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Stähle, P.

2012

Document Version:

Publisher's PDF, also known as Version of record

[Link to publication](#)

Citation for published version (APA):

Stähle, P. (2012, Sep 25). Understanding hydrogen induced degradation of mechanical properties on Zr-alloys using multi-scale structural mechanics approach, MSE-RNS conference Darmstadt, 2012. Orationem Meam.

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Understanding hydrogen induced degradation of mechanical properties on Zr-alloys using multi-scale structural mechanics approach

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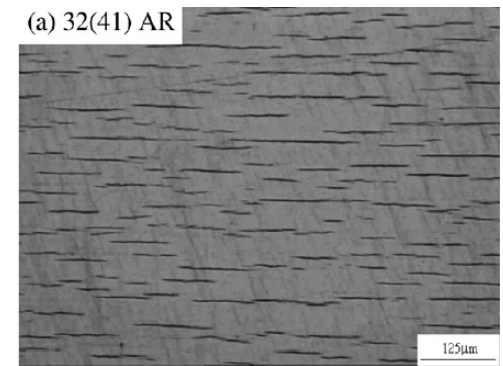
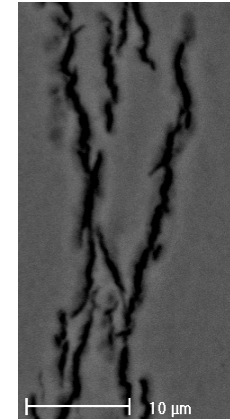
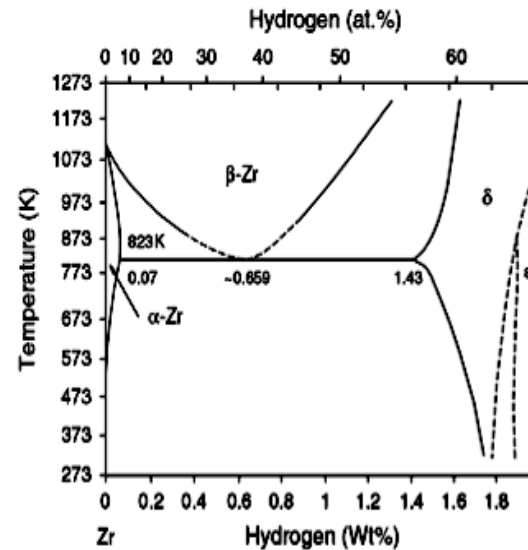
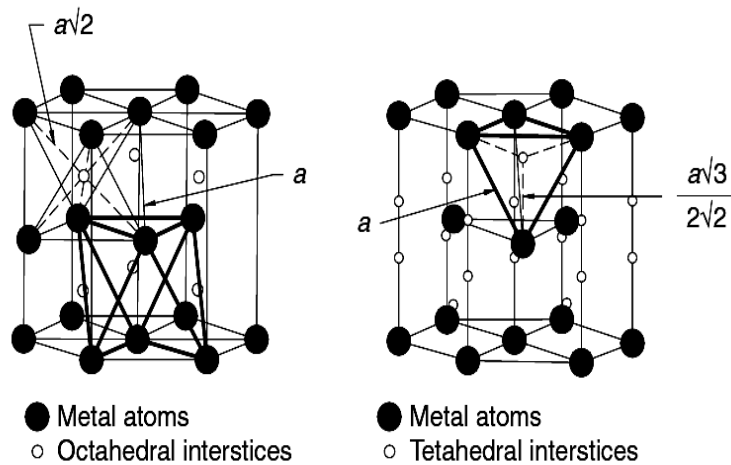
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Zr-H solid solution and hydride

Hydrogen occupies tetrahedral sites in Zr-H solid solution

α -lattice distorts to match the γ and δ structures

Interstitial ordering results in periodic occupation of tetrahedral sites



Zr exhibits two allotropic modification: low T hcp (α) and high T bcc (β) phases

Two stable hydrides (δ and ϵ) and one metastable (γ) hydride forms in this system

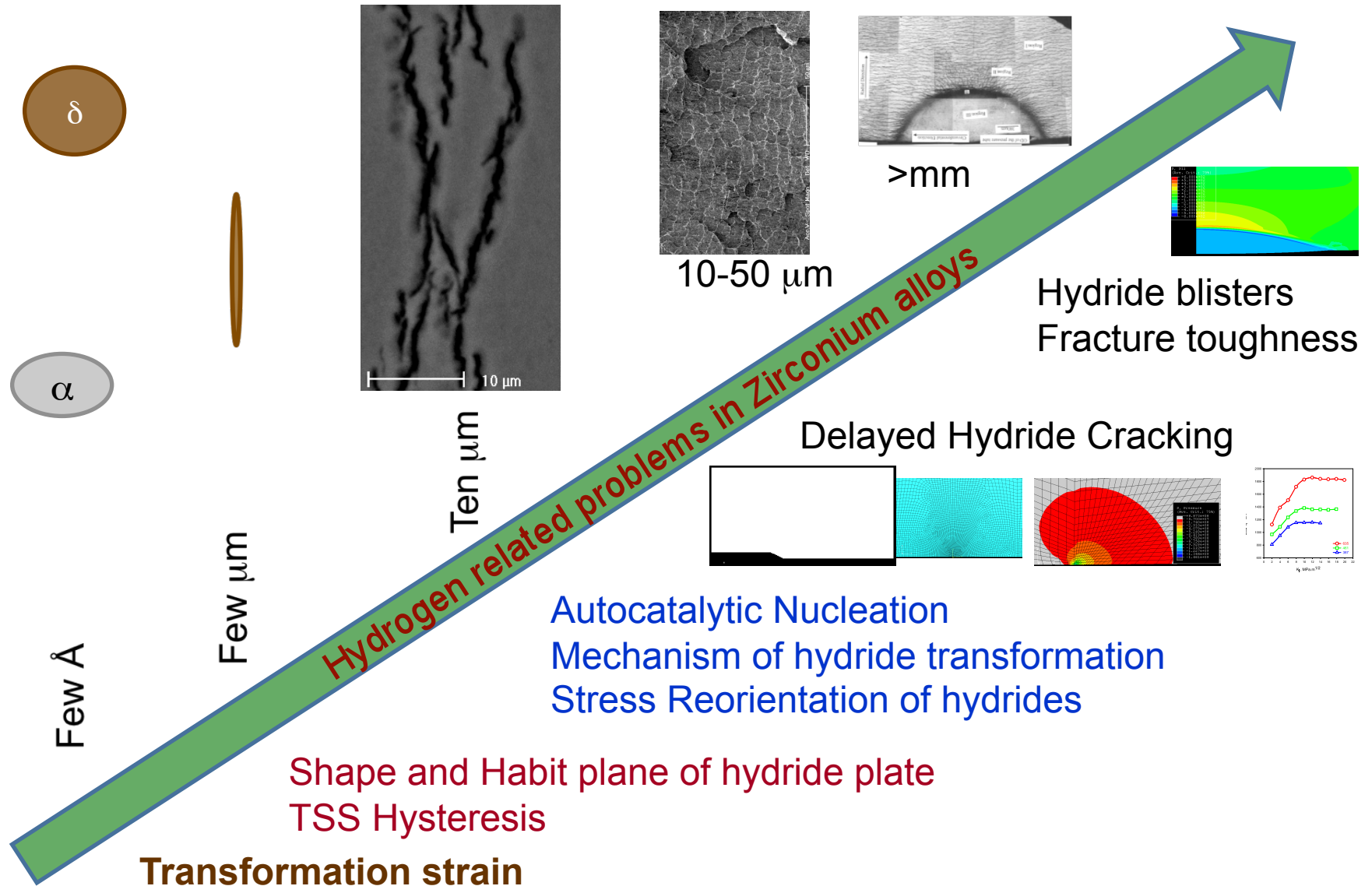
Under optical microscope the traces of hydrides appears as dark lines

At higher magnification each hydride plate is observed to comprise of several smaller entities

Hydride plate comprises of platelets stacked side by side

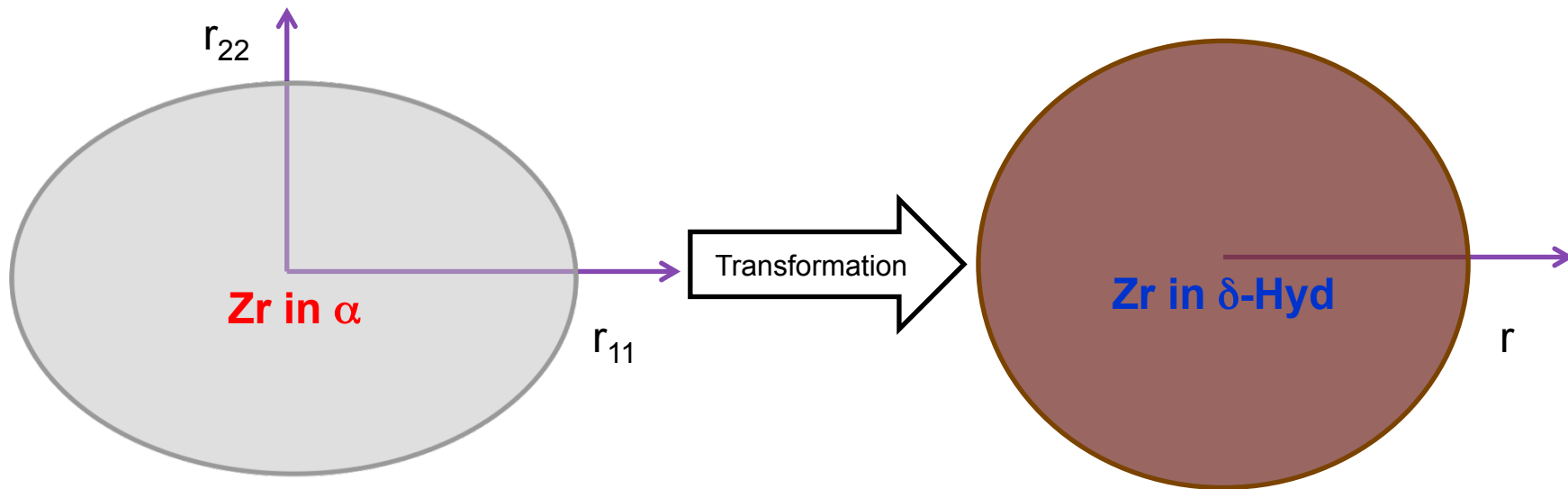
Each platelet comprises of sub-platelets stacked end to end

