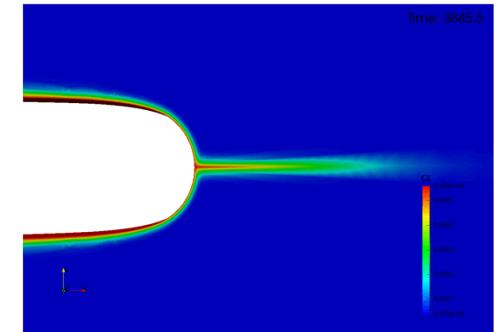
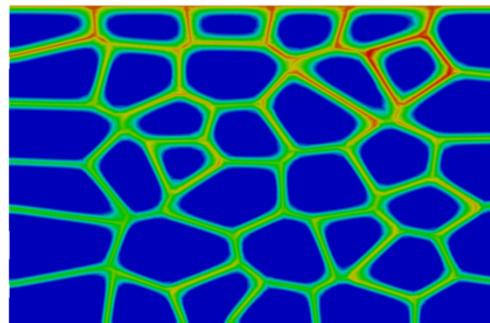
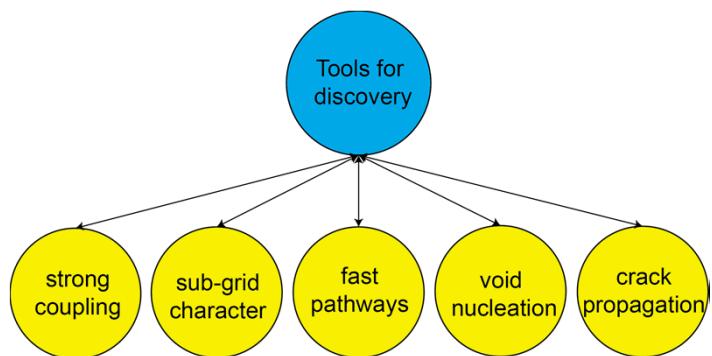


*Exceptional service in the national interest*



## Simulating hydrogen embrittlement and fast pathways for diffusion

J. Foulk III, J. Ostien, A. Mota, Steve Sun, Guy Bergel, Gabriel de Frias  
 Collaborators: Bill Wolfer, C. San Marchi, B. Somerday

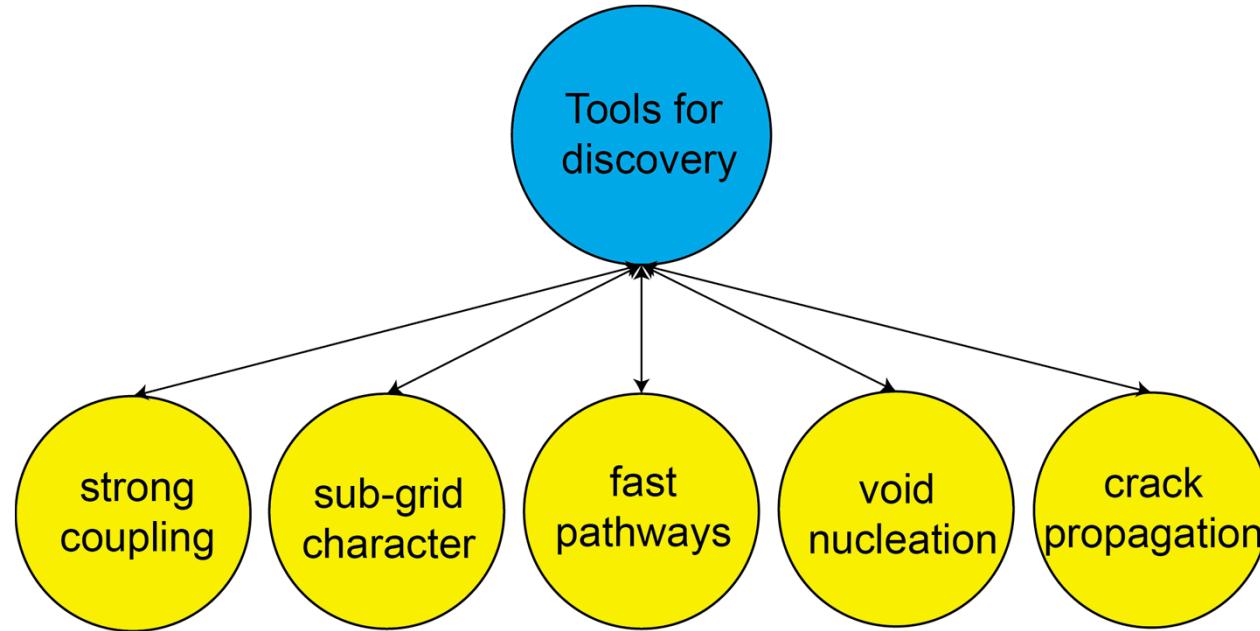
October 27, 2016



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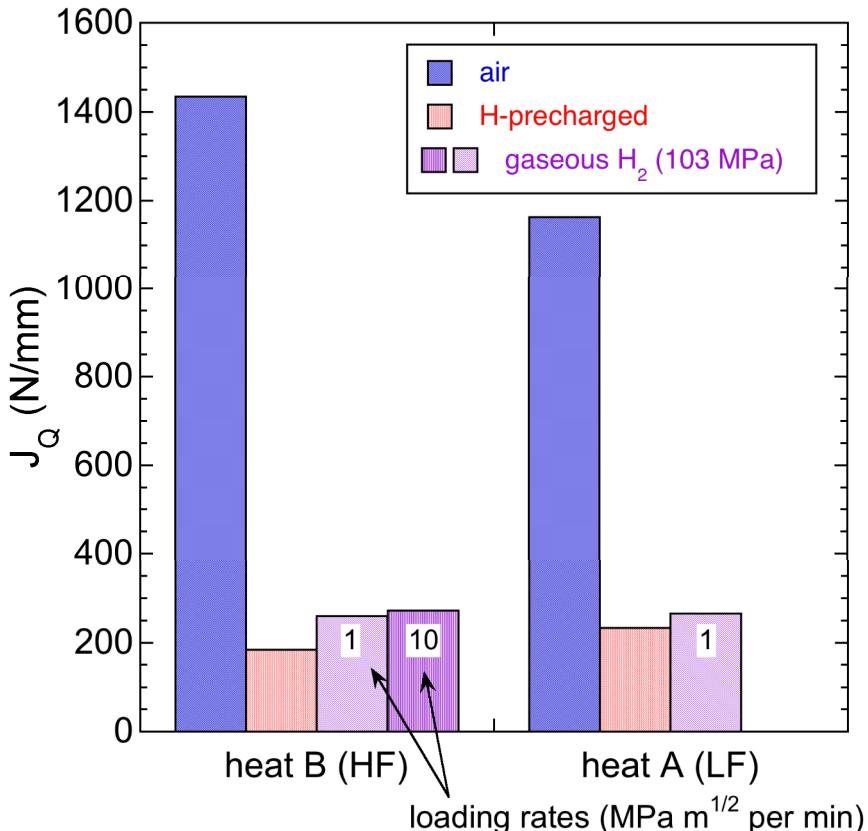
# Tools for discovery and prediction

- Motivated through observation
- Strong chemo-mechanical coupling
- Capture sub-grid processes through a surface approach
- Explore fast pathways for diffusion at structural and microstructural scales
- Develop models for H/T/He embrittlement w/focus on void nucleation
- Demonstrate crack initiation and propagation via the SFC

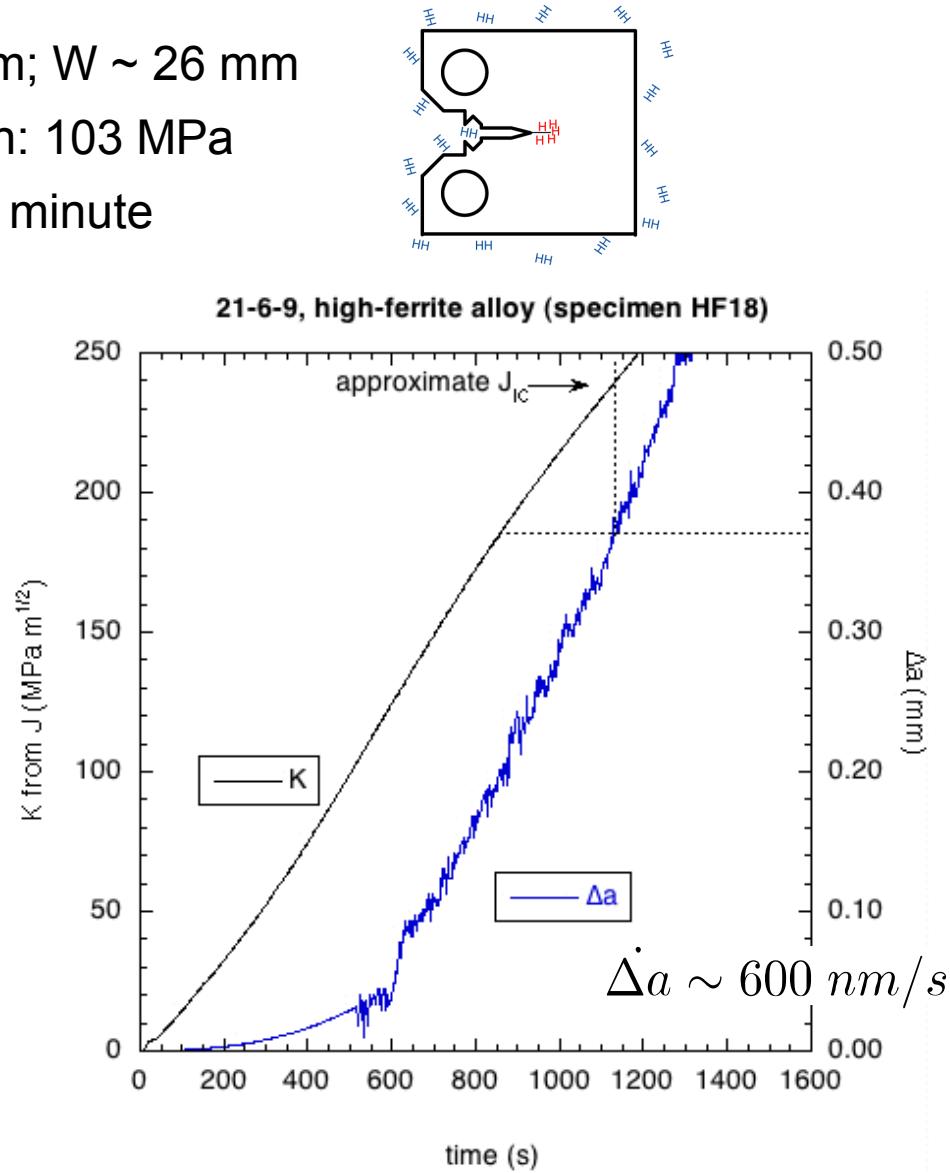


# Initial studies in 21Cr-6Ni-9Mn SS

- Compact tension specimens,  $B \sim 13$  mm;  $W \sim 26$  mm
- Constant pressure of gaseous hydrogen: 103 MPa
- “Loading rates”  $\sim 0.6 - 10$  MPa  $m^{1/2}$  per minute



Note:  $220 \text{ MPa } m^{1/2} = 224 \text{ kJ/m}^2 \text{ (N/mm)}$



(C. San Marchi, SNL)

# Aging of stainless steels in H isotopes

- Fracture toughness degrades with increasing helium concentrations
- Both tritium and helium are requisite for degradation
- Transition from void evolution to fracture along twin and grain boundaries

Morgan and Tosten, Tritium and decay helium effects on the fracture toughness, International Conference on Hydrogen (1994)

