysis, temperature gradients in stress-diffusion analysis, and an explicit notion of the temperature in H mass conservation criterion that dictates precipitation. Such modifications to the stress and stress-diffusion analyses seem reasonably straightforward within the remit of the current multiscale model as earlier PF and FE models have outlined rigorous strategies to do so [Jernkvist and Massih (2014) and Ma et al. (2006)].^{Note 20}

Note 20

Realistic temperature effects

Although it seems trivial to generalise the stress and stress-diffusion analyses to convey temperature, it is more subtle for the diffusion-precipitation analysis, which, in its present form, is already so very nuanced in its efficient algorithmic design that temperature effects could disrupt the sensitive H mass balance criterion and add yet another layer of computational complexity. a conceptual challenge to the simulation efficiency. However, it is straightforward to include the changes to the microstructure induced by heat treatments, such as increasing the grain sizes and annealing certain defects.

FIG. 8.7

Simulated micrographs of the flaw-tip hydrogen profile as a function of the system temperature

The regions of H enhancement and prospective nucleation events ahead of the elliptical notch at three specific temperatures, namely, room temperature (293 K), reactor operating temperature (573 K), and dry storage temperature (673 K), which have industrial relevance to DHC failure during the operation lifetime of the Zr alloy component. (a) A much lower solvus contour at 400 ppm is chosen in order to visualise the abrupt changes in the nucleation event counters because realistic solvus values resulted in zero nucleation events at the higher temperatures; all realisations within the ensembles shared this trait and it is mostly likely attributed to the low intragranular nucleation site density as well as the specific grain morphologies in these simulated microstructures. (b) A bar chart displaying the ensemble averages of the intergranular and intragranular nucleation event counters at the three different temperatures whilst highlighting the large difference between lower room temperature setting in contrasts to the much higher reactor operating and dry storage temperatures. In reality, the number of nucleation events at high temperatures may be vanishing small, especially because the hydride features are typically annealed out of the Zr microstructure during heat treatment and thermal cycles. Such temperature effects do not currently feature in the multiscale model at hand, and a careful modification of the diffusion-precipitation analysis is required in order to improve simulation accuracy at higher temperatures without compromising the simulation efficiency.

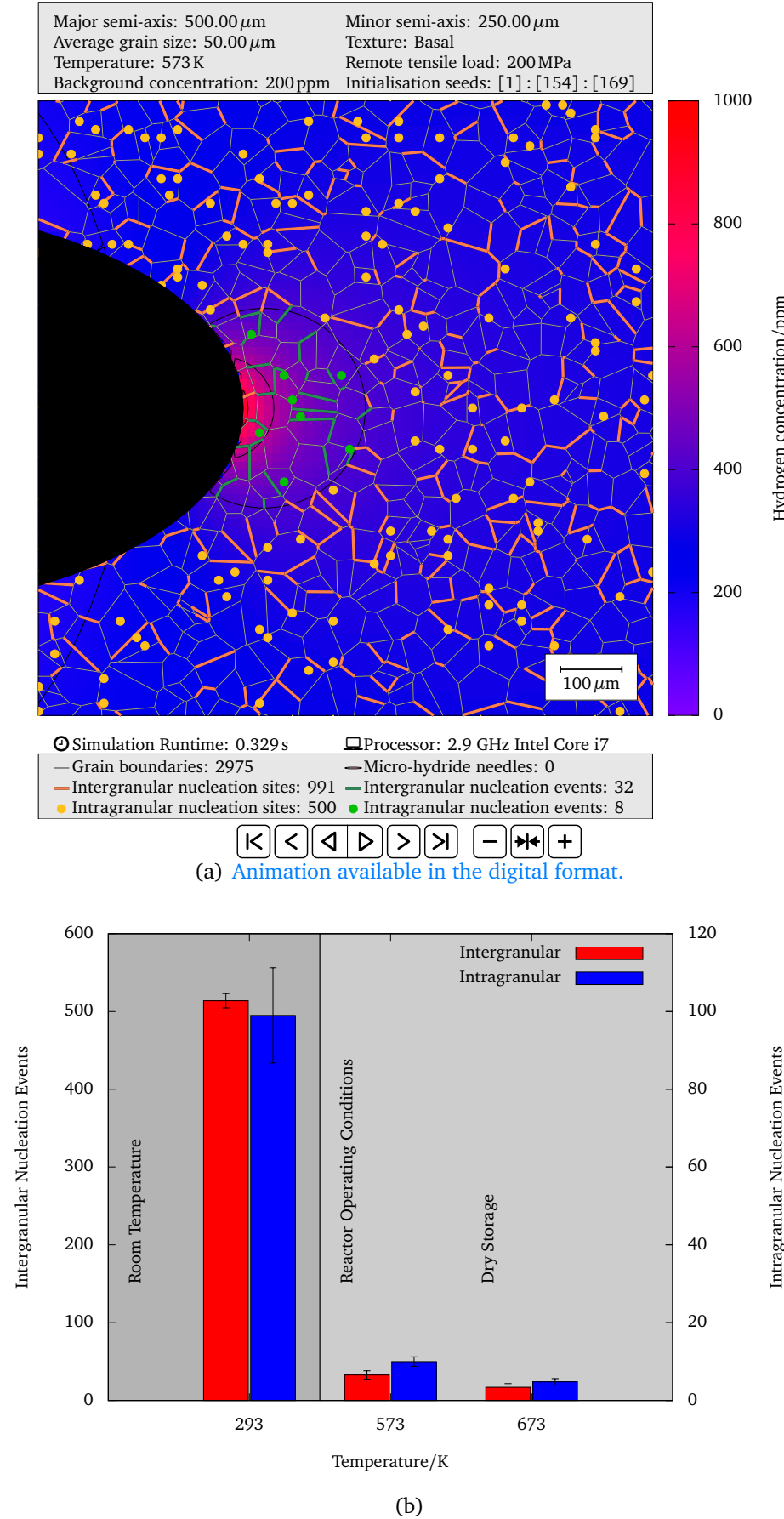
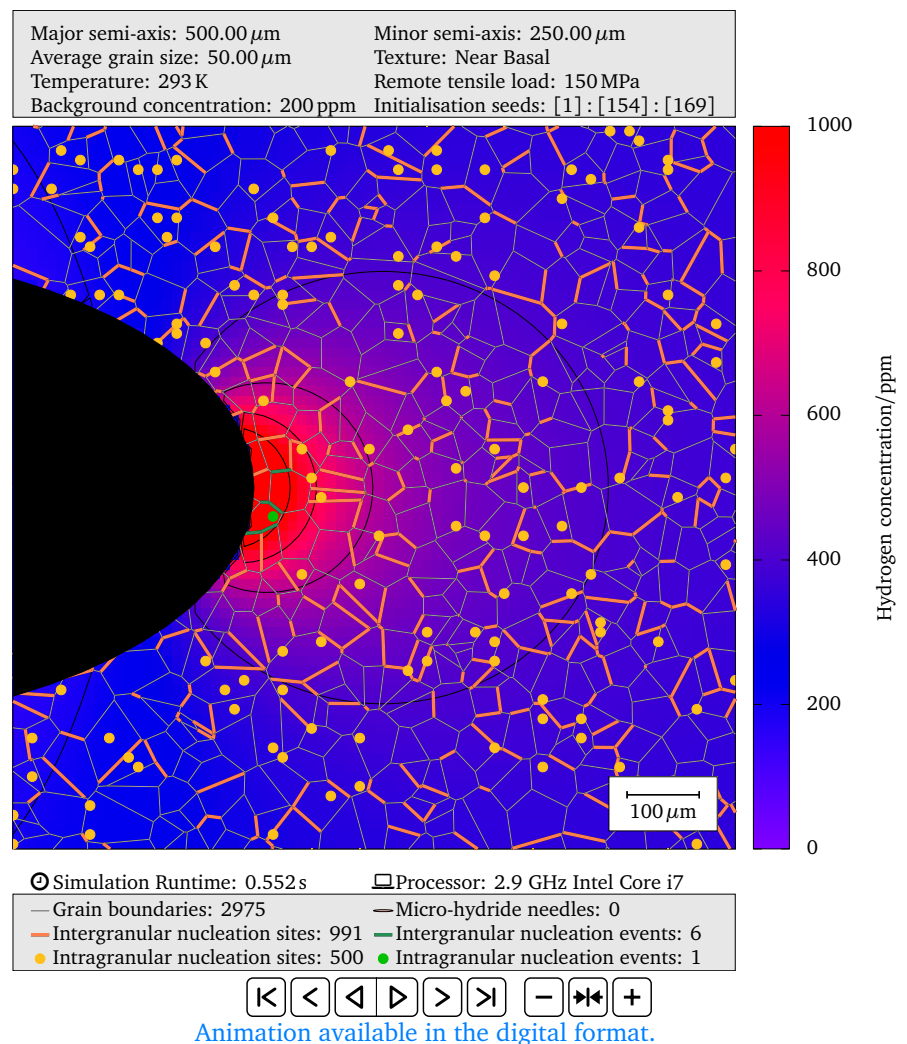


FIG. 8.8

Simulated micrographs of the flaw-tip hydrogen profile as a function of the loading

The contours of H enhancement and prospective nucleation events as the stress state of the increases with the remote tensile loading. A relatively large loading is needed to see many nucleation events in comparison with experiments, and this discrepancy can be attributed to the H mass conservation principle that dictates the precipitation criterion. Note that these loading effects are rudimentary as they merely rescale the stress state contours without introducing the complicated memory effects known in experiments. However, these simulated micrographs indicate that it is possible to devise an efficient algorithm to include such memory effects, and this possibility is better tested with simulated hydride microstructures as opposed to simulated H profiles.



Loading. The remote tensile load exists almost exclusively as a multiplicative prefactor in the analytical formulae for the system stress state. And so load variations directly alter the H contour sizes themselves, as shown in FIG. 8.8, which is expected given how the stress fields contribute to the elastic interaction energy in the stress-diffusion analysis. Although this result is physically reasonable in the early stages of DHC failure, it is far from a complete mechanistic description of the effects of load variation. In reality, the load cycles can also lead to various plastic memory effects as well as concurrent failure mechanisms such as fatigue and creep. Loading can also take the fracture mechanics into the non-linear regime, and process zone approach is much better framework to study these later stages of DHC failure [Martin (2013)]. But the simulated micrographs can be used to parametrise such cohesive zone models.

8.2 Hydride Microstructures

The second series of simulated micrographs displays the key metallographic features of interest to the DHC research, namely, the mesoscale multiphase networks composed of the micro-hydride needles and the macro-hydride colonies. These simulated hydride microstructures utilise the full gamut of the conceived stress-diffusion-precipitation amalgam that underpins the hybrid multiscale model. Of course, some useful information about the hydride features can readily be extracted from the simulated micrographs of the flaw-tip H enhancement, including the distribution and density of the hydride features as functions of the flaw acuity, microstructural properties and thermomechanical cycling, and so it is sufficient to refer to the simulated H profiles for such purposes.

However, the simulated hydride microstructures provide a more direct comparison with experiments because these simulated micrographs explicitly represent the mesoscale hydride networks: macro-hydride colonies whose substructure consists of a staircase-like stacking of micro-hydride needles orientated to reduce the (free) strain and interfacial energies. It is now straightforward to explore how crystalline anisotropy and polycrystalline heterogeneity influence micro-hydride needles and macro-hydride colonies, which is a truly unique computational study that has never been conducted using PF or FE methodologies. Moreover, these simulated hydride microstructures provide a deeper understanding of the precipitation-dissolution memory throughout the histories of thermomechanical cycles; so then opens the gateway into advanced mechanistic models which can predict ratchetting phenomenon that typically precedes DHC initiation. Due to the industrial relevance of these simulations, it is also now an obligation to benchmark the proposed hybrid multiscale modelling strategy against the metrics of simulation accuracy and simulation efficiency.

8.2.1 Mesoscale Networks

The multiscale theory and simulation has thusfar involved a very deliberate and somewhat nuanced mesoscale treatment of hydride features, which has been motivated by experimental images that depict micro-hydride needles and macro-hydride colonies in the Zr alloys. The mesoscopic distinction between needles and colonies has underpinned the development of the hybrid model in which the diffusion-precipitation analyses involves two main concepts: (i) a H mass conservation principle that determines nucleation events where individual microscopic precipitates should appear within the H enhanced region; and (ii) a constitutive rule that generates adjacent nucleation sites near the nucleation events in order to mimic the hypothesised

TAB. 8.1

Properties of the simulated flaw-tip hydride features as a function of the flaw acuity

The overall number of nucleation events increases from the sharp crack regime to the blunt notch regime. However, this trend is reversed for areal density of the flaw-tip hydride, which is defined by the hydride features enclosed within a rectangular region with approximate dimensions of the flaw. The average sizes of the macro-hydride colonies are similar regardless of the flaw acuity.

