SAND2014-17727PE

Hydride Formation and Reorientation in Zircaloy-4 during Dry Storage

Veena Tikare
Sandia National Laboratories

2nd ASTM International Zirconium Alloy Cladding/Hydride Workshop

June 10-12, 2014

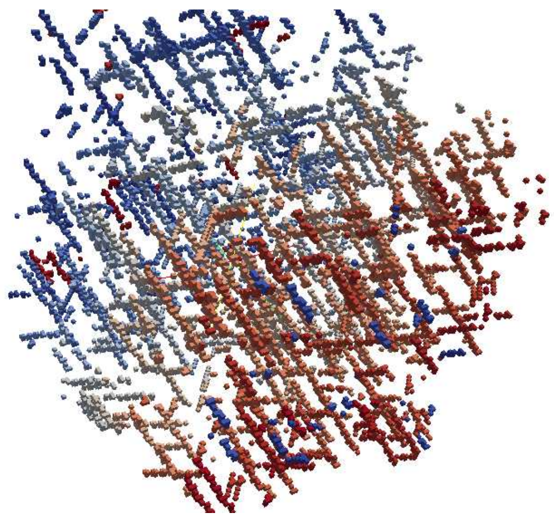
Modeling of hydride precipitate in Zircaloy-4 has been highly successful and can be expanded to address failure.

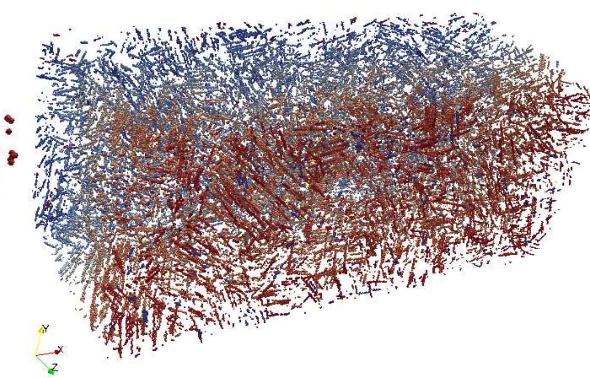
Model objective: to simulate δ-$ZrH_{1.5}$ formation at this microstructural scale.

Accomplishments: Developed a model to simulate precipitation and growth of δ-$ZrH_{1.5}$ precipitates in the α-Zr matrix

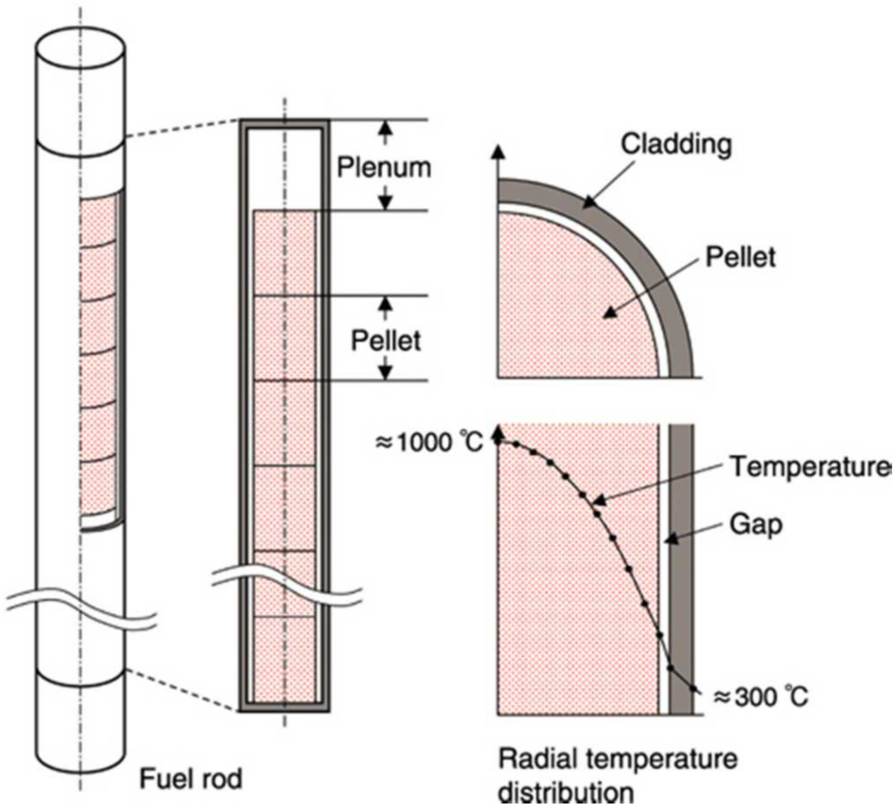
- **In a Zircaloy-4 with correct grain and crystallographic texture**
- **Correct thermodynamic driving forces for the two phases**
- **With kinetic capability for nucleation and growth of precipitates.**

Bradbrook et al, JNM 1972



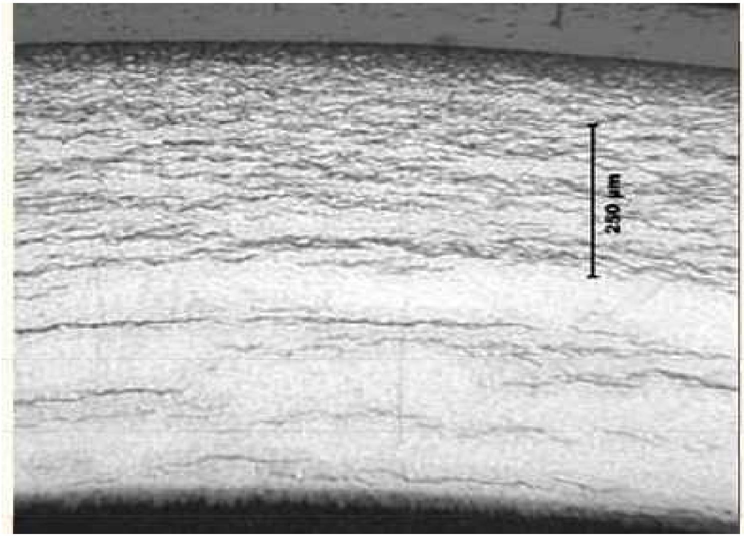


Hydrogen pickup occurs in the reactor by oxidation of the Zr cladding.



Hydrogen Pickup

$$Zr + 2H_2O \rightarrow ZrO_2 + 2H_2$$



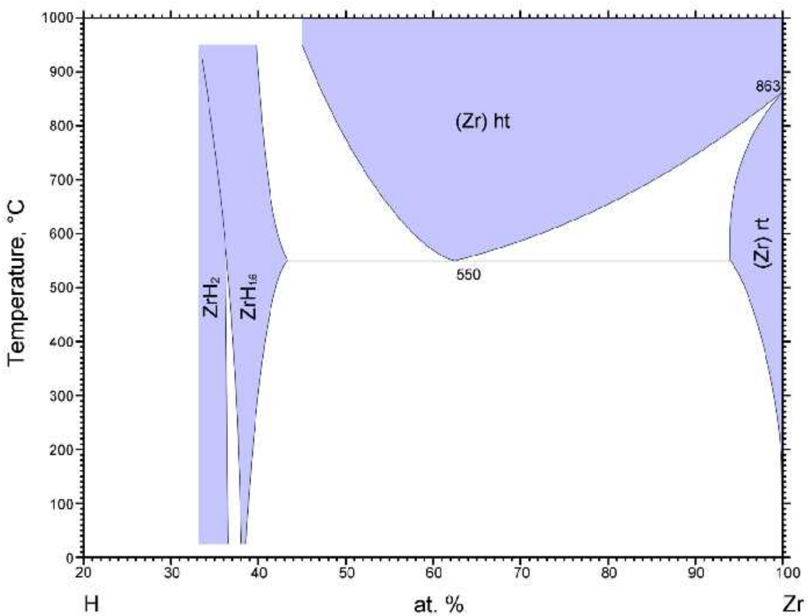
ZrO_2 layer up to 100 μm (600 to 700 ppm H)

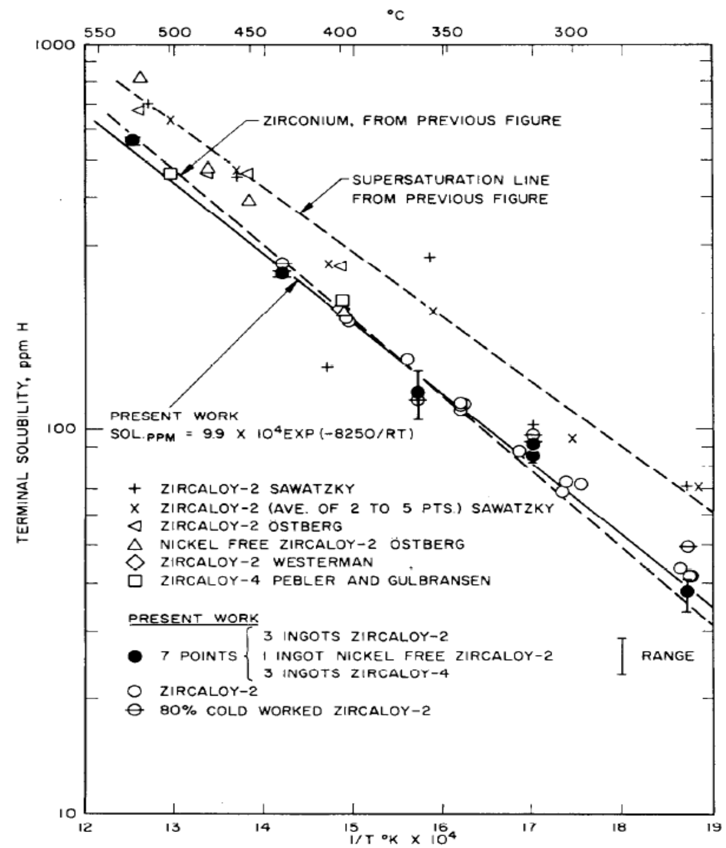
H in Zr-4 <300 wt ppm, 2.7mol%

20 to 40 dpa, 45-60 GWd/MTU

Lanning and al., Corrosion and Hydriding of Reactor Pressure Tubes
Miyashita 2007

Hydrides in Zr-4 will, in most cases, completely dissolve during drying and reprecipitate during dry-storage