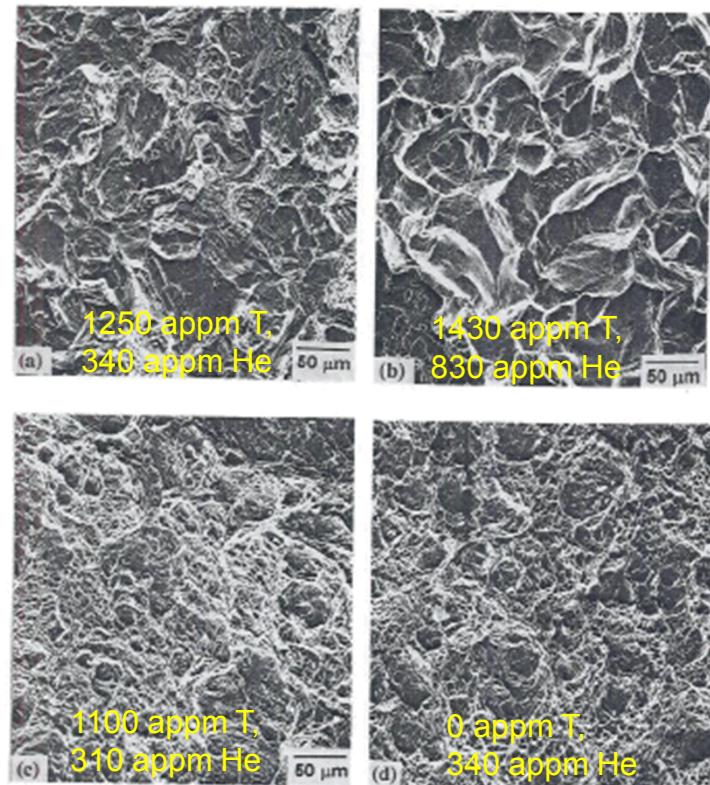
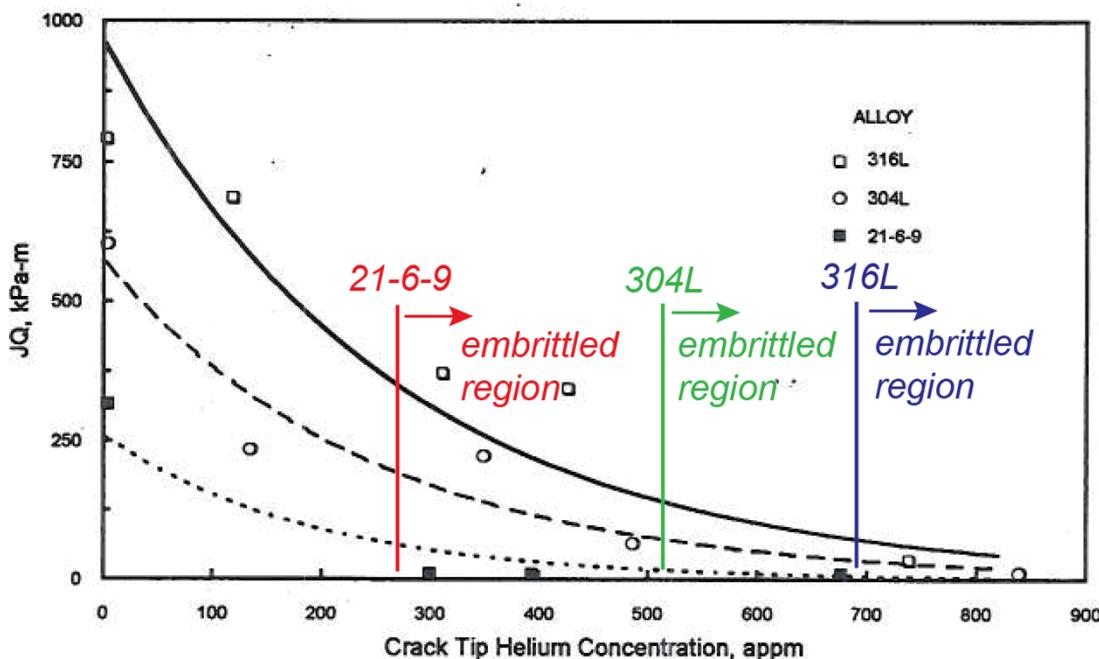


Figure 4 - Fracture Modes in Tritium-Exposed-And-Aged Stainless Steels: (a) Type 304L, 1250 Tritium, 340 appm He; (b) Type 304L, 1430 Appm Tritium, 830 appm He; (c) Type 316L Steel 1100 appm Tritium 310 appm He; (d) Type 304L, Tritium Degassed, ~0 appm T, 340 appm He.

# Finite deformation diffusion of H

This path heavily leverages Sofronis/McMeeking (1989)\* and Krom (1998). Recent work by Leo and Anand (2013).

## *Transport of hydrogen in the current configuration*

$$D^* \dot{c}_l + C^* \operatorname{div} \mathbf{v} - \nabla_{\mathbf{x}} \cdot \mathbf{d}_l \nabla_{\mathbf{x}} c_l - \nabla_{\mathbf{x}} \cdot \frac{c_l}{J} \mathbf{d}_l \nabla_{\mathbf{x}} J + \nabla_{\mathbf{x}} \cdot \frac{c_l V_H}{RT} \mathbf{d}_l \nabla_{\mathbf{x}} \tau_h + \frac{\theta_l}{J} \frac{\partial N_T}{\partial \epsilon_p} \dot{\epsilon}_p - \frac{\theta_t N_T}{J^2} \dot{J} = 0$$

## *Transport of hydrogen in the reference configuration (push back)*

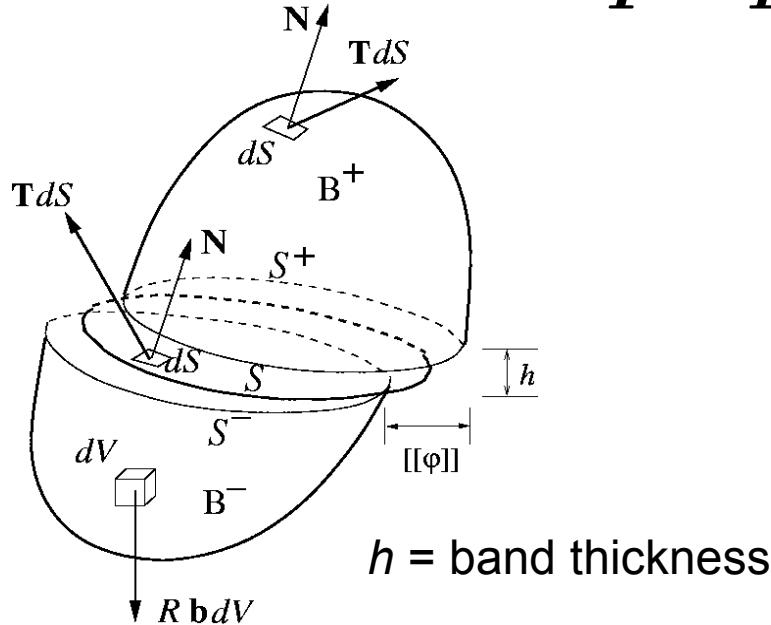
$$D^* \dot{C}_L - \nabla_{\mathbf{X}} \cdot \mathbf{d}_l \mathbf{C}^{-1} \nabla_{\mathbf{X}} C_L + \nabla_{\mathbf{X}} \cdot \frac{d_l V_H}{RT} \mathbf{C}^{-1} \nabla_{\mathbf{X}} \tau_h C_L + \theta_T \frac{d N_T}{d \epsilon_p} \dot{\epsilon}_p$$


  
*transient term*      *diffusion term*      *advection term from pressure*      *source term from trapping*

Deformation-dependent diffusivity     $D_L = \mathbf{F}^{-1} \mathbf{d}_l \mathbf{F}^{-T} = d_l \mathbf{C}^{-1}$

# Capture sub-grid processes for R(a)

Goal: Capture sub-grid processes through methods that regularize the jump

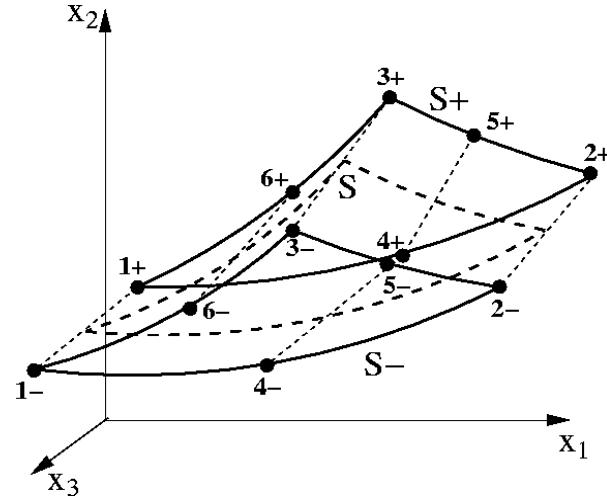


$$\mathbf{F} = \mathbf{F}^{\parallel} \mathbf{F}^{\perp}$$

$$\mathbf{F}^{\parallel} = \mathbf{g}_i \otimes \mathbf{G}^i$$

$$\mathbf{F}^{\perp} = \mathbf{I} + \frac{[\![\Phi]\!]}{h} \otimes \mathbf{N}$$

$$\mathbf{F} = \mathbf{F}^{\parallel} + \frac{[\![\varphi]\!]}{h} \otimes \mathbf{N}$$



Akin to “cohesive” element

Yang, Mota and Ortiz (IJNME, 2005), Armero and Garikipati (IJSS, 1996)

# Extend sub-grid model for multiphysics

Fox and Simo (1990), Callari, Armero, Abati (2010)

*redefine space*  $\mathbf{X} = \Phi(\xi^1, \xi^2, \xi^3) = \bar{\Phi}(\xi^1, \xi^2) + \mathbf{N}(\xi^1, \xi^2)\xi^3$

$$\mathbf{G}_i = \Phi_{,i} = \frac{\partial \mathbf{X}}{\partial \xi^i}$$

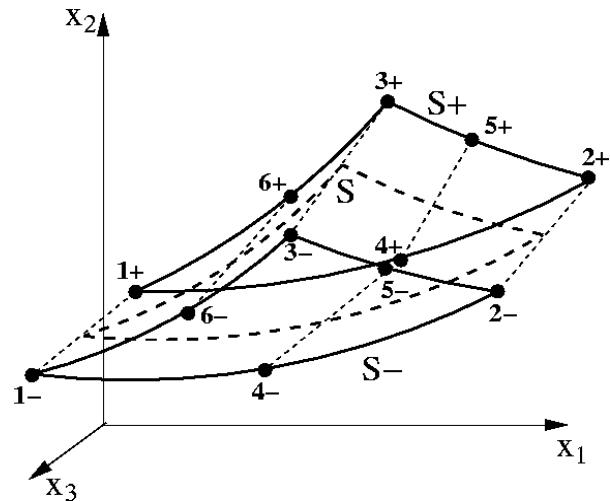
*include jump in C*  $C(\mathbf{X}) = \bar{C}(\phi[\xi^1, \xi^2]) + \frac{[C](\phi[\xi^1, \xi^2])}{h}\xi^3$   $\nabla_{\mathbf{X}} C = (\nabla \Phi)^{-T} \frac{\partial C}{\partial \xi^i}$

Finite element implementation is straightforward

$$\nabla_{\mathbf{X}} C|_{\xi^3=0} = [B] \begin{bmatrix} \{C\}^+ \\ \{C\}^- \end{bmatrix} = [[B]^+ \quad [B]^-] \begin{bmatrix} \{C\}^+ \\ \{C\}^- \end{bmatrix}$$

$$B_{ia}^{\pm} = [G_i^1 \quad G_i^2 \quad G_i^3] \cdot \left[ \frac{1}{2} \frac{\partial N_a}{\partial \xi^1} \quad \frac{1}{2} \frac{\partial N_a}{\partial \xi^2} \quad \pm \frac{1}{h} N_a \right]$$

$i = \# \text{ dimensions}, a = \# \text{ nodes}$



Given this gradient operator, we can use the same PDE for finite-deformation diffusion

$$D^* \dot{C}_L - \nabla_{\mathbf{X}} \cdot d_l \mathbf{C}^{-1} \nabla_{\mathbf{X}} C_L + \nabla_{\mathbf{X}} \cdot \frac{d_l V_H}{RT} \mathbf{C}^{-1} \nabla_{\mathbf{X}} \tau_h C_L + \theta_T \frac{dN_T}{d\epsilon_p} \dot{\epsilon}_p$$