Multi-scale Structural Mechanics



Transformation strain

α -Zr	δ -Zr hydride
hexagonal close packed ($c/a < 1.63$) Ellipsoidal atom	face centred cubic Spherical atom



$$e_{11} = \frac{r - r_{11}}{r_{11}}$$

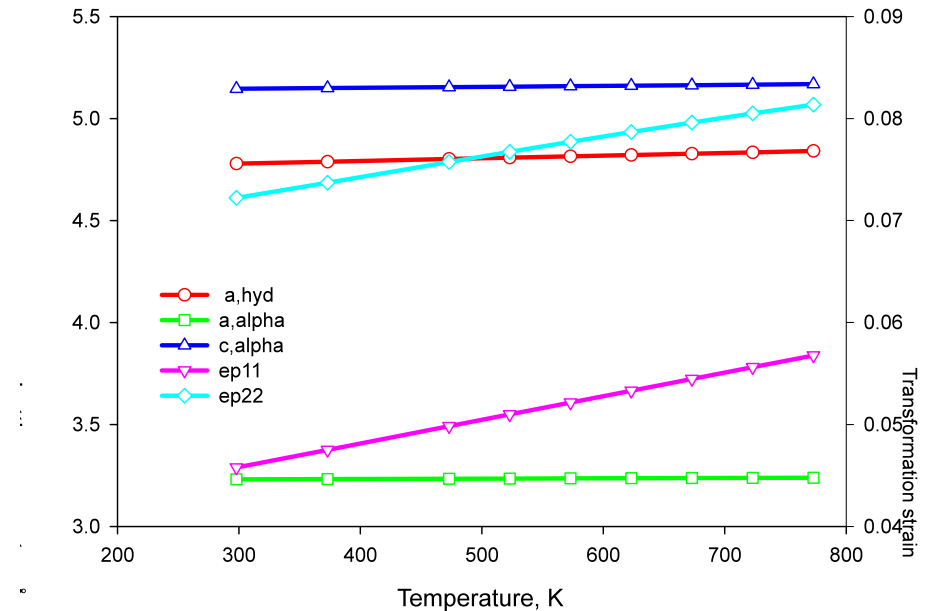
$$e_{22} = \frac{r - r_{22}}{r_{22}}$$

Temperature dependence of transformation strains

Using the afore-described relationship one can calculate the transformation strains from lattice parameters of α -Zr and δ -hydride

e_{11} corresponds to transformation strain parallel to hydride plate

e_{22} corresponds to transformation strain normal to hydride plate



To give some number the formation of δ -hydride is associated with increase in volume of $\sim 17\%$ at room temperature and increases with increase in temperature

Such a large change in volume results in local plastic deformation

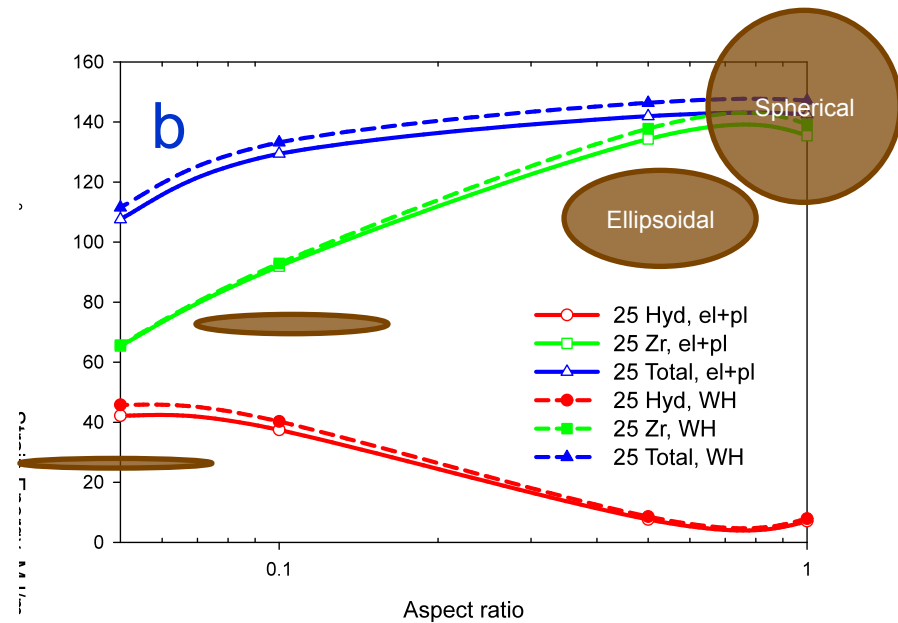
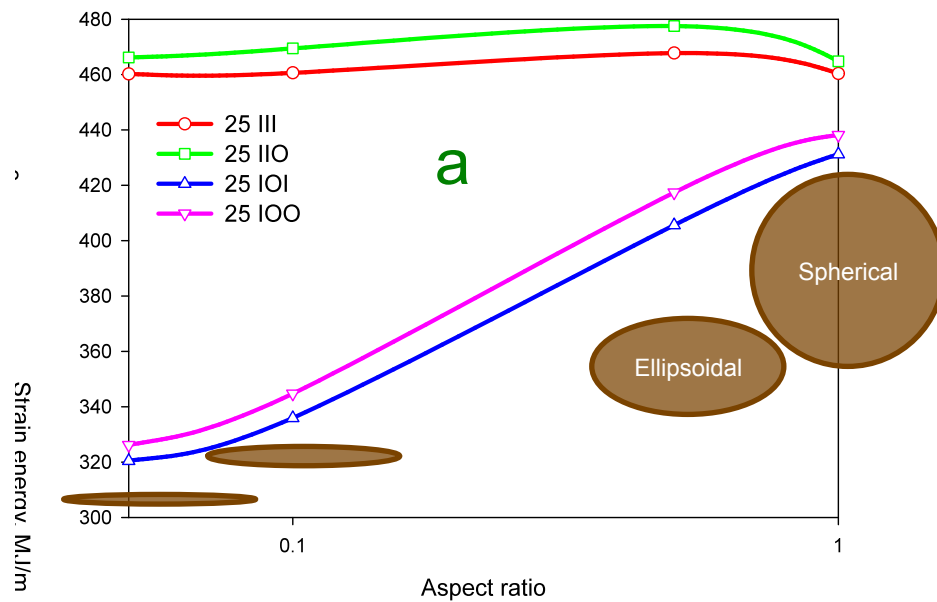
Metal hydride system tries to minimise the strain energy

In the next few slides how minimisation of strain energy governs the shape and habit plane of hydride will be illustrated

Mechanics of Phase transformation

- Types of phase transformation
 - Diffusionless or massive transformation eg. Martensite formation
 - Diffusional transformation-Nucleation & Growth
 - Hybrid transformation – diffusionless transformation of matrix and interstitial ordering eg. Hydride formation
- Driving force - chemical, interfacial and strain energy
- Strain energy is influenced by Anisotropy:
 - Misfit strains or stress free transformation strain
 - Elastic constants of matrix and precipitate
 - Flow stress of matrix and precipitate
 - External and/or residual stress
- Applications
 - Estimation of solvus shift –TSS Hysteresis
 - Shape and Habit plane
 - Quantification of embrittlement

Strain energy and shape of hydride



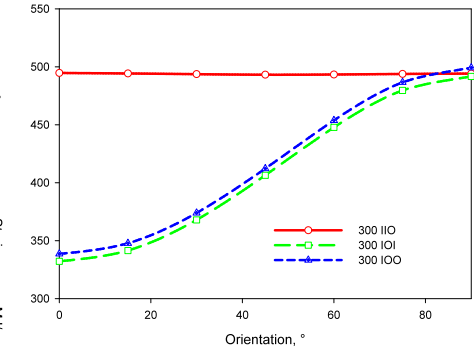
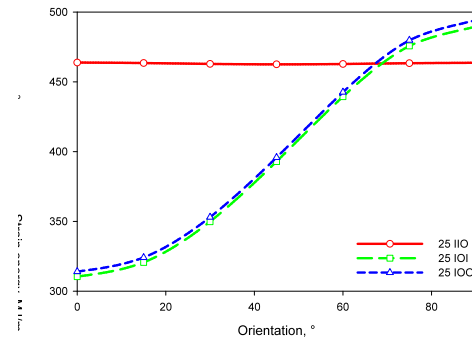
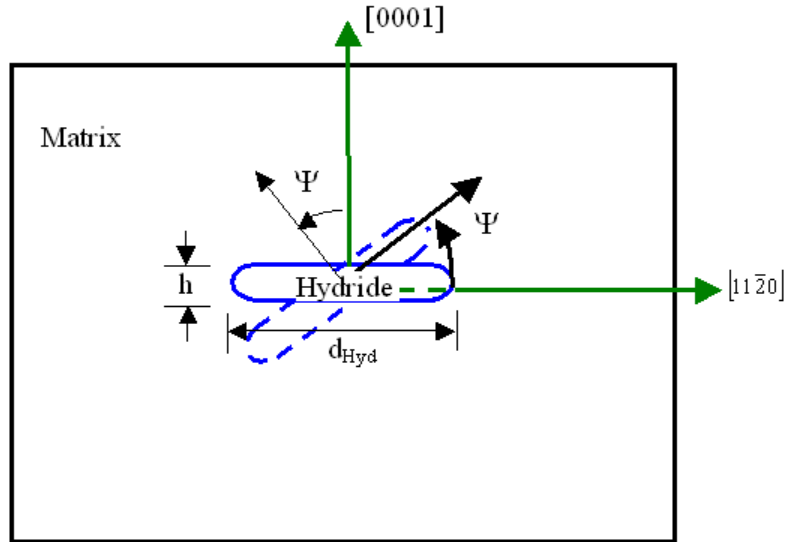
(a) Fully elastic and (b) Elasto-plastic matrix and hydride.

