PAUL SCHERRER INSTITUT

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**Laboratory for
Nuclear Materials**

**Nuclear Energy
and Safety**

Paul Scherrer Institut

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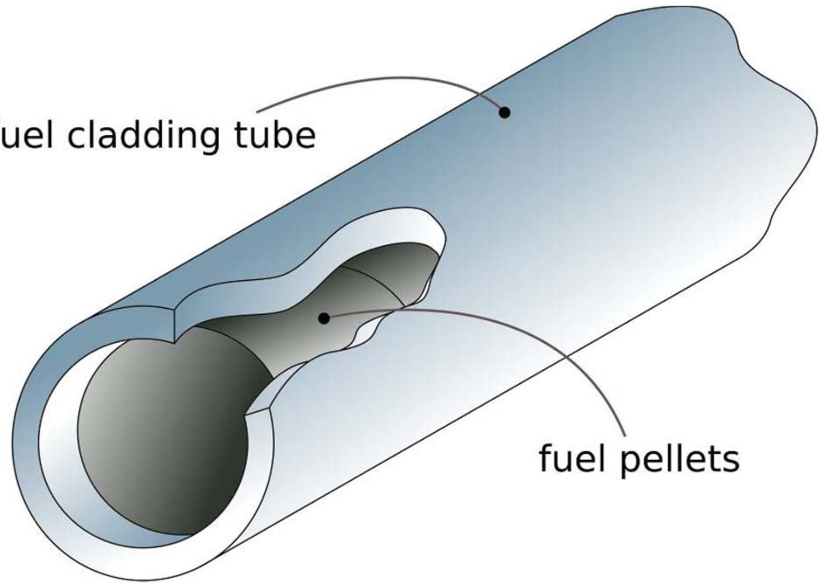
Hydrogen diffusion under stress concentration applied to DHC: a feasibility study using neutron

PSI, December 12, 2011

Hydrogen in cladding tubes

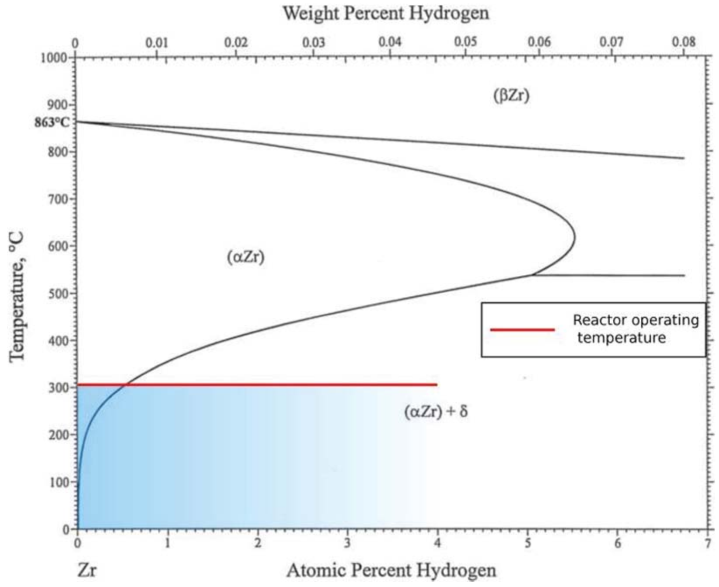
During reactor operation:

- oxidation at the outer side of the cladding;
- released hydrogen is partially absorbed by Zircaloy fuel cladding.

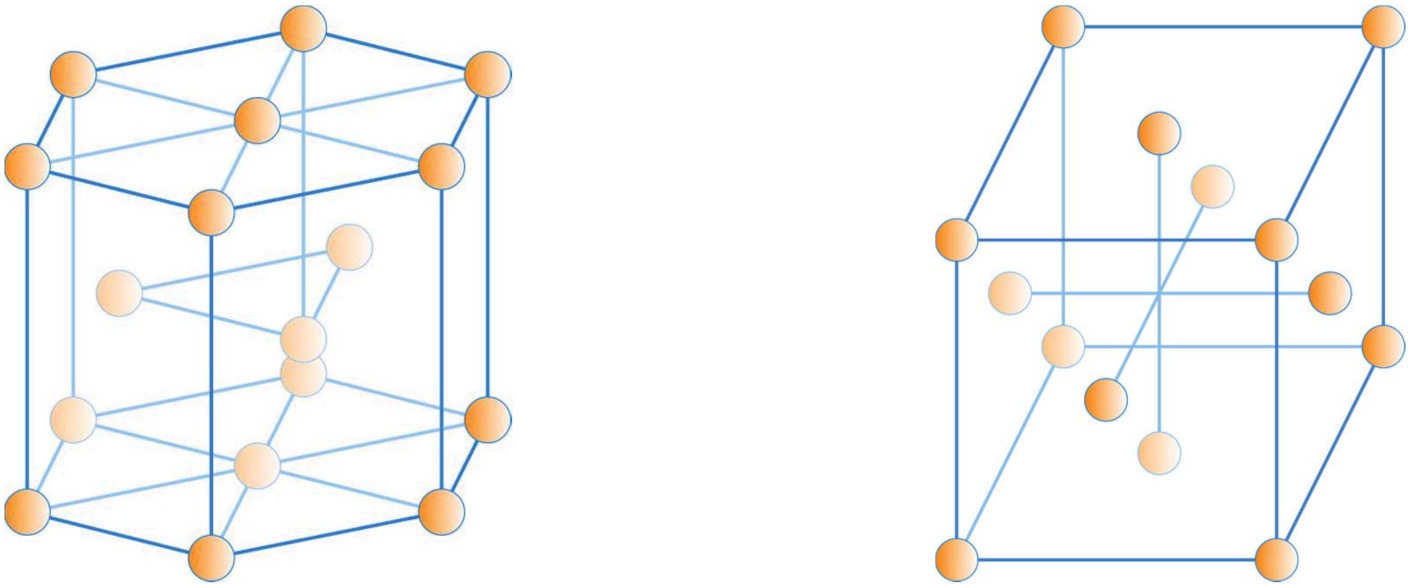


The Zr-H binary system:

- hydrogen in solid solution at operating temperature;
- precipitated hydrides at room temperature.