# Simple channel w/fast pathway

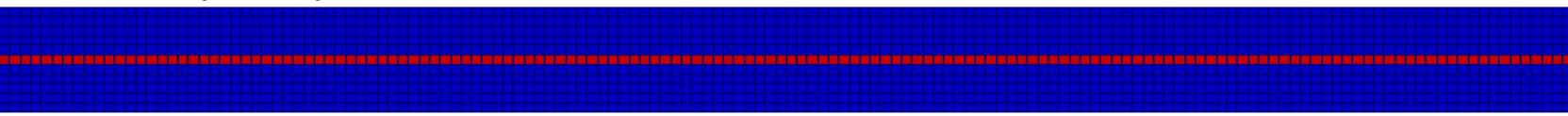
*Implementation of fast pathway (no deformation):*

$$\int_{\mathcal{B}^G} \nabla_{\mathbf{X}} v D_L(\mathbf{X}) \nabla_{\mathbf{X}} C \, dV \approx h \sum_{j=1}^{N_{\text{int}}^M} \bar{W}(\xi_j^1, \xi_j^2) \begin{bmatrix} v_a^+(\xi_j^1, \xi_j^2) & v_a^-(\xi_j^1, \xi_j^2) \end{bmatrix} \begin{bmatrix} \vec{B}^+(\xi_j^1, \xi_j^2) \\ \vec{B}^-(\xi_j^1, \xi_j^2) \end{bmatrix} D_L(\mathbf{X}) \\ \begin{bmatrix} \vec{B}^+(\xi_j^1, \xi_j^2) & \vec{B}^-(\xi_j^1, \xi_j^2) \end{bmatrix} \begin{bmatrix} C_a^+ \\ C_a^- \end{bmatrix}$$

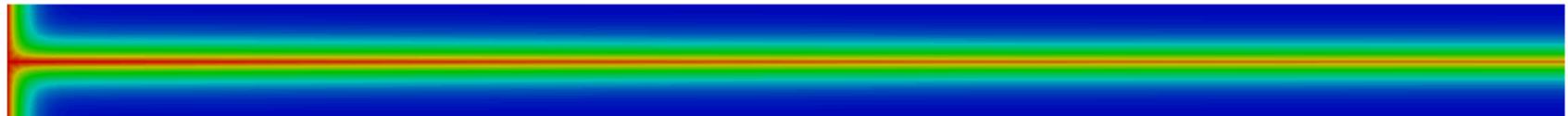
Surface fast pathway



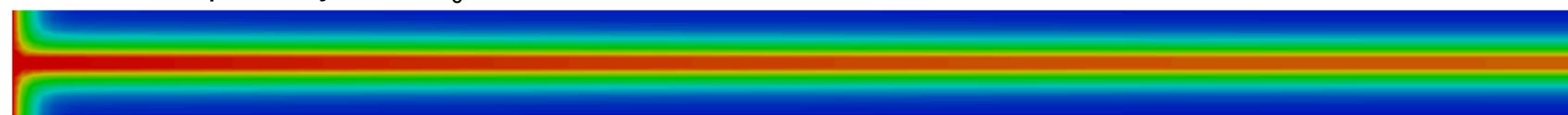
Channel fast pathway



Surface fast pathway,  $10^5 D_0$



Channel fast pathway,  $10^5 D_0$

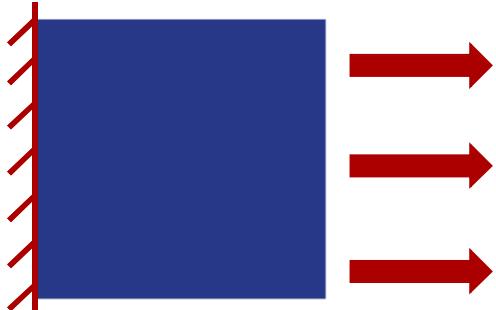


CL



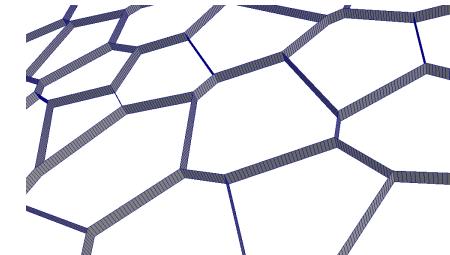
# Polycrystals with fast pathway

*Grain interface diffusion coupled with mechanical loading:*

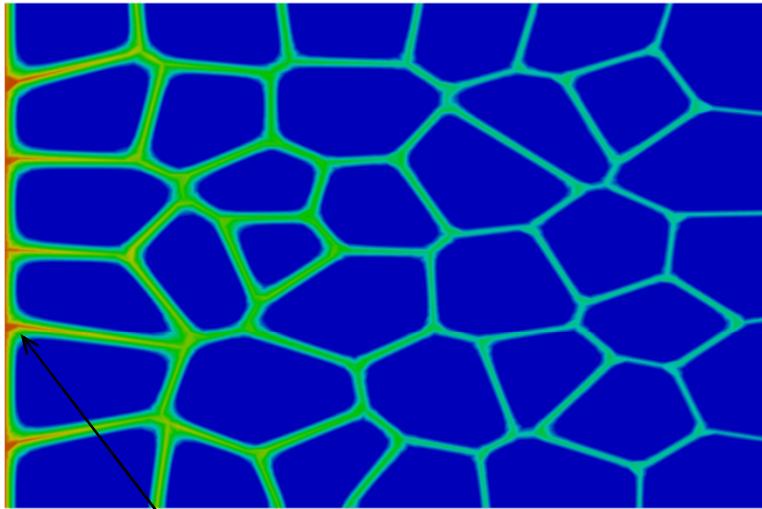


- Stretched in horizontal direction
- Fast pathway =  $10^5 D_0$
- Horizontal diffusion
- Vertical diffusion

$$D_L = F^{-1} d_l F^{-T} = d_l C^{-1}$$



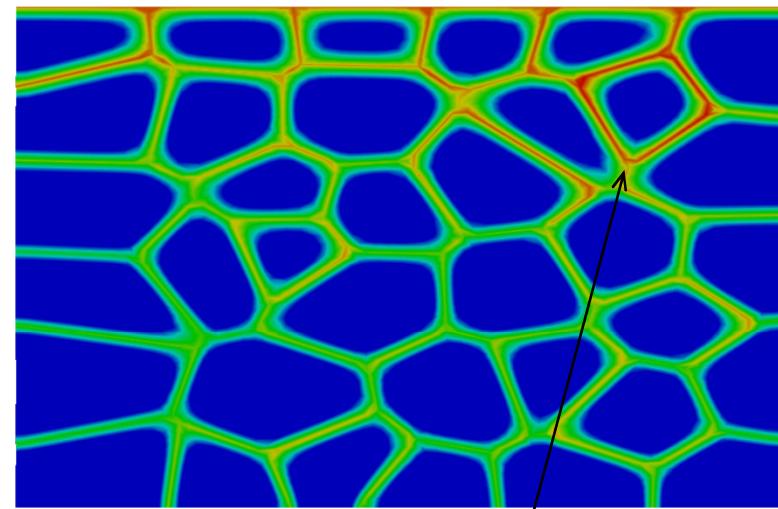
Horizontal diffusion



*Diffusion slows down due to increasing length.*



Vertical diffusion

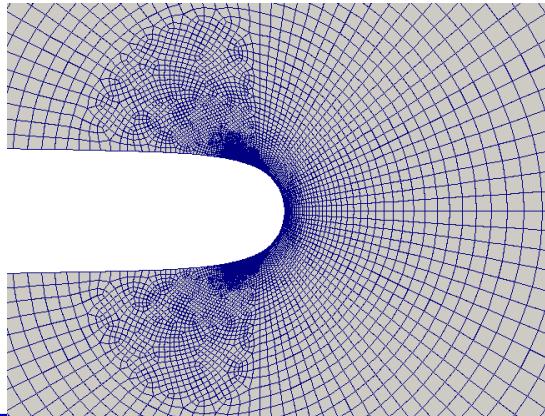
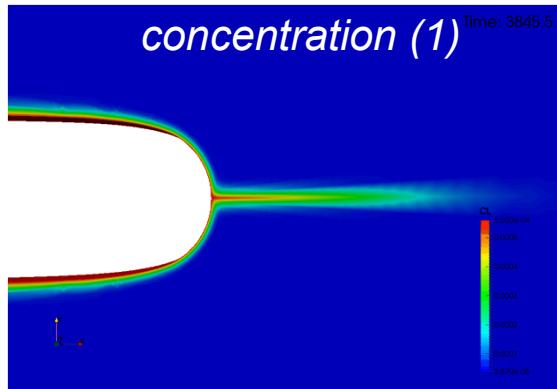


*Diffusion speeds due to decreasing length*

# Solving 5 fields simultaneously

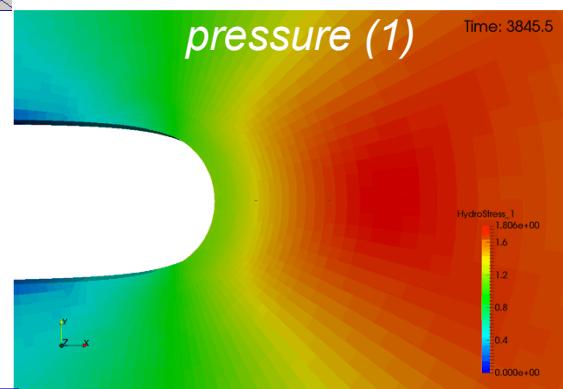
Units are scaled in the balance of linear momentum, conservation of concentration, and  $L_2$  projection to improve condition number of the system