Case	Hydride modulus	Transformation strain	Matrix modulus	Strain energy
III	Isotropic	Isotropic	Isotropic	No reduction
IIO	Isotropic	Isotropic	Orthotropic	No significant reduction
IOI	Isotropic	Orthotropic	Isotropic	Significant reduction
IOO	Isotropic	Orthotropic	Orthotropic	Significant reduction

Note: As aspect ratio decreases interfacial energy increases which counters the decrease in strain energy

Hydride Orientation and Strain energy

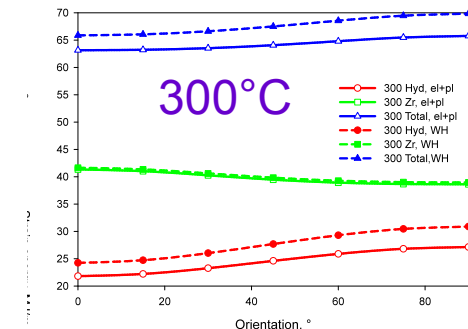
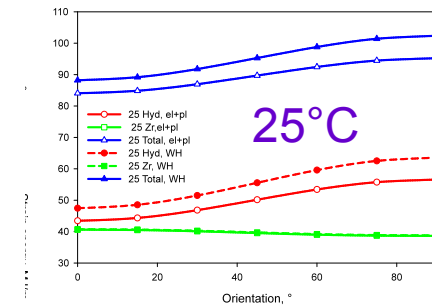
Mesoscopic habit plane reported nearly parallel to basal plane $\{0\bar{1}7\}$
 Microscopic habit plane for delta-hydride is (0001)



Fully elastic case
 Elasto-plastic case

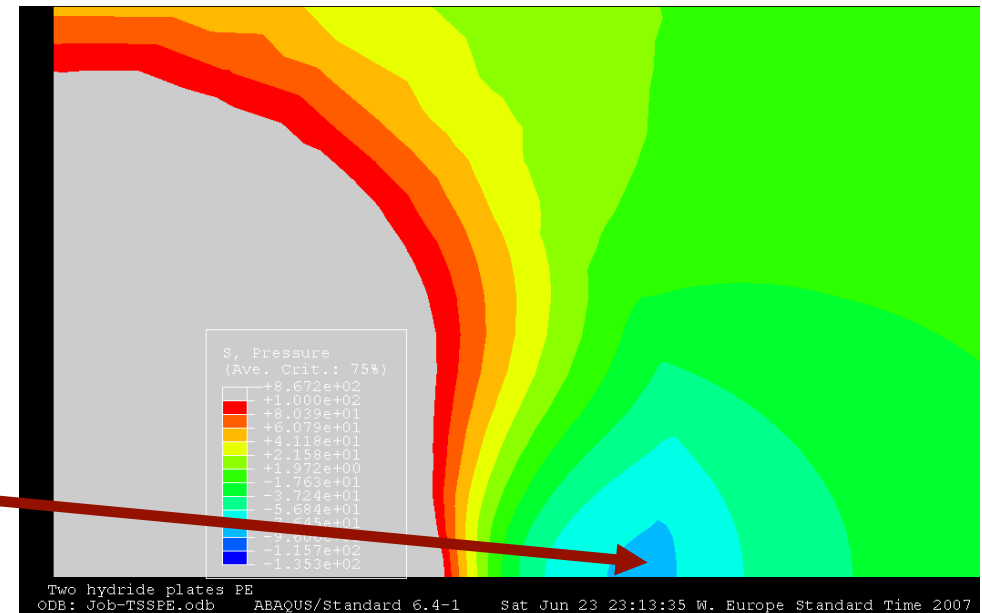
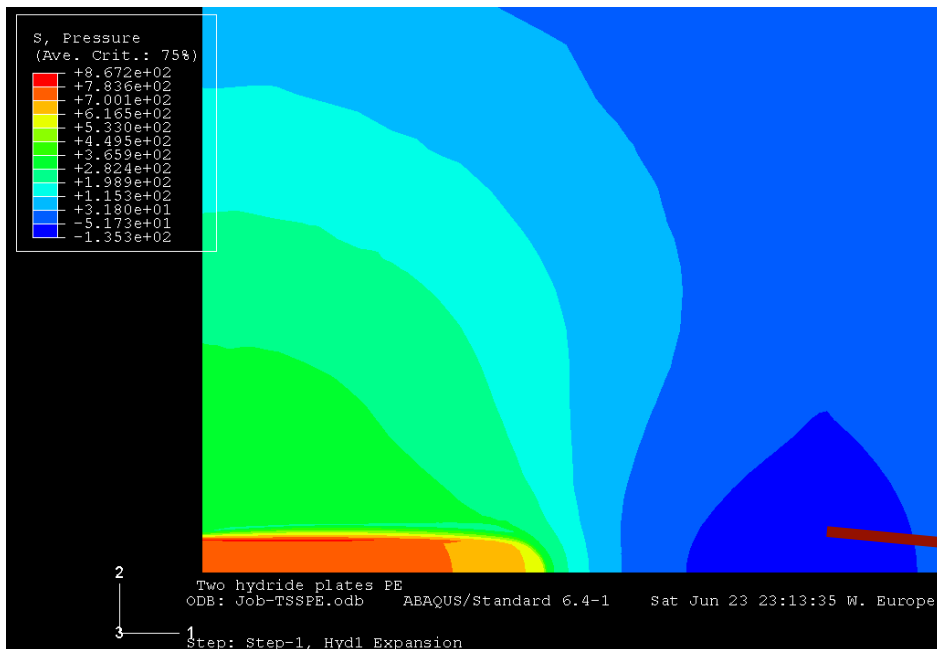
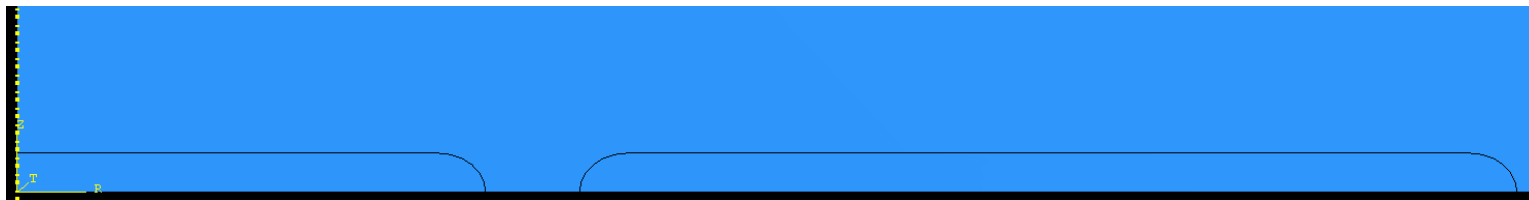
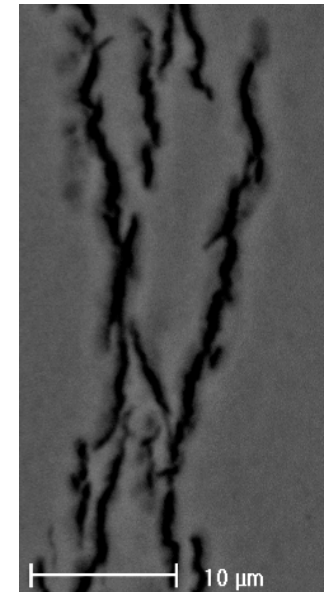
Maintaining OR between matrix and hydride plate orientation changed between 0 to 90 in 15 degrees steps.
 Accommodation energy plotted as a function of plate orientation Ψ

Minimum accommodation energy for 0 degree suggests basal plane as habit plane for fully elastic case
 Note: Hydride interface parallel to basal plane of α -Zr shows minimum strain energy suggesting basal plane as sub-microscopic habit plane for elasto-plastic cases both at 25 and 300 °C.



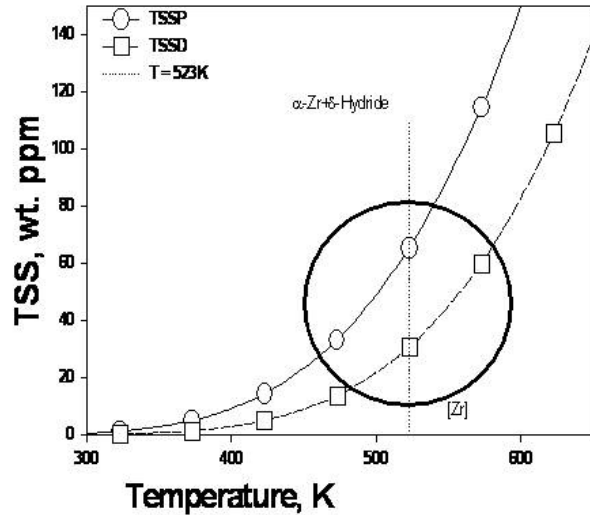
Stress field around hydride plate: Auto-catalytic nucleation

Pressure (-ve hydrostatic stress) variation around hydride plate
Maximum hydrostatic stress away from hydride plate tip
Similar to hydrostatic stress ahead of a crack in elastoplastic materials
Accommodation energy reduces from 105.49 to 94.72 MJ/m³



Terminal Solid Solubility – Temperature dependence & Hysteresis

TSSP(D) = $A \cdot \exp(-Q/RT)$, 'P(D)' for precipitation i.e. cooling (dissolution or heating)
 TSS depends on direction of approach of temperature

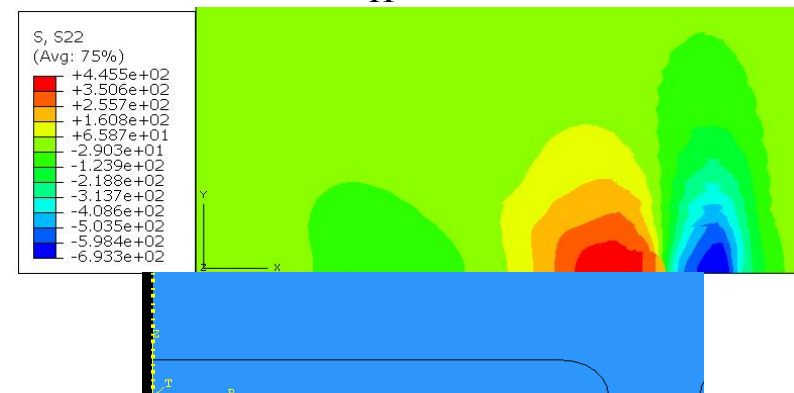
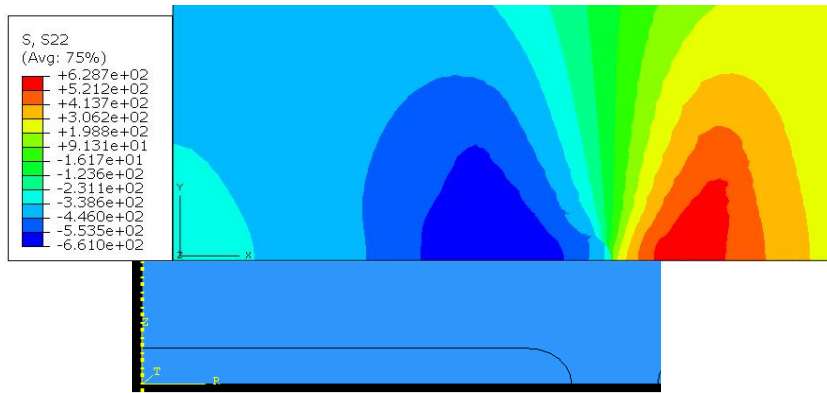


$$C_o^T = C_o \exp\left(\frac{-\Delta H'_s}{RT}\right) \quad \text{No Hysteresis}$$

$$C_o^{Grow} = C_o^T \exp\left(\left(\overline{W}_{el,p}^{acc} + \overline{W}_p^{acc}\right) / RT\right)$$

$$C_o^{Diss} = C_o^T \exp\left(\left(\overline{W}_{el,p}^{acc} + \overline{W}_p^{acc}\right) / RT\right)$$