Property	Value
SHARP CRACK	
Nucleation events	34 nm^{-2}
Flaw-tip density	680 nm^{-2}
Colony size (Inter)	$161.25 \mu\text{m}$
Colony size (Intra)	$67.78 \mu\text{m}$
FINITE ROOT-RADIUS	
Nucleation events	48 nm^{-2}
Flaw-tip density	190 nm^{-2}
Colony size (Inter)	$150.00 \mu\text{m}$
Colony size (Intra)	$63.53 \mu\text{m}$
BLUNT NOTCH	
Nucleation events	68 nm^{-2}
Flaw-tip density	140 nm^{-2}
Colony size (Inter)	$135.58 \mu\text{m}$
Colony size (Intra)	$74.79 \mu\text{m}$

autocatalysis that leads to the formation of macroscopic networks of the microscopic precipitates. The former concept refers to the needles and the latter concept refers to the colonies, and both can be readily applied to simulated H profiles once the thermodynamical free energy optimisation scheme is established. Using the dislocation representation of individual microscopic precipitates in conjunction with the texture map defined by the grain boundaries, it is straightforward to evaluate the two main contributions to the free energy, namely, the strain energy and interfacial energy, and hence determine the minimum free energy configuration of the micro-hydride needles.

A further mesoscale classification has been made to distinguish intergranular and intragranular nucleation event, which is used to configure the position of the adjacent nucleation sites and, hence, the morphologies of the macro-hydride colonies whose substructure constitutes the micro-hydride needles in a staircase-like stacking. Although this hybrid model is far more sophisticated than existing PF and FE models with respect to the phenomenological accuracy, its algorithmic foundations are seemingly efficient enough to treat more needles and colonies than the standard methodologies. Having purposefully built in this simulation accuracy and efficiency into this hybrid model, it is now worth transmuting several simulated H profiles into simulated hydride microstructures using the diffusion-precipitation analysis. In doing so, the mesoscopic representation of the hydride features can be visualised and compared with experimental micrographs.

Morphology and Substructure. As a first comparison between the simulated and experimental micrographs, consider the shape and size of the hydride features in FIG. 8.9, which have been summarised in TAB. 8.1 as a function of the flaw acuity. The staircase-like stacking of the micro-hydride needles leads to the morphological evolution of the macro-hydride colonies which are elongated structures as seen in SEM findings [Puls (2012)]. Intergranular macro-hydride colonies coincide with the grain boundaries whereas the intra-granular nucleation sites are confined within grains. In this variant of the hybrid model, this autocatalysis sequence is limited by either an insufficient H concentration further away from the flaw or the choice of impenetrable grain boundaries that forbid transgranular growth. This simple algorithm is consistent with experimental understanding, and macro-hydride colonies are predicted to grow beyond $\sim 100 \mu\text{m}$ in length, which agrees with SEM findings [Puls (2012) and Chamaa et al. (2018)].

A closer inspection of FIG. 8.9 shows the more detailed mesoscale representation of the hydride microstructure that emerges within the scope of the hybrid model. The sizes of intra-granular macro-hydride colony depend on

the micro-hydride needles residing within the grains; these lenticular precipitates align themselves along the energetically favourable directions on the basal plane as seen in TEM studies but they do not traverse grain boundaries [Carpenter, Watters, and Gilbert (1973)]. The micro-hydride needle configurations are determined by minimising the local strain and interfacial energetics, and so the flaw acuity has a subtle but noticeable influence on the average lengths of the macro-hydride colonies. The average colony size is smaller in the case of the sharp crack for two reasons: (i) the region of the H enhancement is more localised, which impedes the continuation of the autocatalysis sequence if the H concentration is insufficient; and (ii) the azimuthal angle of the colonies to the horizontal is greater in order to minimise the strain energy, but the autocatalytic nucleation sequences are interrupted by impenetrable grain boundaries in fewer algorithmic steps. Therefore, certain textures will also lead also to an earlier truncation in the autocatalysis sequence if the micro-hydride needles are more likely to overlap with grain boundaries at specific orientations, and this truncation would be more pronounced for the finer grain specimens. The hybrid multiscale model is able to provide this mechanistic insight to the experimental observations. ^{Note 21}

Distribution and Density. It is reasonable to hypothesise that the flaw acuity is the main factor governing the arrangement of macro-hydride colonies because hydride features require H accumulation in accordance with causality and hence the stresses of the loaded flaw since the long-range H transport is mediated by the stress gradients; grain boundaries and other lower-dimensional defects also contribute to the local stress state but these secondary effects are responsible for the mid-range H clustering to the nucleation sites. This hypothesis is based on empirical understanding as well as the theory of phase transformation in metals [Puls (2012), Cui et al. (2009), Christian (2002), and Banerjee and Mukhopadhyay (2010)].

This hypothesised effect of the flaw acuity on the macro-hydride colony distributions is visualised in FIG. 8.9 where the macro-hydride colonies emanate radially outwards from the flaw tip to lower the strain energy, which is also observed in seminal experimental studies [Cui et al. (2009) and Schofield (2002)]. Comparing the sharp crack and blunt notch regimes in TAB. 8.1, the blunt notch is a large H attractor whose size leads to twice as many hydride features in the Zr microstructure; however, a significantly denser hydride population ahead of the sharp crack because the H enhancement is more localised to the flaw tip in the case of the sharp crack. These simulations lend credence to empirical claims that implicate the sharper flaw acuities in lowering DHC initiation threshold [Puls (2012)].

Note 21

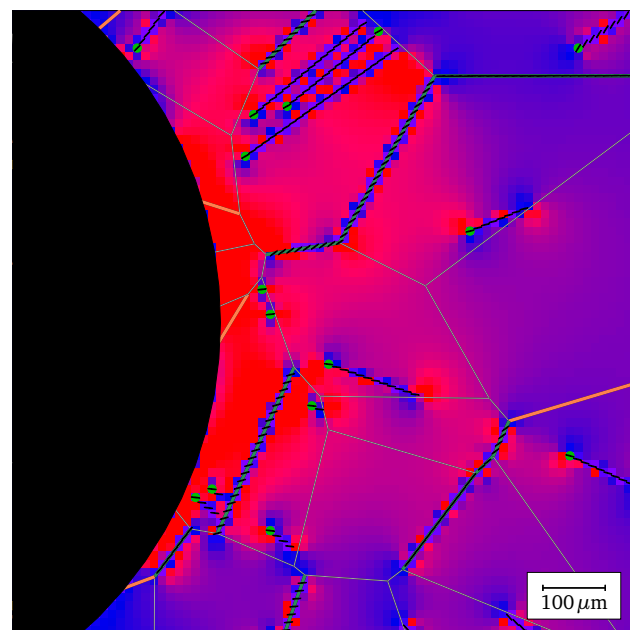
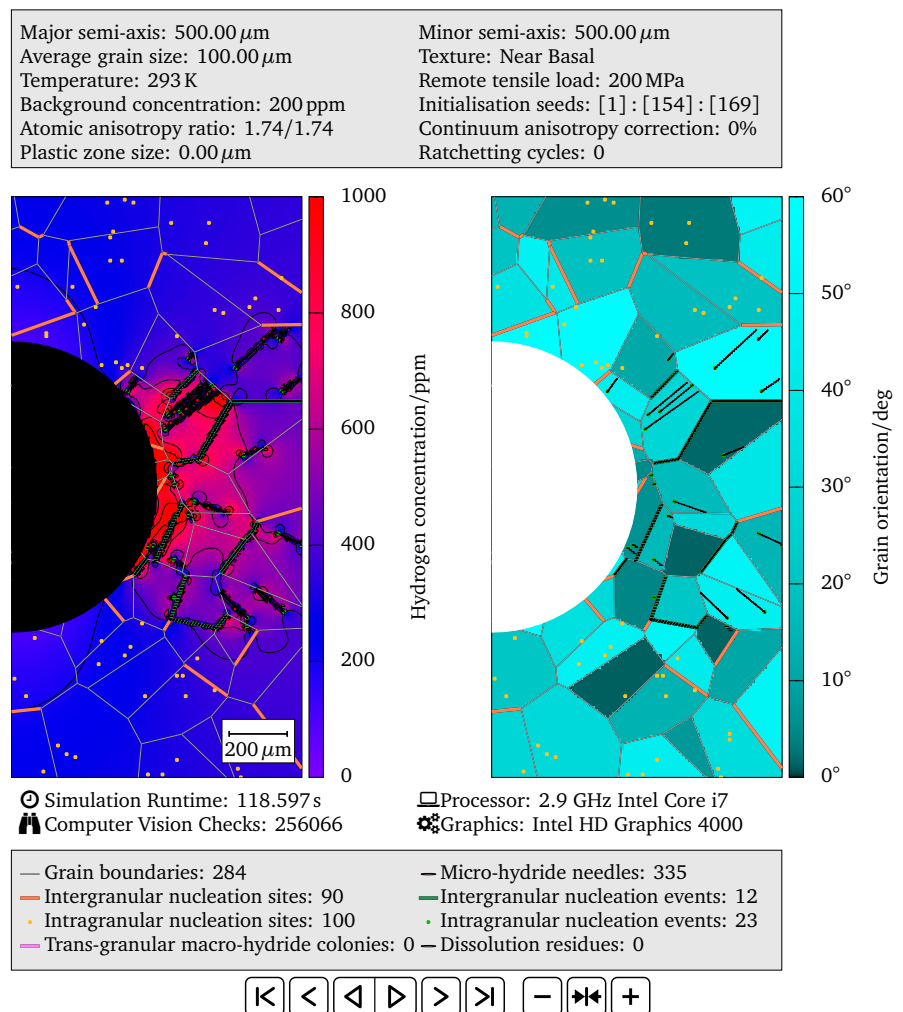
Mechanistic modelling of grain boundaries

It is worth stating again that grain boundaries play a fairly superficial role in the primitive version of the multiscale model. The modelling strategy essentially invokes established SEM and TEM images, which simply confirm the existence of the hydride features at grain boundaries; these experimental evidence suffices in order to construct the basic geometrical rules that are needed to treat intergranular nucleation. However, the actual mechanistic role of the polycrystalline microstructure on the macro-hydride colony distributions requires explicit knowledge of the stresses at the grain boundaries as a function of the anisotropic crystal misorientation, and CPFE modelling is one possibility. However, the continuum stresses may not be the sole criterion that leads to hydride precipitation; localised atomic scale distortions may also control the phase transformation process. In general, further empirical evidence and first-principles computations are required in order to devise a more rigorous mechanistic framework to treat grain boundaries at intergranular nucleation sites.

FIG. 8.9

Simulated micrographs of the flaw-tip hydride microstructure as a function of the flaw acuity

The regions of H enhancement and prospective nucleation events overlaid with the macro-hydride colonies whose substructure is composed of micro-hydride needles in a staircase-like stacking arrangement. The intragranular macro-hydride colonies have been configured to minimise the overall system strain energy whereas the intergranular macro-hydride colonies coincide with the corresponding grain boundary. Micro-hydride needles occupy the orientation that minimises the strain and interfacial energies in accordance with the preferential orientations along specific grain directions; these directions are sampled using the texture map. (a) The micro-hydride needles have been chosen to be $10\mu\text{m}$ in length simply for visualisation purposes. (b) A closer look at the H enhancement around the flaw-tip macro-hydride colonies. For the sharp crack, there are fewer macro-hydride colonies but they reside within a small region ahead of the notch tip. For the blunt notch, there are several more macro-hydride colonies but their distribution is sparser. Observe that the radial orientation of the intragranular macro-hydride colonies is energetically favourable, which agrees with experimental work. These simulated hydride microstructures convey the complexity of the DHC failure mechanism. The diffusion-precipitation analysis is not a trivial extension of the stress-diffusion analysis that underpins the conventional PF and FE models. That is, the mesoscale representation of the macro-hydride colonies cannot be easily extracted from the simulated H profiles alone.



Anisotropy and Heterogeneity. The hybrid model provides the machinery to study the separate and combined mesoscale effects of the HCP crystallography and polycrystalline microstructure. It is apparent that the sizes of the macro-hydride colonies and the distribution density of the hydride population are closely related to the standard microstructural properties such as the grain size, texture, alloy composition [Chamaa et al. (2018) and Puls (2012)]. Large grains allow intragranular macro-hydride colonies to grow without being interrupted by the impenetrable grain boundaries, and long grain boundaries generate extended tensile zones that enable intergranular macro-hydride colonies to grow along the entire interfacial length. Certain alloying additions reside as SPP inclusions in the matrix whilst operating as intragranular nucleation sites; a large number of SPP inclusions can lead to dense hydride microstructures [Chamaa et al. (2018)]. Such microstructural effects are reasonably straightforward to explain through theory and experiment, and these observations agree with the simulated H profiles.