Hydrogen in cladding tubes



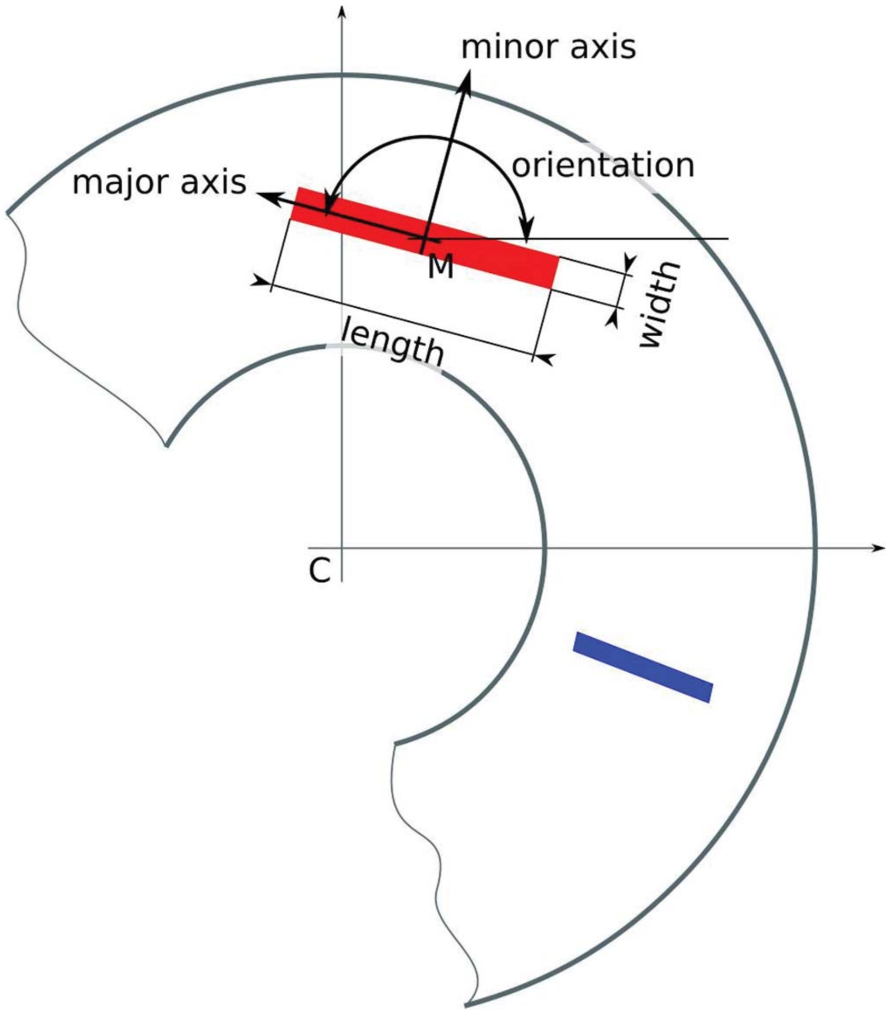
Hydrides *vs.* solid solution:

- α phase is hexagonal compact with hydrogen in solid solution;
- δ phase is face centered cubic with tetragonal sites randomly occupied by hydrogen;
- material behavior properties of α and δ phases are not identical;
- the material can not be considered homogeneous, stress field is modified due to hydrides precipitation.

Hydrogen in cladding tubes

Hydrides behavior:

- brittle at room temperature;
- ductile above 200° C.



Minimization of hydrides impact:

- fabrication process which favor circumferential orientation;
- operating rules;
- regulation limiting fraction of radial hydrides.

Outline

I. Hydrogen diffusion within the delayed hydride cracking mechanism

II. Neutron radiography

Outline

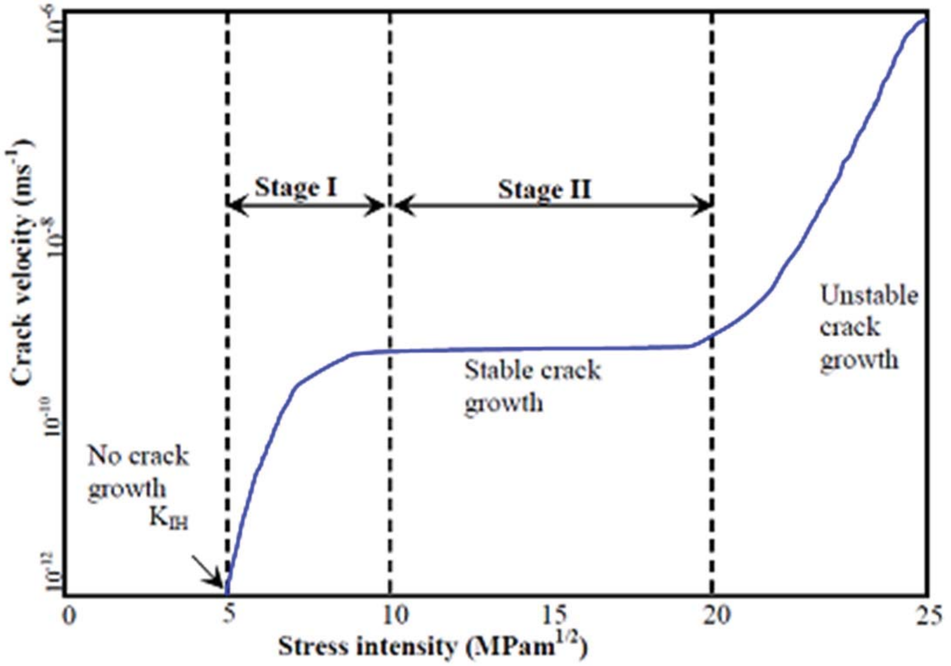
I. Hydrogen diffusion within the delayed hydride cracking mechanism

- Delayed Hydride Cracking
- models and experiments for hydrogen diffusion

Delayed Hydride Cracking

Delayed Hydride Cracking:

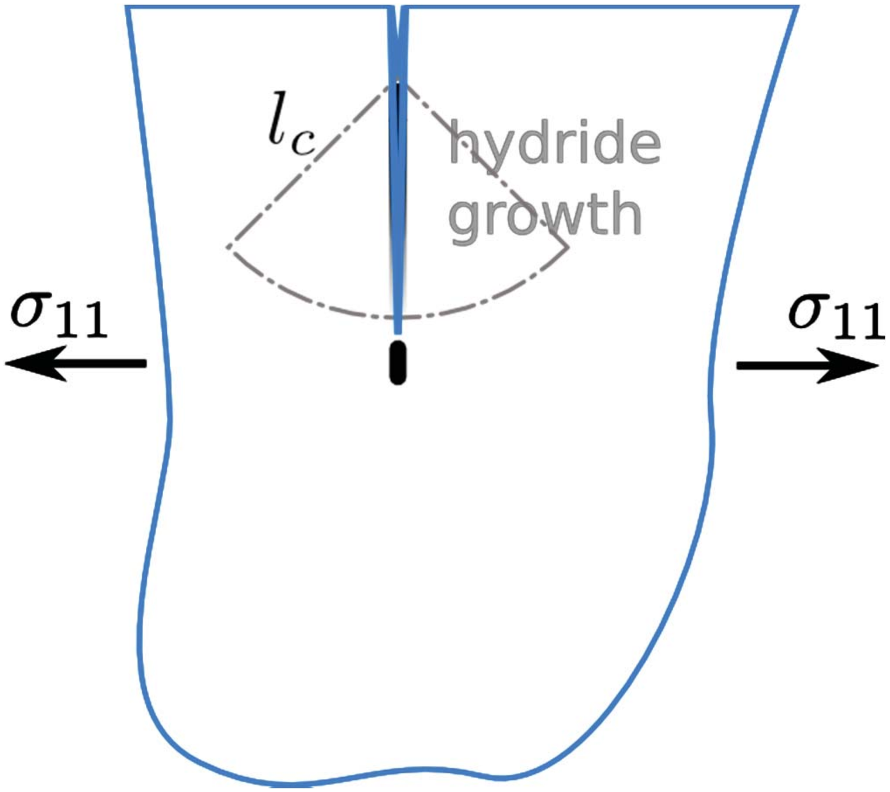
- under-critical failure mechanism;
- arise due to interplay between hydrides precipitation and stress raisers;
- stepwise cracking velocity;
- can lead to complete fracture of cladding tubes under low mechanical loading.



Delayed Hydride Cracking

Phenomenological description:

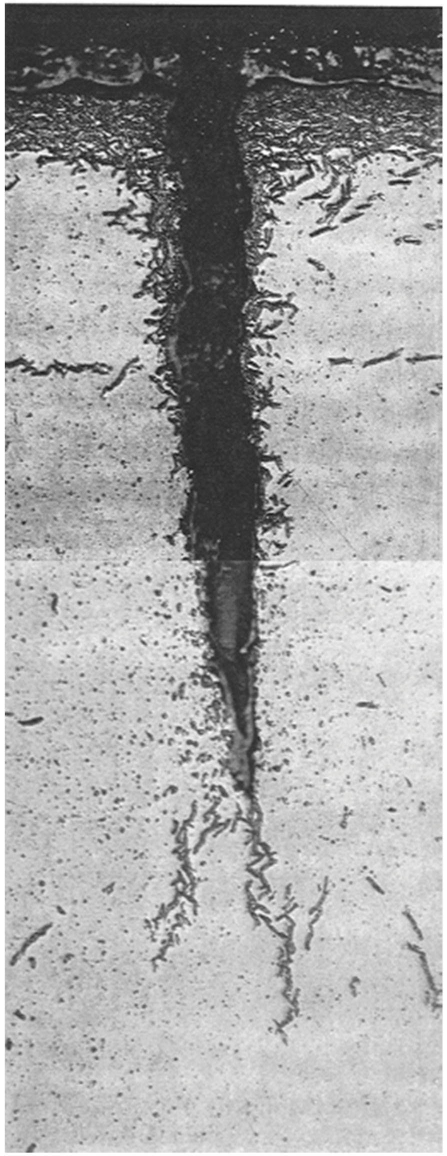
- reoriented hydride nucleation at crack tip;
- hydride growth;
- hydride reaches critical length;
- hydride failure under stress;
- cycle repetition until complete failure.