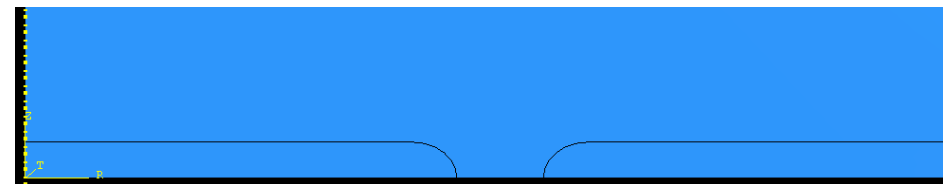
- Growth - size increases \Leftrightarrow Dissolution - decrease in size
- At 250 °C, TSSP=60 wt ppm for α -Zr and for δ -Hydride $C_H=16000$



Growing hydride induces tensile while shrinking hydride induces compressive stress in the matrix

Mechanistic simulation of precipitation and dissolution

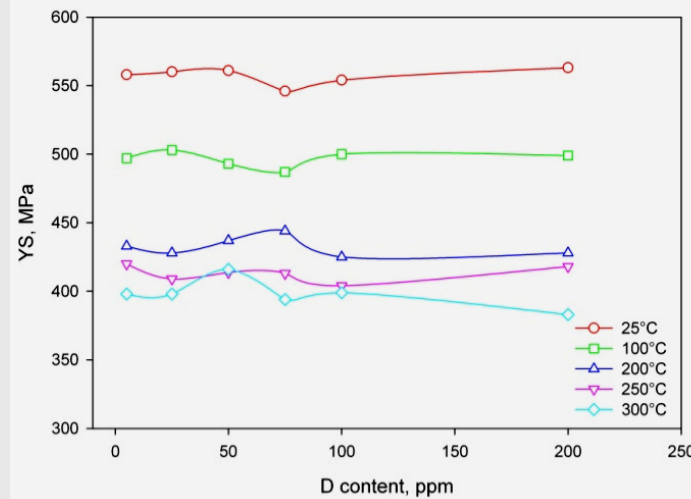
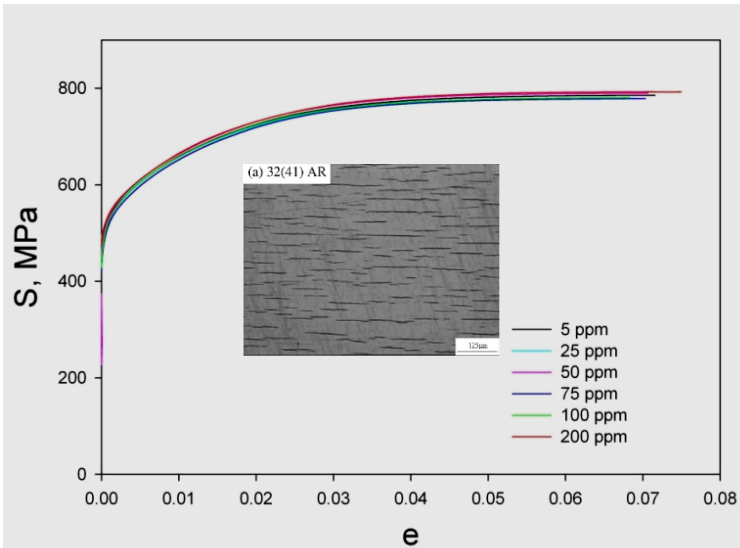
	Single step (Axysymmetric)	Single step (Plane Strain)	Auto catalytic (Plane Strain)
Elastic –Pptn. (Dissn.)	35.82 (-24.02)	35.53 (-12.41)	29.42(-15.62)
Plastic -Pptn. (Dissn.)	78.73 (59.42)	69.96 (290.00)	65.30 (35.27)
Total - Pptn. (Dissn.)	114.55 (35.40)	105.49 (277.60)	94.72 (19.65)



Hydride plate

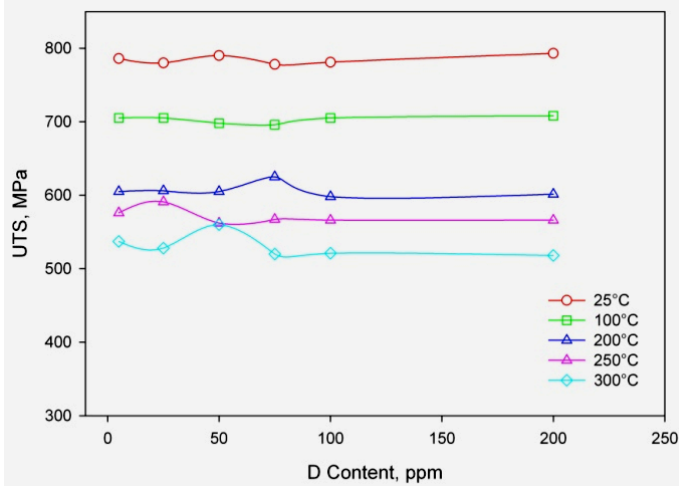
Autocatalytic nucleation
of next Hydride plate

Influence of Hydride on Tensile properties of Zr-2.5Nb PT alloy

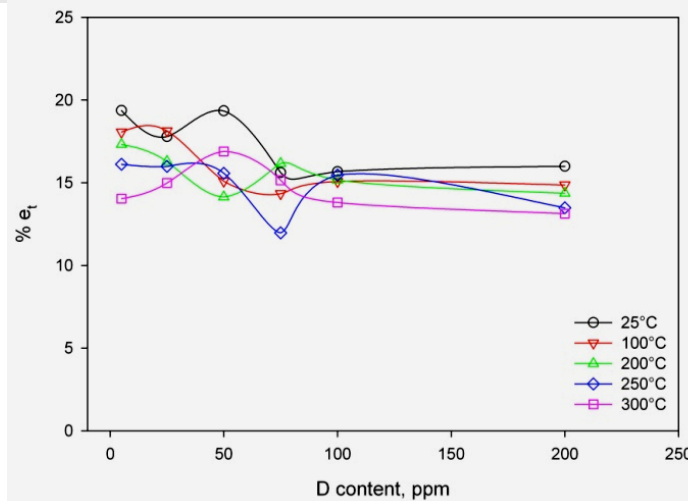


Upto 200 wppm of hydrogen/ deuterium as circumferential hydride

Tensile strength is practically unaffected

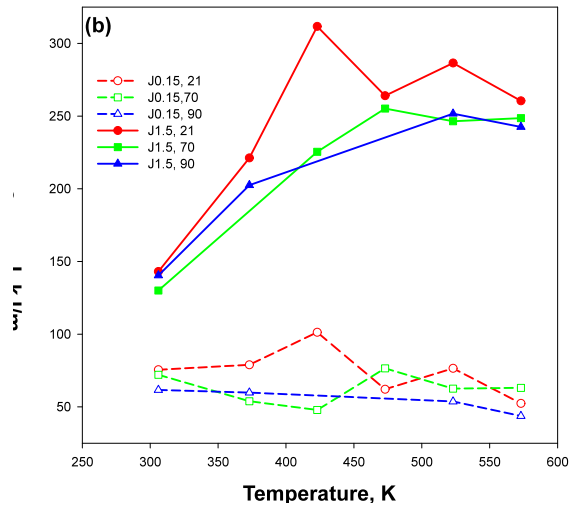


though marginal reduction in elongation

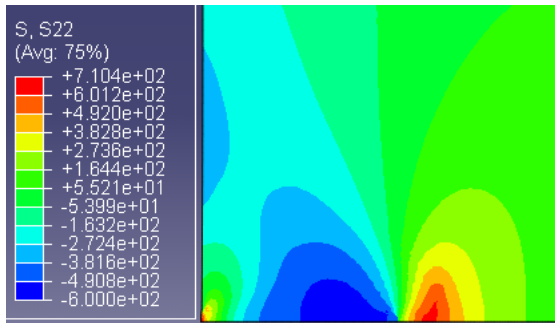
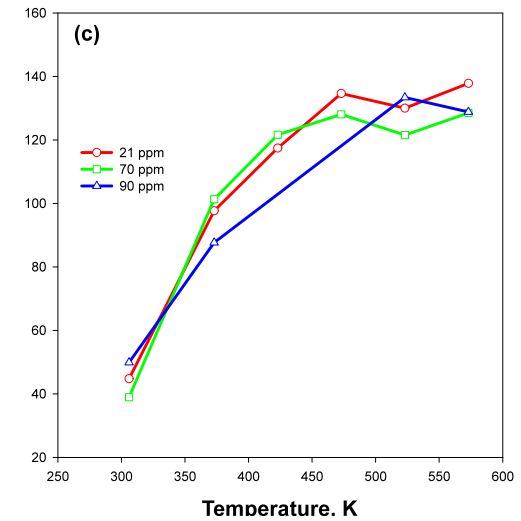


However if hydride plate is normal to tensile stress i.e. radial hydride significant reduction in ductility is observed

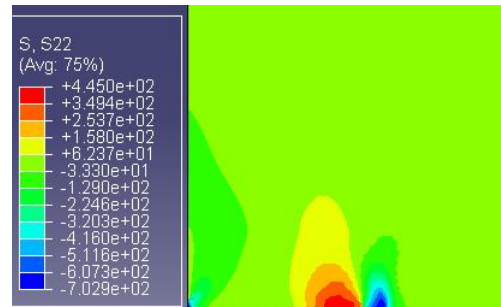
Fracture toughness Zr-2.5%Nb PT (Double melted)



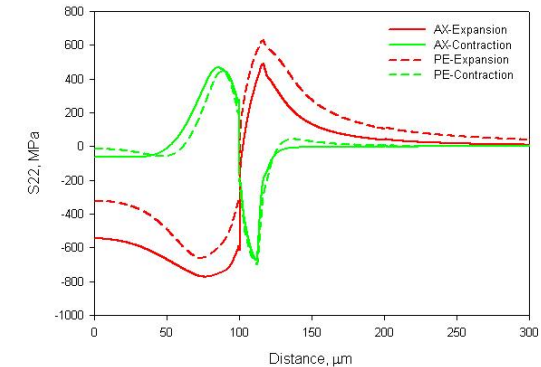
Fracture initiation toughness parameter shows marginal decrease with increase in Temp. whereas fracture propagation toughness parameters increases with increase in temp



Expanding hydride imposes tensile stress field in the matrix thereby enhancing susceptibility to embrittlement