Quantifying the effects of the texture is arguably a more challenging problem to decipher with simple reasoning. The HCP crystallography of Zr contributes to the overall anisotropic properties and behaviour of the heterogeneous metal at various length scales.^{Note 22} Nevertheless, an attempt is made here to quantify the effects of texture through two multiscale parameters: (i) the atomic anisotropy ratio of the components of the elastic dipole tensor for H in Zr as obtained through DFT calculations or APT experiments; and (ii) the continuum anisotropy correction to the stress state which has its origins in the dislocation distribution model of fracture in anisotropic continua [Nazarov et al. (2016) and Barnett and Asaro (1972)]. The latter is particular crude but it is a starting point as a means to bridge the length scales without affecting the simulation runtime.

Consider the H profile visualised in FIG. 8.10, in which the relative orientation a single critical grain near the flaw tip is varied. As the misorientation changes, intergranular nucleation sites appear and disappear whilst the contours of H enhancement become distorted. This distortion is quite tame for the near basal texture but, as shown in FIG. 8.11, it can be quite drastic on the anisotropic prism and pyramidal planes even without the compatibility stress corrections at grain boundaries.

Industrial Application. These simulated hydride microstructures deconstruct the multiscale complexity of the early stages of DHC failure into simple mesomechanical cause-and-effect relationships. These parametric studies imply that ideal Zr alloy design would have finer grain sizes to restrict colony growth as well as controlled texture and fewer alloying additions to respectively minimise intergranular and intragranular nucleation sites.^{Note 23}

Note 22

Multiscale representation of crystalline anisotropy and polycrystalline heterogeneity

At the continuum scale, the compatibility stresses due to misorientated grains distort the otherwise smooth and continuous stress contours. At the microstructural scale, the hydride-matrix interfacial energies characterise specific orientation relationships that promote precipitate growth in one direction and inhibit it other directions. At the atomic scale, the tetrahedral interstitialcy biases H diffusion along the [0001] directions due to the trigonally symmetric bonding with the Zr atoms. So the mesoscale effects of the texture cannot be easily linked to a single modelling parameter.

Note 23

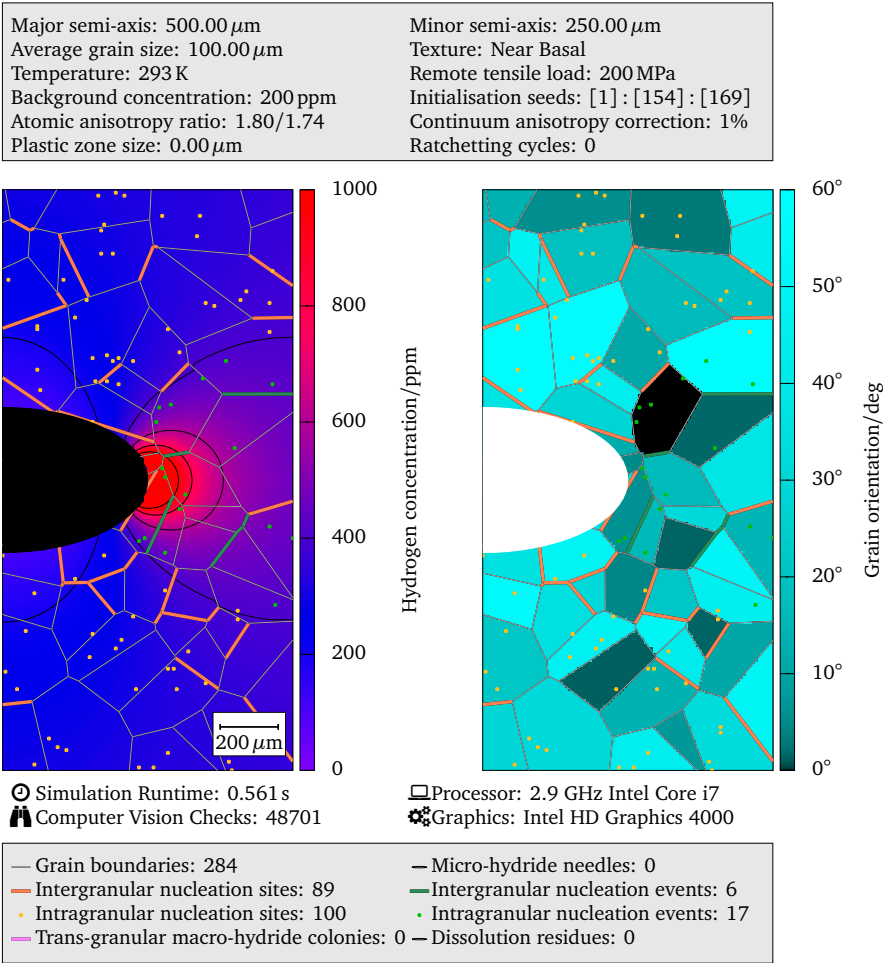
Inexpensive parameter space exploration

Commercial alloys do indeed possess such microstructures but these have been found through extensive trial-and-error empiricism that requires expensive experimentation. The hybrid multiscale model provides the computational framework to endlessly explore the full parameter space and finetune the component properties to mitigate the risk of DHC failure given a specific flaw acuity.

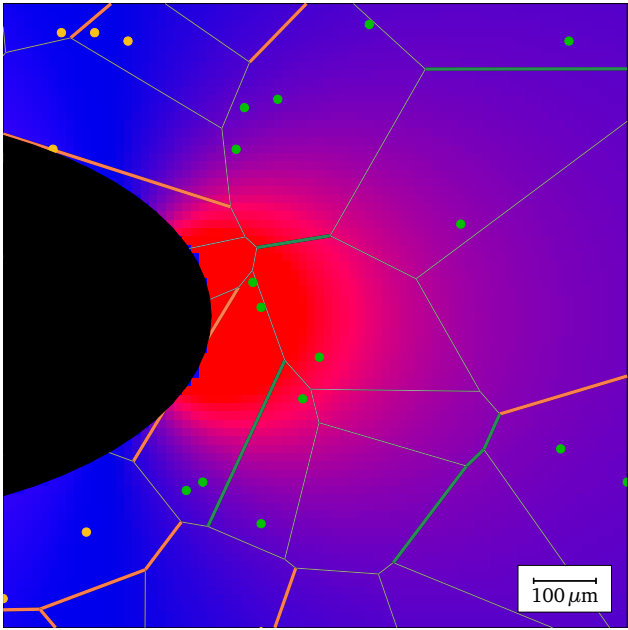
FIG. 8.10

Simulated micrograph of the flaw-tip hydrogen profile as a function of the local texture

The regions of H enhancement and prospective nucleation events in a polycrystalline Zr specimen with a randomly fixed near basal texture except for a lone critical grain whose orientation can freely vary. The chosen elastic dipole component ratio and stress correction percentage reflect a near basal regime at both atomic and continuum scales of the description. (a) The overall microstructure and the corresponding texture map. (b) A closer look at the H enhancement and the changes in the intergranular nucleation sites and events. Moreover, these findings indicate that there is some critical combination of the flaw acuity, grain size and texture which would exacerbate the risk of DHC initiation. But further model development is required to shed more insight on the role of the flaw acuity and the microstructure on the distribution of macro-hydride colonies in the Zr materials used in industry.



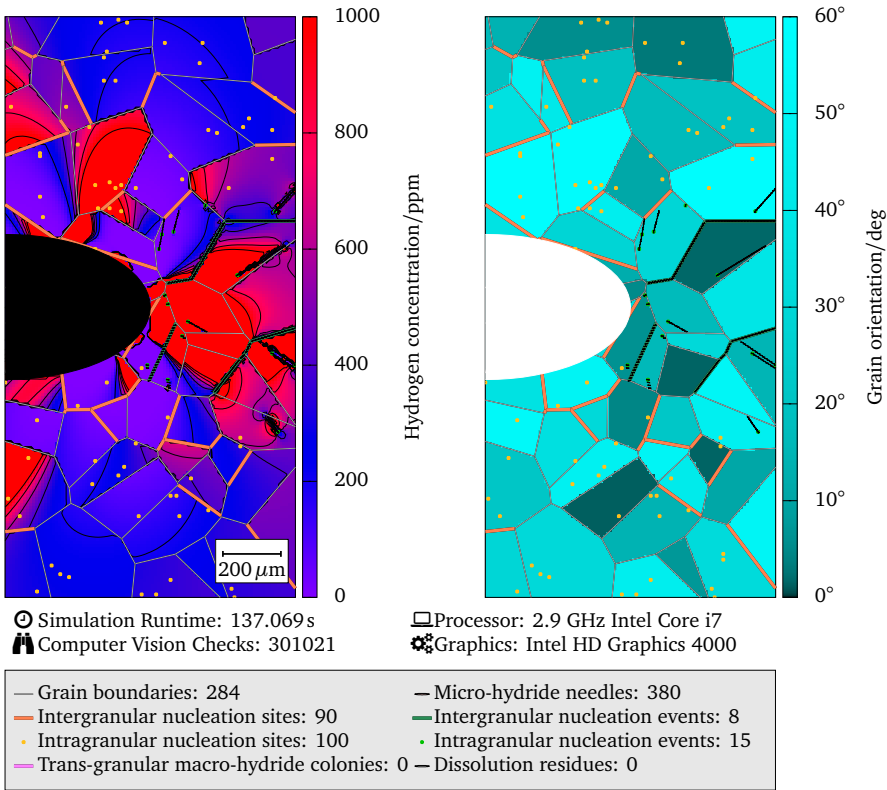
(a) Animation available in the digital format.



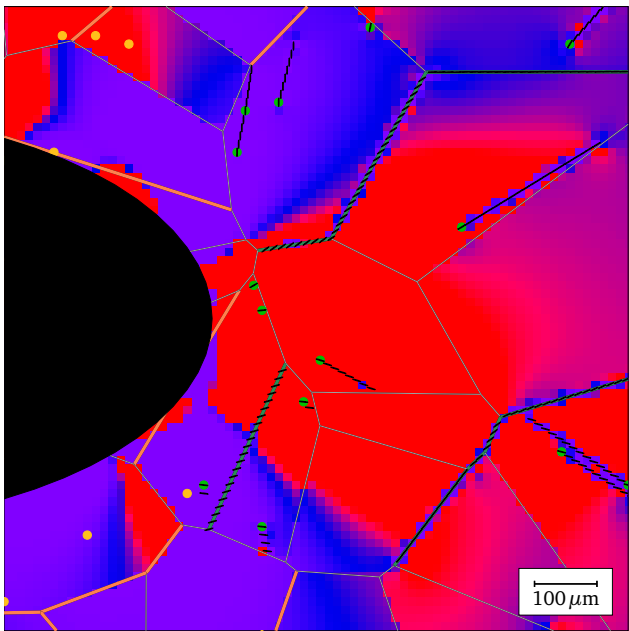
(b) Animation available in the digital format.

Major semi-axis: 500.00 μm
Average grain size: 100.00 μm
Temperature: 293 K
Background concentration: 200 ppm
Atomic anisotropy ratio: 2.36/1.74
Plastic zone size: 0.00 μm

Minor semi-axis: 250.00 μm
Texture: Misorientated Prism
Remote tensile load: 200 MPa
Initialisation seeds: [1] : [154] : [169]
Continuum anisotropy correction: 10%
Ratchetting cycles: 0



(a) [Animation available in the digital format.](#)



(b) [Animation available in the digital format.](#)

FIG. 8.11

Simulated micrograph of the flaw-tip hydrogen profile as a function of the global texture

The regions of H enhancement and prospective nucleation events overlaid with the hydride features in a polycrystalline Zr specimen with increasingly anisotropic textures as quantified by the atomic scale and continuum scale anisotropy parameters. The three texture labels are inexact but they do provide a rough description of the possible Zr alloy texture in the simulation. (a) The entire flaw-tip hydride microstructure alongside the texture map. (b) A closer look at the hydride microstructure and clear demonstration of the one of the key limitations of the multiscale model in its current form, namely, the absence of stresses due to the misorientated grains. But it is apparent the elastic dipole tensor creates many discontinuities in the H profile, which would also be the case with the compatibility stress corrections in advanced CPFE models. These simulations suggest that the CPFE models should also account for the atomic scale anisotropy, which would also be necessary for overall self-consistency.