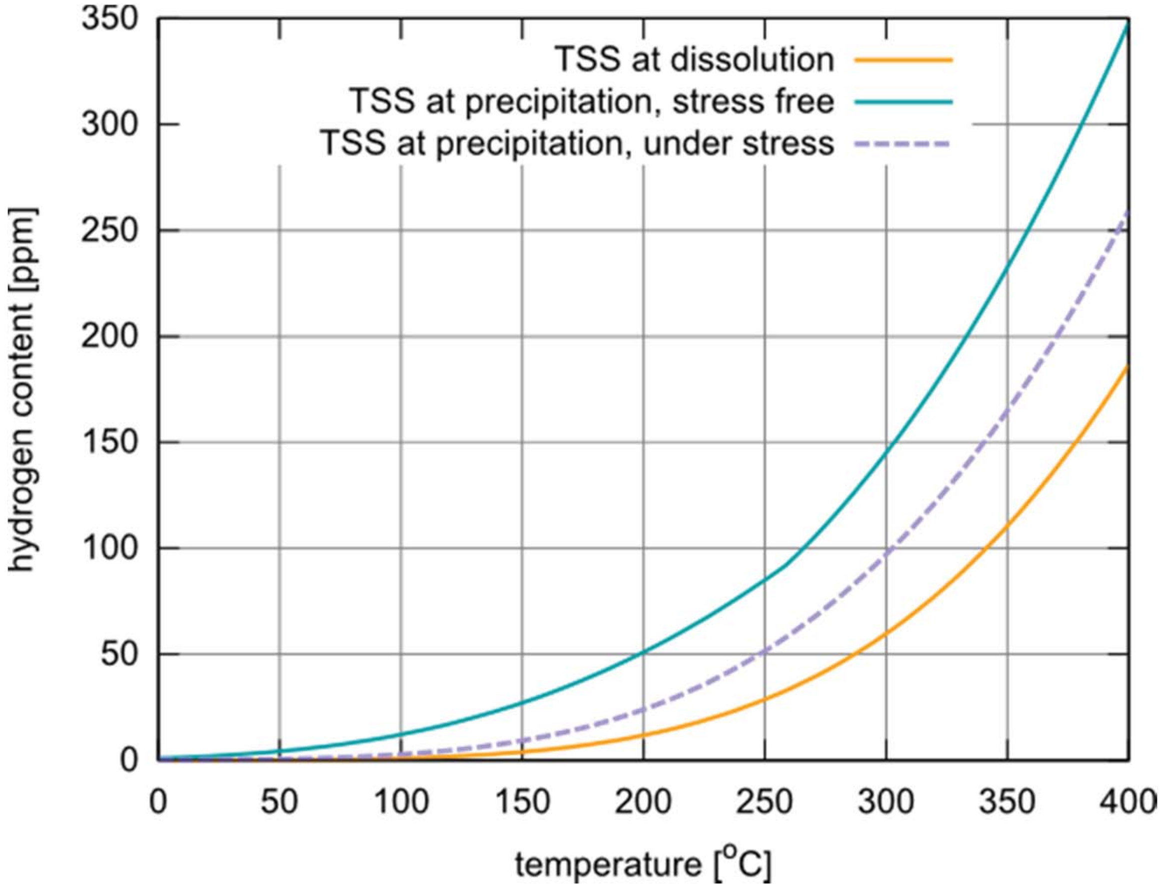
Delayed Hydride Cracking

Involved physical mechanisms:

- modification of the Temperature of Solid Solution at Precipitation due to stress;
- hydride brittle behavior;
- modification of the interaction energy at nucleation site due to stress;
- modification of crack tip stress singularity due to hydride;
- **hydrogen diffusion under concentration gradient and stress gradient**.



Driving force for crack tip hydride formation



Terminal solid Solubility (TSS):

- depends on dissolution and precipitation;
- during precipitation, depends on the effective stress state

Consequences for DHC:

- change of TSS solvi line at the crack tip;
- earlier hydride precipitation at crack tip might induce concentration gradient.

Driving force for crack tip hydride formation

DHC analytical models:

- hydrogen flux [Varias & Massih, 1999]:

$$\underline{J}^H = -(1-f)\frac{D^H C^H}{R\theta}\underline{\nabla}\mu^H$$

- chemical potential [Varias & Massih, 1999; Varias & Feng, 2004]:

$$\mu^H = \mu_0^H + (\tfrac{1}{2}\underline{\underline{\sigma}} : \underline{\underline{\underline{\underline{M}}}} : \underline{\underline{\sigma}} - \tfrac{1}{3}tr(\underline{\underline{\sigma}}))\bar{V}^H$$

$$\mu^H = \mu_0^H - \tfrac{1}{3}tr(\underline{\underline{\sigma}})\bar{V}^H$$

Rational thermodynamics, diffusion in mixture:

- hydrogen flux [Müller, 2001]:

$$\underline{J}^\alpha = \textstyle\sum_{\beta=1}^{\nu-1}(D_J^{\alpha\beta})^{-1}\underline{\nabla}(-\frac{\mu_\beta-\mu_\nu}{\theta}) - (D_J^{\alpha\beta})^{-1}D_T^\beta\underline{\nabla}(\frac{1}{T})$$

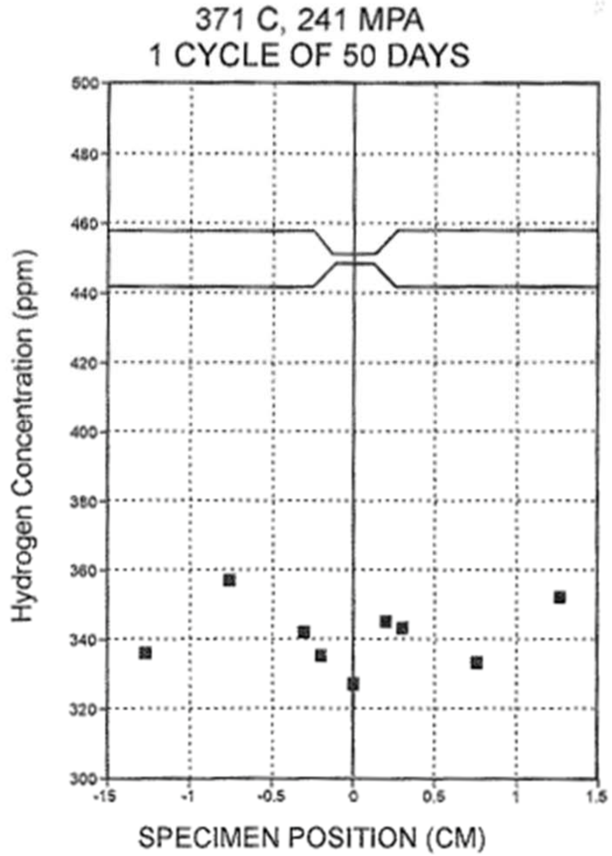
- chemical potential [de Boer & Bluhm, 1996]:

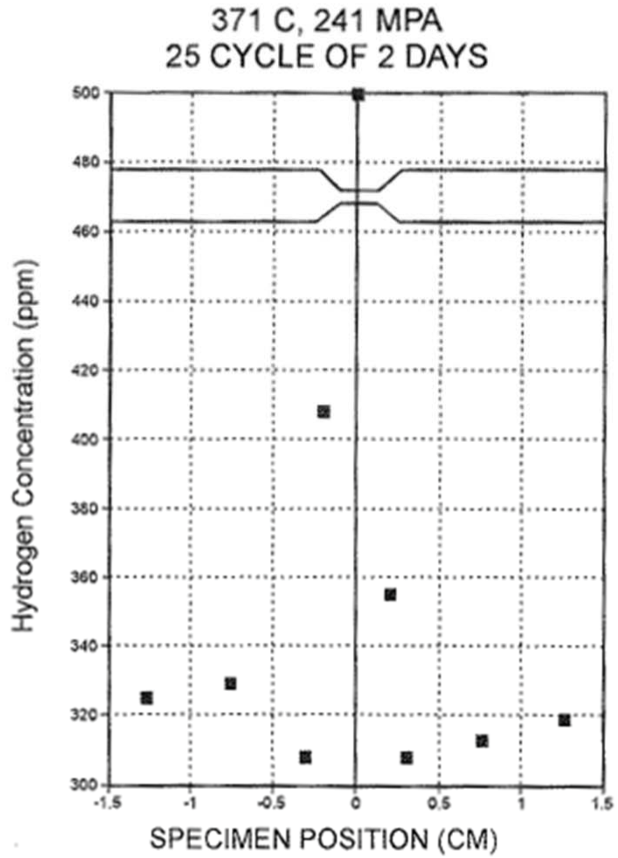
$$\mu^\alpha = \Psi^\alpha - \frac{1}{3\rho^\alpha}\underline{\underline{T}}^\alpha : \underline{\underline{Id}} - \tfrac{1}{2}\underline{\dot{x}}^\alpha \cdot \underline{\dot{x}}^\alpha$$