$$D^* \dot{C}_L$$

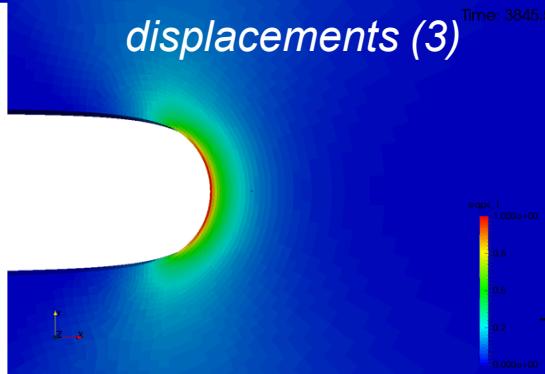


<https://software.sandia.gov/albany/>

- Path:  $10^5 D_0$
- $K_{app}$ : 85 MPa  $m^{1/2}$
- Time: 3850 s



$$\nabla_x \cdot d_l C^{-1} \nabla_x C_L$$

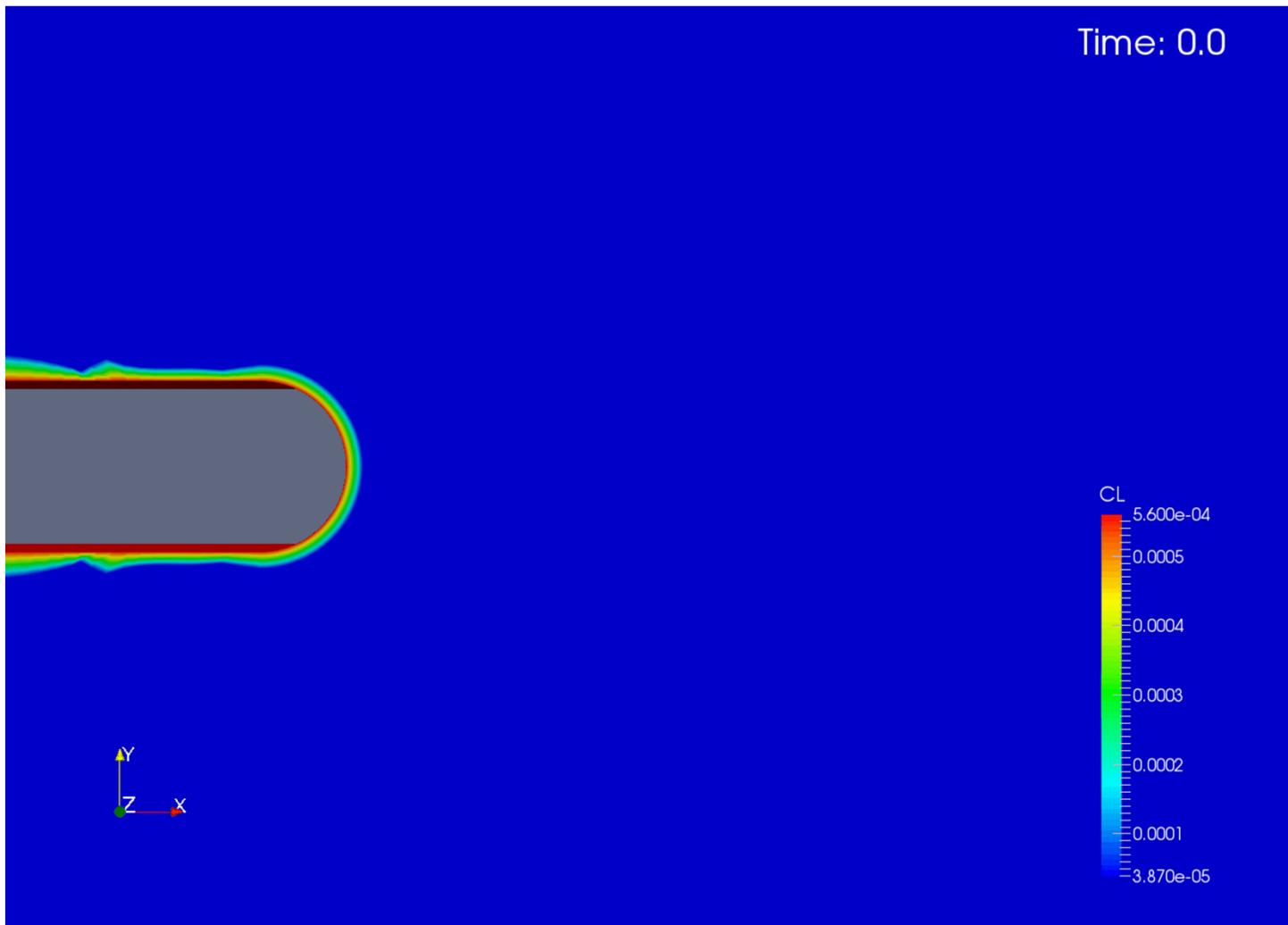


$$\nabla_x \cdot \frac{d_l V_H}{RT} C^{-1} \nabla_x \tau_h C_L$$

NOTE: 85 MPa  $m^{1/2}$  is well below  $J_Q$  for 21Cr-6Ni-9Mn (220 MPa  $m^{1/2}$ )

$$+ \theta_T \frac{dN_T}{d\epsilon_p} \dot{\epsilon}_p$$

# Evolution of concentration at crack tip



# H isotope diffusion w/ He bubbles

We seek to find descriptors of helium bubble formation that result from the radioactive decay of tritium (T) to He.

- Schaldach and Wolfer (2004) focus on the total number of clusters (total bubble density)

1000s of ODEs for helium clusters are condensed into 3 coupled ODEs written in

- Single He (monomers)  $N_1$ , total bubble density,  $N_b$ , and bubble volume fraction  $S_b$
- ODEs are nonlinear. We can integrate them implicitly with Newton's method
- Chemo-mechanical solution ( $T, \mathbf{u}$ ). Solve ODEs (dependent on  $T$ ) at integration points.

$$\frac{dN_1}{dt} = G(t) - 16\pi(r_1 + r_1)DN_1^2 - 4\pi DN_1 \left( \frac{3}{4\pi} \right)^{\frac{1}{3}} S_b^{\frac{1}{3}} N_b^{\frac{2}{3}}$$

$$\frac{dN_b}{dt} = 8\pi(r_1 + r_1)DN_1^2$$

$$\frac{\eta}{\Omega} \frac{dS_b}{dt} = 16\pi(r_1 + r_1)DN_1^2 + 4\pi DN_1 \left( \frac{3}{4\pi} \right)^{\frac{1}{3}} S_b^{\frac{1}{3}} N_b^{\frac{2}{3}}$$

$$C_{He} = N_1 + \left( \frac{\eta}{\Omega} \right) S_b$$

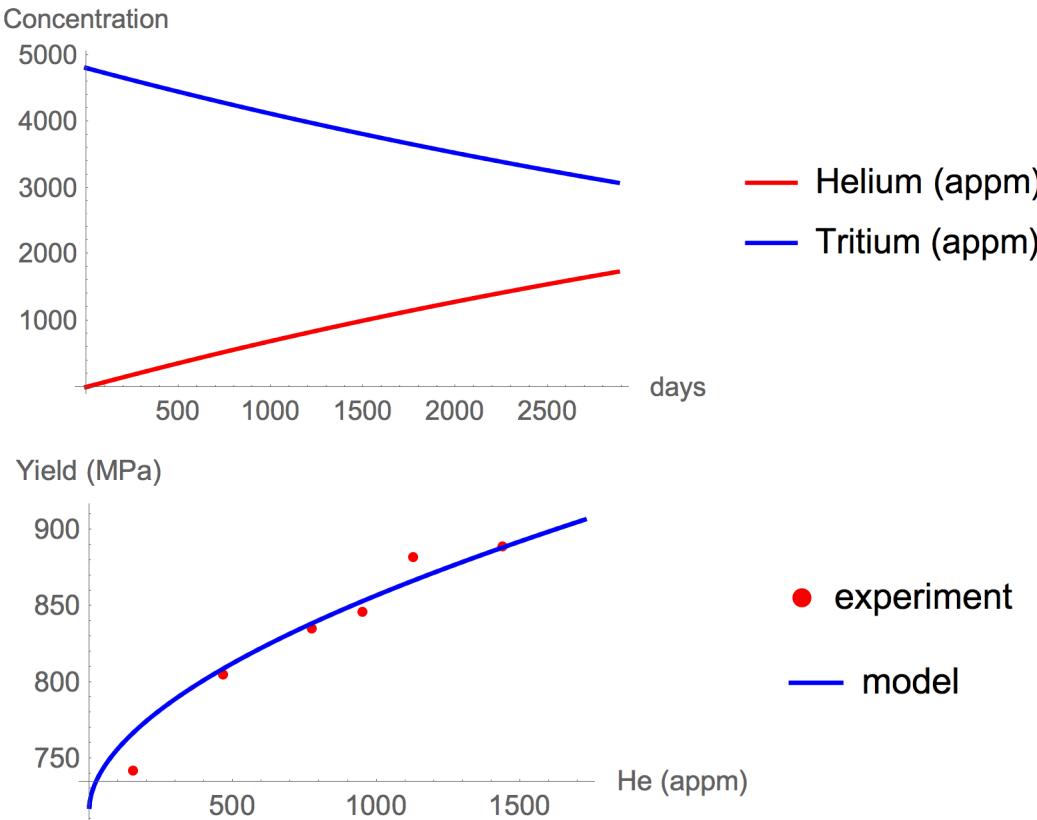
$G(t)$  – helium source term

$r_1$  - initial bubble radius

$\eta$  - number of He atoms/vacant site

$\Omega$  - partial molar volume

# Effects of tritium & helium on yield



Comparison of current model to experimental data by Robinson and Thomas (1991). Data from hydrogen yields  $\alpha_1$  (hydrogen = tritium). Nonlinearity in fit stems from average bubble radius, not fitting parameter  $\alpha_2$ . Both parameters are needed to accurately fit Robinson's data.

From helium bubble ODEs, we have:

$N_b$  total bubble density

$S_b$  bubble volume fraction

Calculate average bubble radius:

$$\bar{R}_b = \left( \frac{3S_b}{4\pi N_b} \right)^{\frac{1}{3}}$$

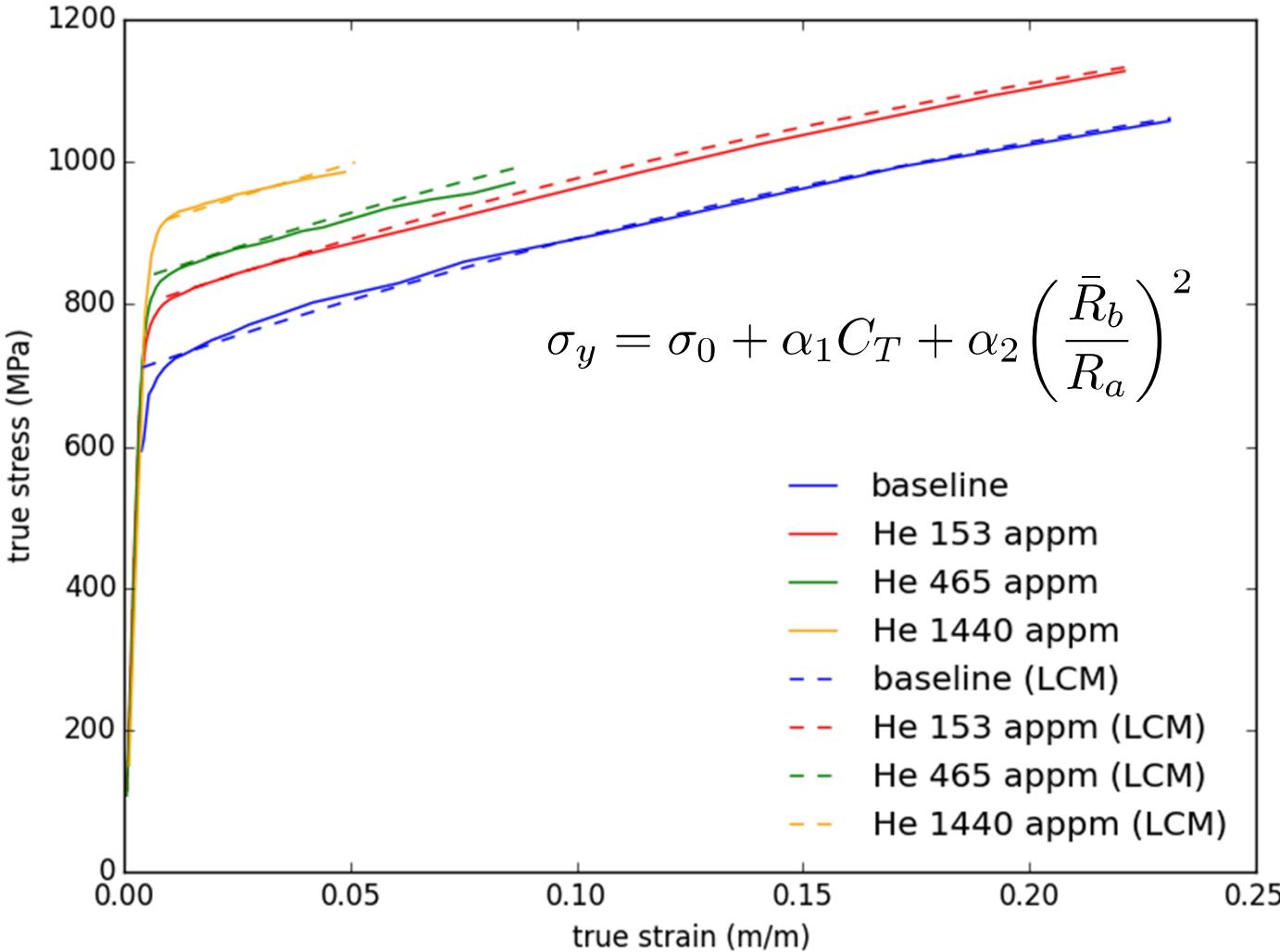
Assumptions for yield stress  $\sigma_y$ :

- Rate independent yield stress  $\sigma_0$
- Proportional to T concentration,  $C_T$
- Misfit strengthening from He is dominant (Arsenlis, Wolfer, JNM)
- Misfit strengthening varies w/ $R_b^2$
- Normalize w/He atomic radius  $R_a$

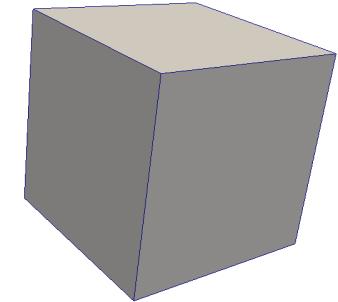
$$\sigma_y = \sigma_0 + \alpha_1 C_T + \alpha_2 \left( \frac{\bar{R}_b}{R_a} \right)^2$$