8.2.2 Precipitation-Dissolution Memory

The simulated H profiles and hydride microstructures thusfar do not explore the role of history, which is an essential precursor to the ratchetting phenomenon that leads to DHC initiation over thermomechanical cycles. In standard FE models of DHC failure, temperature and loading histories are effectively inputs based on the empirical two-solvus TSSp/d hysteresis rather than outputs that should be a natural consequence due to an explicit treatment of the memory mechanisms [Jernkvist and Massih (2014) and Shek and Xu (2015)]. As a simple demonstration, one such rudimentary mechanistic memory effect is considered within the scope of the hybrid multiscale model. It is understood that repeated precipitation-dissolution cycles deform the Zr matrix as plastic energy is dissipated into microstructure, and TEM studies do indeed show the presence of dislocations around the micro-hydride needles [Darby, Martin, and Scarth (2013) and Carpenter, Watters, and Gilbert (1973)]. These dislocations can operate as the agents of the memory mechanism because they are stress generators that can trap H atoms. Each precipitation event leads some plastic relaxation around the micro-hydride needles and each dissolution event leaves behind some residual stress in the vicinity of the nucleation site; repeated precipitation-dissolution cycles augment the intensity of the residual stresses. ^{Note 24}

Note 24

Mechanistic foundations of the precipitation-dissolution hysteresis

There is still much speculation about the exact nature of the memory effects that underpin thermal ratchetting. Nevertheless, it is still worthwhile to demonstrate one possible origin of the ratchetting phenomenon which is straightforward to simulate within the current scope of the hybrid multiscale model. (No significant modifications must be made to the stress, stress-diffusion and diffusion-precipitation analyses in order to convey the dissolution history.) However, a mechanistic approach is necessary because the standard TSSp/d hypothesis is inconsistent with the phase rule for the two-component thermodynamic system with a solid solution phase and a stable hydride phase composed of the chemical species, Zr and H, which implies only two degrees of freedom, namely, temperature and pressure.

In the hybrid multiscale model, this precipitation-dissolution memory must be consistent with the H mass conservation criterion that presides over the nucleation events. In the forward phase transformation direction, diffusible H atoms in solid solution are locked into the precipitating hydride phase. In the reverse phase transformation direction, these H are reintroduced into the diffusible concentration profile as the hydride phase dissolves but another stress update can be applied to represent the residual. Accordingly, the self-consistency of the H mass conservation principle remains intact but the memory mechanism is reflected in the changes to the local stress state after each cycle. This concept is realised in FIG. 8.12 which shows the simulated hydride microstructure over ten thermomechanical cycles. After the first thermomechanical cycle over which the hydride features are annealed, some H trapping occurs where macro-hydride colonies once resided. After the tenth thermomechanical cycle, the trapped H concentration has increased drastically, which is a clear demonstration of the mechanistic foundations of the precipitation-dissolution memory effect. Subsequent nucleation events may occur at higher temperatures upon cooling because the trapped H concentration is sufficient enough to satisfy the H mass conservation principle. That is, it is not necessary to assume the TSSp/d hysteresis; ratchetting can be explained by the residual stress build-up.

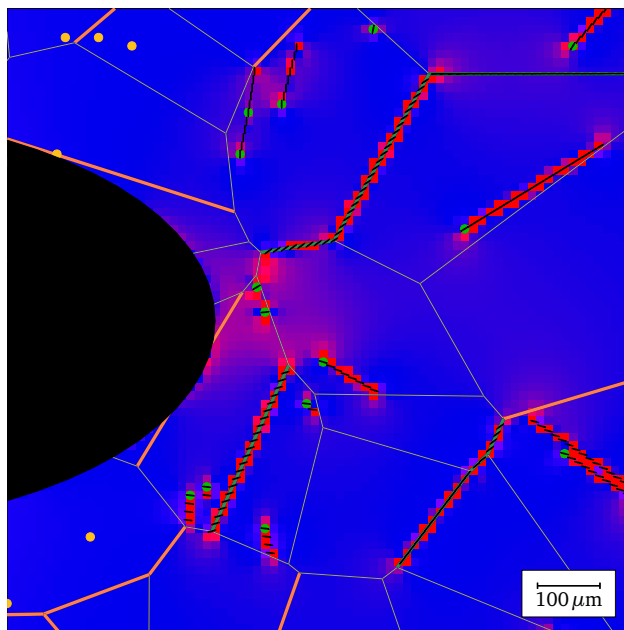
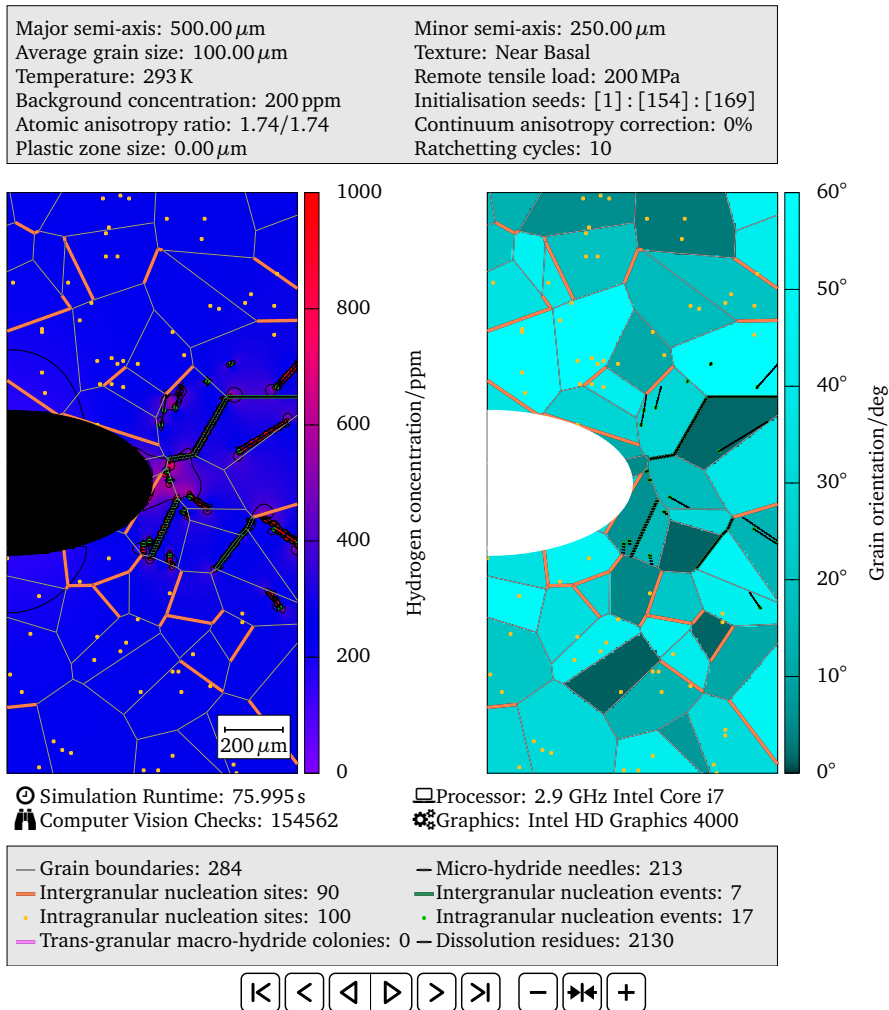


FIG. 8.12

Simulated micrograph of the flaw-tip hydrogen profile and hydride microstructure as a function of the histories of thermo-mechanical cycles

The regions of H enhancement and prospective dissolution residues over a series of ratchetting cycles during which micro-hydride needles and macro-hydride colonies are formed upon cooling down and annealed upon heating up. The first precipitation-dissolution cycle leaves behind a tensile hydrostatic stress source at the original site of every nucleation event. The tenth precipitation-dissolution cycle doubles the intensity of this initial residual hydrostatic stress. This tensile dissolution residue is represented by a Volterra dislocation dipole in an analogous manner to the precipitate features, but the slip vectors have opposite signs; the reasoning behind this approach is justified in a later discussion on the mechanistic origin of the TSSp/d hysteresis. (a) The memory effect is evident as the dissolution residues generate the tensile stresses to trap the H and hence facilitate precipitation at existing nucleation sites during cooling. The contours of the H trapping coincides with the morphologies of the intergranular and intragranular macro-hydride colonies. (b) A closer view of the flaw-tip H enhancement where it is clear that there is ratchetting in the H concentration from the first to the tenth cycle. As previously stated, further model development is required to improve the temperature dependencies in the stress, stress-diffusion and diffusion-precipitation analyses so this demonstration of the memory effect must be considered in accordance with these limitations. Nevertheless, this promising result justified the need to include a mechanistic treatment of the dissolution kinetics in order to predict ratchetting without resorting to the empirical TSSp/d curves.

Note 25*Relative simulation accuracy*

Acknowledging that total quantum mechanical energies provide the most complete representation of the material properties and behaviour, one possible classification system has been adopted in this multiscale endeavour, which adheres to the following relative definitions: (i) quantitatively accurate methodologies compute quantum energetics within some numerical precision; (ii) qualitatively accurate methodologies estimate the trends in quantum energetics; (iii) phenomenologically accurate methodologies attempt to capture the microscopic consequences of the quantum energetics but usually without any explicit references to the quantum mechanical state; and (iv) topologically accurate methodologies do not consider the quantum energetics at all but utilise some macroscopic benchmark that can be readily measured in experiments. Note that each category has its own advantages and disadvantages in terms of usage, and these definitions do not say anything about the relevance of the modelling strategy in practical settings. Of course, in general, some experimental comparison is necessary in model validation and it is clear that phenomenologically and topologically accurate modelling strategies provide the most suitable connection to experimental studies in the context of DHC research. Conventional PF models tend to be phenomenologically accurate whereas FE models may be described as topologically accurate.

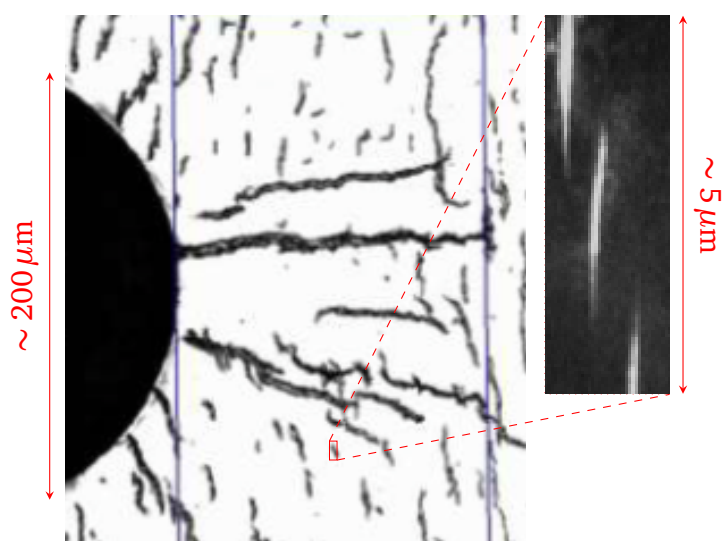
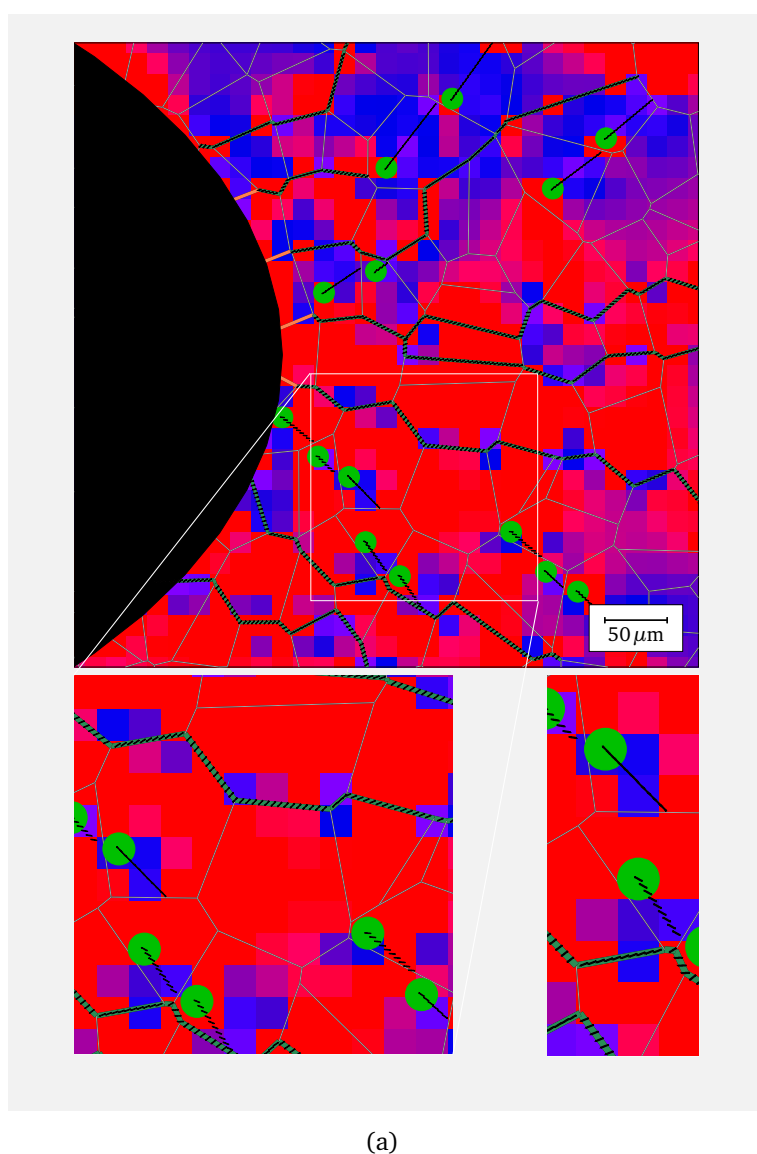
8.2.3 Accuracy-Efficiency Paradigm

There has been a running commentary about the importance of simulation accuracy and simulation efficiency throughout the development of the hybrid model because the balance between these two computational metrics is essential to nuclear fuel performance codes that can be employed within nuclear safety assessments. At the beginning of this investigation, the respective notions of simulation accuracy and simulation efficiency were introduced in a fairly superficial manner without any prelude to the DHC failure mechanism. Now that the capabilities of the hybrid model have been demonstrated—following a deep dissection of the DHC phenomenon as well as a detailed breakdown of the standard modelling methodologies—it is a more opportune moment to revisit and recontextualise the accuracy-efficiency paradigm.