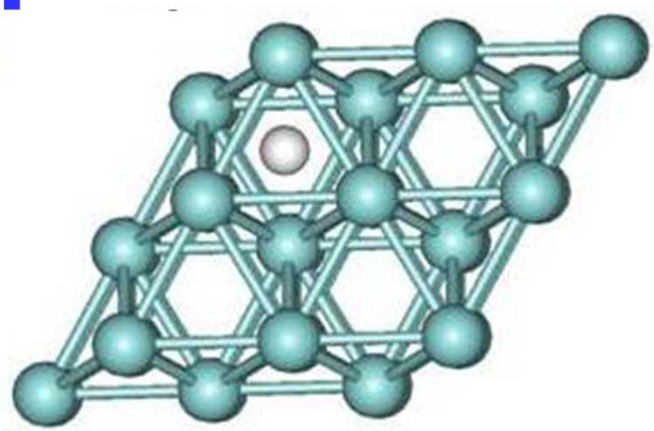




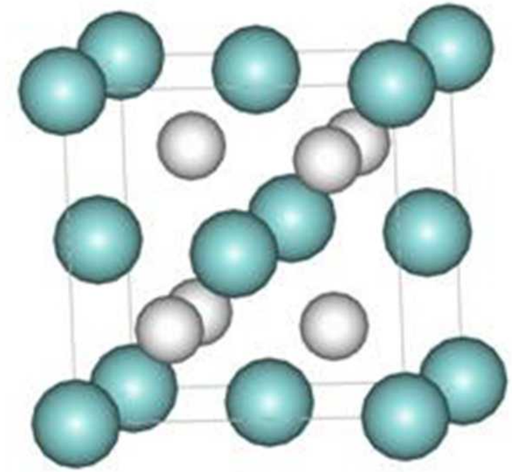
400 °C, 210 ppm H
350 °C, 120 ppm H
300 °C, 68 ppm H
200 °C, 15 ppm H

M. Glazoff, INL
Kearns, JNM, 1967

Precipitate form by a phase transformation from α–Zr with dissolved H to δ–$ZrH_{1.5}$



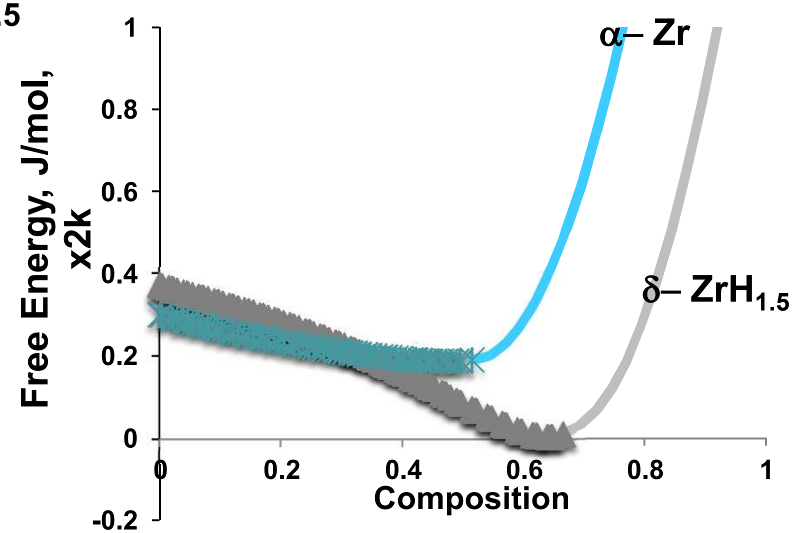
HCP Zr with H dissolved



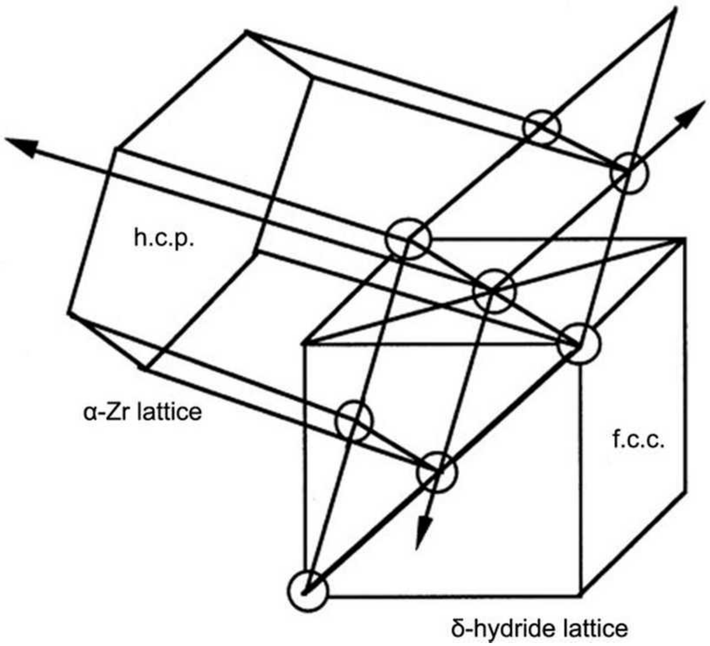
FCC $ZrH_{1.5}$

$$\varepsilon = \begin{bmatrix} .048 & 0 & 0 \\ 0 & .048 & 0 \\ 0 & 0 & .072 \end{bmatrix} = .17\ Vol$$

M. Glazoff, INL



δ–$ZrH_{1.5}$ Precipitates *always* form in the α–Zr basal plane along three specific directions.



Orientation relationship:

$\delta(111)$ // $\alpha(0002)$

$\delta[1\bar{1}0]$ // $\alpha[11\bar{2}0]$

http://journals.iucr.org/j/issues/2014/01/00/he5611/he5611fig7.html

Bradbrook et al, JNM 1972

δ–$ZrH_{1.5}$ platelets are assumed to form, but have never been observed, so assumed needles.

The strain associated with α-Zr to δ-$ZrH_{1.5}$ transformation

$$\varepsilon = \begin{bmatrix} .048 & 0 & 0 \\ 0 & .048 & 0 \\ 0 & 0 & .072 \end{bmatrix} = .17\ Vol$$

was assumed to result in platelet formation, but never observed.

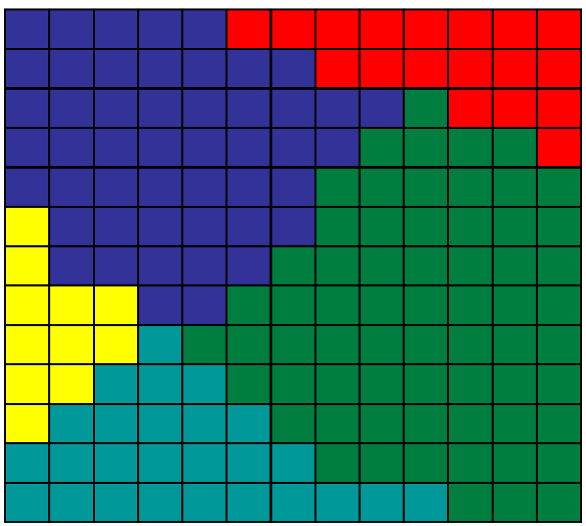
Only platelets are shown in TEM micrographs.

Bradbrook et al, JNM 1972
Bailey, Acta Met 1963
Chung, 13th Int Symp. Zr Nuc Ind, 2002

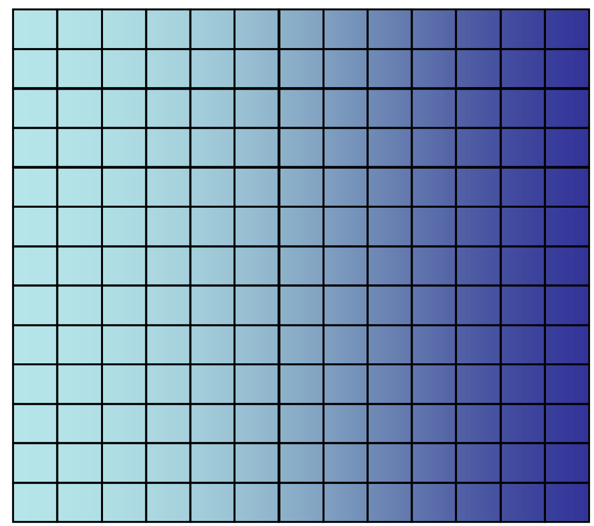
Representation of Microstructure and Composition: Hybrid Model

- Potts kMC digitizes represents microstructure using spins q_i
- Phase field represents composition with field variable C_i
  - Both are on the same grid

Microstructure



Composition



Equation of State (Thermodynamics) Hybrid Model

- **EOS is a function of volume free energy and interfacial energies.**

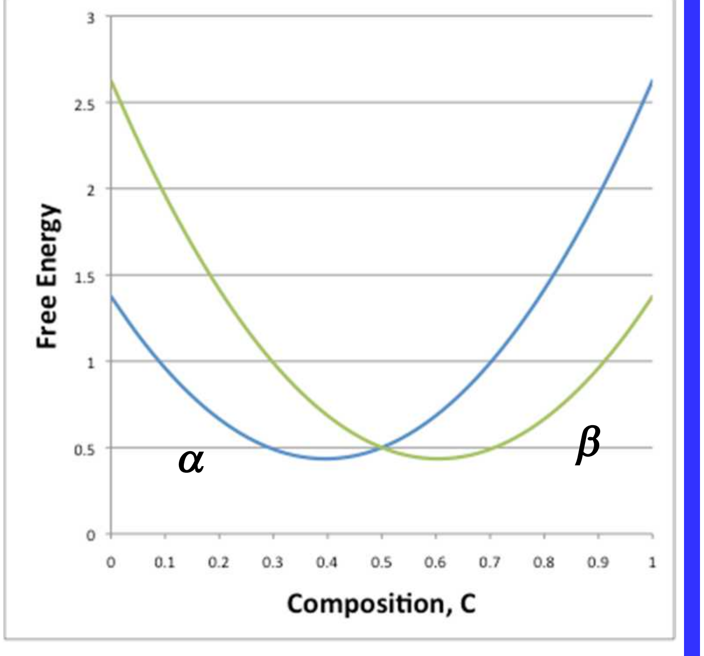
$$E_{hyb} = \sum_{i=1}^{N} \left(E_v(q_i, C) + \frac{1}{2} \sum_{j=1}^{n} J(q_i, q_j) \right) + E_{dC}$$

Volume free energy (first term) ***Interfacial free energy*** (second term)

$$E_{dC} = \int 2\kappa_C (\nabla C)^2 dV$$

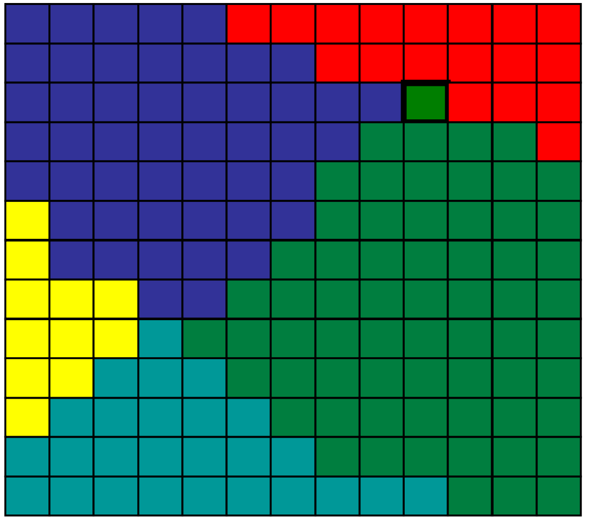
An example of E_v

$$E_v = a\left[(C - C_1)^2 + (C_2 - C)^2\right] + b\left[(C - C_3)q_\alpha + (C_4 - C)q_\beta\right]$$



Representation of Microstructure and Composition: kMC

- Potts kMC digitizes space into discrete 'bits' of material
  - An ensemble of particles populate the lattice
  - Each color can represent a membership in a phase and / or feature (i.e. grain)
  - Each color can also represent composition, but true gradients in composition would require huge simulations