$\alpha_1$  and  $\alpha_2$  are constants fit to experiments

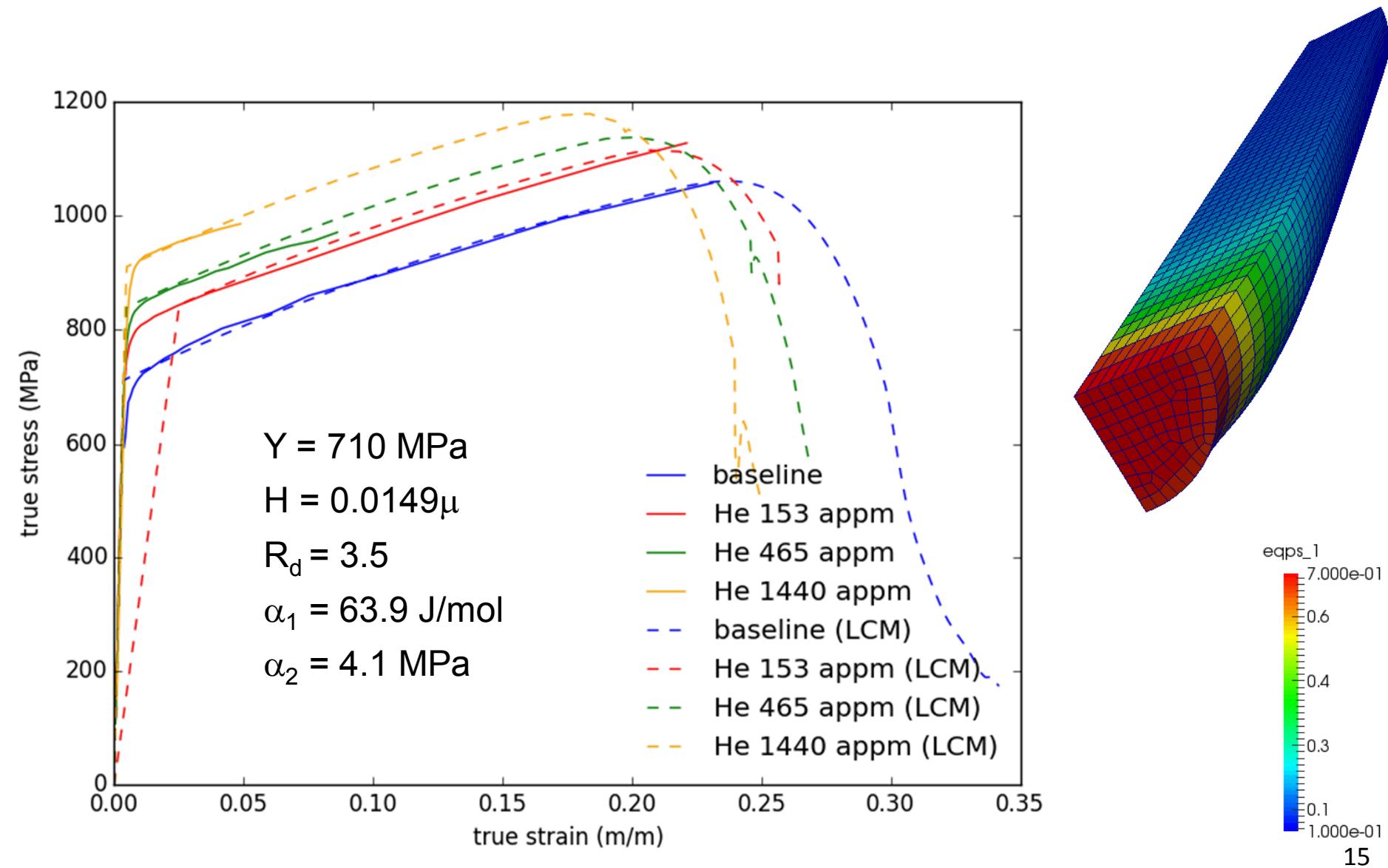
# Yield dominant in flow behavior



$$\begin{aligned}
 \sigma_0 &= 710 \text{ MPa} \\
 H &= 0.0149 \mu \\
 R_d &= 3.5 \\
 \alpha_1 &= 63.9 \text{ J/mol} \\
 \alpha_2 &= 4.1 \text{ MPa}
 \end{aligned}$$



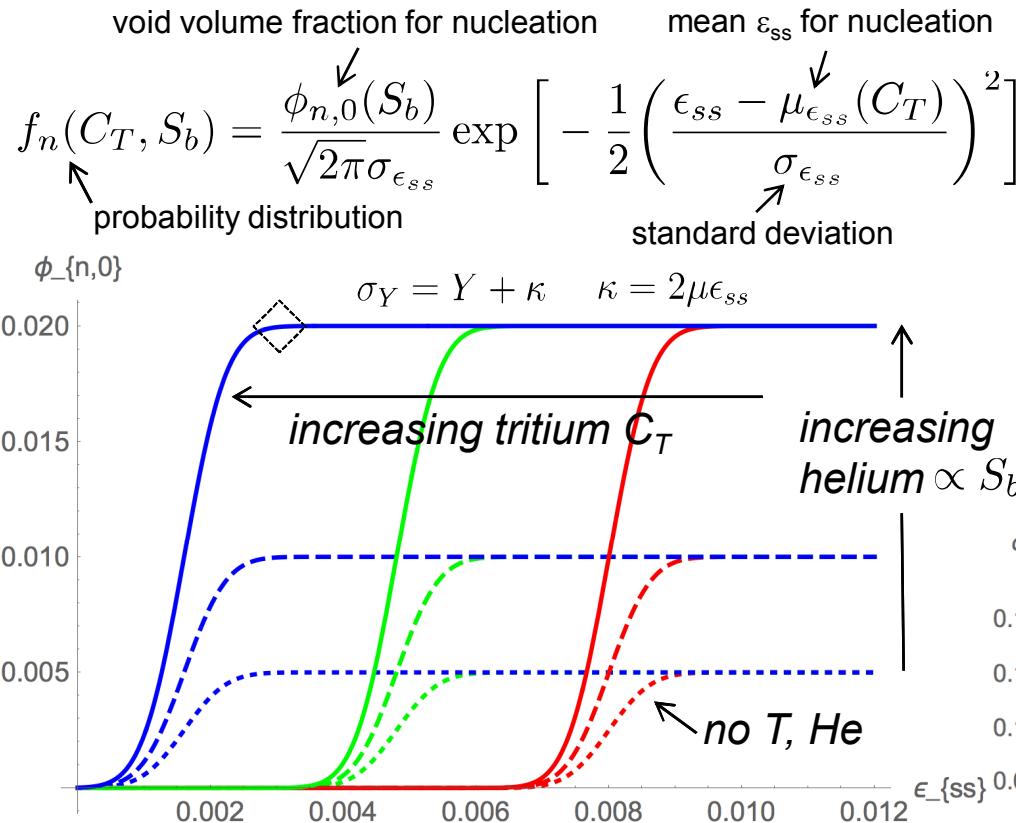
# T/He nucleation needed for failure



Model results reduced through volume preservation to create true stress-strain curves.

# T/He nucleation, growth, coalescence

In spirit of Chu and Needleman (1980) we choose an appropriate state variable to capture void nucleation through elevated stresses at pile-ups.



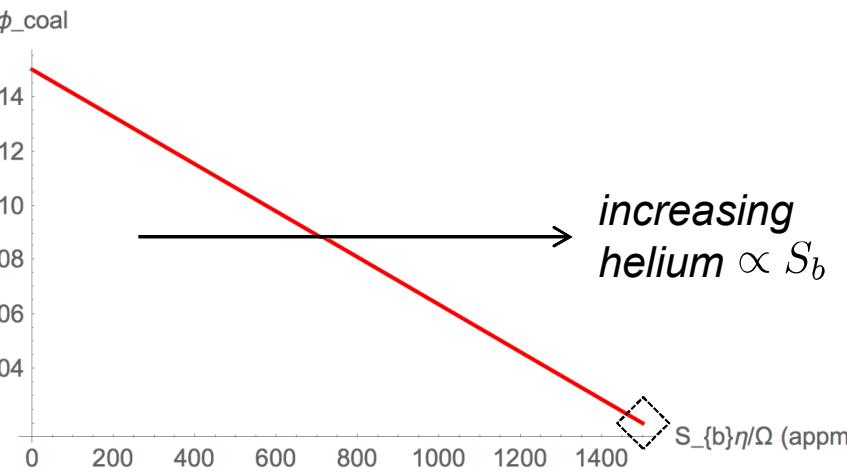
*Statistical nucleation:* Tritium localizes deformation and enables voids to nucleate earlier in the deformation.

Helium-hardened microstructure nucleates more voids.

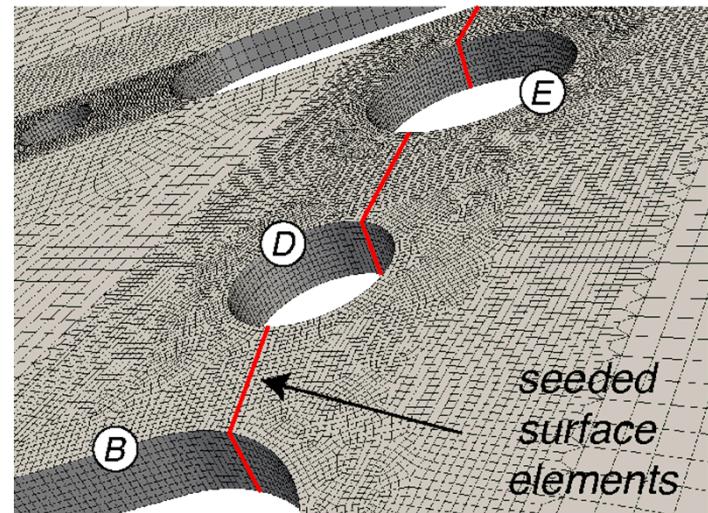
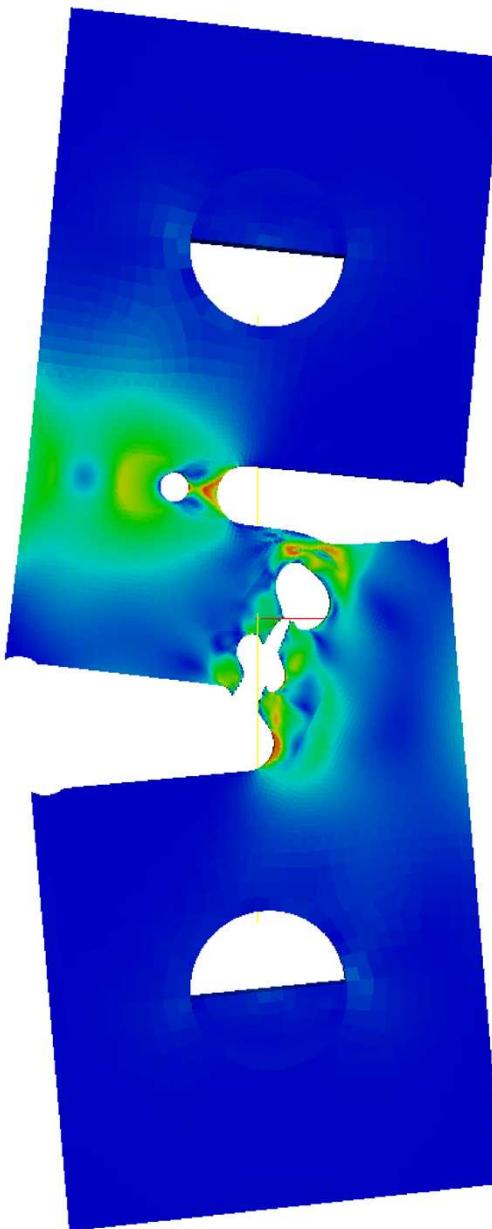
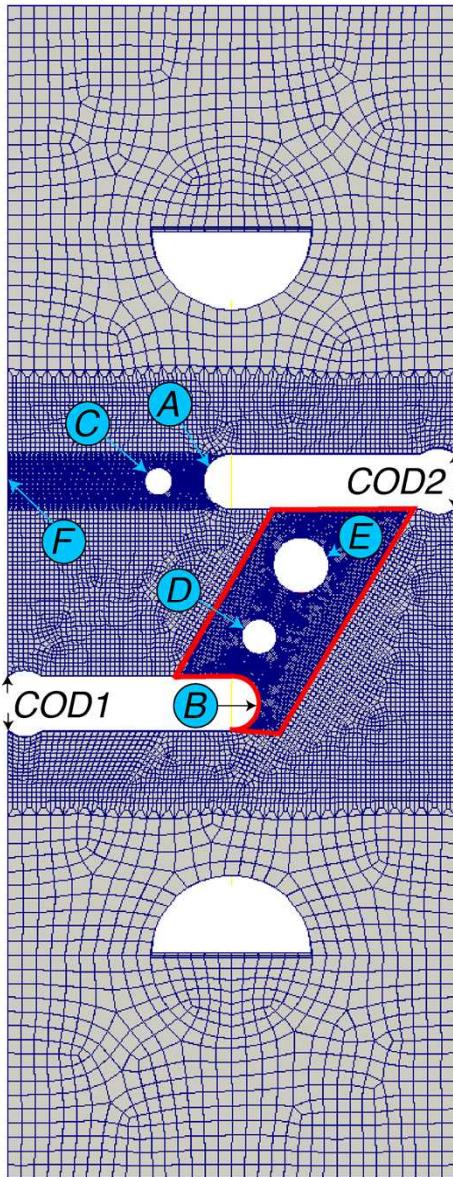
A tritium-embrittled, helium-hardened microstructure can move from nucleation to coalescence ◇