Simulation Accuracy. Several definitions and classification systems have been suggested as a means of categorising the standard modelling strategies according to their overall accuracy.^{Note 25} In general, multiscale methodologies are seldom confined to one particular definition [Vvedensky (2004) and Curtin (2017)]. But the hybrid multiscale model may be classified as phenomenologically accurate because the simulated micrographs attempt to capture the SEM and TEM observations using the diffusion-precipitation analysis whose mesoscale formulation has been guided by experiments as well as earlier DFT, PF and FE modelling strategies.

The hybrid multiscale model is intermediate to the PF and FE models in terms of the length scales, and modelling concepts at each length scale have different simulation accuracies. Quantum energetics cannot be reliably inferred from the simulated micrographs but *ab initio* calculations have been used to parametrise the elastic dipole tensor that underpins the stress-diffusion analysis. However, the main contributions to the free energy are consistent with PF models which have inspired the algorithmic diffusion-precipitation analysis. The complete stress state is unavailable in the simulated hydride microstructures as the linear stress analysis only explicitly treats certain micromechanical defects, namely, the flaw, micro-hydride needles and H interstitials, whereas there is only an implicit notion of the stresses due to other defects such as grain boundaries, inclusions and dislocations; however this partially accurate stress state puts the hybrid multiscale on par with the FE models, albeit with a lower topological precision.

After qualifying the simulation accuracy with respect to other modelling strategies, experiments provide a more definitive measure. The most detailed simulated micrograph in FIG. 8.13 can be meaningfully compared with SEM and TEM images, which is completely novel in DHC research.



(b) Adapted from Shek and Xu (2015) and Perovic, Weatherly, and Simpson (1983).

FIG. 8.13

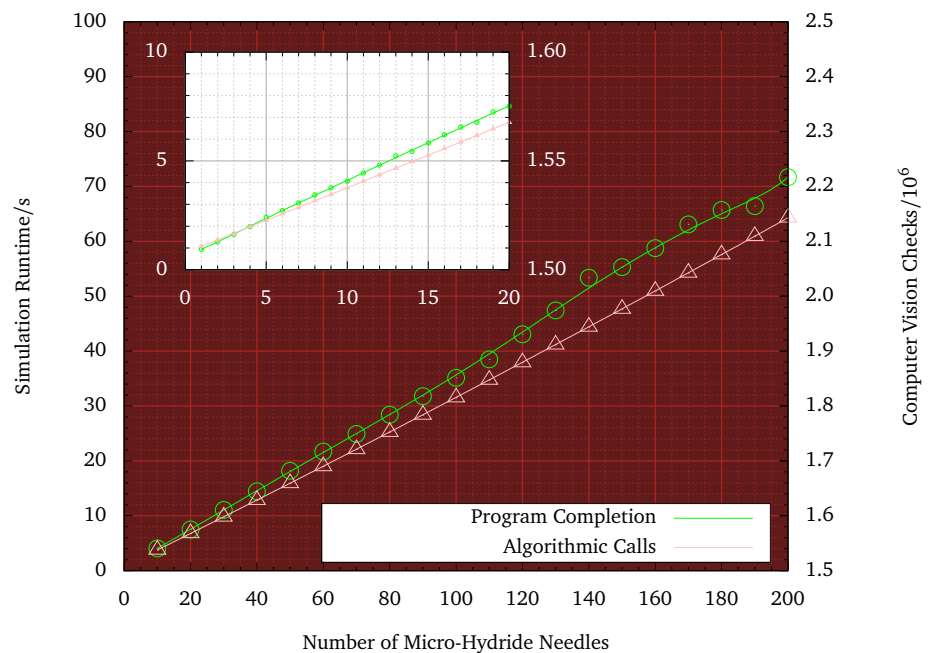
Mesoscale comparison of the simulated micrographs with SEM and TEM images

The phenomenological accuracy of the hybrid multiscale model as measured through a highly detailed simulated micrograph that can be placed alongside experimental SEM and TEM studies in understanding how DHC failure may transpire. Simulation parameters are carefully selected to match the chosen experiments, including the $2\mu\text{m}$ lengths of the micro-hydride needles as well as an average grain size of $50\mu\text{m}$, which is a typical upperbound for commercial Zr alloy specimens. A low intragranular nucleation site is assumed but transgranular continuation of the autocatalytic sequence is permitted. (a) A simulated hydride microstructure with ~ 100 nucleation sites and ~ 1000 micro-hydride needles as well as a dozen transgranular macro-hydride colonies which themselves are composed of networks of smaller intergranular and intragranular macro-hydride colonies. Despite these quantities, the simulation runtime was still relatively short at $\sim 300\text{s}$, which is a testament to the simulation efficiency. (b) A SEM image showing infamous flaw-tip hydride patterns in which the hydride features emanate radially outwards from the notch; the TEM inset shows the possible staircase-like substructure. In comparison to these experiments, the simulated micrograph shows similar hydride distributions and densities, which have been determined using the same thermodynamic concepts that underpin PF modelling but through a more optimised algorithmic scheme to minimise the free energy. The hybrid multiscale model correctly predicts the morphologies of the transgranular macro-hydride colonies whose mean size $136.2\mu\text{m}$ agrees with hydride process zone length of $132.6\mu\text{m}$ in this particular experiment.

FIG. 8.14

Algorithmic complexity of the hybrid multi-scale model

The post-initialisation simulation runtime to program completion and the number of geometric PIP, PLSI and LSI checks as a function of the number of micro-hydride needles in the simulated micrographs. Each micro-hydride needle must be positioned within a grain using a PIP algorithmic call, and then it must be subsequently reviewed with PLSI and LSI algorithmic calls which monitor forbidden microstructural configurations. The linear scaling is optimal because it ensures that continued statistical modelling remains within the realm of possibilities. By inspection, the number of grains and grain boundaries would also have a multiplicative effect on the scaling.



Simulation Efficiency. It is worth estimating the computational complexity before any further model development. Computational complexity can be defined in terms of the processing time as well as computing memory requirements. Accordingly, the simulation runtime and the number of geometric checks can be used to gauge the simulation efficiency. As plotted in FIG. 8.14, the hybrid multiscale modelling strategy scales linearly with the number of micro-hydride needles. The typical simulation runtimes range from seconds to minutes, which is convenient in the industrial setting where statistical modelling is important. Additional microstructural rules based on computational geometry should not be too problematic as long as any microstructural positioning is handled by the graphics card, which has dedicated hardware that is needed to implement computer vision.

Acknowledging the phenomenological accuracy of the hybrid multiscale model, the simulation runtimes should really only be compared with the PF methodology, but these PF models require numerical PDE solvers, which is similar to the FE methodology. In such PF and FE models, finer spatial resolutions and smaller temporal gradations increase the simulation runtime; convergence of the numerical PDE solution is the limiting factor. The hybrid multiscale model bypasses this limitation through the use of analytical and semi-analytical formulae in the stress and stress-diffusion analyses. Any extensions must adhere to this modelling philosophy and preserve this simulation efficiency.

8.3 Advanced Extensions

As it stands, the proposed framework captures two of three primary factors that govern DHC initiations, namely, the flaw acuity and microstructure. However, the third of these factors—thermomechanical cycling—is arguably the most important to industry and hence it requires a more serious consideration here. In order to address this omission, two modelling extensions are formalised to capture the reorientation of circumferential hydrides and the increase in the volume fraction of radial hydrides over a series of thermal cycles. These two modelling extensions together serve as predictive tools for studying thermal ratchetting within the proposed framework.

8.3.1 Thermal Ratchetting

Thermal ratchetting is often attributed to the TSSp/d hysteresis, and FE models of DHC typically assume this empirical two-solvus relationship as input [[Jernkvist and Massih \(2014\)](#) and [Shek and Xu \(2015\)](#)]. In principle, the same assumption can be made within the current framework. However, from the standpoint of thermodynamics, such a two-solvus system is non-physical for the two-component Zr-H system in accordance with the Gibbs phase rule. Therefore, it cannot be used to develop a predictive framework for modelling the ratchet phenomenon.

Instead, it is postulated that the ratchet phenomenon is fundamentally a consequence of the irreversible dislocation-based plastic relaxation around misfit caused by the newly formed micro-hydride needles. That is, some dislocations punched out by precipitates to relax the elastic stresses remain in the matrix when precipitates are dissolved on heating. These dislocations can trap H and hence the overall H content in the nucleation site increases with each cycle. This hypothesis is supported by experimental observations of a larger TSSp/d hysteresis being exhibited by irradiated Zr alloys. Conversely, annealing out the radiation damages shifts the TSSp/d values to their unirradiated counterparts [[McMinn, Darby, and Schofield \(2003\)](#)].

Dislocation Dynamics. In order to predict the ratchet phenomenon, the current treatment of hydride precipitation must then be modified to include the kinetics of growth and dissolution. This requires a mechanistic model that captures the evolution of the dislocation microstructure around a micro-hydride needle as it precipitates and dissolves. A sensible starting point is to embed within a DDP simulation the dislocation dipole model of micro-hydrides. As a multiscale methodology in its own right, DDP explicitly evaluates the many-body interactions between crystallographic dislocations whilst enforcing constitutive rules that dictate nucleation from Frank-Read

sources and annihilation in close proximity as well as pinning to obstacles and pile-ups at impenetrable barriers such as sites of irradiation damage and grain boundaries [van der Giessen and Needleman (1995)]

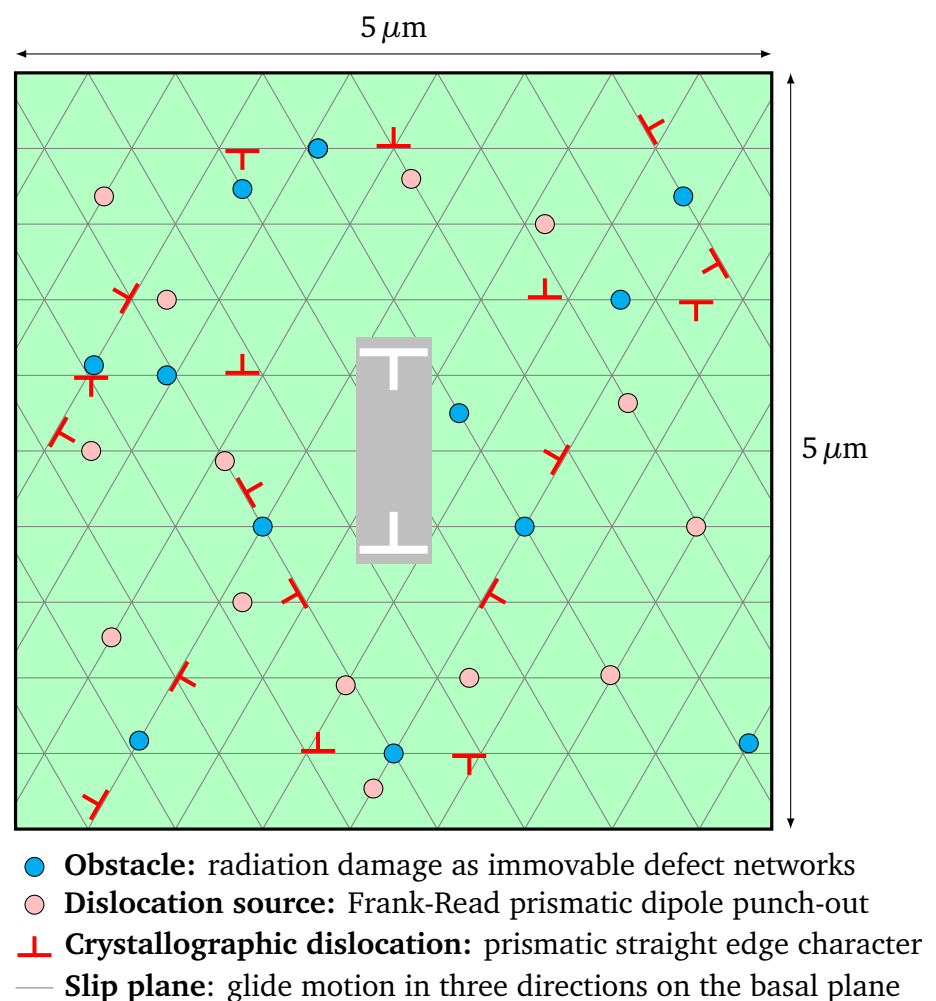
In the following, a simple planar DDP methodology is proposed to demonstrate plastic relaxation associated with hydride precipitation and the non-recoverability of this plastic strain energy upon hydride dissolution [Patel et al. (2017)]. As this work concerns the micro-hydride needles in the bulk, it is justifiable to assume an infinite continuum as usual but also restrict attention to the scale of an individual nucleation site by working within a $5\ \mu\text{m} \times 5\ \mu\text{m}$ simulation cell around one micro-hydride needle. This setup is shown in FIG. 8.15, which is an adaptation of the standard DPP framework. Supposing a coherent interface and surface diffusion of H atoms to and from the long edges of the hydride-matrix interface, it is possible to depict the micro-hydride thickening (or thinning) by increasing (or decreasing) the hydride Burgers vector.