- Helmotz free energy [Truesdell, 1969]:

$$\Psi^\alpha = \hat{\Psi}^\alpha(\rho^\alpha, \underline{\nabla}\rho^\alpha \cdot \underline{\nabla}\rho^\alpha, \theta)$$

Driving force for crack tip hydride formation





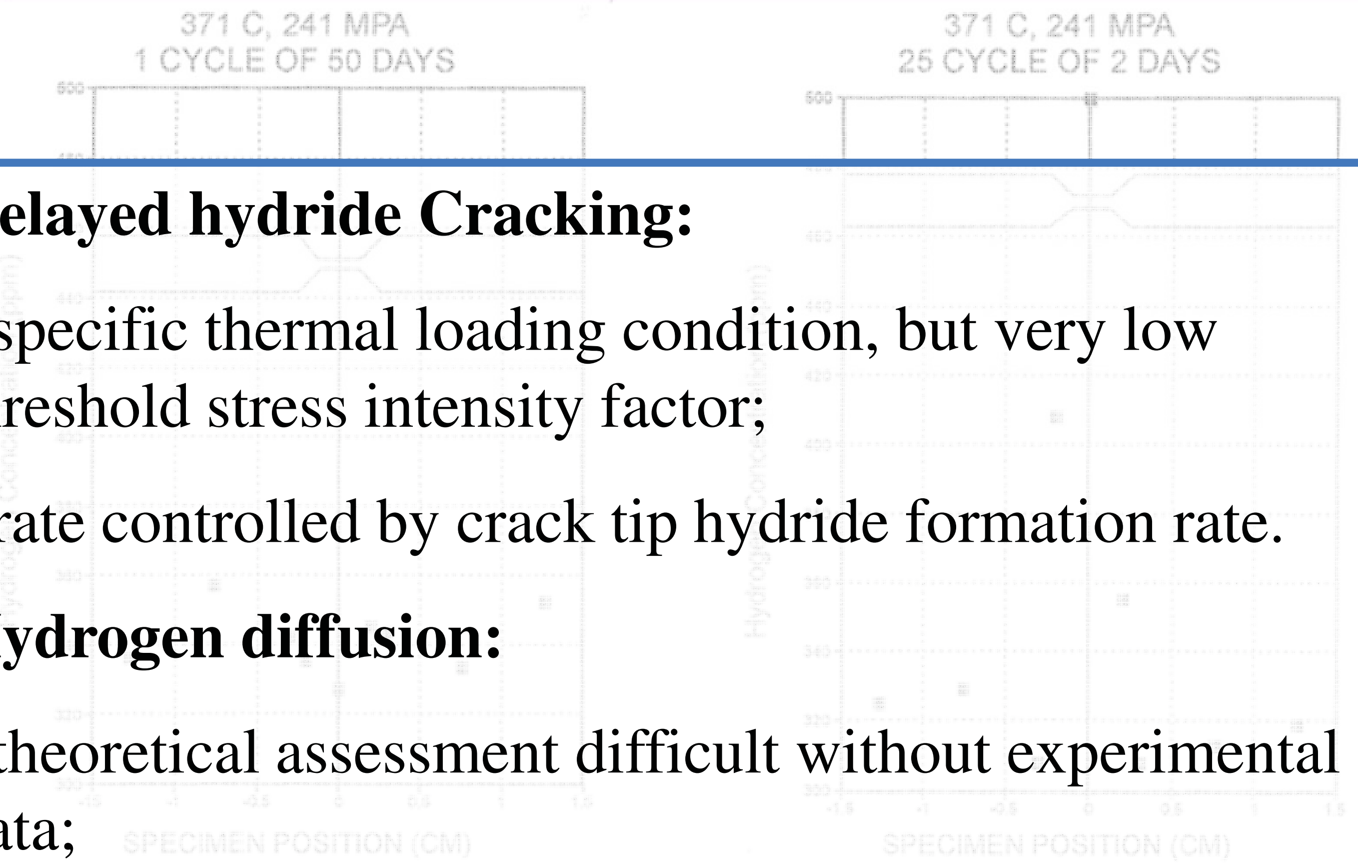
Post-mortem investigation:

- assumes hydrides give a good picture of hydrogen content when in solid solution;
- with only one dissolution cycle, no ‘stress induced diffusion’.

Validity:

- results depends on the number of cycles, and material annealing conditions;
- how many cycles to consider that hydrides are a good marker?

Outlook



Delayed hydride Cracking:

- specific thermal loading condition, but very low threshold stress intensity factor;

- rate controlled by crack tip hydride formation rate.

Hydrogen diffusion:

- theoretical assessment difficult without experimental data;

- sound experimental investigation can not rely on *post-mortem* hydrogen analysis.

Post-mortem investigation:

- assumes hydrides give a good picture of hydrogen content when in solid solution;
- with only one dissolution cycle, no ‘stress induced diffusion’.