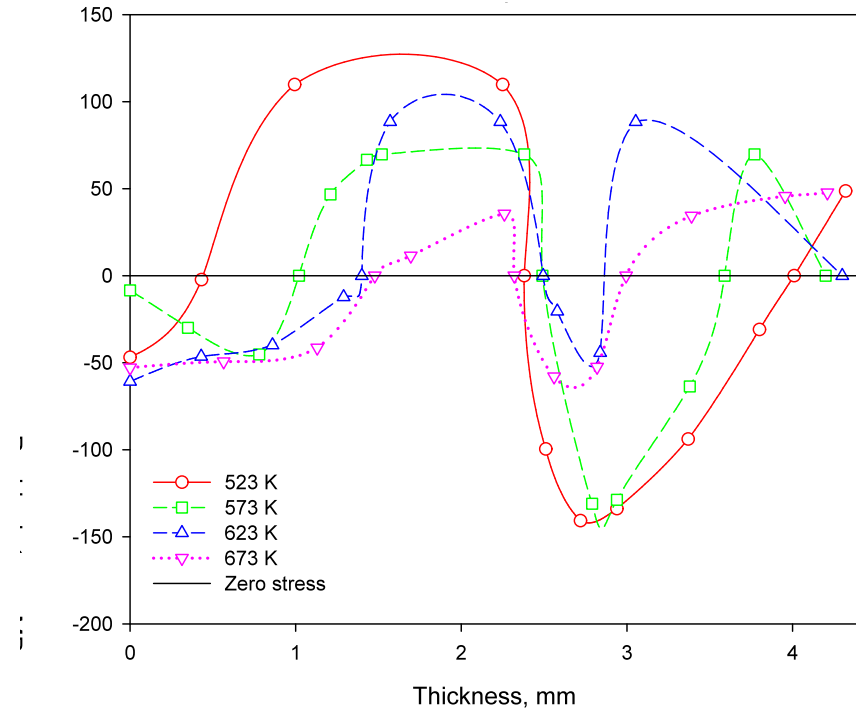
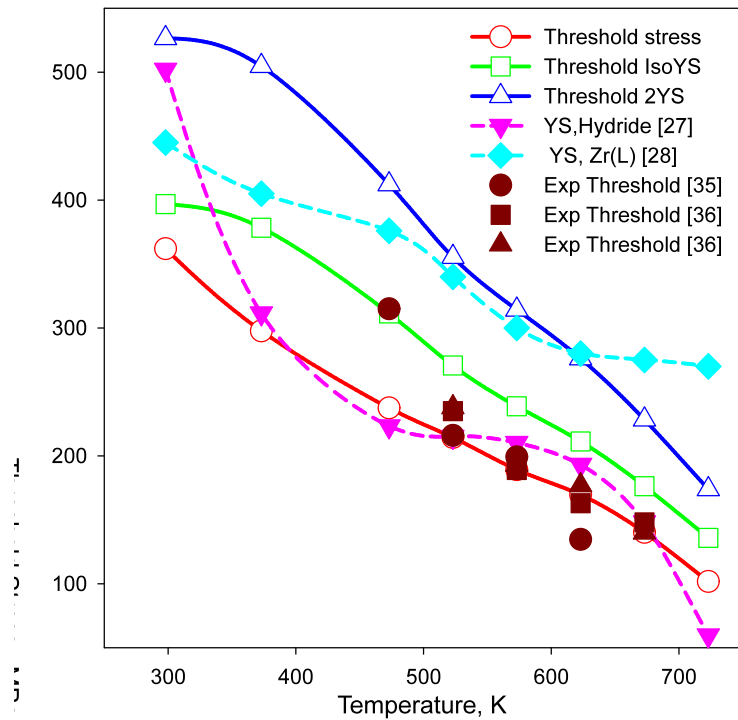
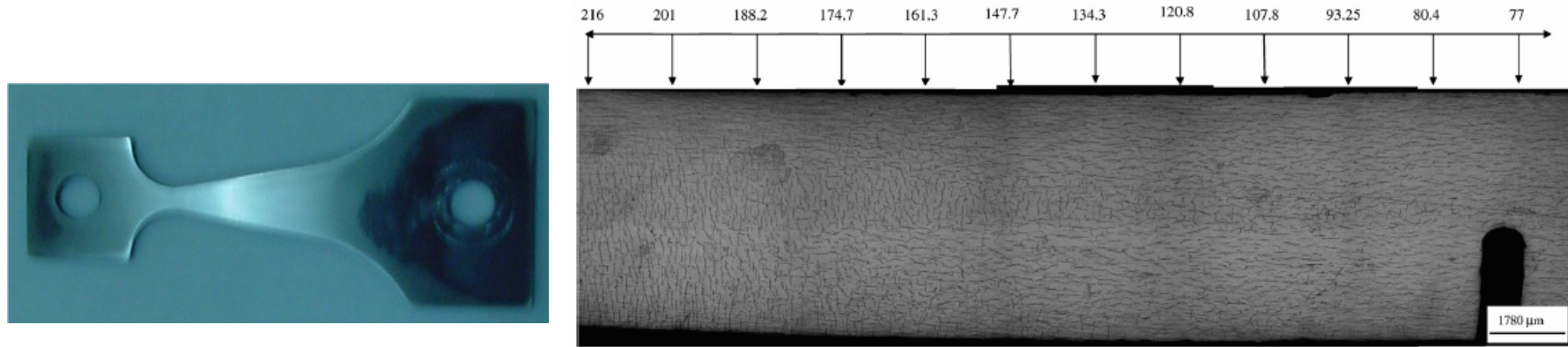
Contracting hydride imposes compressive stress field in the matrix thereby reducing susceptibility to embrittlement



Critical crack length (CCL), mm

Temp. °C	21 wt. ppm	70 wt. ppm	90 wt. ppm
250	65.6	61.8	57.2
300	57.2	58.0	55.2

Threshold stress determination & Modeling



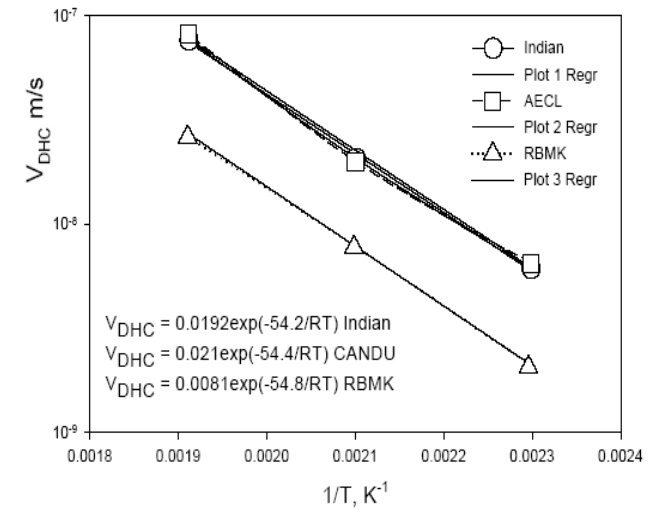
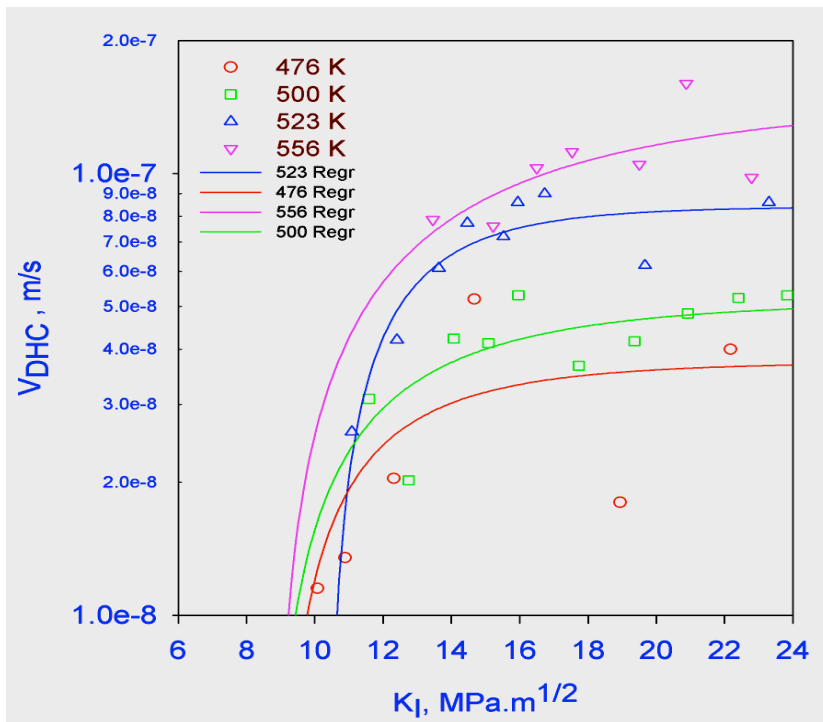
SRT model predicts the existence of threshold stress for reorientation and the predicted value of threshold stress is in good agreement with the experimentally determined values

Delayed Hydride Cracking-Experimental

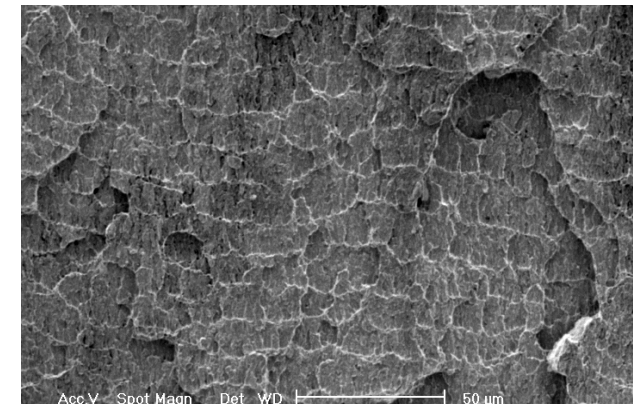


- Hydrogen migration
- Radial hydride precipitation
- Growth to critical size
- Crack growth by fracture