FIG. 8.15

A discrete dislocation plasticity model of a micro-hydride needle

As the micro-hydride needle grows during the cool down stage of the thermal cycle, the stress increases in the surrounding matrix, which eventually leads to plastic deformation. Plasticity occurs through the nucleation and glide of a large number of discrete dislocations on prismatic slip planes.

Adapted from Patel et al. (2017).



Dissolution Residues. As hydrogen accumulates in the nucleation site, the micro-hydride needle continues to grow until it reaches a critical size, at which point its misfit accommodation results in plastic relaxation and the dissipation of plastic strain energy into the Zr matrix. As seen in **FIG. 8.16**, this plastic relaxation is represented by the extensive dislocation network. In particular, the dislocation pile-ups may be viewed as sections through the concentric loops of prismatic dislocations observed in experiments [Carpenter, Watters, and Gilbert (1973)]. Upon dissolution, however, a substantial residual dislocation density remains in this region, which corresponds to the non-recoverability of the plastic strain energy associated with hydride formation.

As evident from **FIG. 8.16**, a residual tensile hydrostatic stress state exists at the nucleation site after dissolution, which provides a positive potential for H diffusion in the Zr specimen. This residual tensile state is also obtained for the different realizations. This is because dislocations nucleate and configure so as to minimize the total strain energy of the system by counteracting the compressive field of the micro-hydride needle. Thus, a residual tensile stress state remains upon dissolution of the compressive field. These dislocation networks may play a role in trapping H from dissolving hydrides as well as acting as an enhanced stress-raiser in the vicinity of the nucleation site to drive H diffusion from the bulk, both of which make subsequent re-precipitation more favorable; this is consistent with the observation that hydrides increase in number as thermal cycling progresses.

The evolution of the dislocation density over sequential thermal cycles is shown in **FIG. 8.17**. The dislocation density reaches a peak at maximum precipitate thickness, after which it begins to decrease as dissolution occurs. However, as noted previously, a residual dislocation density remains even after dissolution. It can be seen that there is a steady increase in the residual dislocation density following multiple dissolutions. This ratcheting in the dislocation density suggests that over time a nucleation site may become more effective at precipitating hydrides due to the interaction between hydrogen interstitials and an increasing dislocation population. Recall that this hypothesis was tested in **FIG. 8.12**, which lends some support to this dislocation mechanism as the origin of the TSSp/d hysteresis.

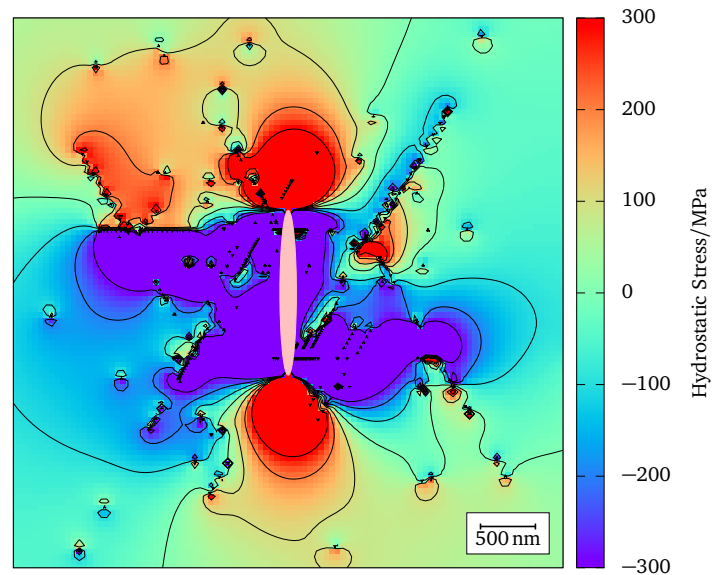
Furthermore, obstacles were introduced to study the effects of irradiation damage; for example, it is known that interstitial clusters can impede dislocation motion. As evident, the dislocation density is higher for the irradiated material as the obstacles help to confine the dislocation network to a smaller region around the nucleation site. This supports the experimental findings in TSSp/d hysteresis is identified to be greater for irradiated Zr alloy components [McMinn, Darby, and Schofield (2003)].

FIG. 8.16

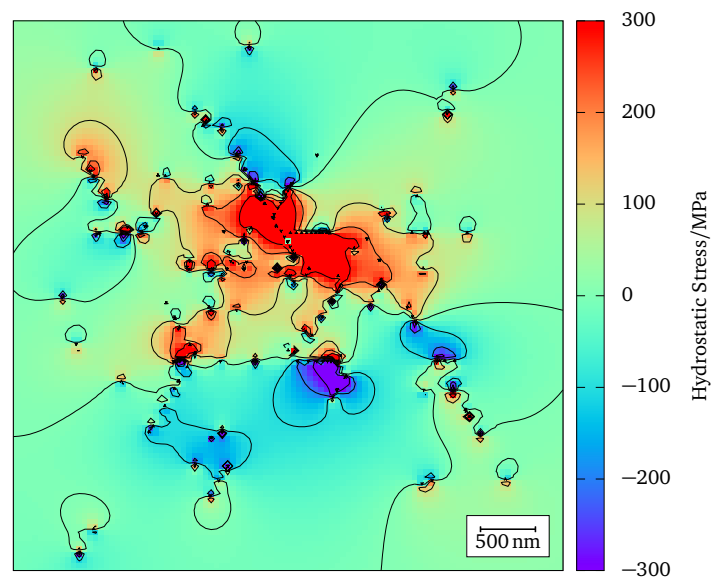
The evolution of the dislocation microstructure around a micro-hydride needle

A typical realisation of the dislocation structure at (a) maximum hydride thickness and (b) upon dissolution. Observe the residual tensile stress state in the vicinity of the nucleation site upon dissolution.

Adapted from [Patel et al. \(2017\)](#).



(a)



(b)

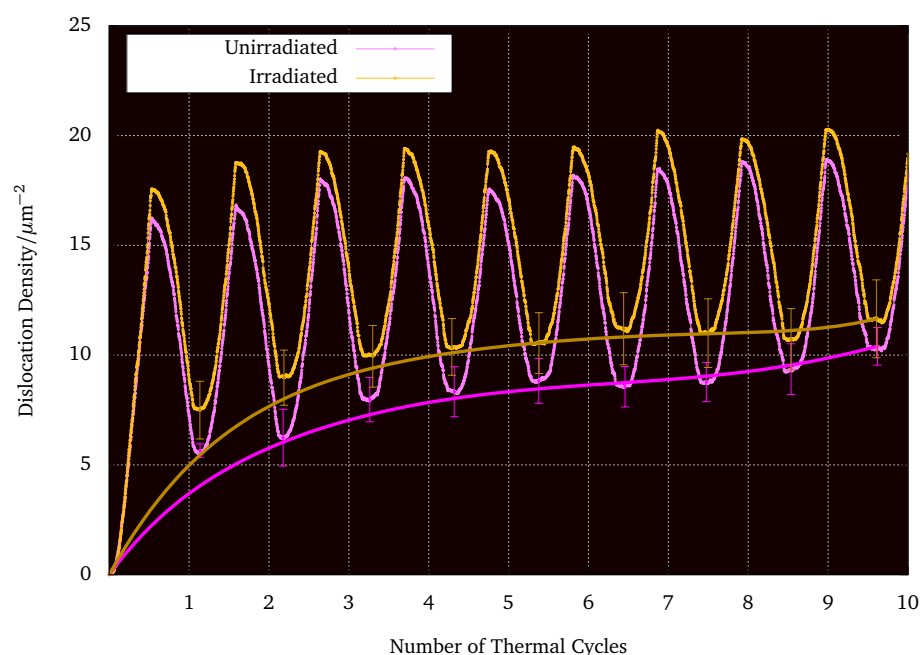


FIG. 8.17

The ratchetting of the dislocation density
 The ratchetting of dislocation density in unirradiated (without obstacles) and irradiated (with obstacles) zirconium for (a) a series of thermal cycles and (b) repeated dissolutions. The results are averaged over three DDP realizations and error bars are shown in (b) for the residual dislocation density. Adapted from [Patel et al. \(2017\)](#).

Implementation Strategy. The question remains as to how this microscale discrete dislocation-based mechanism can be incorporated within the hybrid multiscale model whilst preserving its simulation efficiency. One simple approach is to treat the fully formed micro-hydride and its dislocation microstructure as a sub-model for precipitation events. That is, the entire DDP simulation cell can be added as a precipitate class upon the activation of a nucleation site. Then upon dissolution, this sub-model can be replaced by the residual dislocation network. In this way, the residual tensile field can be coupled to the stress-diffusion analysis to reproduce the effects of TSSp/TSSd hysteresis and hence predict thermal ratchetting.

Further work is required to justify this claim but, as previously stated, this premise was crudely applied in [FIG. 8.12](#) with some success, and so this approach does appear to be somewhat promising in terms of the stress-diffusion and diffusion-precipitation analyses. It is essential to confirm that the dislocation ratchetting corresponds to increased strength in the residual tensile stress field, as this will quantify a time scale over which the H retention occurs. The respective sub-model stress states can be evaluated as ensemble averages over multiple realisations, and hence the eliminate any stochastic variations due to the simulated microstructural randomness.

8.3.2 Polycrystalline Microplasticity

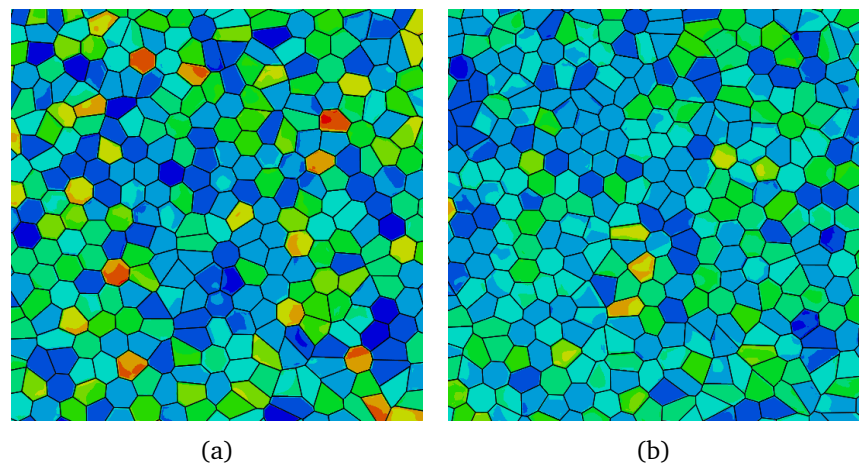
Experimental micrographs show conclusively that intergranular macro-hydride colonies do not reside along every grain boundary in the Zr alloy microstructure [Chamaa et al. (2018)]. That is, only certain grain boundaries operate as favourable intergranular nucleation sites; the underlying reason can be attributed to the microscale elastoplasticity in the vicinity of the interfaces between highly misorientated HCP crystallites. Hence, the absence of the compatibility corrected stresses is a major oversight because it is not possible to predict which grain boundaries can drive the mid-range clustering of H or control the morphological evolution of macro-hydride colonies. Therefore, the hybrid multiscale model must appropriately convey the stress state in anisotropic heterogeneous Zr alloys.