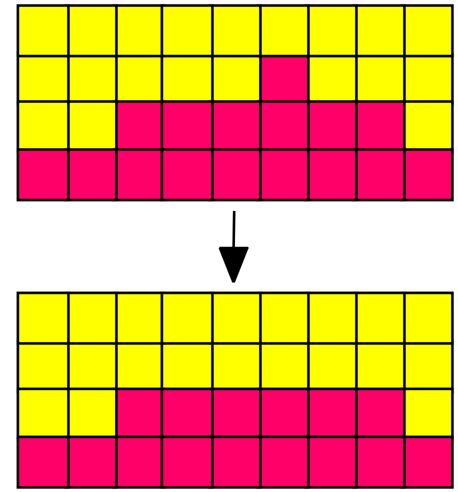
Kinetic of Evolution Hybrid Model

- **Microstructure is evolved in the same manner as Potts in response to local free energy using E_{hyb}**
  - **Metropolis algorithm**
- **Composition evolved as a phase field parameter.**

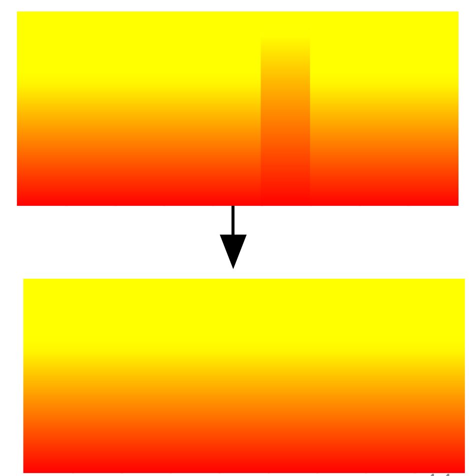
$$\frac{\partial C}{\partial t} = -M_c\left(\nabla^2 \frac{\partial E_v}{\partial C} - \kappa_c \nabla^4 C\right)$$

- **Where E_v is from the hybrid Free Energy**

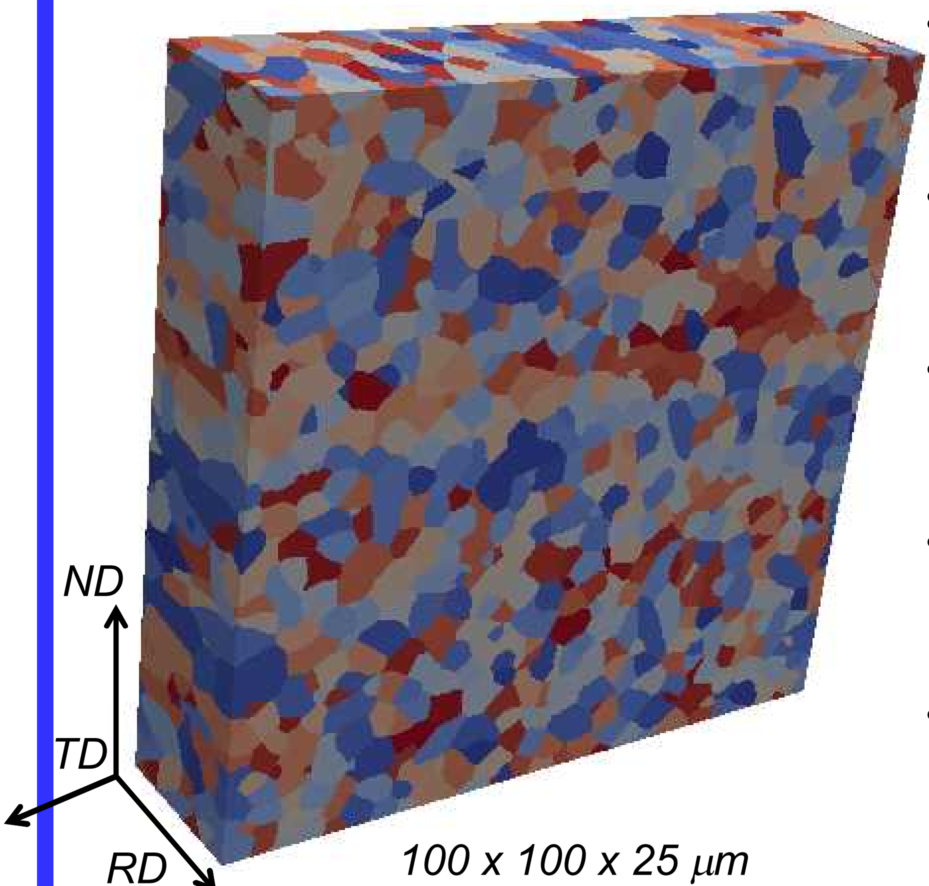
grain growth change pixel color



Composition change by diffusion



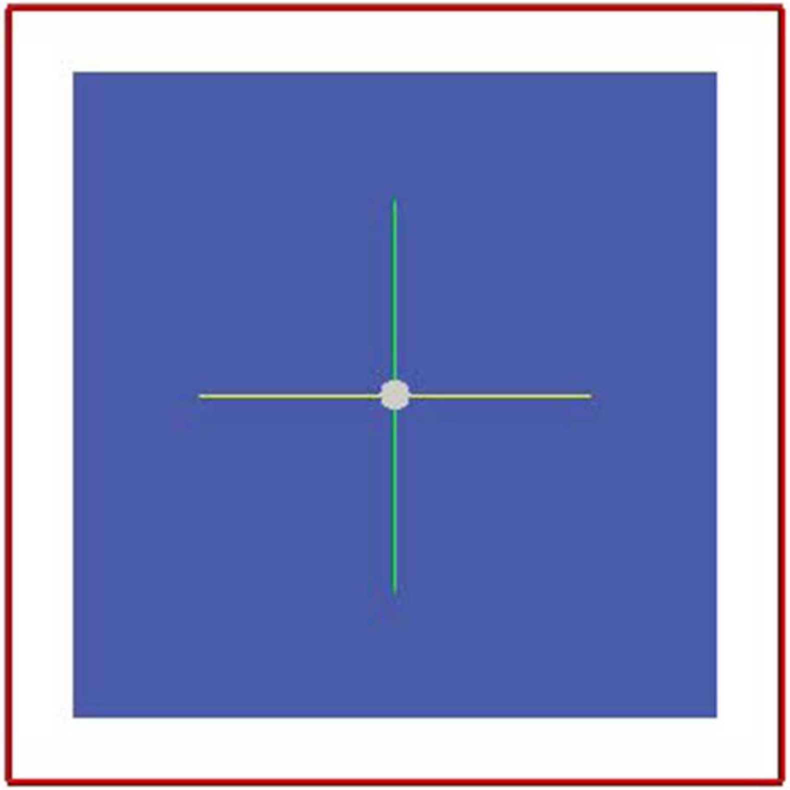
Simulation of δ–$ZrH_{1.5}$ precipitation in rolled α–Zr with randomly oriented grains.

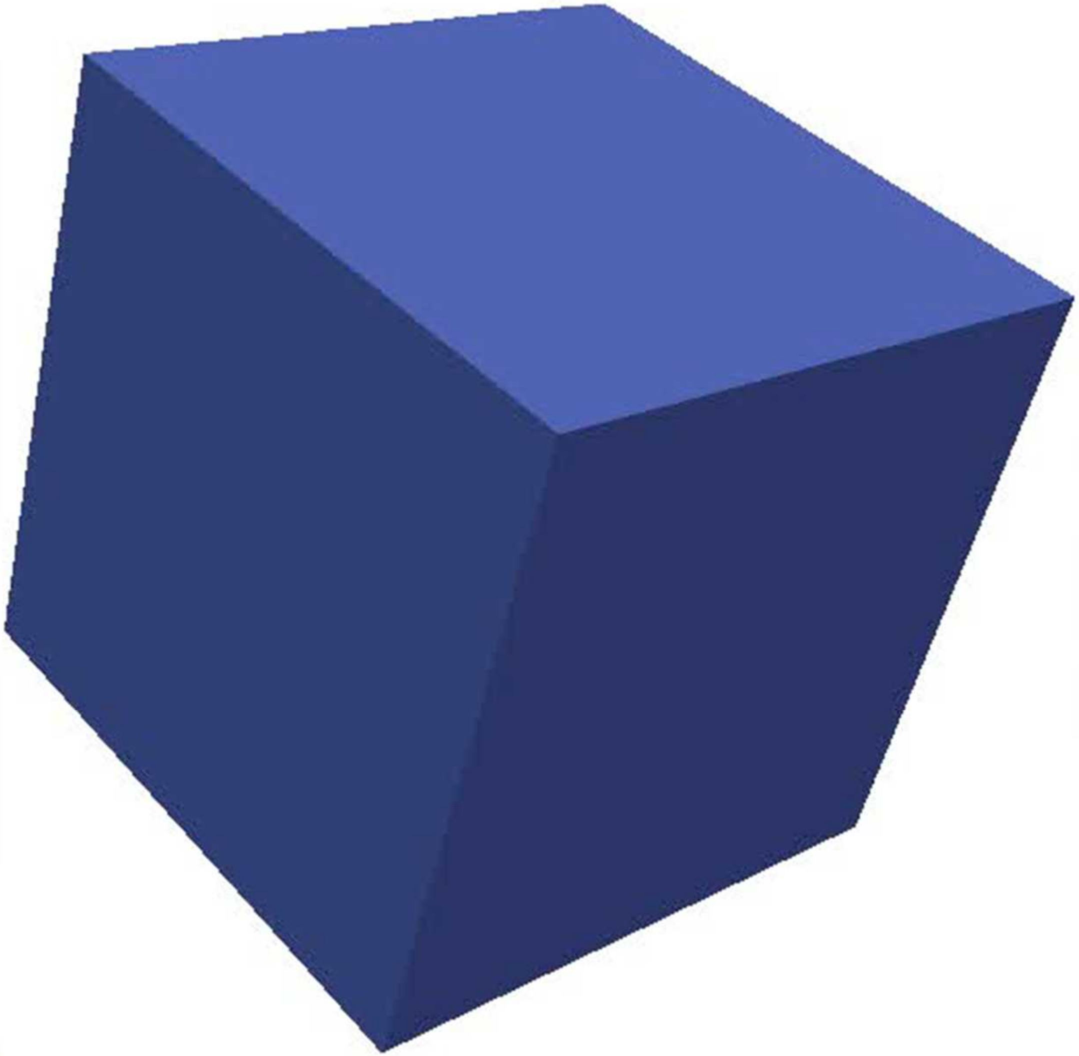


- **Same microstructure as rolled Zircaloy-4 with elongation in rolled direction.**
- **Grain are randomly oriented with uniform distribution in all directions.**
- **Starting condition is supersaturated Zr with H, cooled to 350 °C.**
- **Precipitates form in basal plane with correct orientation δ(111) || α(0001), δ[1-10] || α(11-20)**
- **Nucleation at randomly selected sites with uniform distribution in each grain.**