Plot of DHC velocity with stress intensity factor



Striations
evidence of
discontinuous



DHC velocity to assess operator response time (t) for meeting LBB criteria

$$t = \frac{CCL - a_{Leak}}{2V_{DHC}}$$

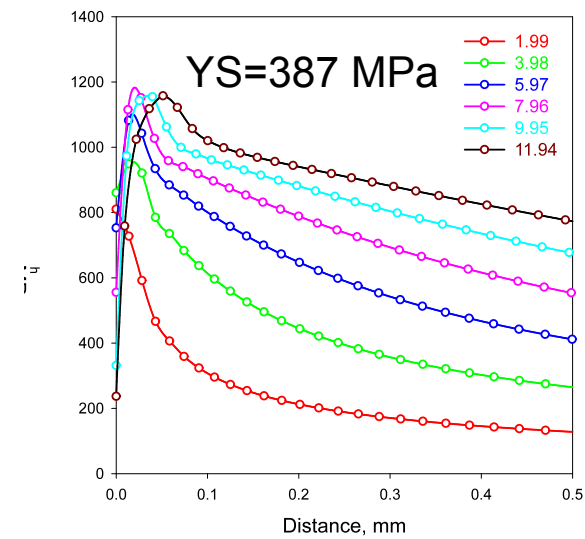
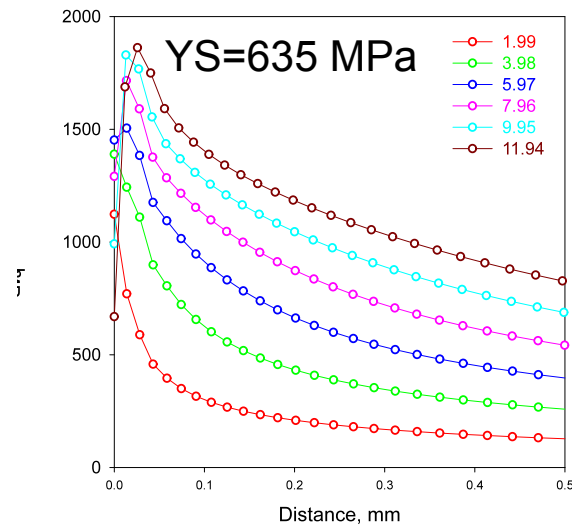
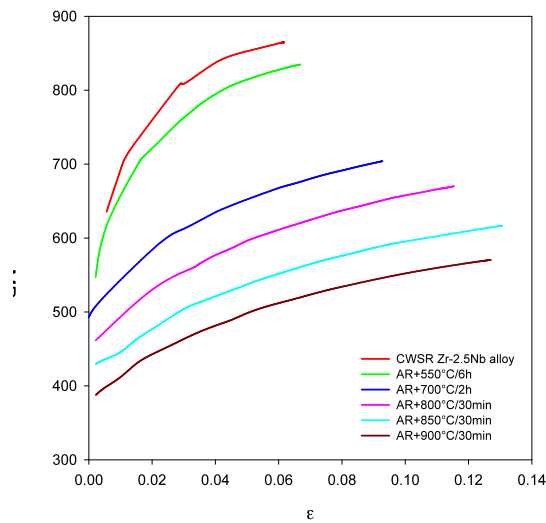
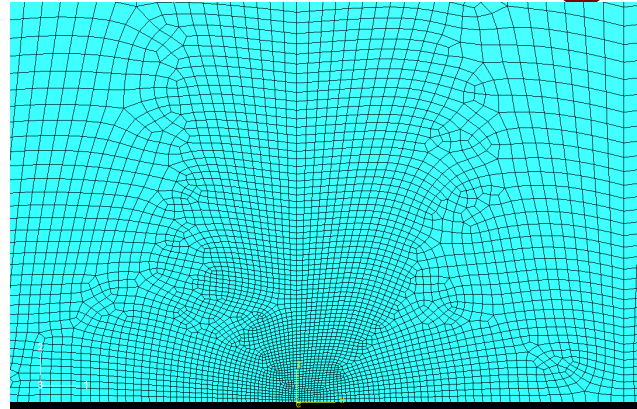
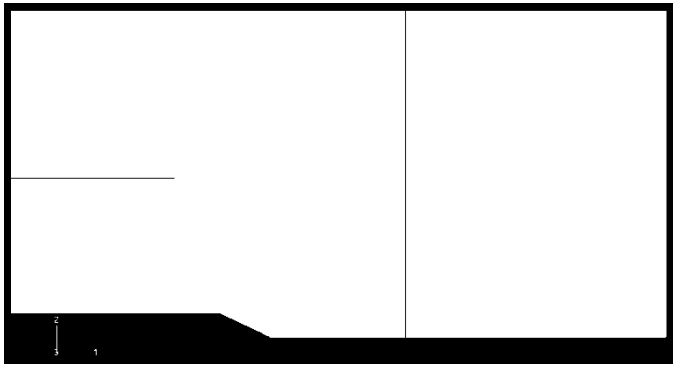
Modeling of Threshold stress intensity factor

- To impose threshold stress gradient for hydrogen migration towards the crack tip
- To facilitate precipitation of radial hydrides
- To cause fracture of radial hydride matrix composite

Approaches

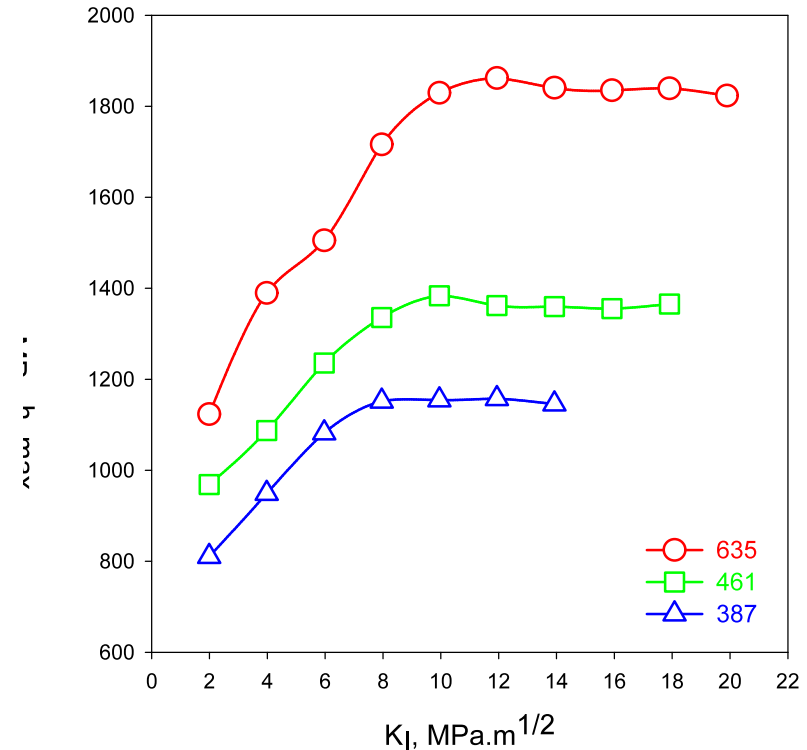
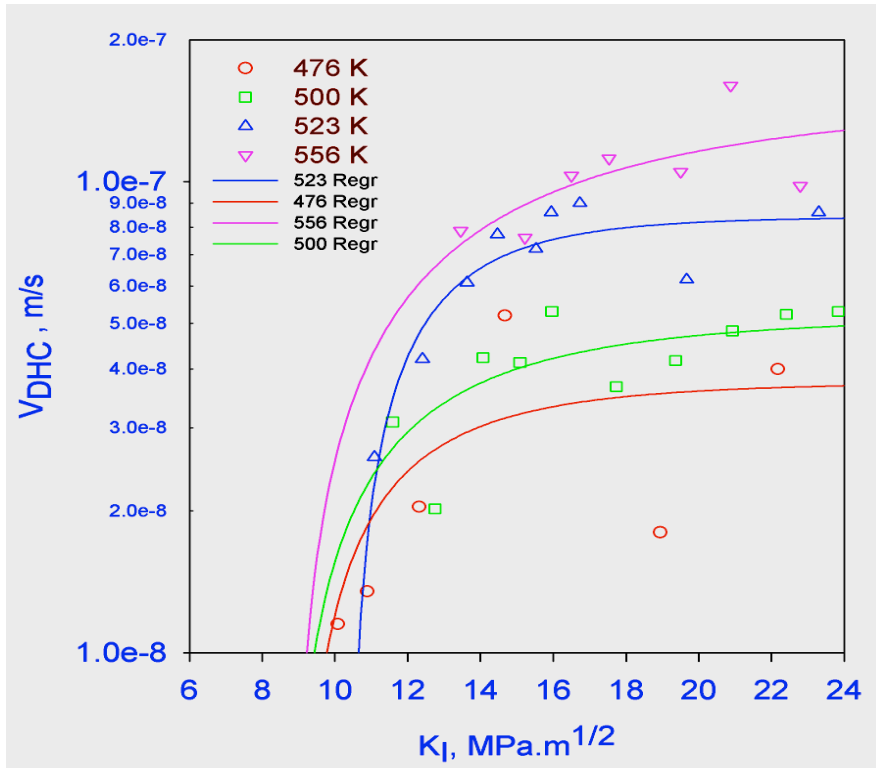
- Treat radial-hydride-matrix as composite (Sagat et. al. ASTM-STP1245) $K_{IH} = K_{IC}^{\delta} + K_{IC}^{\alpha}$
- Relating the fracture stress of constrained hydride with stress intensity factor (series of publication by Puls et al)
- Relating with hydrostatic stress and rest of the conditions will automatically be satisfied

Delayed Hydride Cracking-Modeling



Evolution of hydrostatic stress in the crack plane ahead of a sharp crack tip as a function of stress intensity factor (MPa.m^{1/2})

Variation in Maximum hydrostatic stress with stress intensity factor (YS)

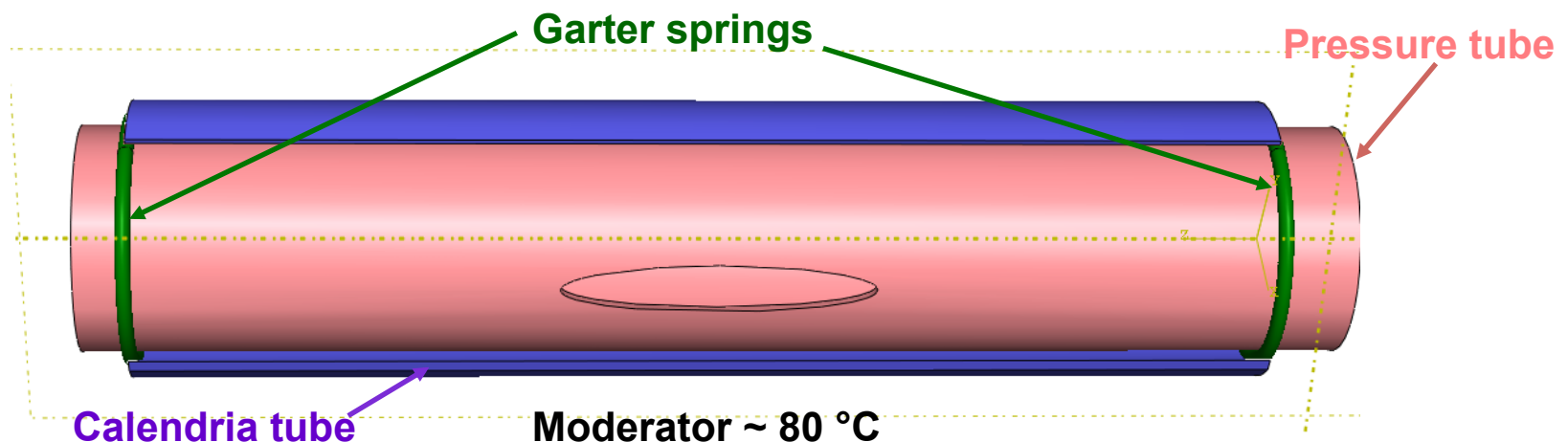


Hydrostatic stress reaches a saturation with increase in Stress intensity factor for elasto-plastic materials – responsible for stable crack growth during DHC

The computation of max. hydrostatic stress ahead of a sharp crack suggests a saturation in driving force for hydrogen migration during DHC for $SIF > K_{IH}$.