Initial model for void evolution:

- Void nucleation driven by deformation (dislocations, twins)  $\propto \epsilon_{ss}$ 
  - Tritium  $C_T$  hastens process
  - Helium amplifies process
- Void growth through Gurson
- Void coalescence governed by  $S_b$ 
  - Nucleated voids connected by smaller helium bubbles



# Crack initiation and growth in SFC

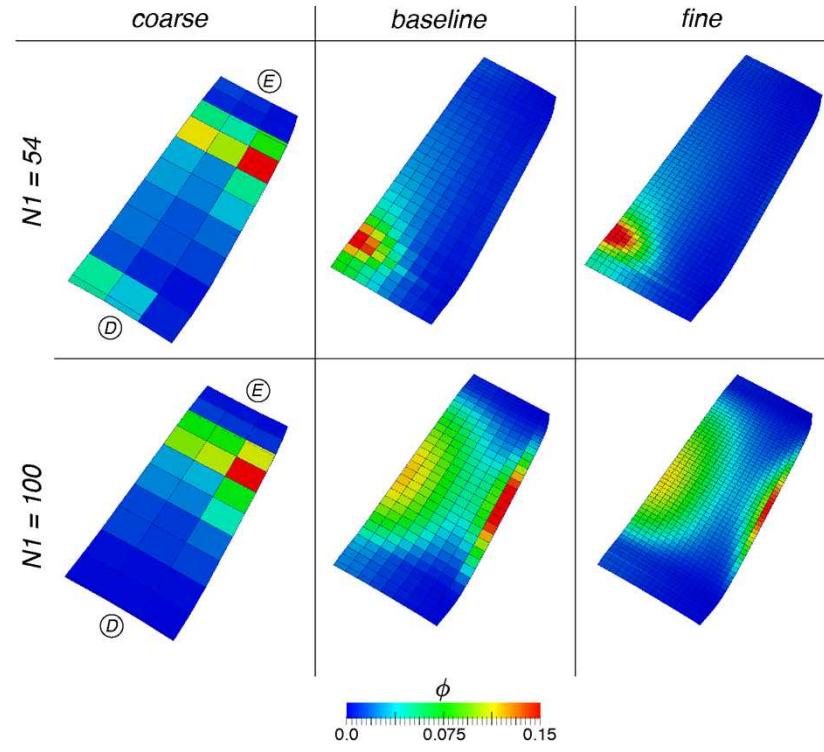
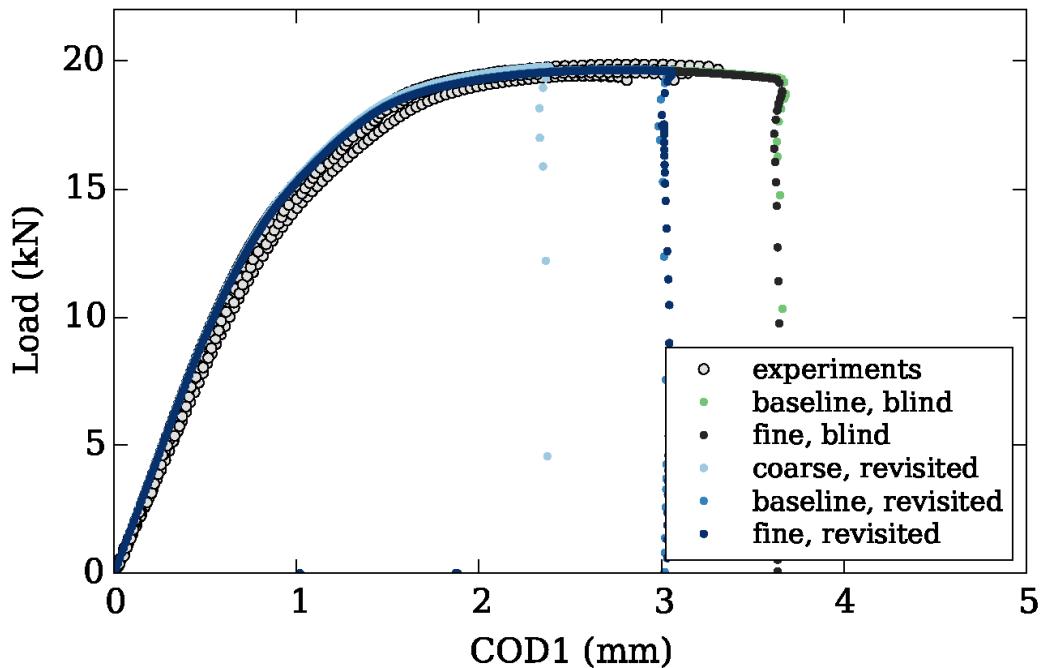


## 2<sup>nd</sup> Sandia Fracture Challenge (SFC)

- Ti-6Al-4V plate
- Anisotropy
- Mixed-mode loading
- Slow/fast rates of loading
- Thermomechanical coupling
- Dynamics (unstable propagation)
- Employed surface elements
- Multiple damage models
- Implicit solution
- *Sierra SolidMechanics*

# Regularized solution

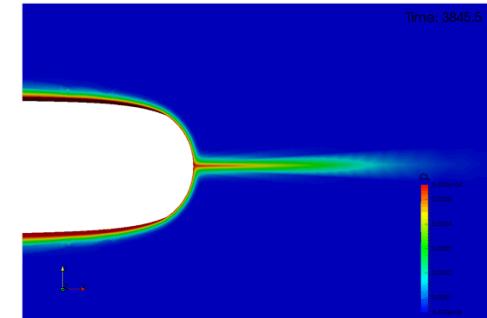
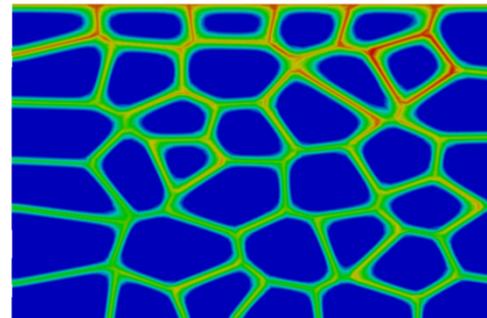
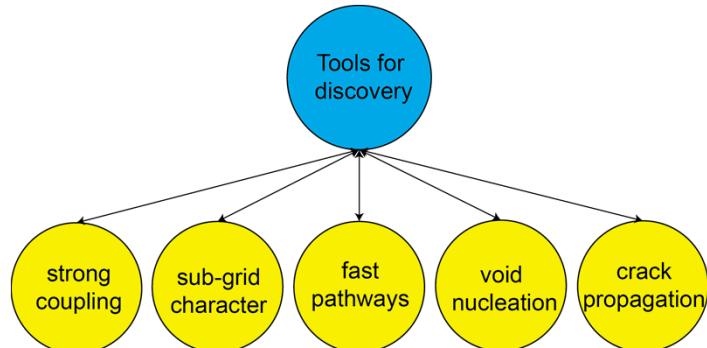
- Localization elements yield convergence in the load displacement curve at slow, isothermal rates
- Constitutive model incorporates anisotropy in yield and shear nucleation in damage evolution



- Convergence in both the far-field and near-field quantities
- Increasing the role of shear nucleation ( $N1$ ) transitions crack initiation from the interior to the surface

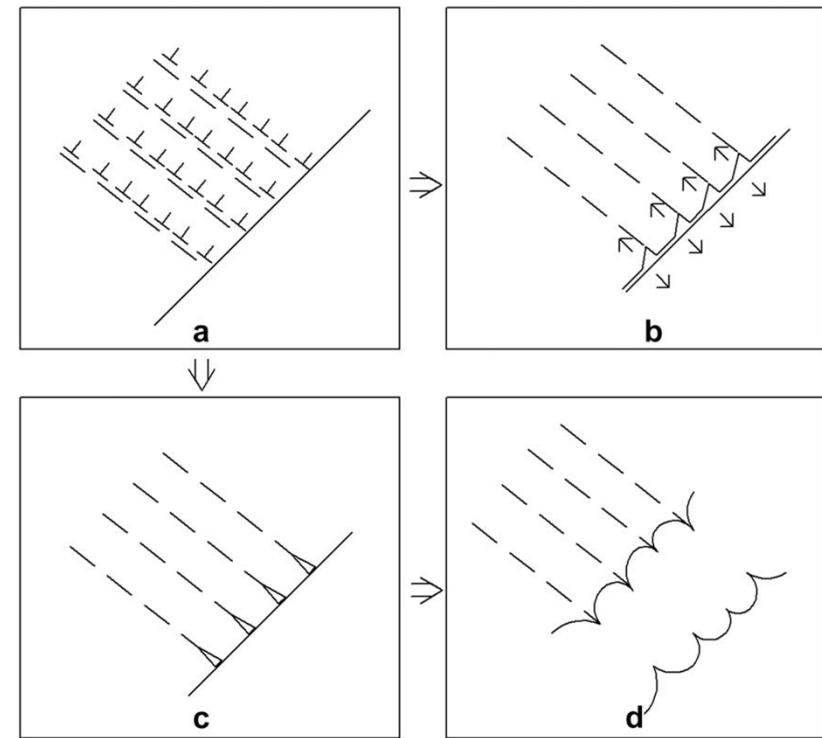
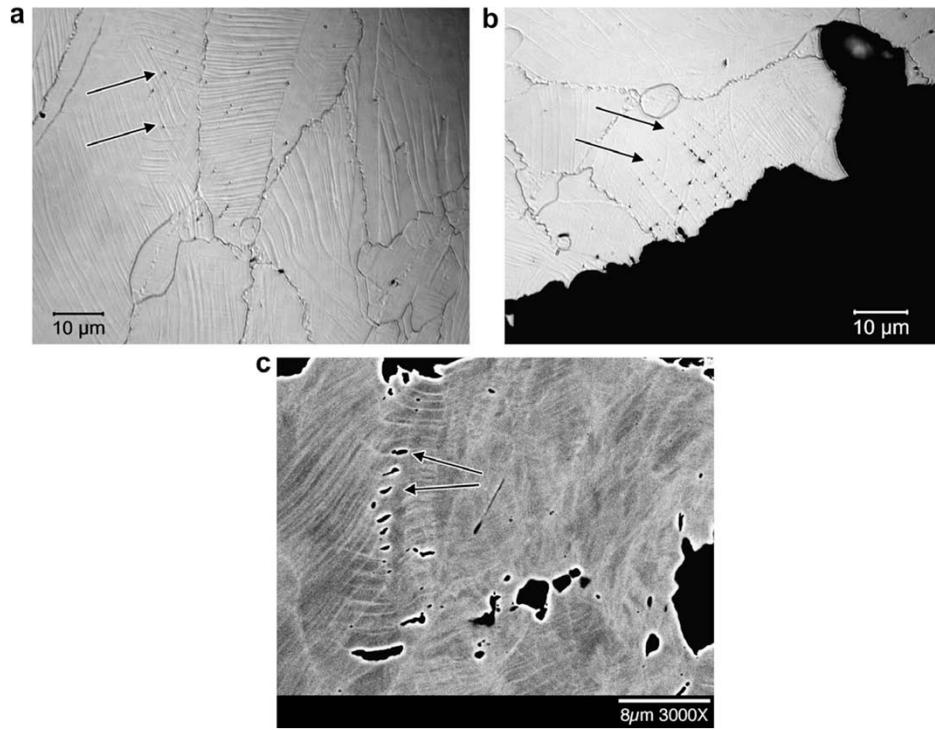
# Summary and path forward