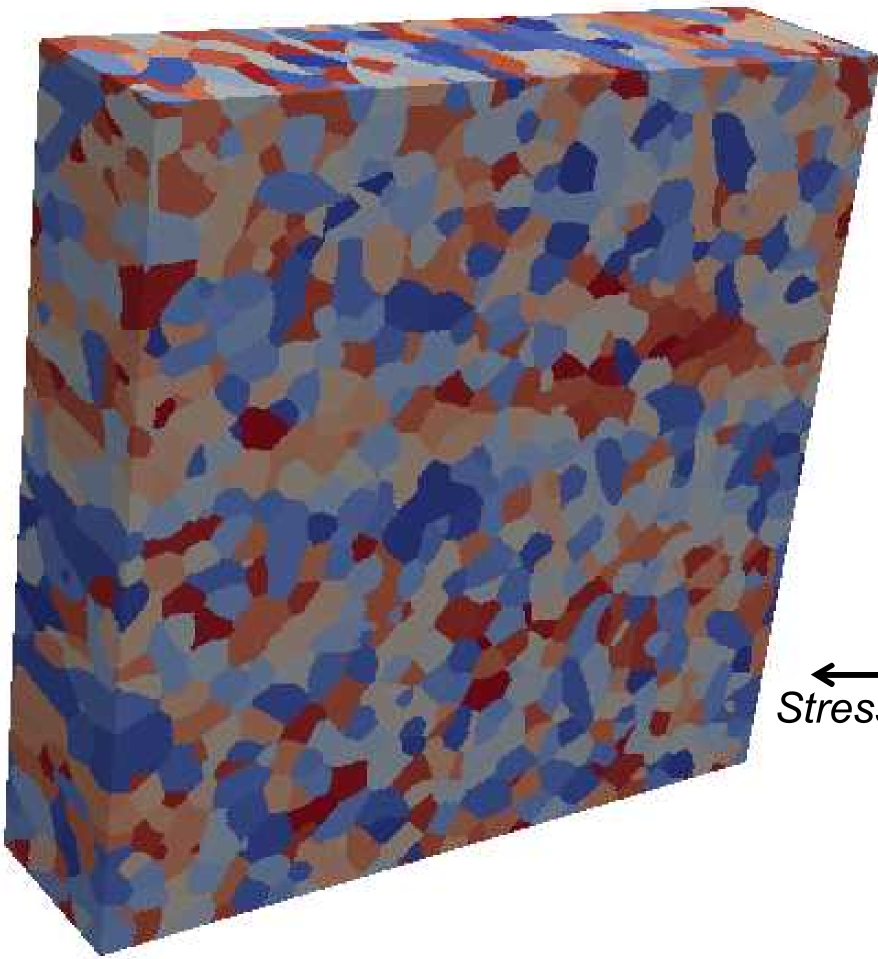
Precipitation of δ–$ZrH_{1.5}$ in single crystal α–Zr on cooling from super-saturation.

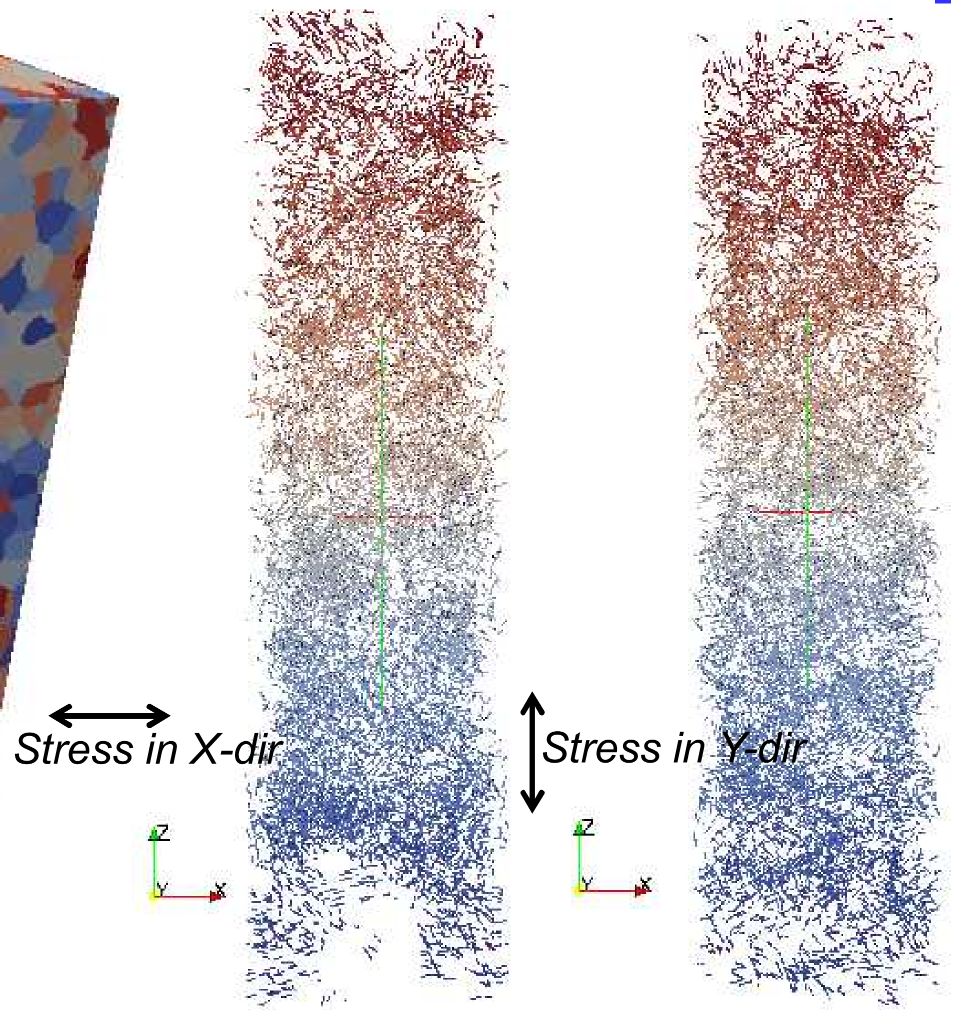
Diffusion of H to δ–$ZrH_{1.5}$ precipitates controls growth rate in single crystal



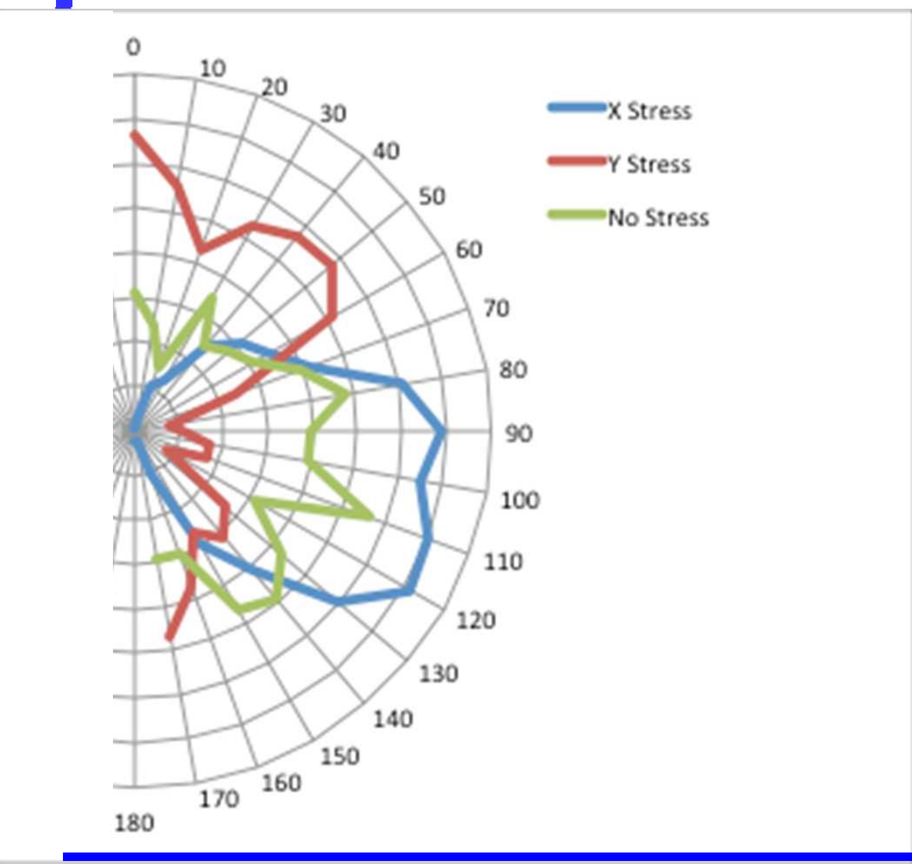


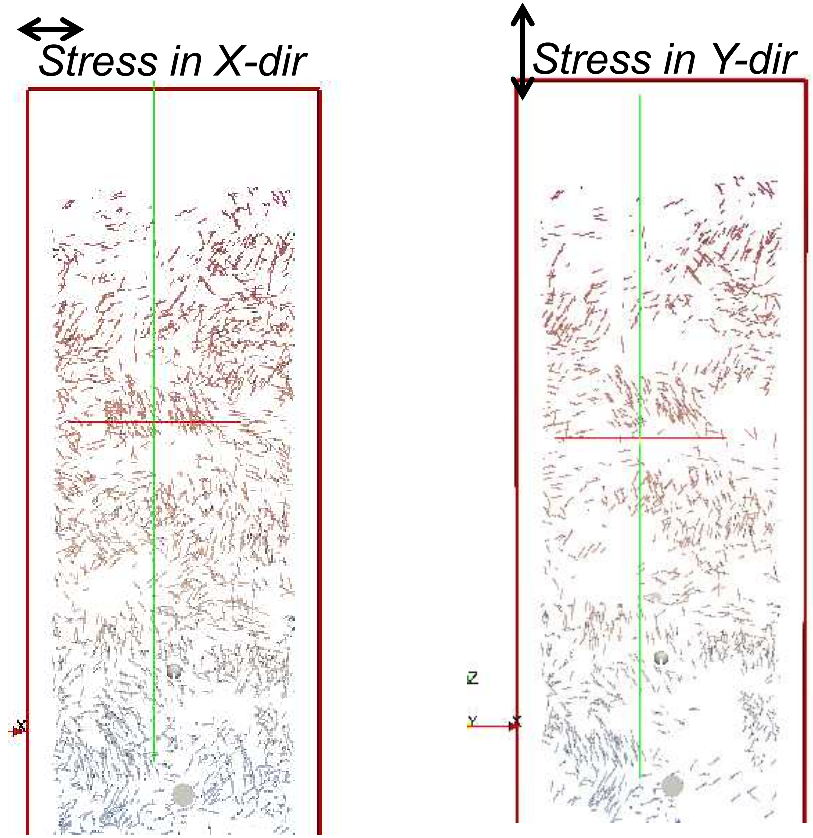
Simulation of δ–$ZrH_{1.5}$ precipitation in rolled α–Zr with randomly oriented grains.





Simulation of δ–$ZrH_{1.5}$ precipitation in rolled α–Zr with randomly oriented grains.