Validity:

- results depends on the number of cycles, and material annealing conditions;
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Outline

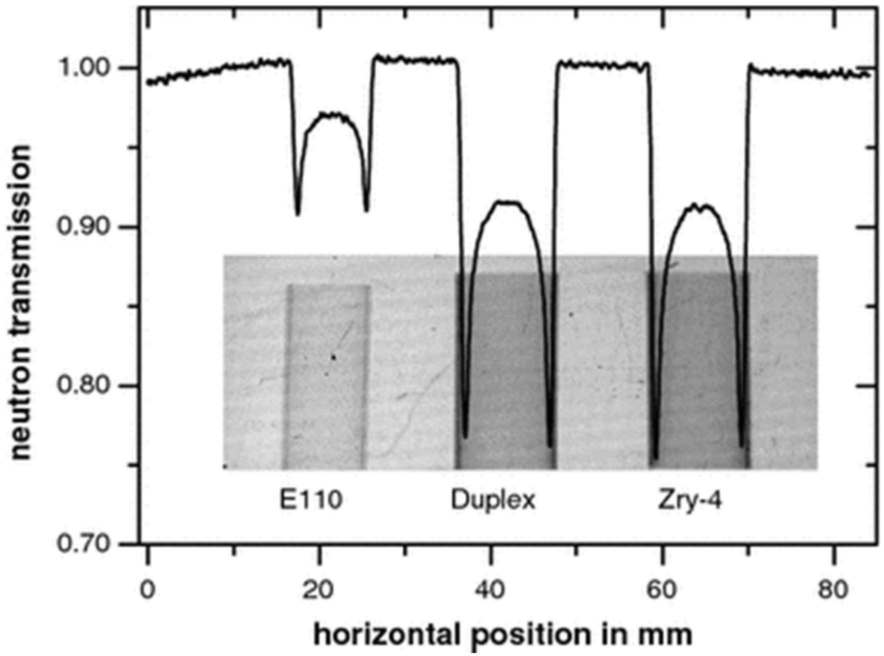
II. Neutron radiography and hydrogen diffusion

- experimental setup and purposes
- feasibility results

Experimental setup and purposes

Cold neutrons radiography:

- hydrogen presents higher neutron attenuation than zirconium;
- possibility of *in-situ* radiography;
- feasibility tests carried this summer at the ICON beam of SIN-Q.



[Grosse & Al., Kinetics of Hydrogen Absorption and Release in Zirconium Alloys During Steam Oxydation]

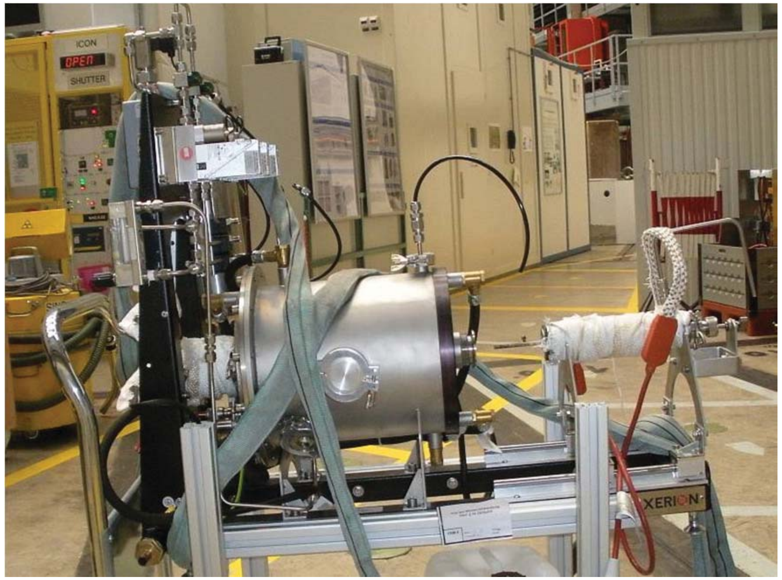
Objective:

- *in-situ* measurement of effect of stress gradient on hydrogen diffusion;
- observation of pre-hydrogenated samples and online hydrogenated samples;
- observation under stress in presence of stress riser – notch or fatigue crack.

Experimental setup and purposes

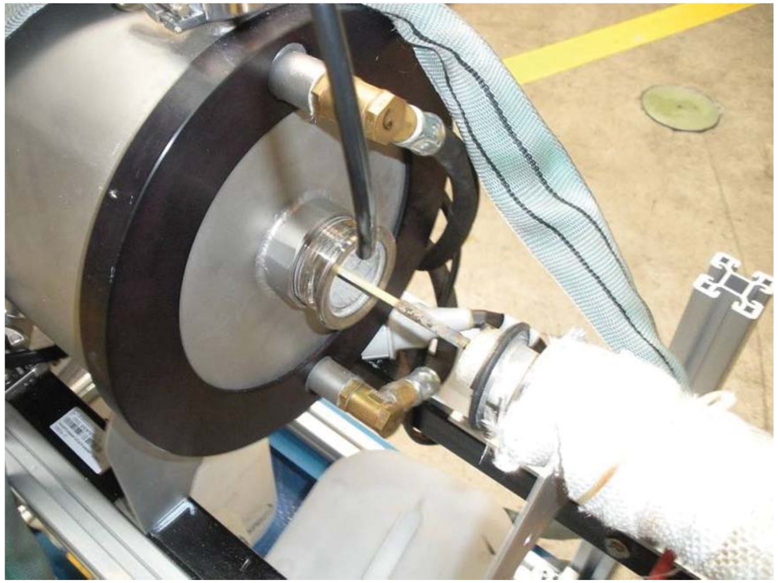
INRRO furnace:

- thermal loading up to 1500° C;
- well defined flowing gas atmosphere;
- useable area is a cylinder of diameter 30mm.