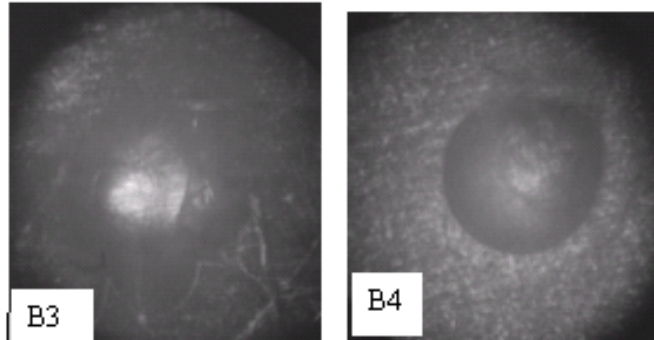
Hydride Blister

1. Hydrogen migration down the thermal gradient
2. Hydride precipitation at or around the cold spot
3. Increase in specific volume resulting in a bulge formation.
4. Because of its appearance is called hydride blister.
5. Though the formation of one isolated blister is not defying the leak before break (LBB) criterion of pressure tube design, but an array of blisters by interlinking together may exceed the critical crack length required for catastrophic failure.
6. A major reason for the premature replacement of the pressure tubes from the operating reactors.



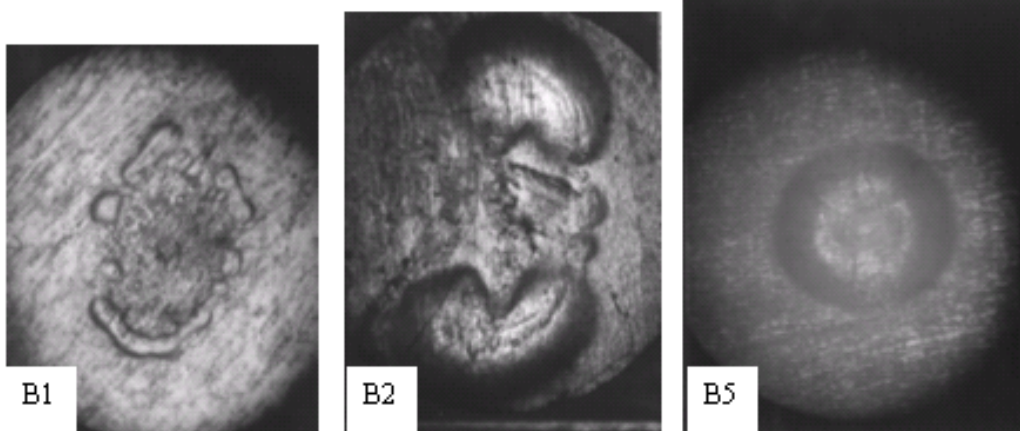
Hydride Blister

Prior solution annealing



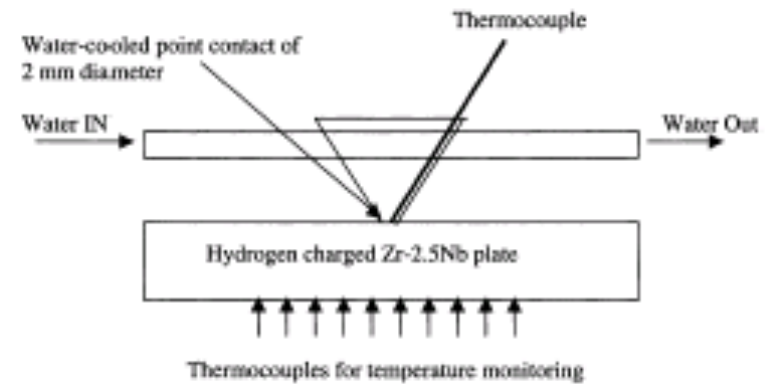
(a) Type I

Before cold finger is struck all the hydrogen is solid solution.
As cold finger makes contact hydride precipitation occurs at cold spot which grows with the arrival of thermally migrated hydrogen resulting in single blister



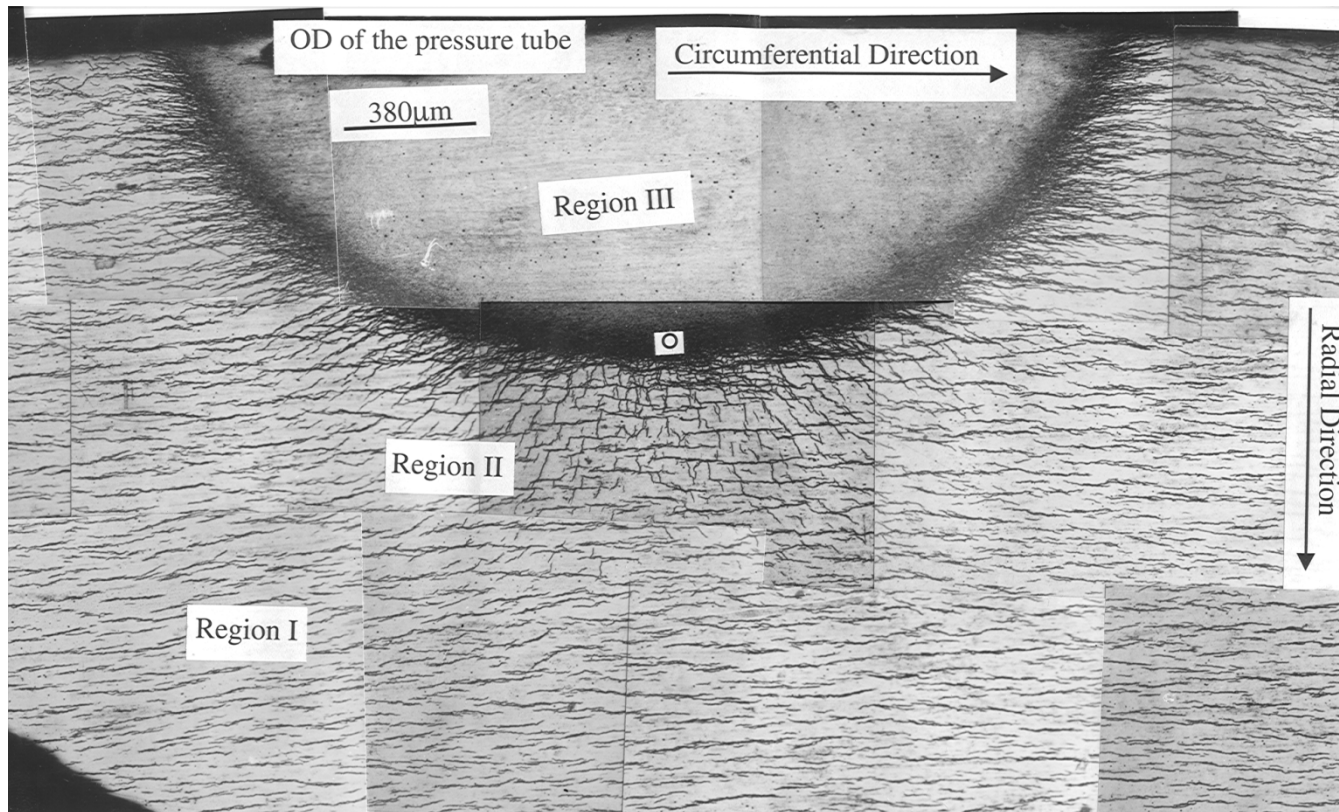
(b) Type II

Without solution annealing



Cold finger is in contact all the time
Hydride precipitation occurs around the cold spot resulting in ring of blisterets

Hydride Blister section



Optical micrograph of hydride blister section, grown in Zr-2.5wt.% Nb pressure tube material. Three regions - Region I - matrix & circumferential hydrides, region II - matrix containing both radial and circumferential hydrides and region III - mainly of δ -hydride.

The basis of radial hydride formation is the stress field of blister in the matrix surrounding it.

Blister formation - Stress field computation- Single step

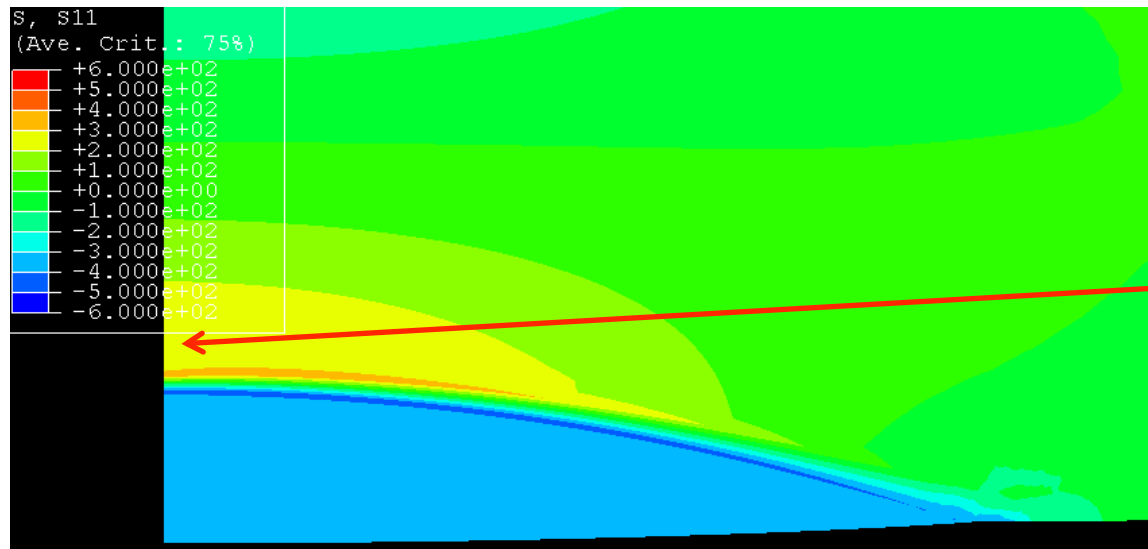
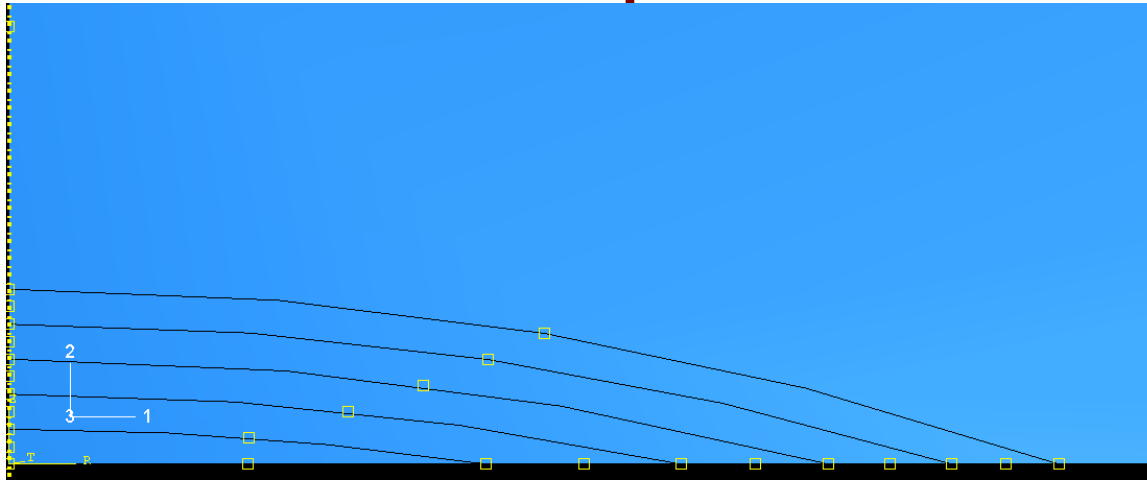
Modelling blister