Crystal Plasticity. Stresses in polycrystalline media can be approximated using the multiscale CPFE methodology which numerically solves elastomechanical equilibrium PDE under the requirements of the strain compatibility criteria as well as constitutive material behaviour response equations and specific initial and boundary conditions. The compatibility corrected stresses have important micromechanical consequences [Dunne and Petrinic (2005)]. Considering the stress states of the two different polycrystalline Zr microstructures shown in FIG. 8.18, it is evident that the texture affects the overall stress profile. In particular, there are more tensile pockets in the randomly textured material, which may be attributed to existence of highly misorientated crystallites. Grain boundaries in the vicinity of these tensile pockets would most likely act as potent intergranular nucleation sites in accordance with the stress-diffusion and diffusion-precipitation analyses.

FIG. 8.18

Stress state of polycrystalline zirconium
A two-dimensional CPFE model of uniformly loaded polycrystalline Zr specimen with the compatibility stress corrections. The red and blue regions respectively correspond to pockets of tensile and compressive hydrostatic stresses. (a) A randomly textured polycrystalline Zr microstructure that is characteristic of welds. (b) A highly textured polycrystalline Zr microstructure that is characteristic of rolled plates.

Adapted from Wilson and Patel (2017).



Implementation Strategy. Computational expenditure is the main drawback of explicitly calculating these compatibility corrections as part of the stress analysis. In particular, irregular boundary conditions due to complicated grain morphologies have to be solved numerically by brute force. Such a taxing overhead would undoubtedly compromise the simulation efficiency. Instead, consider a simplified alternative based on the computer vision of the tensile pockets.

The first step is to identify of a set of microstructural rules that reflect the statistical relationship between the different textures for a given morphology of grains and relative positions of the tensile pockets. This involves using an ensemble of CPFE simulations to deduce these rules. For example, one possible rule could dictate how these tensile pockets are usually located in the vicinity of grain boundaries that are shared amongst a group of grains with a particular set of relative misorientations. Then experimental studies could be used to confirm whether such grain boundaries do indeed operate as intergranular nucleation sites. If this proves to be case, additional microstructural rules can be devised to reflect the morphological growth of macro-hydride colonies at these intergranular nucleation sites as well as the configuration of micro-hydride needles within their substructure.

The second step is to determine a characteristic length scale that quantifies the distance ahead of the flaw tip beyond which the grain boundary stresses dominate over those of loaded flaw. This requires comparing the differences in the stress state in the isotropic and anisotropic heterogeneous representations of the microstructure. For a given average grain size and texture, this characteristic length scale should be parametrised by the flaw acuity and the loading regime.

The final step is then to initialise the intergranular nucleation sites within the simulation cell by using computer vision to locate the relevant sites beyond the characteristic length scale and then constructing their polygonal geometries. It is entirely possible that this characteristic length scale is negligibly small, in which case every grain boundary within the simulation cell would have to be checked. In this way, intergranular nucleation can be efficiently implemented within the hybrid multiscale model whilst implicitly accounting for the compatibility corrected stresses due to the polycrystalline microplasticity. [Note 26](#)

Note 26

Hydride reorientation during ratchetting

It is reasonable to state that this approach would enable the model to predict the formation of circumferential macro-hydride colonies whose morphological growth may be governed by the local microstructure rather than the tensile fields at the flaw tip. Such circumferential hydride patterns are observed prior to any thermomechanical cycling but a swirl distribution of macro-hydride colonies can be seen following industrial tests [[Cui et al. \(2009\)](#) and [Schofield \(2002\)](#)]. In conjunction with the previous analysis on the hysteresis, this newly extended framework should also, in theory, be able predict the swirl pattern that would inevitably occur as the dislocation microstructure naturally evolves over repeated thermal cycles as a response to negate any long-range grain boundary stresses, and thereby establish the flaw as the dominant stress-raiser in the system. Further work is needed to justify this hypothesis but this mechanistic framework provides the necessary tools to explore and predict the effects of thermal ratchetting.

8.3.3 Machine Learning

This investigation into DHC failure has delved deeply into multiscale mechanistic modelling through a careful review and application of experimental findings, theoretical concepts and computational methodologies. This physical insight into the hydrogenated and hydrided Zr alloy material properties and behaviour has preceeded the development of this bespoke software: an industrial code which can rapidly generate simulated micrographs that can be readily compared with experimental SEM and TEM images. Given the complexity of the DHC phenomenon, such a breakthrough modelling strategy could not have been conceived without understanding stress-driven diffusion of H interstitials and diffusion-controlled precipitation of hydrides across a spectrum of length and time scales. But there is an alternative modelling strategy involving machine learning that could entirely sidestep the tremendous effort required to gain this insight and understanding, which is becoming increasingly fashionable due to the advent of artificial intelligence in computational materials science [[Schmidt et al. \(2019\)](#)].

The explosive interest in machine learning has coincided with the data deluge that is touted as the fourth pillar alongside the experimental, theoretical and computational pillars of science [[Tansley and Tolle \(2009\)](#)]. In general, however, mechanistic modelling should not be substituted with trending techniques whose interpretation is shrouded in uncertainty and value is questionable at best. It is certainly not advisable to completely replace the foundational scientific rigor with data-centric pattern recognition, especially considering the dire consequences of DHC failure to the nuclear industry. However, artificial intelligence can complement this hybrid multiscale model as computer vision may be improved through machine learning.

This complementary modelling strategy involves supervised learning algorithms which can identify the spatial relationships between various classes of defects in experimental SEM and TEM images, and, in particular, positioning of hydrides features relative to intergranular and intragranular nucleation sites. Such supervised learning can be used to deduce microstructural rules that reflect the free energetics with a greater degree of phenomenological accuracy, which can then be adapted into the hybrid multiscale model as part of the diffusion-precipitation analysis with improved geometrical checks. Therefore, simulated micrographs should, in principle, display increasingly realistic hydride configurations based on the microstructural rules learned from the experimental images. Such superhuman image classification techniques can be powerful but caution must be exercised due to restricted training data, that is, very large data sets of SEM and TEM images are not available in the field of DHC research.

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9

Conclusions

Chapter Overview

This work was motivated by the need for an accurate and efficient model of DHC failure for safety assessments of Zr alloy components in the nuclear industry. After collectively reviewing the experimental literature on the Zr-H system, the multiscale complexity of the DHC mechanism and its constituent sub-mechanisms became more appreciable. It was concluded that this multiscale complexity is beyond the capabilities of existing nuclear fuel performance codes that rely on DFT, PF and FE models.

For this reason, it was proposed that a bespoke model of DHC must be conceived. This would be an entirely novel microstructural solver that simulates the stress-driven diffusion of H and the diffusion-controlled precipitation of hydrides in Zr alloys. This work has put forward a prototype candidate for such a multiscale framework: a hybrid computational model for simulating notch-tip H concentration profiles and hydrided microstructures. In this chapter, the main findings from the model development are summarised and the possible avenues of further work are explored.

This investigation has spanned many domains of materials science and engineering: continuum mechanics and elastic field theory of defects; linear irreversible thermodynamics and generalised diffusion potentials; structural phase transformations and classical nucleation theory; quantum chemistry and electronic structure simulations; microstructural modelling at the interface of computational science and computer science. During the course of this investigation, several general developments have been made in these respective areas. These developments are highlighted in the following alongside the overall progress in the research field of DHC modelling.

Chapter Outline

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9.1 Summary

The multiscale model proposed in this work is based on an understanding of experimental TEM and SEM studies as well as the insight offered by existing DFT, PF and FE simulations. The proposed model can be outlined as follows. Upon specifying the notch geometry, microstructural details and thermomechanical conditions, a planar simulation cell is initialised with spatial meshes representing the elastic fields of the system as well as the diffusible H concentration. In this setup, the grains are represented by a space-filling Voronoi tessellation of convex polygons and intra-granular nucleation sites are represented by circles that are populated randomly within grains. First the system stress state is computed. Then H concentration is either evolved iteratively or equilibrated in the limit in which the elastochemical diffusion potential vanishes. In order to account for the anisotropic interstitial diffusion of H in α -Zr, the elastic interaction component of the diffusion potential is computed using the anisotropic elastic dipole tensor. Nucleation sites are routinely checked to see if the precipitation criterion is satisfied; this involves integrating the H concentration over the spatial domain of the nucleation site. If there is sufficient H concentration for a micro-hydride needle of a fixed length and thickness in accordance with mass-balance stoichiometry, the nucleation site is activated. The micro-hydride needle itself is represented by a line segment and its stress state is approximated by a dipole of Volterra edge dislocations. Possible micro-hydride configurations are sampled; this procedure mimics the conventional free energy minimisation approach by testing possible needle orientations and positions that lower the elastic contribution to the overall free energy as well as employing computational geometry checks to eliminate non-physical configurations. Secondary nucleations sites are subsequently added in the vicinity of an activated nucleation site to replicate the characteristic autocatalysis that leads to the formation of large macro-hydride colonies. These steps are appropriately repeated until the local H reservoir has been depleted. The simulated H concentration profile and hydrided microstructure can be determined in this manner.

The primary output of the computational model is a simulated micrograph that depicts the geometries, morphologies and contours of key metallographic features: (i) the geometries of the notch, grains and intra-granular nucleation sites; (ii) the morphologies of micro-hydride needles and macro-hydride colonies; and (iii) the contours of the notch-tip H concentration enhancement and the hydrided microstructure stress state. Simple parametric studies were conducted to showcase the diverse capabilities of the model. The exhibited effects of notch acuity, texture and grain size showed good qualitative agreement with experimental observations.

Considering **FIG. 9.1**, it is evident that this hybrid model outperforms existing FE and PF methodologies in several key areas. Most notably, the simulation cell sizes can be relatively large ($\sim 1000\ \mu\text{m}$) and the resolution ($\sim 0.1\ \mu\text{m}$) can be quite fine, which provides a direct comparison with both SEM and TEM studies. This is attributed to the analytical approximations, geometrical simplification and algorithmic optimisations that underpin the proposed computational methodology, which allows simulation runtime to be ~ 1000 times faster than standard FE and PF simulations. As simulation speed is highly desired in the industrial setting, this approach provides a means for statistical averaging of ensembles of simulated micrographs.

The outlook for this work begins with a more thorough verification than what has been possible within the scope of this investigation. Following this, the model can be validated using TEM and SEM experiments, and further parametrised using supplementary small scale DFT, PF, DDP and CCP simulations. Several of these next steps are explored in more depth in the following. But, for now, it can be said that the present work provides a suitable starting point for incorporating more sophisticated mechanistic models of DHC into advanced nuclear fuel performance codes.

FIG. 9.1

Comparison of modelling methodologies

A side-by-side look at the capabilities of the proposed model in comparison with analogous FE and PF models. It is clear that the present work has attempted to incorporate many modelling features that have so far eluded the standard computational methodologies. In particular, the detailed description of the hydrided microstructure exceeds by far what is possible with current FE and PF models. Moreover, the simulation scaling here is not restricted by the system size and resolution because of the extensive use of analytical solutions; the scaling is instead limited by the density of micro-hydride needles with which the frequency of computational geometry checks increases. The main limitation of the proposed model is the inherent two-dimensionality of the framework. Although it is possible to extend some of the features to a three-dimensional framework, it is not clear what additional theoretical and computational challenges must be overcome for the model to retain its efficiency. For now, the obvious next steps in the development of this planar model are highlighted as further work.

Feature	Finite Element Model	Phase-Field Model	Proposed Model
Reference	[Jernkvist-2014]	[Bair, Zaeem, and Tonks (2015)]	Present work
Dimensionality	3D	2D ^(a)	2D ^(a)
Microstructure			
Polycrystalline heterogeneity	✗	✗	✓
Crystalline anisotropy	✗	✗	✓(*)
Nucleation sites	✗	✓	✓ ^(b)
Alloy composition effects	✗	✓	✓
Mechanics			
Stress analysis	Numerical ^(c)	Numerical ^(c)	Analytical ^(d)
Loaded notch stress state	✓	✓	✓
Macro-hydride stress state	✗	✓	✓
Micro-hydride stress state	✗	✗	✓
Dislocation stress state	✗	✗	✓
Elastoplasticity	✗	✓ ^(e)	✓ ^(e)
Diffusion			
Diffusion solver	Numerical	Numerical	Analytical
Stress-driven transport	✓	✓	✓
Temperature-driven transport	✓	✓	✗ ^(f)
Interstitial anisotropy	✗	✗	✓
Precipitation			
Phase transition modelling	Point kinetics	Free energy	Mass balance
Macro-hydride growth	✗	✓	✓
Macro-hydride orientation	✓	✓	✓
Intra-granular macro-hydrides	✗	✓	✓
Inter-granular macro-hydrides	✗	✗	✓
Trans-granular macro-hydrides	✗	✗	✓
Micro-hydride nucleation	✗	✗	✓
Micro-hydride habit planes	✗	✗	✓
Kinetics of dissolution	✓	✓	✓(*)
Predictive ratchetting	✗	✗	✓(*)
Fracture			
Fracture mechanics	Cohesive zone	N/A	N/A
Non-linear material fracture	✓	✗	✗
Crack propagation pathways	✗	✗	✗ ^(h)
Accuracy-Efficiency Paradigm			
Simulation scaling	Mesh resolution	Mesh resolution	Hydride density
Simulation runtime	Hours–days	Hours–days	Seconds–minutes
Experimental validation	✓	✗	✓(*)

^(a) Extendible to 3D at the cost of computational expenditure on higher-dimensional stress analysis as well as diffusion and precipitation kinetics.