- Illustrated strong chemo-mechanical coupling
- Surface approaches capable of capturing multiphysics on multiple scales
- Progress in H/T/He embrittlement w/focus on void nucleation
- SFC illustrates the applicability of approach to H/T/He embrittlement
- Future work will focus on
  - Parameterization of nucleation processes and transition to coalescence
  - Predicting the time-dependent toughness of 21Cr-6-9Mn
  - Transitioning technology from research environment to production



# *BACKUP SLIDES*

# Damage nucleation model w/H

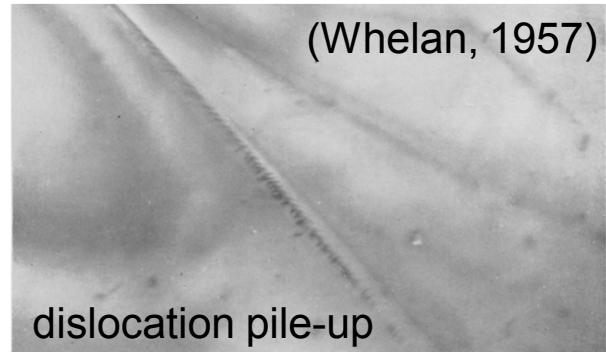
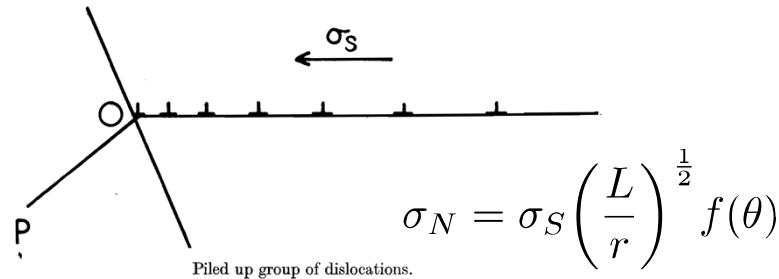


IDEA: Hydrogen enables the premature formation of planar deformation bands that impinge on boundaries of grains, annealing twins, and/or other deformation bands. The stress concentration induced by the intersection may nucleate a void of large aspect ratio (cylinder) that will evolve, coalesce and create the observed “fluted” fracture surface.

*The fracture process is still ductile! Need to capture the premature nucleation of voids in the presence of hydrogen. Can we first construct a simple model to aid our intuition?*

# Analytical basis for nucleation

Stroh, A Theory of the Fracture of Metals, 1957



Using a work argument, the normal stress  $\sigma_N$  for nucleation can be derived from the shear stress  $\sigma_S$  given the fracture energy  $\gamma$  and the number of dislocations  $n$  in a pile-up (band) along a boundary.

$$\sigma_{S,crit} = \frac{3\pi^2 \gamma}{8n(\rho_{ss}, \theta_T)b} \quad n = A(\theta_T)\rho_{ss} = hs(\theta_T)\rho_{ss} \quad \kappa = \mu \epsilon_{ss}$$

$$\epsilon_{ss} = b \sqrt{\rho_{ss}}$$

Given  $b$  is burgers vector and  $A$  is an effective area characterized by the grain size  $h$  and the pile-up spacing  $s$ . We relate the pile-up spacing to the occupancy of hydrogen in the traps  $\theta_T$ . If we approximate  $\sigma_S$  through the yield stress  $\sigma_y$  and the isotropic hardening variable  $\kappa$ , we can express nucleation in terms of a scalar strain metric  $\epsilon_{ss}$  that is reflective of the dislocation density  $\rho_{ss}$ .

$$\epsilon_{ss,crit}^3 + \frac{\sigma_y}{\mu} \epsilon_{ss,crit} - \frac{3\pi b \gamma}{4hs(\theta_T)\mu} \quad \text{permits analytical solution (1 real root)}$$

If we assume heavily worked materials,  $\rho_{ss} \sim 10^{15}$ , the specification of  $s(\theta_T)$  becomes problematic. We need to construct a simplified model for nucleation in the correct state variable  $\epsilon_{ss}$  that can capture a statistical sampling of boundary orientations having dislocation pile-ups (bands) which are stabilized and extended through hydrogen transport.

$$\theta_T = \frac{C_T}{N_T}$$

Occupancy of hydrogen in the traps  $\theta_T$  derives from trapped concentration  $C_T$  and the number of traps  $N_T$ .

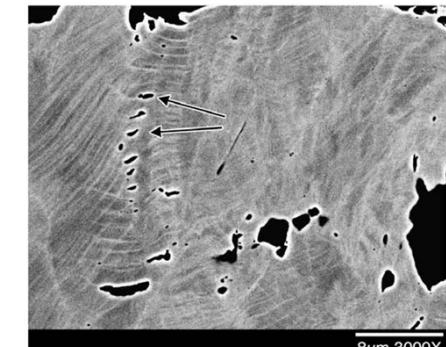
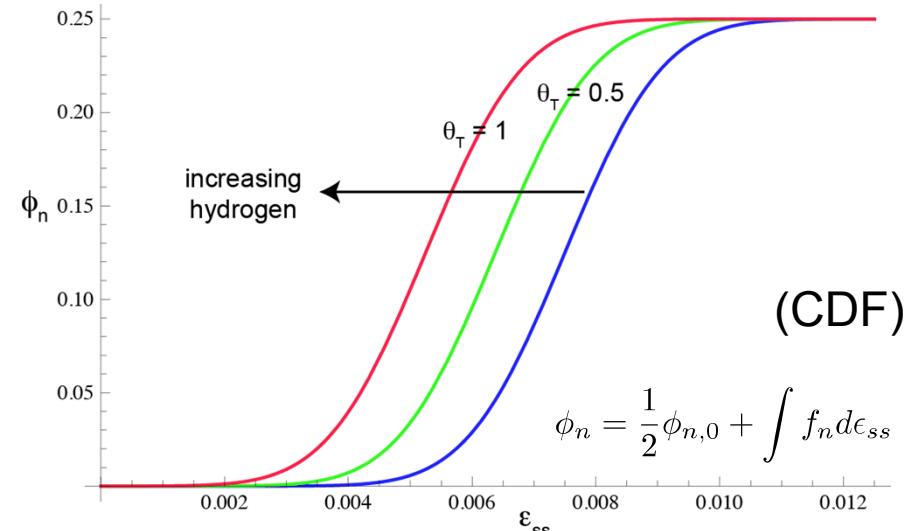
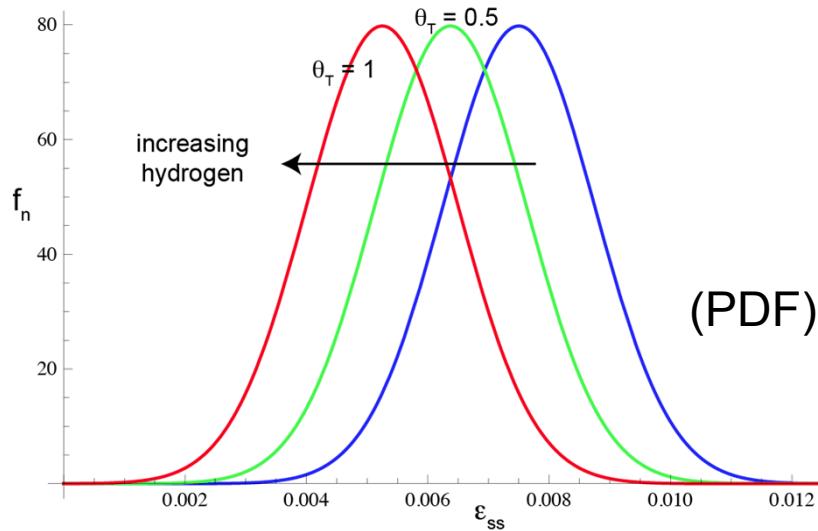
# Phenomenological extension

The deformation bands that evolve under large deformations cannot be easily idealized

$$f_n = \frac{\phi_{n,0}}{\epsilon_{ss, std} \sqrt{2\pi}} \exp \left[ -\frac{1}{2} \left( \frac{\epsilon_{ss} - \epsilon_{ss, mean}}{\epsilon_{ss, std}} \right)^2 \right]$$

In spirit of Chu and Needleman (1980) we choose an appropriate state variable to capture void nucleation through elevated stresses at pile-ups. We assume the probability of void nucleation  $f_n$  follows a normal distribution.

We assume that hydrogen affects the mean  $\epsilon_{ss, mean}$  and not the standard deviation  $\epsilon_{ss, std}$  through the occupancy of hydrogen in the traps  $\theta_T$ . The nucleated void volume fraction  $\phi_n$  can be found through integration and is limited by  $\phi_{n,0}$ .



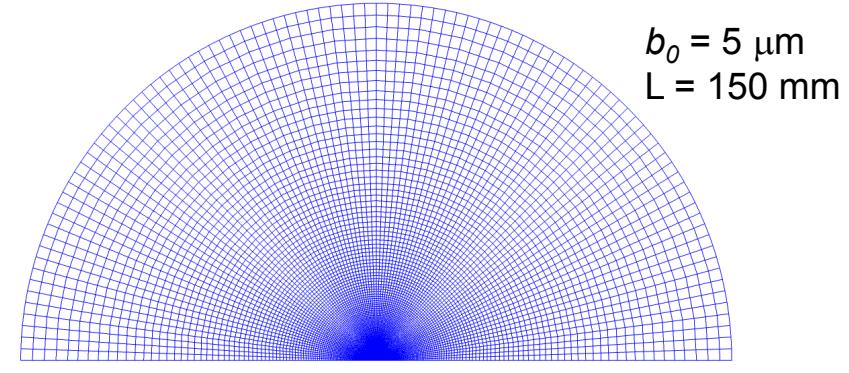
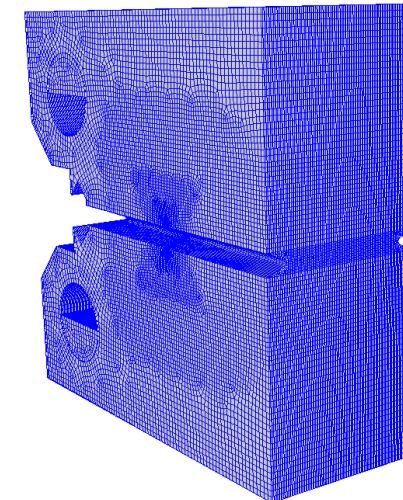
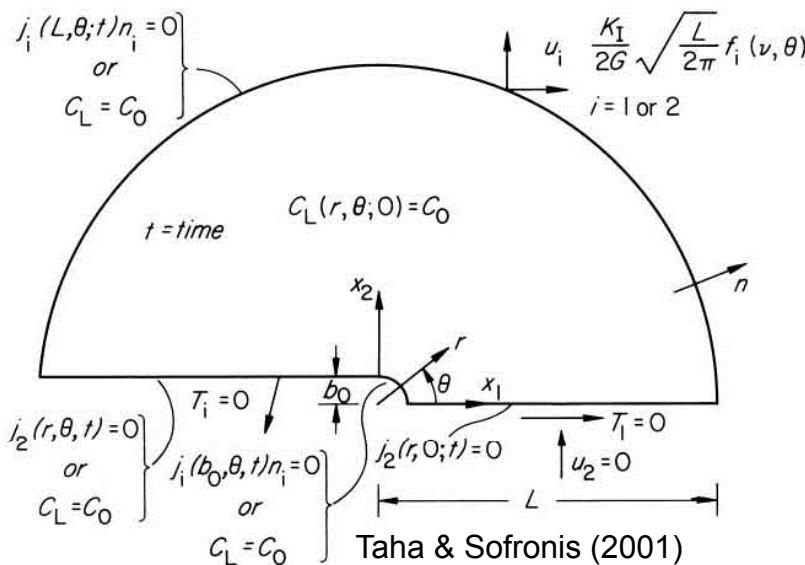
(Nibur, 2009)

NOTE: In this case, we assume that  $\phi_{n,0}$  is 0.25. Nucleation will account for 25% of porosity

# Modeling 21Cr-6Ni-9Mn in H<sub>2</sub> gas

*Before moving to complex and computationally challenging fracture geometries, we need to understand phenomena in plane strain*

*Mechanical analysis should be performed to help experimentalists reduce driving forces from non-standard fracture geometry. Iteration required.*



nodes: 189,312  
h: 40 nm x 200 nm

*NOTE: Not pre-charged, constant concentration C<sub>L,applied</sub> applied to crack faces*

# Coupled hydrogen transport

This path heavily leverages Sofronis/McMeeking (1989)\* and Krom (1998).