Axisymmetric about axis 2

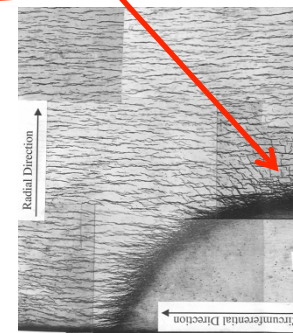
5 partitions

YS ratio of matrix/Hydride 1.0

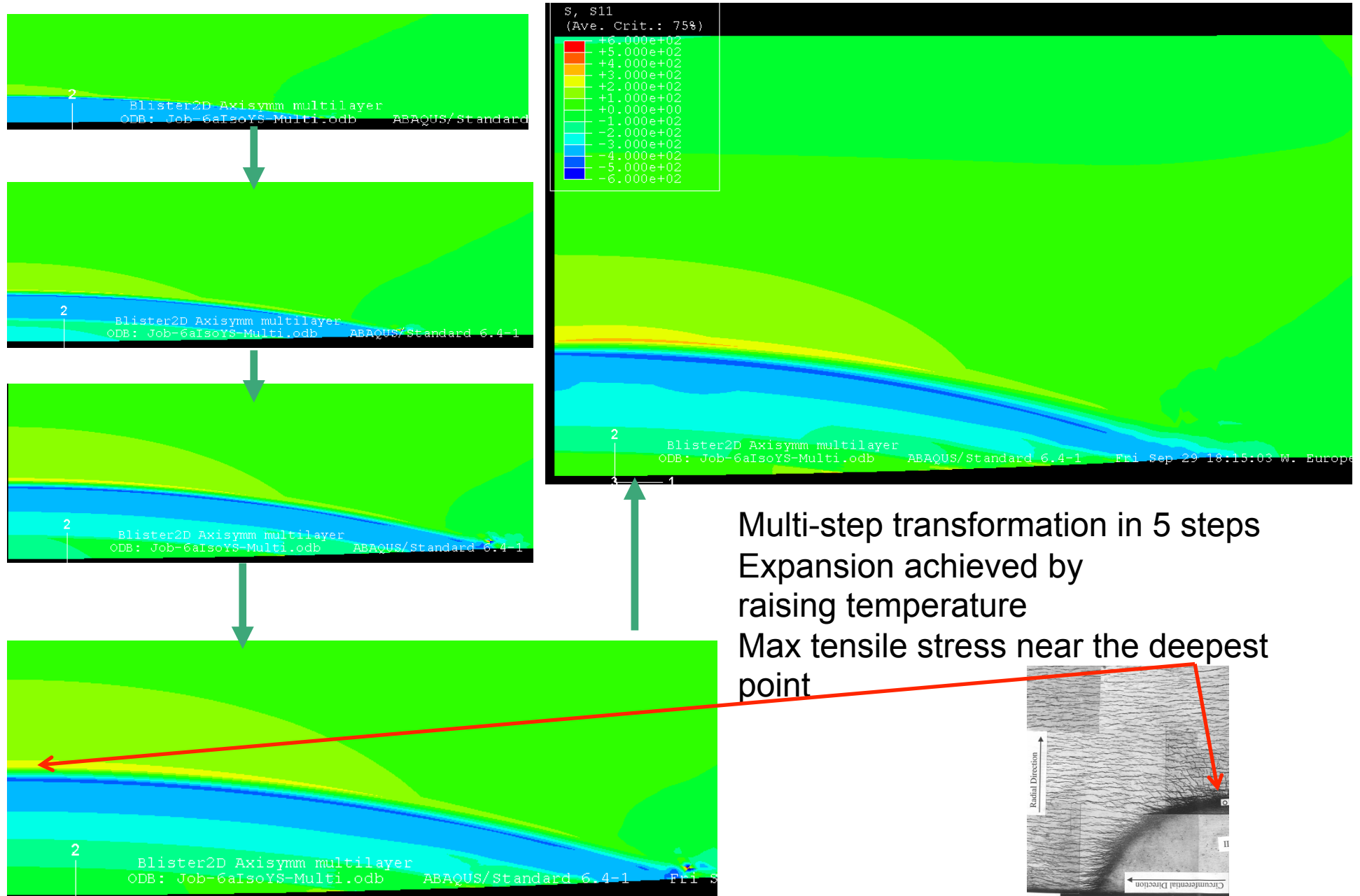
Misfit strain 5.7 percent



Single step transformation
Expansion achieved by
raising temperature
Max tensile stress near the
deepest point

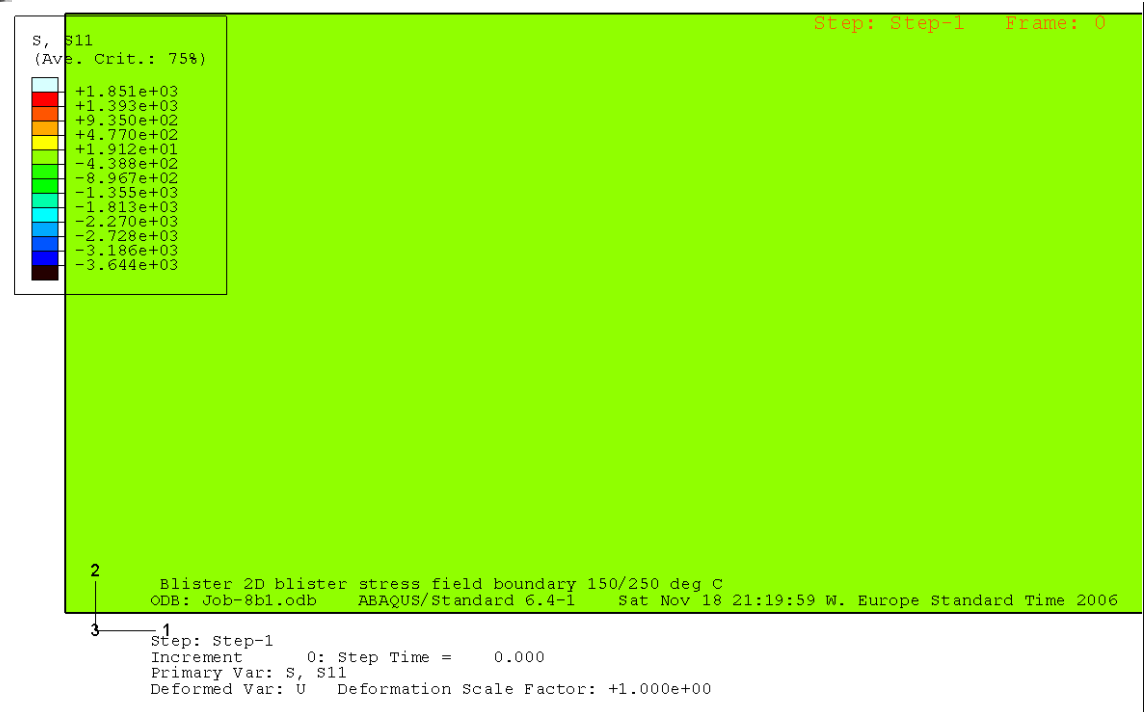
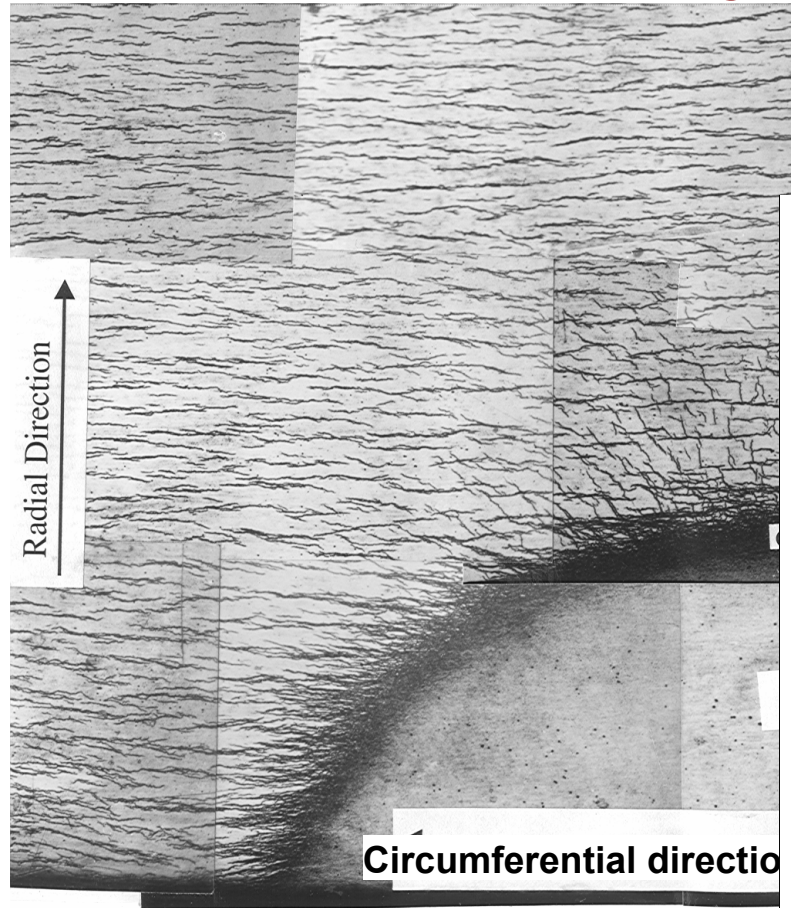


Blister formation - Stress field computation – Multi step



Blister formation - Radial hydride formation around blister

Expansion due to hydride blister formation
Achieved gradually



Computed stress field explains the formation of radial hydride in the matrix surrounding the blister.

The computed effective stress obtained by carrying out the single step transformation of a hydride is higher as compared to that obtained by a multi-step transformation.

Conclusions

- An attempt has been made to understand the hydrogen induced degradation of mechanical property of Zr-alloy using multi-scale structural mechanics approach.
- Computation of stress free transformation strains, prediction of shape and habit plane of hydride precipitate using strain energy minimization technique is performed.
- Tensile, fracture toughness and DHC parameters are presented.