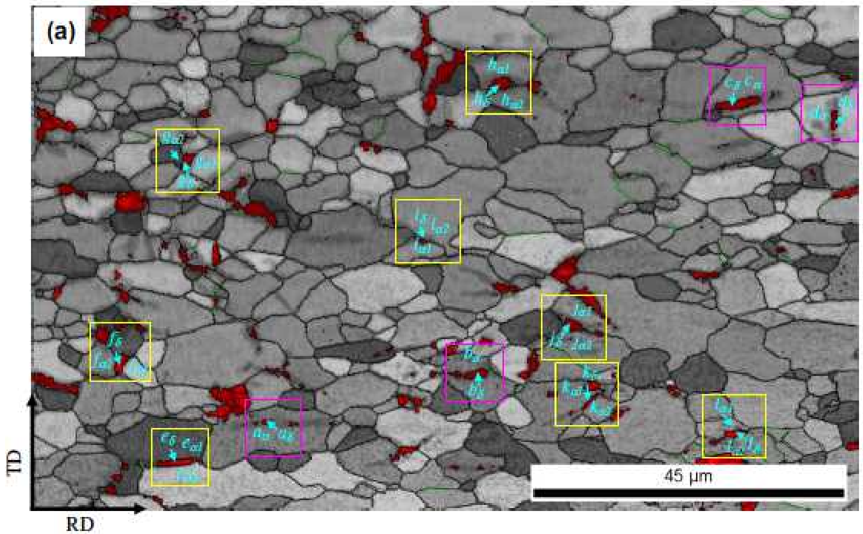


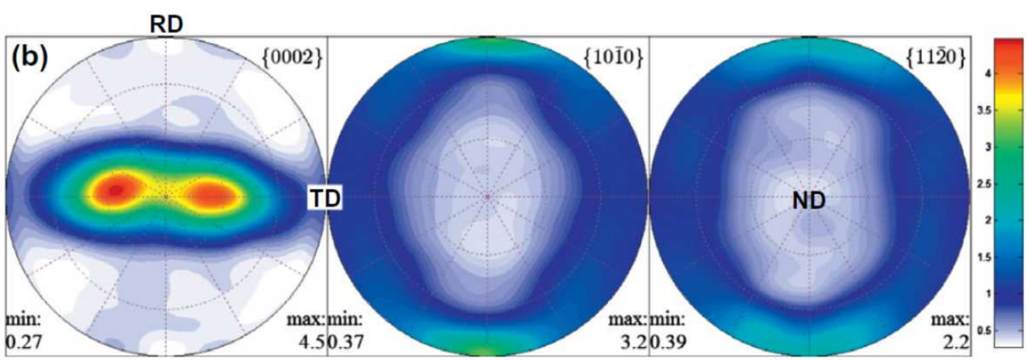


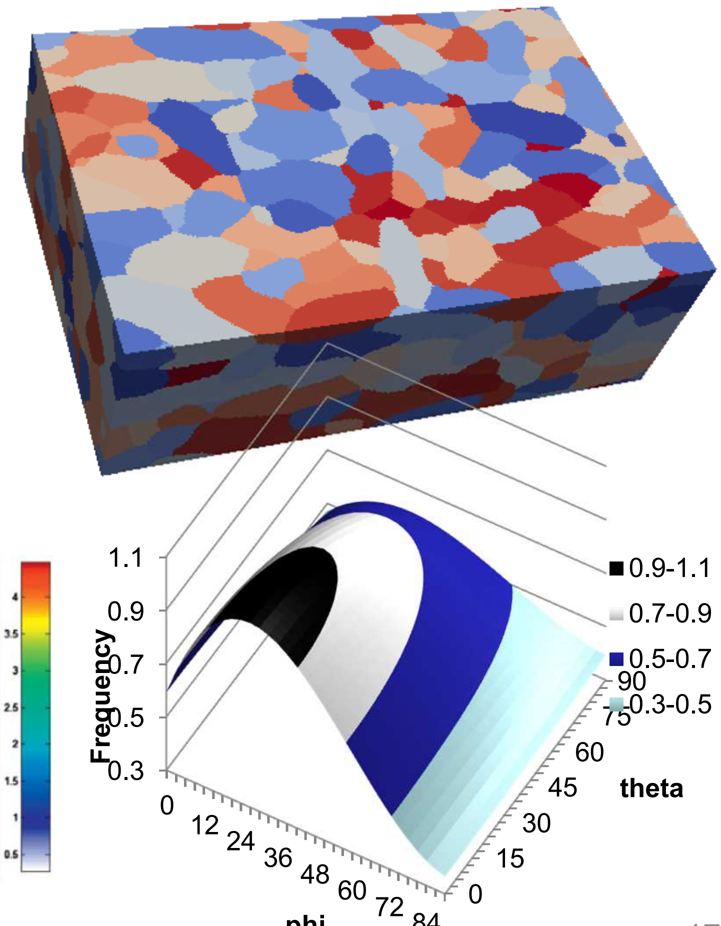
Reorientation occurs by precipitates in different grains that are favorably oriented precipitating to form "continuous" looking precipitates.

Generated a Digital Zr-4 Microstructure

from information available in the literature on grain and crystallographic texture

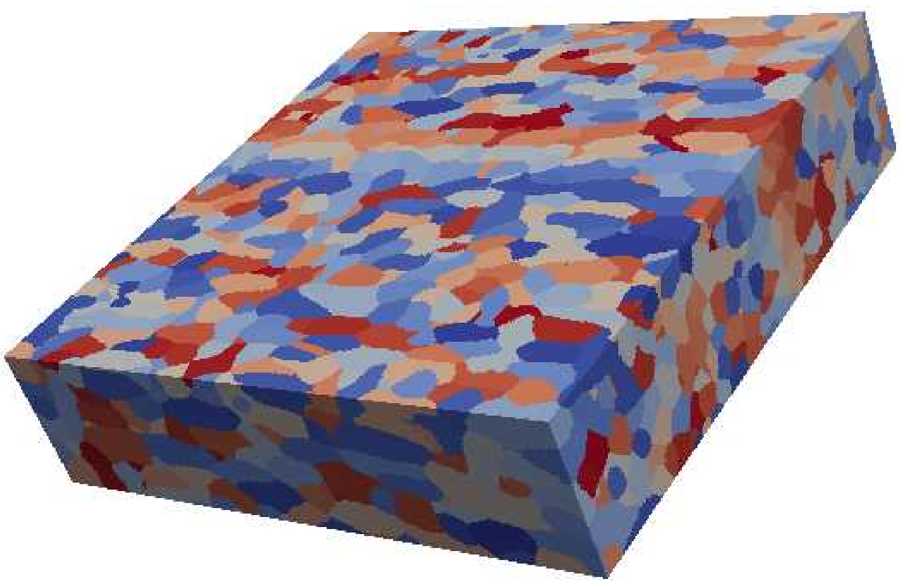


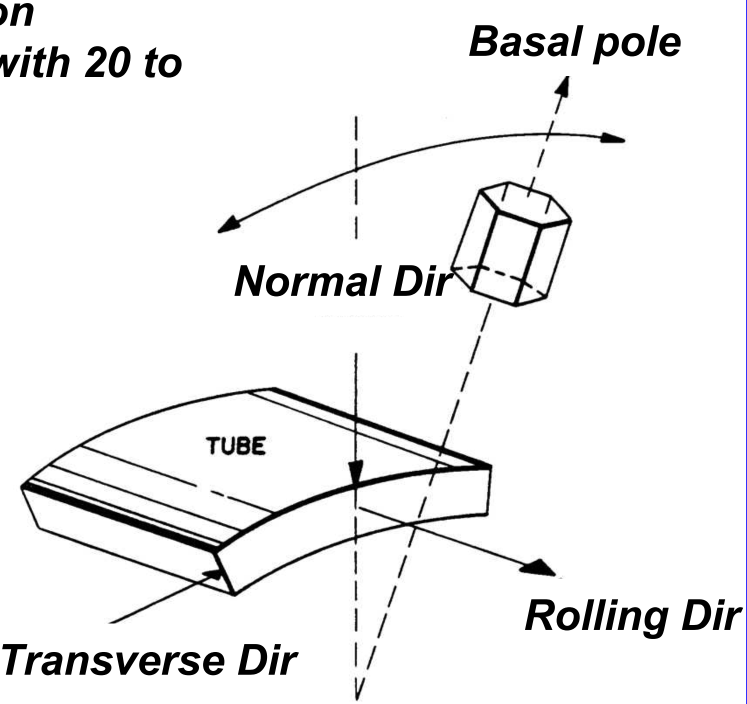




Zircaloy-4 and other Zr-based claddings are known to have texture

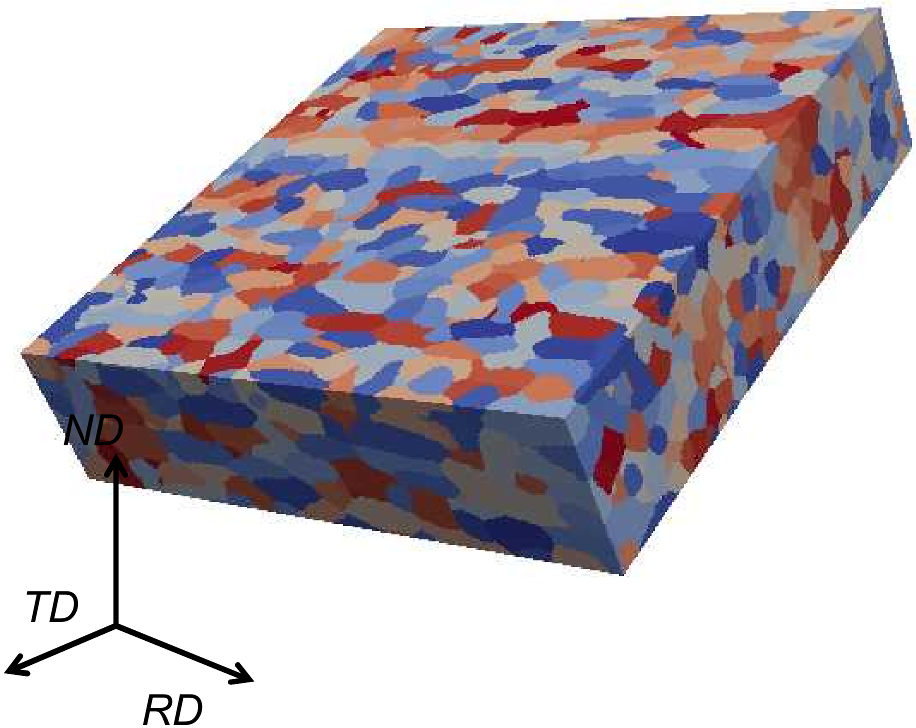
Pilgering process imparts texture
- *Grain shape, elongated ~2x in rolling direction*
- *Crystallographic, basal plane parallel to ND with 20 to 40^{o} rotation around TD*