^(b) Extendible to a hierarchy of heterogeneous nucleation sites to distinguish grain boundaries, second-phase particles, dislocation networks and point defect clusters.

^(c) Finite-element analysis solver for system stress state whose accuracy and speed varies with spatial mesh resolution.

^(d) Mathematical formulae obtained using the planar theory of elasticity in an infinite linear continua.

^(e) In the present work, plasticity occurs naturally through the motion of dislocations, whereas, in phase-field models, elastoplasticity is described by additional strain energy terms in the free energy of the system that must be calibrated by constitutive relationships.

^(f) Temperature gradient terms can be incorporated into the current model straightforwardly using linear irreversible thermodynamics, that is, in the same capacity as multi-field models.

^(g) Although fracture mechanics is beyond the scope of this work, quantifiable information from simulated micrographs of notch-tip hydrides can be used to parametrised larger scale models.

✗ Partially tested within the model but further work is required.

The original findings of this investigation in approximate order of their dissemination can be summarised as follows:

- *Elastoplastic Slit Cracks in Anisotropic Continua.* As a requirement in the proposed model of DHC, computational stress analyses must be rapid. This rapidity can be achieved by employing closed-form analytical expressions for the elastic fields. The most widely known analytical solutions are only applicable to isotropic continua. But α -Zr has a hexagonal crystal structure, and this crystalline anisotropy is important in quantifying DHC failure. This work introduces an original derivation for the elastic fields around an elastoplastic slit crack in Zr by extending the DBCS distributed dislocation model to a transversely isotropic continuum using the elastostatic Green tensor formalism. This permits the comparison of mode I cracks whose fronts lie on, say, the basal plane or the prism plane. The derivation can also be extended to other topological defects which can be represented by a network of dislocations, which includes precipitates, grain boundaries and notches.

Reference: **Chapter 4**

Publication: [[Patel et al. \(2018a\)](#)]

- *Elastic Dipole Model of Point Defects in Anisotropic Crystals.* A crucial detail of the Zr-H is the tetrahedral interstitialcy of H atoms in the hexagonal α -Zr crystal. The atomic environment of the tetrahedral site exhibits a trigonal symmetry, that is, the H atom forms three equivalent bonds with the Zr atoms on the basal plane and one non-equivalent bond with the Zr atom in the transverse direction. This has important consequences on H mobility which must be accounted for in the treatment of H migration in the Zr matrix. The conventional misfitting sphere model of point defects is accordingly inadequate. In order to truly capture this anisotropy, this work invokes the elastic multipole model of point defects. The leading term in the multipole expansion of point defect forces is the elastic dipole tensor, which can be evaluated using first-principles quantum mechanical calculations or deduced from experimental studies of a related quantity. Original to the study of DHC is the use of the anisotropic elastic dipole tensor for H in Zr in conjunction with the stress fields of higher-dimensional defects in the transversely isotropic Zr continuum.

Reference: **Chapter 4**

Publication: [[Nazarov et al. \(2016\)](#)]

- *Multiscale Model of Stress-Driven Diffusion in Polycrystalline Materials.*

The stress-assisted migration of H solute atoms in the Zr matrix is most certainly influenced by the local microstructure given that hydrides are only found at distinct sites in the Zr alloys. These microstructural effects cannot be described through a standard continuum thermodynamic approach. Instead this work introduces a heterogeneous treatment of stress-driven diffusion through a PDE that incorporates the anisotropic elastic interaction energy through the elastic dipole tensor. For a polycrystalline system in which grains are represented by a Voronoi tessellation of convex polygons, this PDE can be solved efficiently by applying a PIP algorithm. In this work, equilibrated H concentration profiles are computed using an analogous strategy by assuming the limit in which the elastochemical potential vanishes. As a first in this field of study, the effects of crystalline anisotropy and polycrystalline texture can be straightforwardly introduced into coupled stress-diffusion analyses of H in Zr alloys.

Reference: **Chapter 5**

Publication: [Patel et al. (2018b)]

- *Dislocation Dipole Model of Precipitate Needles.* Micro-hydride precipitate platelets are known to have a lenticular needle-like morphology. This facilitates the computational treatment of the micro-hydrides both in terms of their geometrical representation and stress state computation. The geometry of needle-like hydrides can be represented by simple shapes such as lines, rectangles or ellipses, which reduces computational expenditure associated with boundary conditions. In particular, the choice of lines (or thin rectangles) means that micro-hydride needles can be effectively described by a dipole of Volterra-Somigliana edge dislocations. The Burgers vectors of these stress-generating virtual dislocations can be calibrated to mimic the experimentally observed misfit stains. This is an analytical approximation that expedites the simulated mechanics of micro-hydride needles as they self-assemble into macro-hydride colonies. The dislocation dipole model of micro-hydride needles allows the proposed framework to surpass existing PF models in terms of both the size and resolution of the simulation cell.

Reference: **Chapter 4**

Publication: [Patel et al. (2017)]

- *Multiscale Model of Diffusion-Controlled Precipitation.* In general, the process of diffusion-controlled nucleation and growth is an exceptionally difficult problem from the standpoint of computational mod-

elling because of the spectrum of length and time scales involved. But this is particularly true for the case of hydride precipitation in Zr because it involves the long-range transport of H atoms to tensile regions, the mid-ranged clustering of H atoms to vicinity of energetically favourable nucleation sites, and the short-ranged martensitic motion of Zr atoms and the reordering of H atoms as the hydride-matrix interface advances. Coupling the respective stress-diffusion and diffusion-precipitation analyses has proved to be particularly challenging in PF and FE models because of this multiscale nature. As a strategy to overcome this mismatch in scales, this work tests a mass-balance approach in which the stress-diffusion analysis is treated independently from the diffusion-precipitation analysis. This approach provides a physical justification for local changes in the diffusible H content by explicitly connecting the micro-hydride needle geometry to the necessary stoichiometric composition.

Reference: Section 6

Publication: In preparation.

- *Multiscale Model of Stress-Driven Diffusion-Controlled Precipitation in Anisotropic Polycrystalline Materials.* This paradigm is the principal theoretical innovation of this investigation as it unifies the aforementioned original findings into one self-consistent framework. This hybrid model of the early stages of DHC is further discussed in depth in the ensuing discussion.

Reference: **Chapter 7**

Publication: In preparation.

- *Computational Framework for the DHC Mechanism.* A strategy for implementing the proposed model within a software package was conceived during this investigation. This involved the careful design of the algorithmic workflow and program architecture to optimal simulation performance. The computational methodology itself is based on fast algorithms pertaining to the computational geometry of convex polygons. In particular, the significance of PIP, PLSI and LSI algorithms was emphasised as a necessity for efficient modelling of the evolution of the hydrided microstructure.

Reference: **Chapter 7** and in particular **FIG. 7.14**

Publication: In preparation.

- *Discrete Dislocation Plasticity Model of Thermal Ratchetting.* The factor that primarily governs DHC failure is the series of thermomechanical

mechanical series over which hydrides repeatedly precipitate and dissolve. The proposed model adequately treats precipitation but not dissolution. Therefore, as a possible extension to the existing version of the model, a mechanistic sub-model of hydride precipitation-dissolution cycles was introduced. In this sub-model, the dislocation microstructure around a micro-hydride needle was simulated using a modified variant of the planar DDP framework. The DDP study showed the irreversibility of the plastic relaxation around the micro-hydride needles. This irreversibility corresponds to a residual tensile stress state that provides an attractive potential for H retention upon dissolution, which supports a long-standing hypothesis concerning the origin of the TSSp/d hysteresis.

Reference: **Chapter 8**

Publication: [[Patel et al. \(2017\)](#)]

9.2 Further Work

There are several possible avenues for future progress on this multiscale modelling methodology. These next steps can be categorised with respect to the short-term, mid-term and long-term visions of DHC research and nuclear fuel performance codes. The short-term future work involves verifying and validating the existing variant of the proposed model. The mid-term future work involves modelling extensions that provide a more realistic portrayal of DHC failure. The long-term future work involves transforming the computational framework into a fit-for-purpose software that can be readily deployed within the nuclear industry. A possible pathway for achieving this ambitious target would include the following milestones:

- *Verification and Validation.* First a more systematic approach for verification is required because this modelling methodology has several novel computational steps. It is important to ensure that there are no internal discrepancies between the various interfaces, dependencies and inheritances in the program architecture so that the entire simulation can be fully automated, which is essential for statistical modelling. It is then necessary to complete a more rigorous sensitivity study to identify the choices of physical parameters such as the length scales associated with the nucleation site domain, the micro-hydride needle size, and the autocatalysis mimicry. This also applies to details of the algorithmic workflow such as the order in which nucleation events are allowed to unfold. Then it would be possible to compare the simulated micrographs with their experimental TEM and SEM counterparts, and adjust the computational rules that govern the microstructural evolution. More specifically, this would begin with a more accurate treatment of the formation of intra-granular macro-hydride colonies in the high H concentration and large grain size limits by modifying the geometrical rule set that governs the interactions between networks of the micro-hydride needles. Once these rules are established, simulated micrographs can be validated. The validation metric would focus on quantities that describe the hydride density, average orientation and overall connectivity.
- *Modelling Extensions.* Further model development requires both theoretical and computational advancements. Theoretical advancements are particularly necessary for the multiscale coupling of H diffusion and hydride precipitation. The diffusion-precipitation analysis should move beyond the confines of linear irreversible thermodynamics, and ideally incorporate a complete treatment of heterogeneous nucleation. This would offer a more predictive framework for understanding the

evolution of complex hydrided microstructures. For this to be possible, several concurrent computational advances are also necessary. In particular, inter-granular nucleation sites must be introduced and ranked according to potency. The latter is a challenge because the micromechanical computations must account for the anisotropic polycrystallinity of Zr alloys. The problem lies in the fact that analytical elastic field solutions are only known in very rare cases for heterogeneous media whereas the CP methods can suffer from a slow FE overhead [Dunne and Petrinic (2005)]. So an alternative modelling strategy must be conceived in order to preserve both accuracy and efficiency. In addition, hydride dissolution and thermal ratchetting are also much needed additions to the existing model because of the importance of thermomechanical cycles in the reactor environment. The theoretical basis for the TSSp/d hysteresis has already been established using the planar DDP sub-model at the TEM scale. The local dislocation microstructures, however, need to be scaled up to the SEM scale. In principal, substituting a dislocation microstructure around a dissolving micro-hydride needle is not a difficult task within the current framework. However, this simplistic substitution would most likely compromise the computational speed and memory management. It may be more practical to then approximate the residual tensile field with a coarser dislocation network. Finally, the extensive use of computer vision in this model opens up the prospect of adapting more refined and optimised techniques from various trending areas of computer science research such as machine learning and big data.

- *Industrial Code.* The overarching aim of this investigation has been intimately tied with industrial safety economics. In the context of industrial DHC research, the proposed multiscale model as it stands seems promising in its early stages of development. However, there is a considerable amount of work that needs to be done in order to package the program into a robust industrial code that can be used in anger. In addition to the scientific challenges outlined above and the technical challenges of software design, there is an everchanging regulatory standard to satisfy. In fact, the present work itself was driven by the recent regulatory changes which intend to transition the nuclear fuel performance codes away from the dated burn-up calculations and towards less conservative models that are based on mechanistic criteria such as H pick-up [Strasser, Adamson, and Garzarolli (2008), Puls (2012), and Coleman (2003)]. The mechanistic concepts that underpin the proposed model are, in part, inspired by the DFT, PF and FE models that came before it. Any further model development must,

therefore, continue to exploit the advances in other all areas of computational material science. This is a crucial counterweight to the increasingly stricter regulations which demand less and less conservatism.

Given the ubiquity of Zr alloy components in day-to-day operation around the world—and in particular the hope that dry storage casks can maintain their integrity as shields against radiotoxic emissions for up to a century—a predictive framework for DHC failure would undoubtedly serve as a critical tool that could shape the future of nuclear energy and environmental safety. To this end, the present work has outlined a blueprint for predicting the early stages of DHC through multiscale modelling.

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