Recent work by Leo and Anand (2013).

*chemical potential*  $\mu_l = \mu_0 + RT \ln(\theta_l) - v_h \sigma_h$

$$\mathbf{F} = \frac{\partial \mathbf{x}}{\partial \mathbf{X}} \quad J = \det[\mathbf{F}]$$

$$\theta_l = c_l/n_l \quad \theta_t = c_t/n_t$$

*model for flux*  $\mathbf{j}_l = -\mathbf{m}_l c_l \nabla_{\mathbf{x}} \mu_l$

$$n_l = N_L/J \quad n_t = N_T(\epsilon_p)/J$$

$$v_h = V_H J \quad \tau_h = J \sigma_h$$

$$\mathbf{d}_l = RT \mathbf{m}_l$$

*conservation of hydrogen*  $\frac{d}{dt} \int_B c dv = - \int_{\partial B} \mathbf{j} \cdot \mathbf{n} da \quad \dot{c} = \dot{c}_l + \frac{\partial c_t}{\partial c_l} \dot{c}_l + \frac{\partial c_t}{\partial n_t} \frac{\partial n_t}{\partial \epsilon_p} \dot{\epsilon}_p + \frac{\partial c_t}{\partial n_t} \frac{\partial n_t}{\partial J} \dot{J}$

$$c_t = c_t(c_l, \epsilon_p, J)$$

*equilibrium of lattice/trap sites*  $\theta_t = \frac{1}{1 + \frac{1}{k_t \theta_l}}$   $C^* = c_l + \frac{n_t}{1 + \frac{n_t}{k_t c_l}} \quad D^* = 1 + \frac{\partial c_t}{\partial c_l}$

$$D^* \dot{c}_l + C^* \text{div} \mathbf{v} - \nabla_{\mathbf{x}} \cdot \mathbf{d}_l \nabla_{\mathbf{x}} c_l - \nabla_{\mathbf{x}} \cdot \frac{c_l}{J} \mathbf{d}_l \nabla_{\mathbf{x}} J + \nabla_{\mathbf{x}} \cdot \frac{c_l V_H}{RT} \mathbf{d}_l \nabla_{\mathbf{x}} \tau_h +$$

$$\frac{\theta_l}{J} \frac{\partial N_T}{\partial \epsilon_p} \dot{\epsilon}_p - \frac{\theta_t N_T}{J^2} \dot{\mathbf{j}} = 0$$

\*P. Sofronis and R.M. McMeeking, J. Mech. Phys. Solids 37 (1989) 317

# Baseline properties for 21Cr-6Ni-9Mn

## Transport\*

$$D_0 = 5.4E-7 \text{ m}^2/\text{s}$$

$$Q = 53.9E3 \text{ J/mol}$$

$$R = 8.314 \text{ J/(mol K)}$$

$$T = 300 \text{ K}$$

$$D_L = 2.2E-16 \text{ m}^2/\text{s}$$

$$N_A = 6.0232 \text{ atoms/mol}$$

$$V_M = 7.116E-6 \text{ m}^3/\text{mol} - \text{molar volume of Fe}$$

$$V_H = 2.0E-6 \text{ m}^3/\text{mol} - \text{partial molar volume of H}$$

$$N_L = 8.46E28 \text{ atoms/m}^3 = 1.40E5 \text{ solvent lattice mol/m}^3$$

$$C_{L,0} = 38.7 \text{ mol/m}^3 \text{ (from 316 alloys, assumes 5 wppm)}$$

$$C_{L,applied} = 560 \text{ mol H/m}^3 \text{ (280 moles H}_2\text{/m}^3\text{)}$$

$$N_{T,total} = \alpha N_T = 10N_T = 10^{(26.6 - 1.5\exp(-6.96ep))} \text{ mole/m}^3$$

$$C_{T,0} = 3.94E24 \text{ atoms/m}^3 = 6.542 \text{ mol/m}^3$$

$$W_B = 9.65E3 \text{ J/mol}$$

$$K_T = 47.9$$

## Mechanics – non-charged, forged, transverse, LF

$$\rho = 7806 \text{ kg/m}^3$$

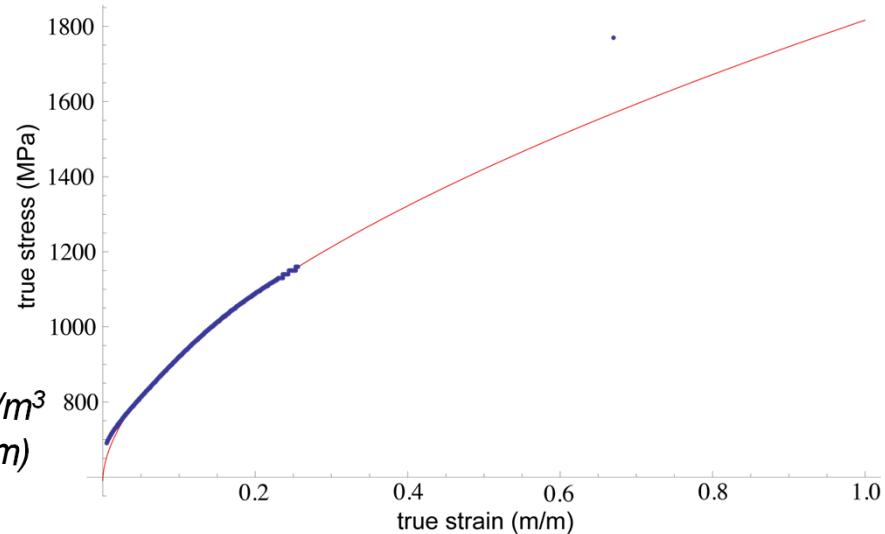
$$E = 196.6 \text{ GPa}$$

$$\nu = 0.3$$

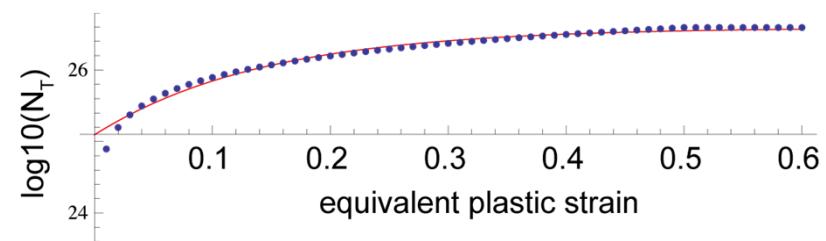
$$\sigma_0 = 590 \text{ MPa}$$

$$H = 1227 \text{ MPa}$$

$$m = 0.563$$



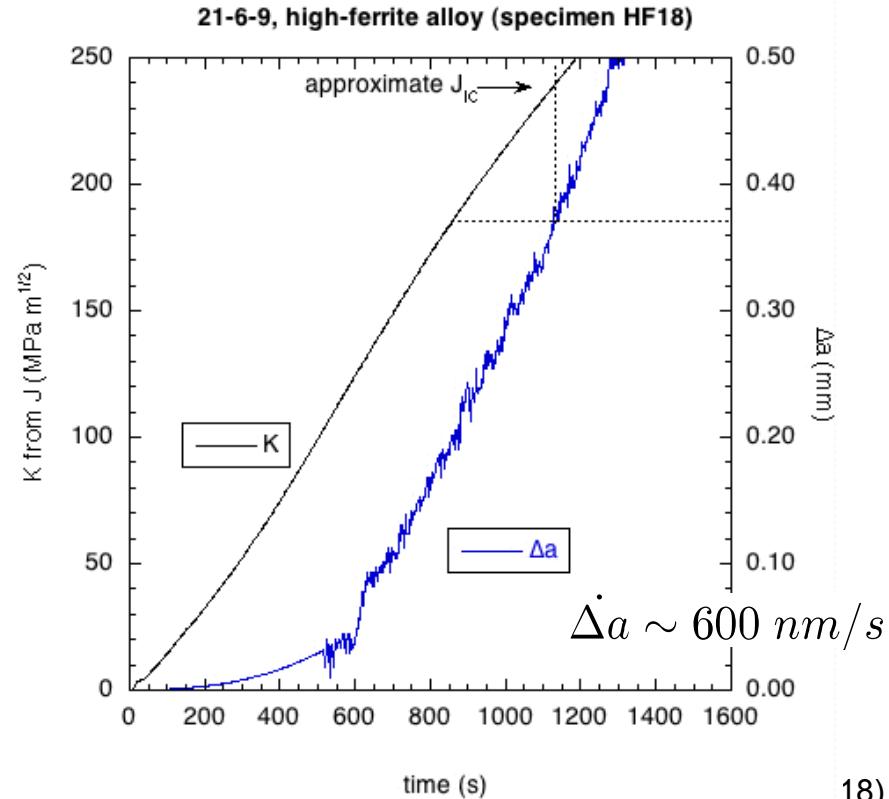
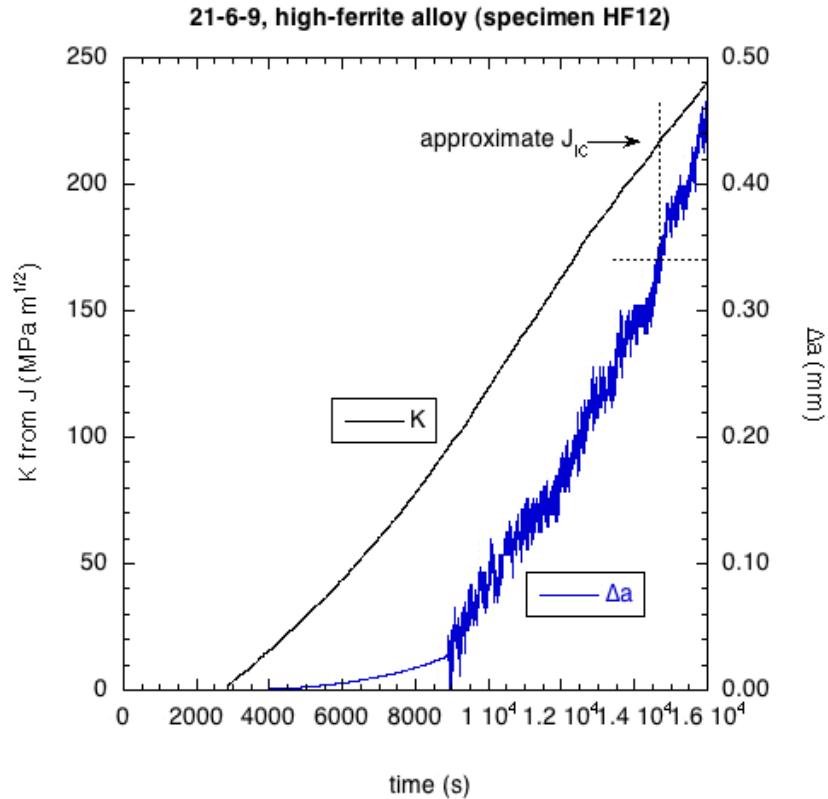
$$C_{L,applied} = K f^{\frac{1}{2}} \quad \text{San Marchi, et al., IJHE, 2007}$$



\*Transport properties aligned with Somerday, et al., Met Trans, 2009

NOTE: Constant concentration, not chemical potential, is applied. Will fix.

# Initial studies in 21Cr-6Ni-9Mn SS



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