Nucleation and growth of hydride precipitates

Initial microstructure

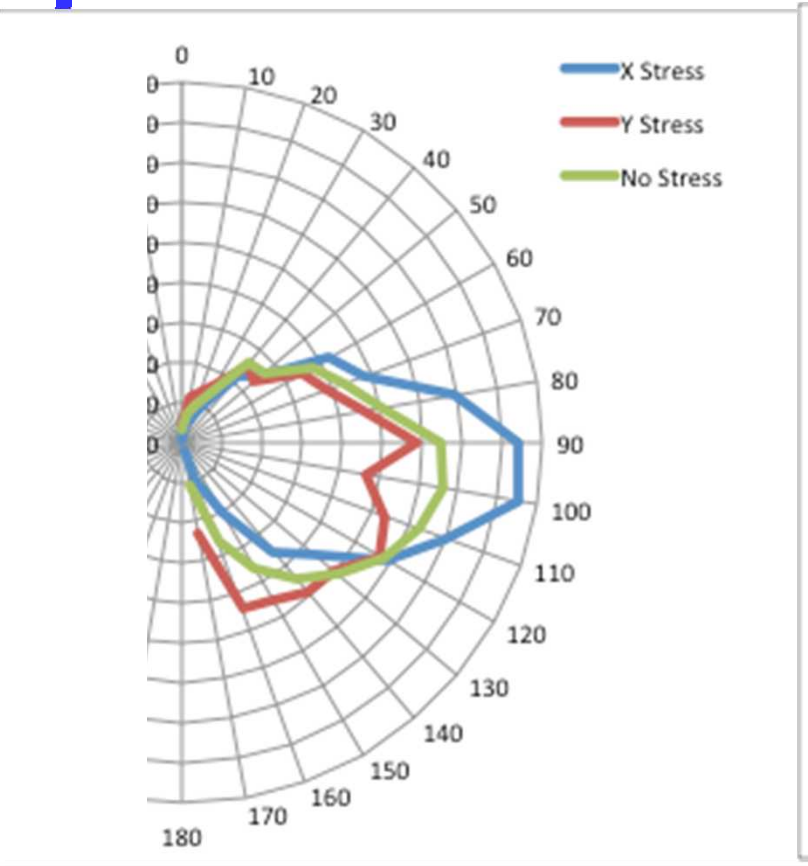


100 x 100 x 25 μm

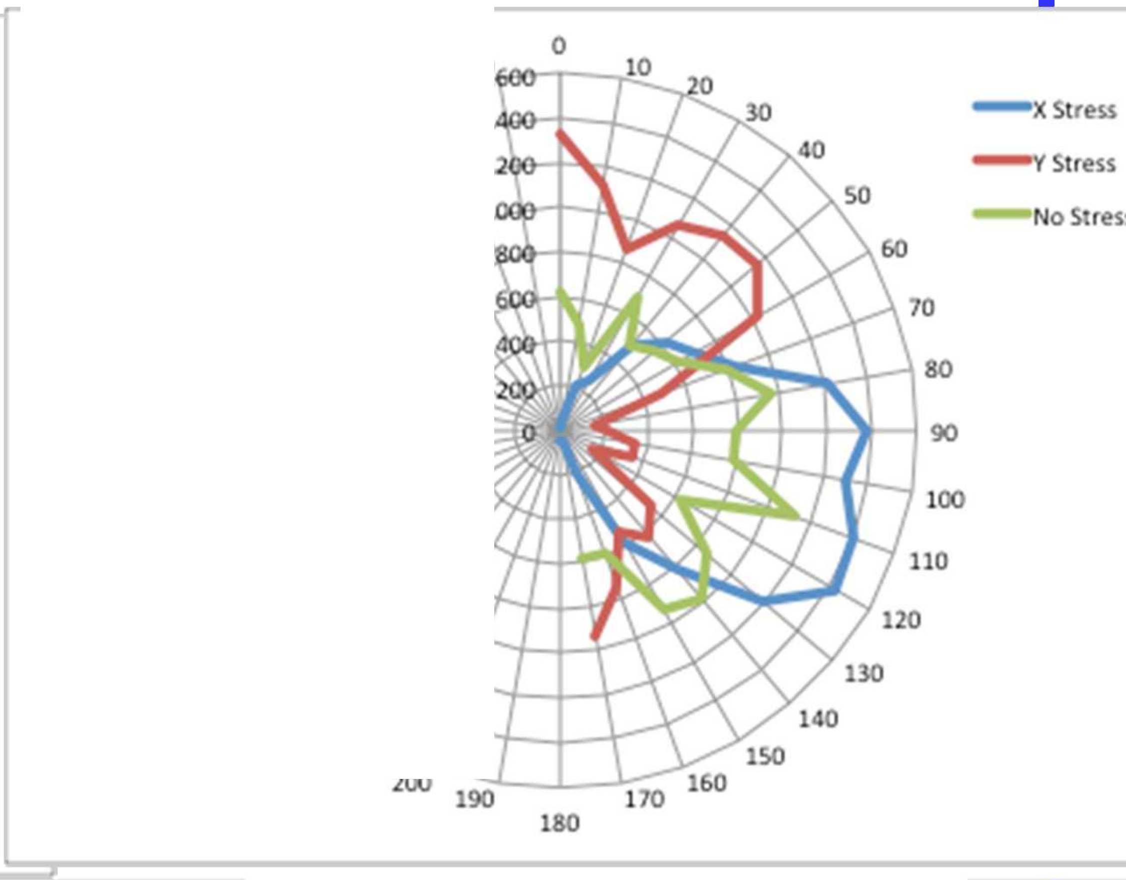
Simulation:

- **Microstructure of rolled Zr-4.**
- **Basal plane of α–Zr aligned with rolling direction.**
- **Precipitates form in basal plane with δ(111) || α(0001), δ[1-10] || α(11-20).**
- **1000 ppm H.**
- **Zr-H thermodynamics with free energy curves for α–Zr and δ–$ZrH_{1.5}$**
- **Nucleation and growth of precipitates at randomly selected sites**
- **Diffusion controlled kinetics**

Simulation of δ–$ZrH_{1.5}$ precipitation in rolled α–Zr with Zr-4 crystallographic texture.

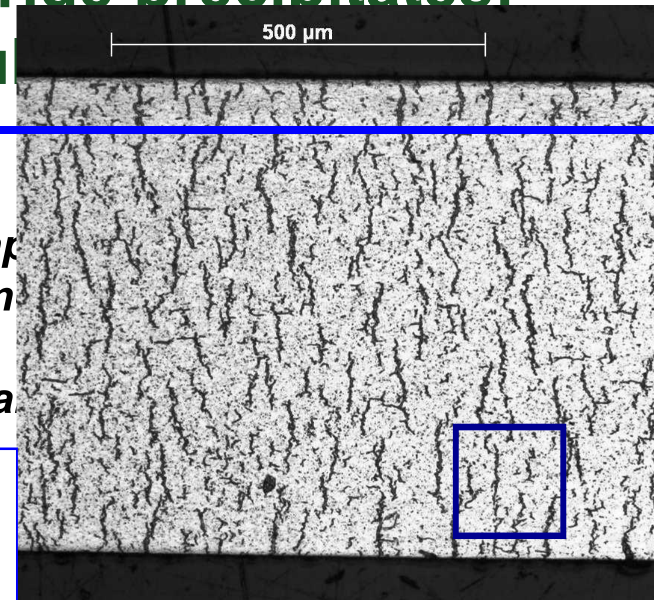


With crystallographic texture



Without crystallographic texture

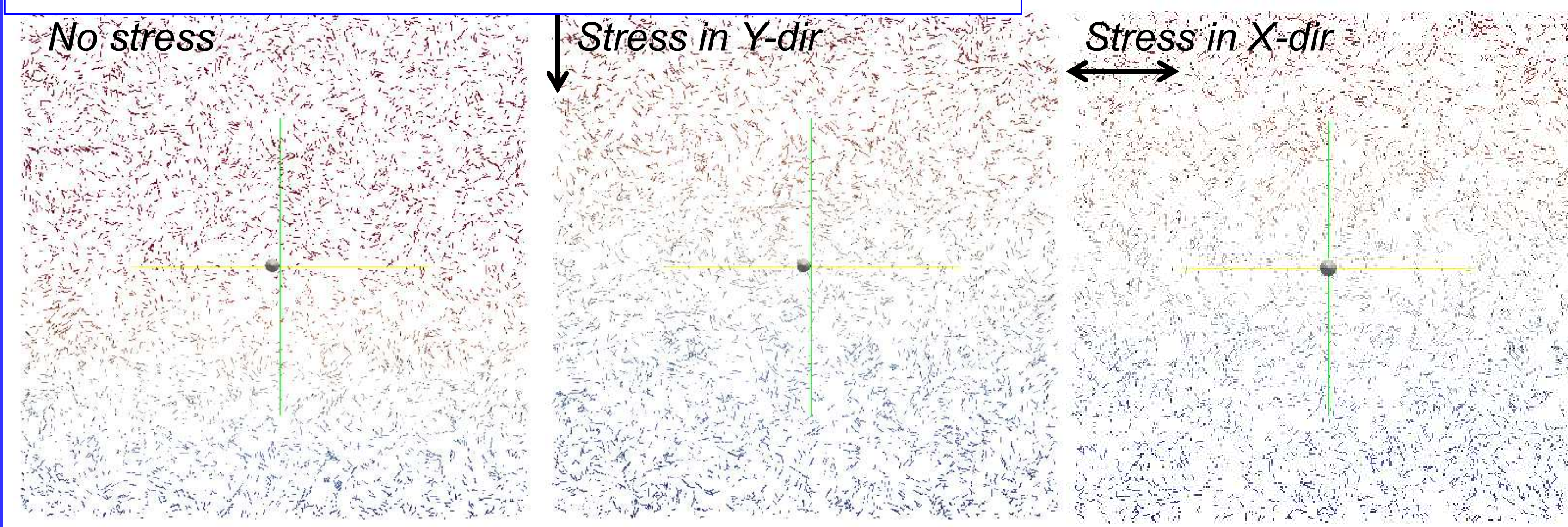
Nucleation and growth of hydride precipitates: Simulation resul



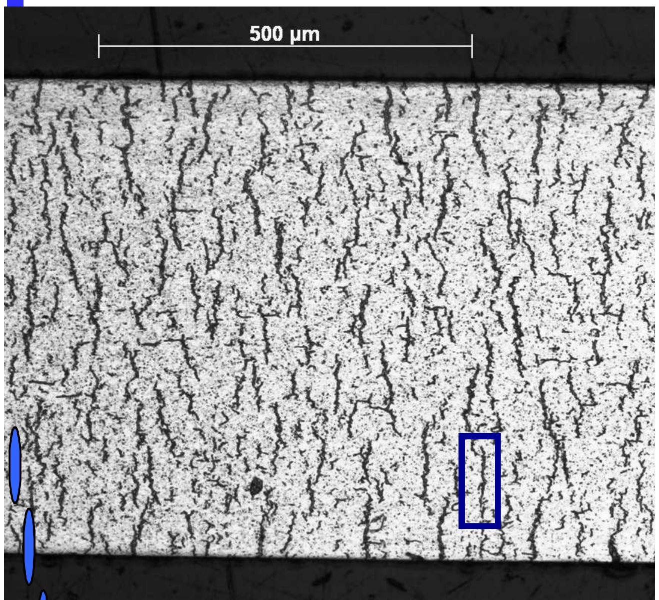
Precipitates align themselves perpendicular to the ap