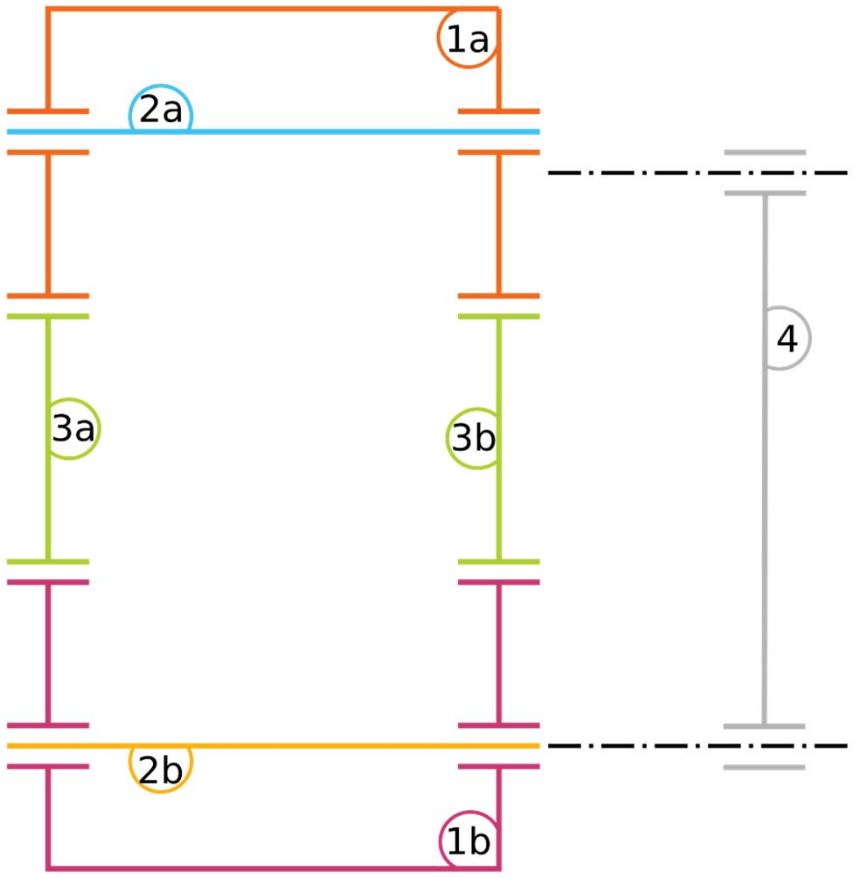


Constraint for the mechanical loading device:

- no external power source;
- no external control;
- temperature resistant up to 450° C;
- compact;
- transparent to neutrons at the sample gage section.



Experimental setup and purposes



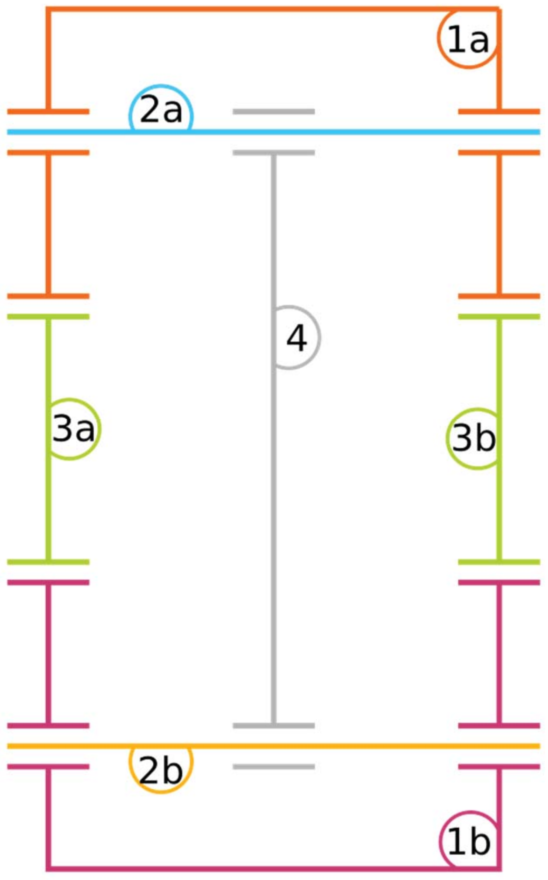
Principle:

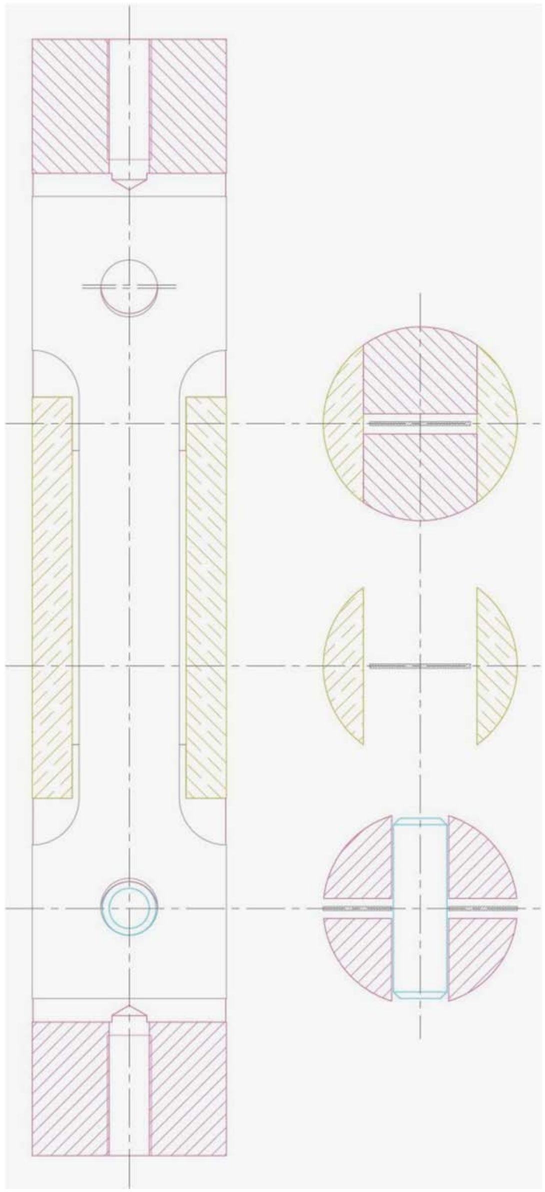
- sample is loaded outside the furnace;
- sample length between holes is smaller than pin spacing on the frame;
- exact loading can be obtained using, during mounting, a strain gauge on the sample;
- displacement controlled loading device.

Side aspects:

- frame stiffness larger than sample stiffness;
- materials chosen to get a temperature independent loading;
- load level can be tuned using pins of different diameters.

Experimental setup and purposes





Feasibility results

Non hydrogenated samples:

- heat up to 350° C;
- observe the sample by neutron radiography.