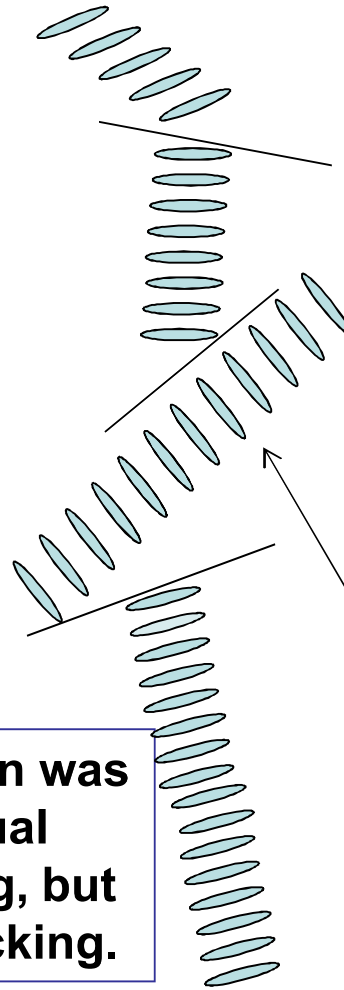
- ***No stress, alignment is ~random along basal plan***
- ***Stress along Y-dir, alignment is perpendicular***
- ***Stress along Z-dir, alignment is less perpendicula***

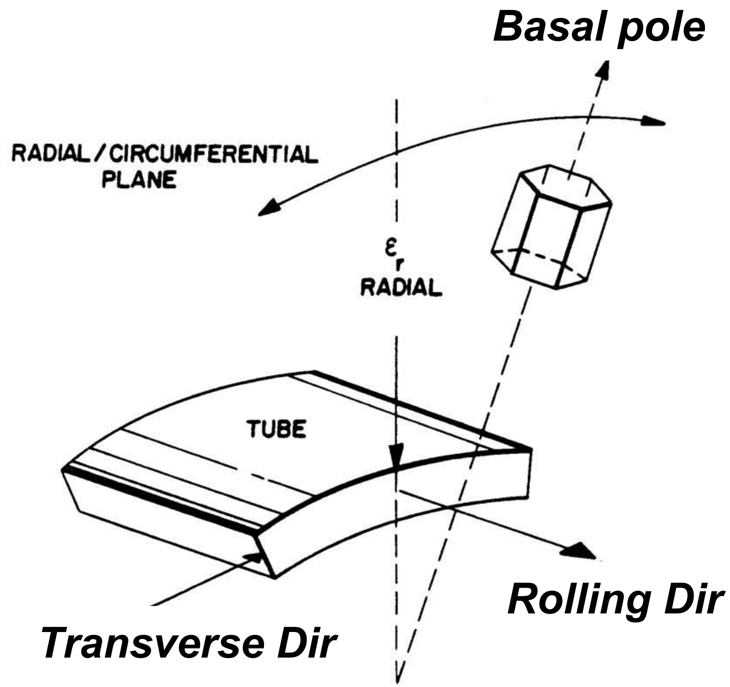
However, simulated precipitates are uniformly distributed, individual precipitations do not re-align sufficiently to explain observed behavior

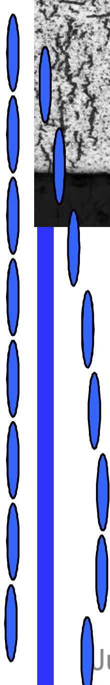


Individual hydride precipitates stack, rather than reorient, to give overall reorientation.









Precipitate reorientation was pictured as individual precipitates re-aligning, but reality is probably stacking.

Individual precipitates align themselves in the basal plane, but stack to reorient.

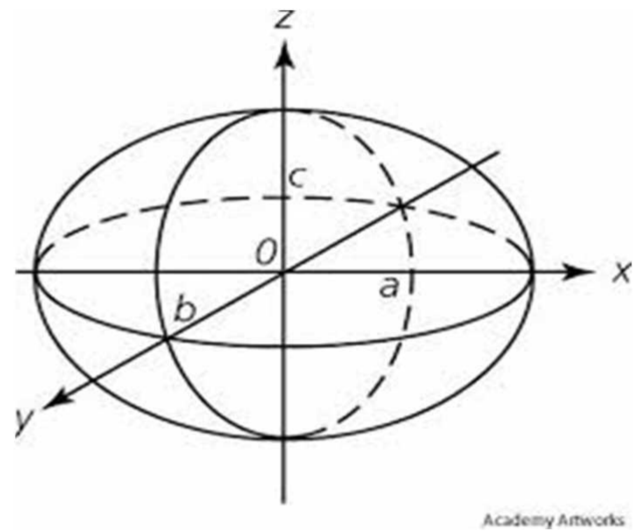
Current Modeling Capabilities

- Have a microstructural and compositional evolution model for hydride formation and reorientation
  - Incorporates underlying microstructure of Zr-based cladding
  - Based on actual thermodynamics (bulk chemical free energy, interfacial energy, strain energy)
  - Can treat the kinetics that are relevant (H diffusion-controlled growth or interfacial-controlled growth, nucleation rate and sites)
  - Can incorporate radiation effects (dislocation loops that are nucleation sites, increase in diffusivities)
  - Can simulate temperature gradients
  - Can treat large volumes, sufficient to obtain contiguity of precipitates
- Model is ready to simulate a wide range of Zr-based claddings under many different conditions, but is not predicting the stacking of precipitates.

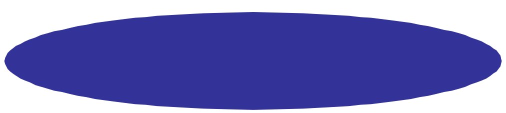
Critical Missing Physics

- Stress state around precipitate:
  - Accompanying hydride precipitation is volumetric dilation

$$\varepsilon = \begin{bmatrix} .048 & 0 & 0 \\ 0 & .048 & 0 \\ 0 & 0 & .072 \end{bmatrix} = .17\ Vol$$



  - The precipitate is ellipsoidal
  - Can apply Eshelby analysis

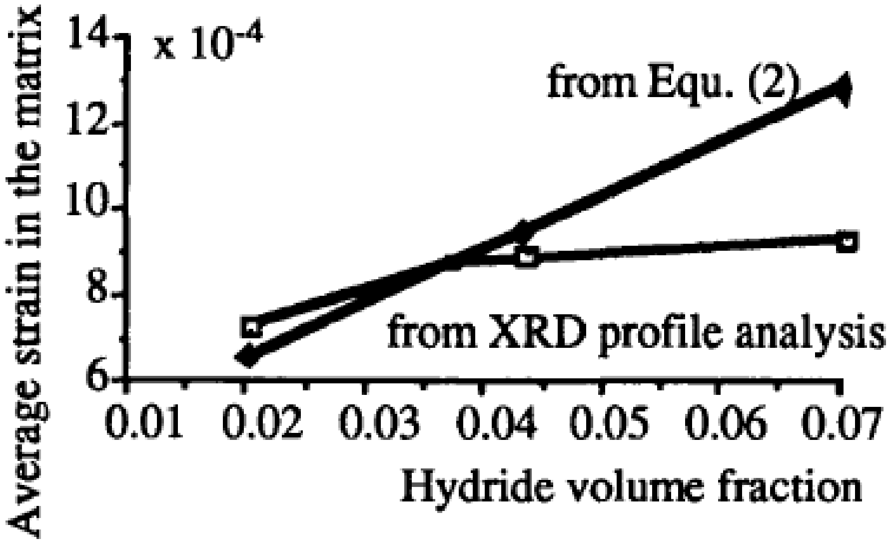


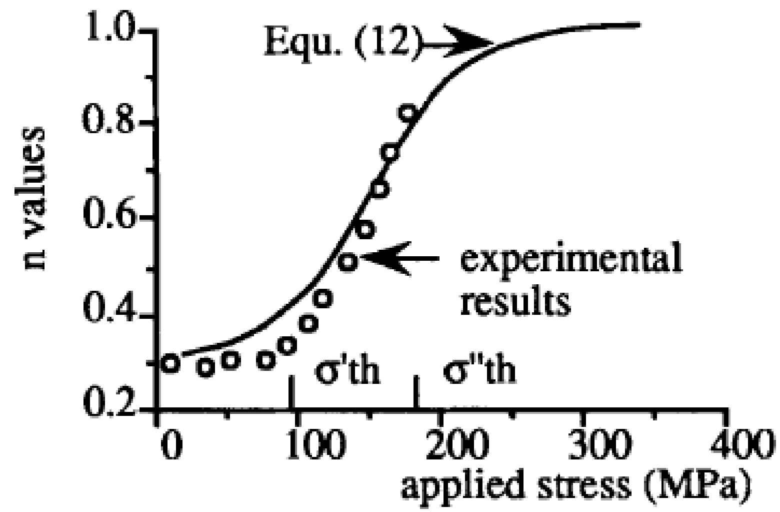
  - Should grow as a disc with short direction parallel to the basal-plane, but … maybe needle-like
  - Puts the matrix in compression, suppressing precipitation growth and nucleation.

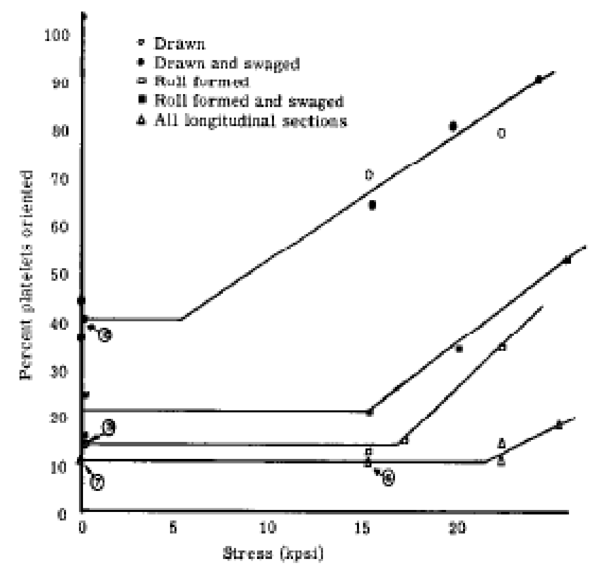
Proposed work to address this

- Original goal: develop capability to predict hydride reorientation in all Zr-based claddings during dry-storage.
  - Done in Zr-4 and can be more easily extended to other Zr-based claddings.
- Proposed new goal is 2-fold:
  - Redirect microstructural effort to predict degree of reorientation and contiguity as a function of Zr-cladding material, hydrogen content, irradiation history in reactor, thermal history during and post-drying using rate-theory.
    - *Need micro-mechanical coupling model to predict stress state around precipitates.*
  - Engineering prediction of crack propagation and failure
    - *FEM modeling of cladding given hydride reorientation and contiguity.*

Reorientation of hydride is observed when large tensile hoop stresses are applied, Zr-4

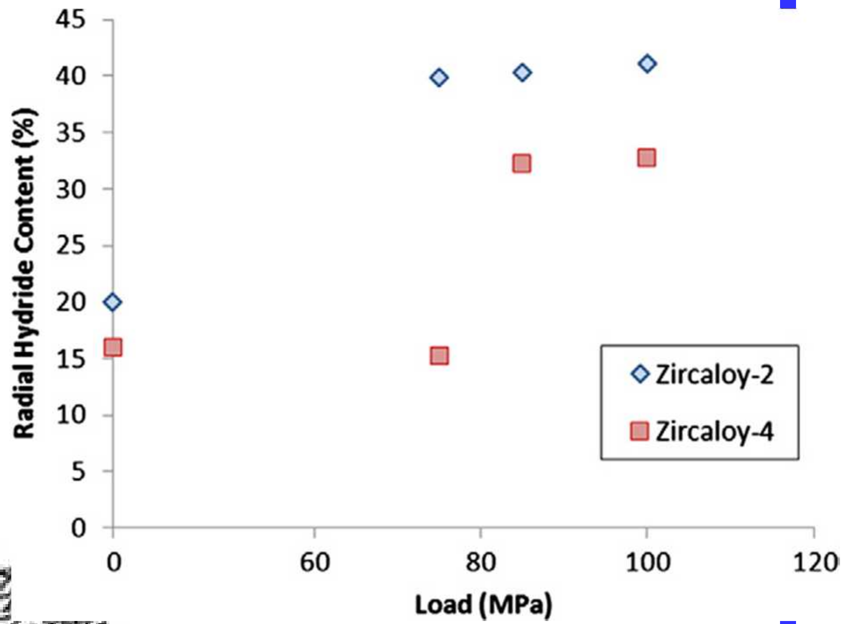




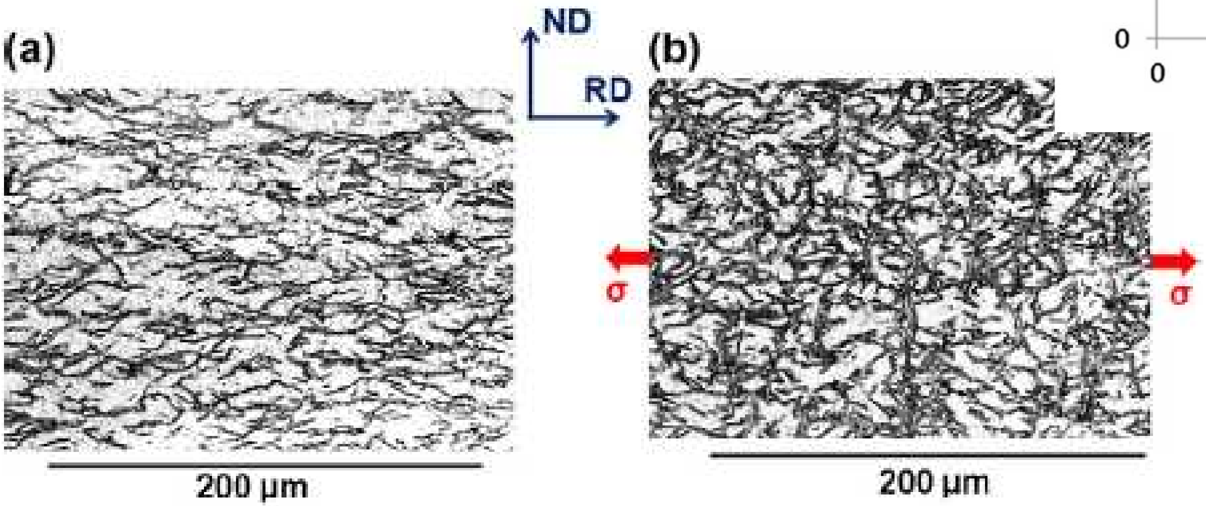


Bai et al, Met Trans 25A, 1994
Louthan et al., JNM 9. 1963

Reorientation of hydride is observed when large tensile hoop stresses are applied.



Reorientation in Zr-4 at 85 MPa and 600 wt ppm H

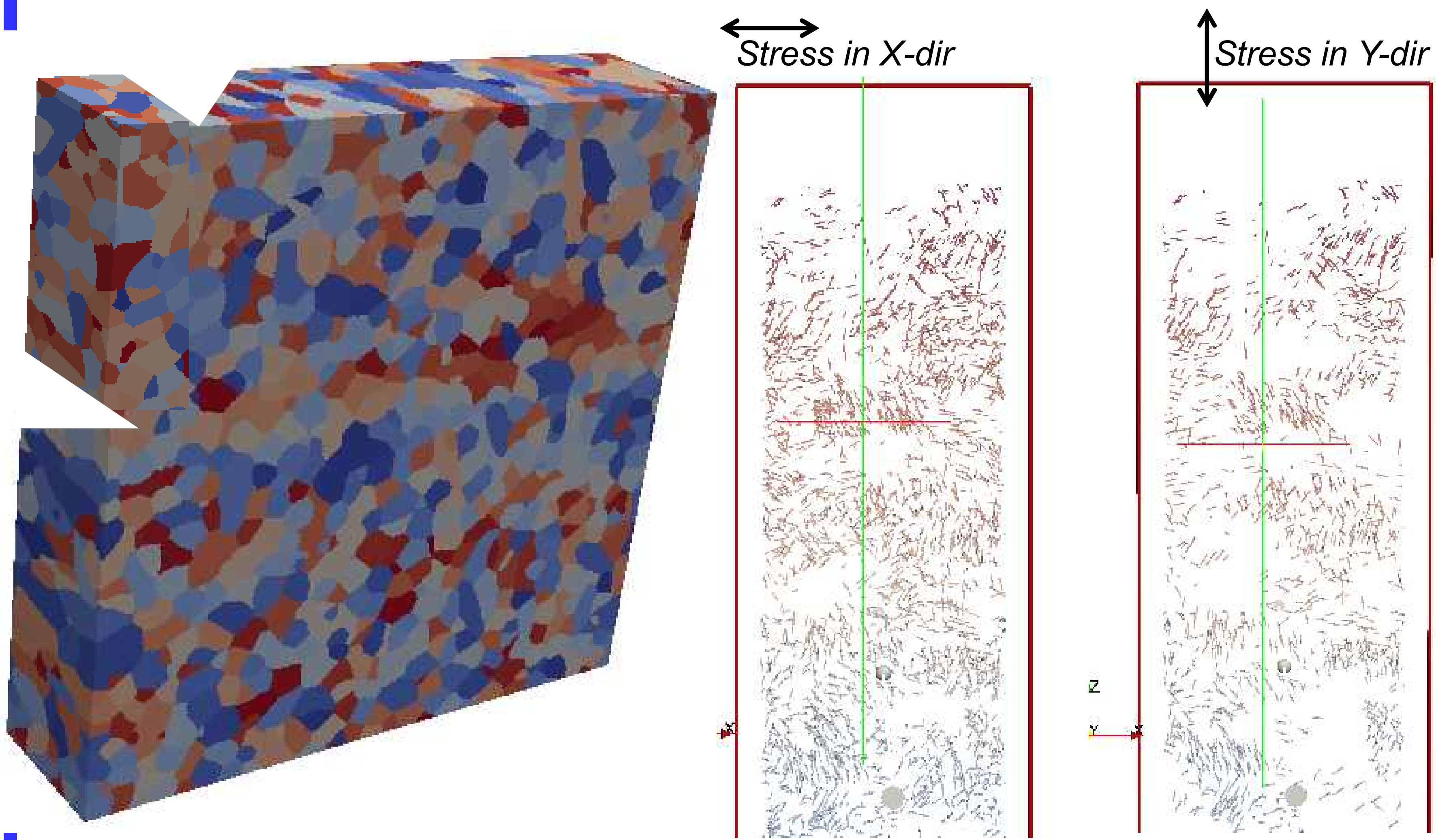


Colas et al., Acta Met 58, 2010

Requested experiments for discovery & validation

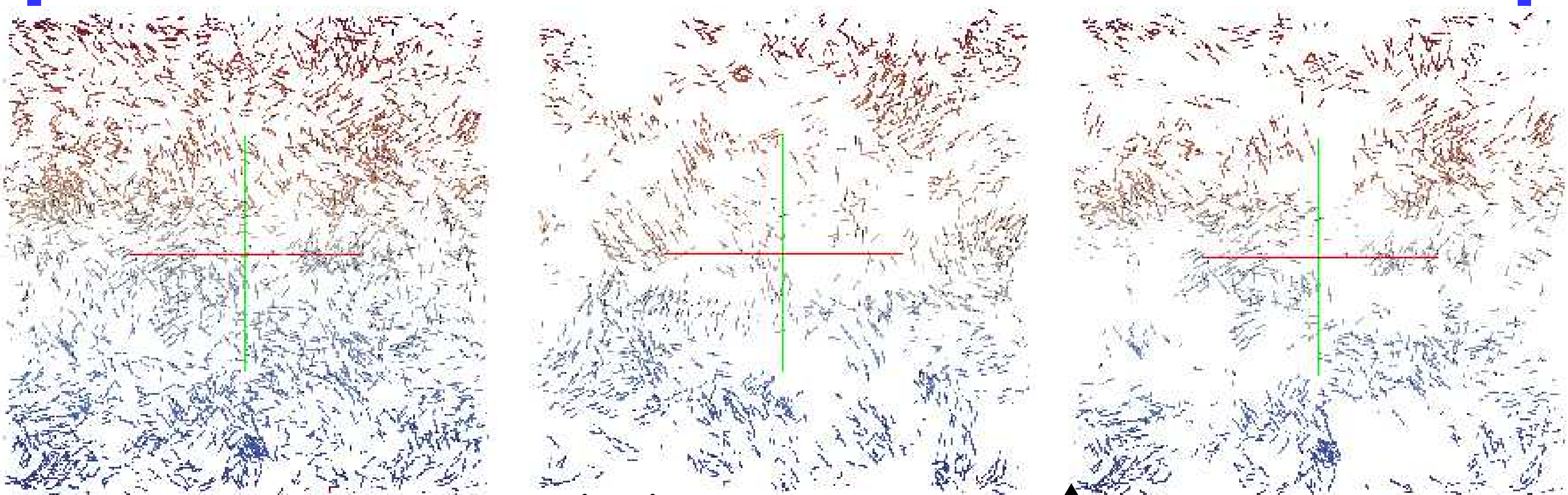
- Precipitate morphology
  - Shape, size (disc or needle)
  - Ordering with respect to each other (stacking)
- Zr-based cladding microstructure
  - Grain size & shape
  - Crystallographic and shape texture
- Threshold stress for re-orientation
- stress on cladding as a function of burnup
- Radiation effects
- Fracture toughness of hydrided, and hydrided & irradiated Zr-claddings
- Note: Most of this can be obtained on hydrided, but un-irradiated samples.

Simulation of δ–$ZrH_{1.5}$ precipitation in rolled α–Zr with randomly oriented grains.



Simulation of δ–$ZrH_{1.5}$ precipitation in rolled α–Zr with randomly oriented grains.

δ–$ZrH_{1.5}$ under conditions of no stress, stress in Y- and X-directions.



No stress *Stress in X-dir* *Stress in Y-dir*

Reorientation occurs by precipitates in different grains that are favorably oriented precipitating to form "continuous" looking precipitates.

Nucleation and growth of hydride precipitates