Hydrogenated samples:

- heat up to 350° C;
- let Ar+H2 gas in;
- observe the sample by neutron radiography

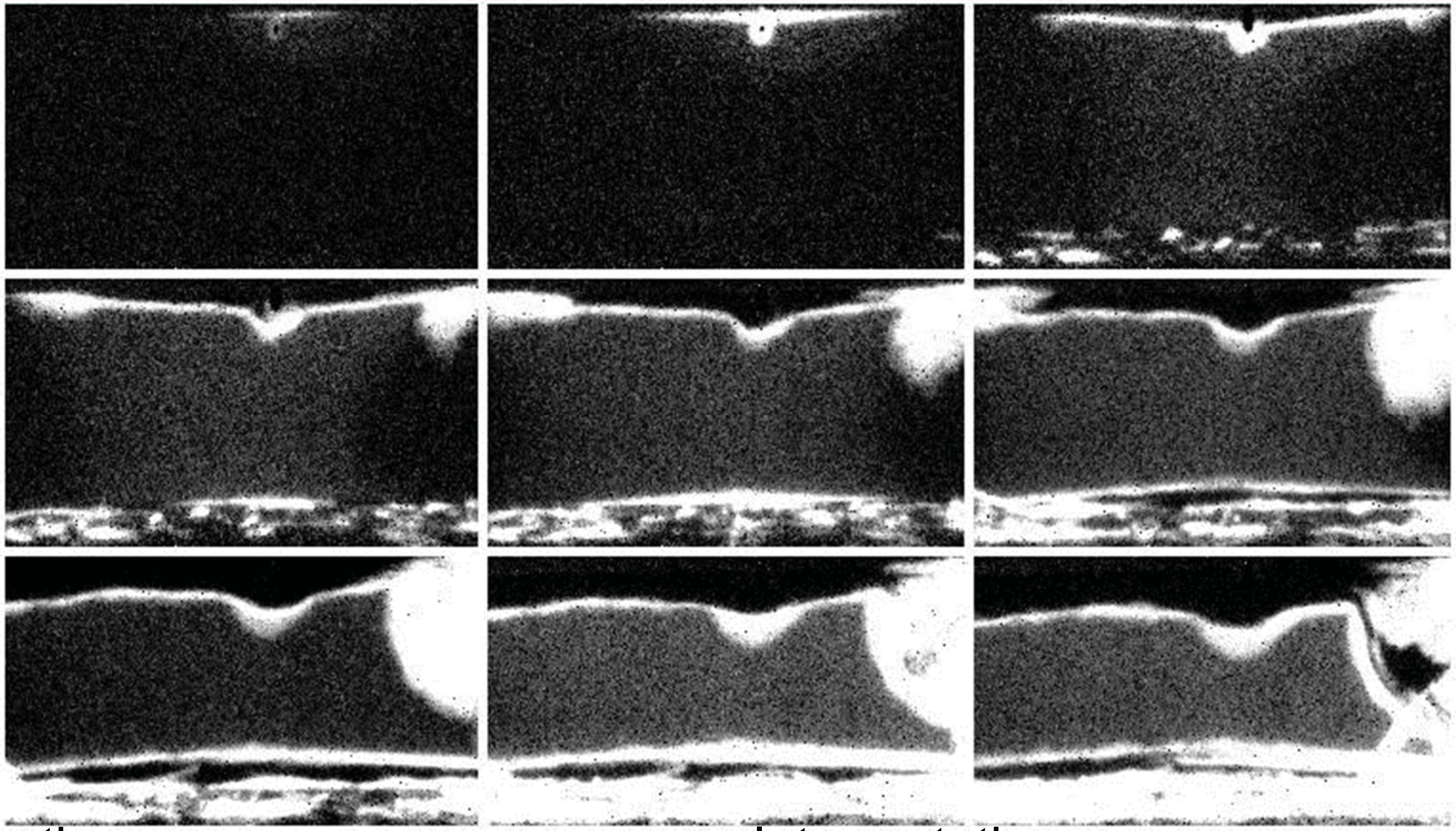
Sample #	H cont.	Notch	Fatigue crack	Output
1	~300.ppm	Yes	Yes	Image illumination time too long.
2	~300.ppm	Yes	Yes	Hydrogen already diffused
3	0.ppm	Yes	Yes	Hydrogen ingress and diffusion primarily in stressed area.
4	0.ppm	Yes	No	Hydrogen ingress and diffusion primarily in stressed area.

Feasibility results

Sample #4:

- notched specimen, no fatigue pre-crack;
- tensile loading around 80MPa;
- temperature 350° C
- Ar+H2 atmosphere at partial pressure 4kPa.

Feasibility results



Observations:

- hydrogen absorption at stressed area;
- diffusion and embrittlement first in the stressed area, then on top end;
- higher H concentration in front of stress raiser.

Interpretation:

- stress gradient and/or oxide layer cracking;
- higher stressed area encounter earlier diffusion.

Outlook

n-radiography:

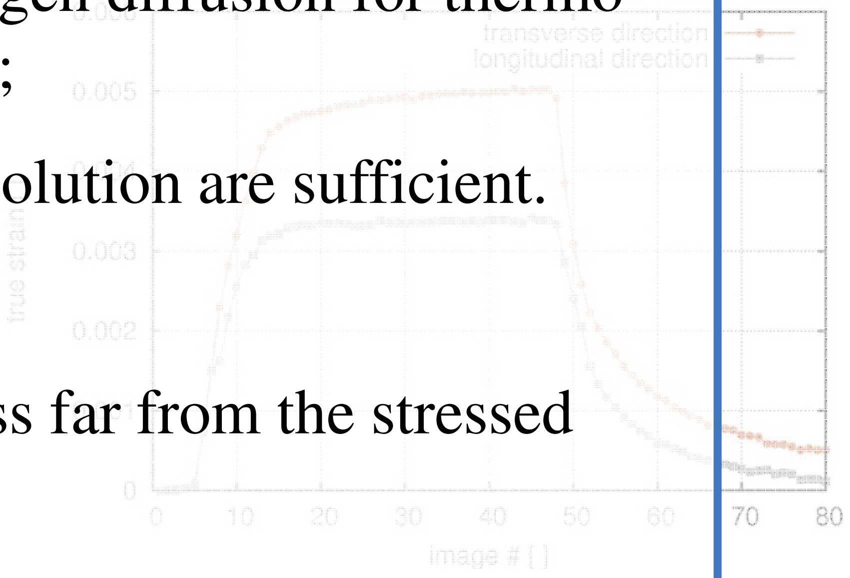
- *in-situ* observation of hydrogen diffusion for thermo-mechanically loaded samples;

- spatial, time and H cont. resolution are sufficient.

Future test conditions:

- channel the hydrogen ingress far from the stressed area;

- use of thermo-mechanical loading suitable for DHC to arise.



Driving force for hydrogen to the crack tip is a central piece for a fine understanding and sound modeling of DHC.

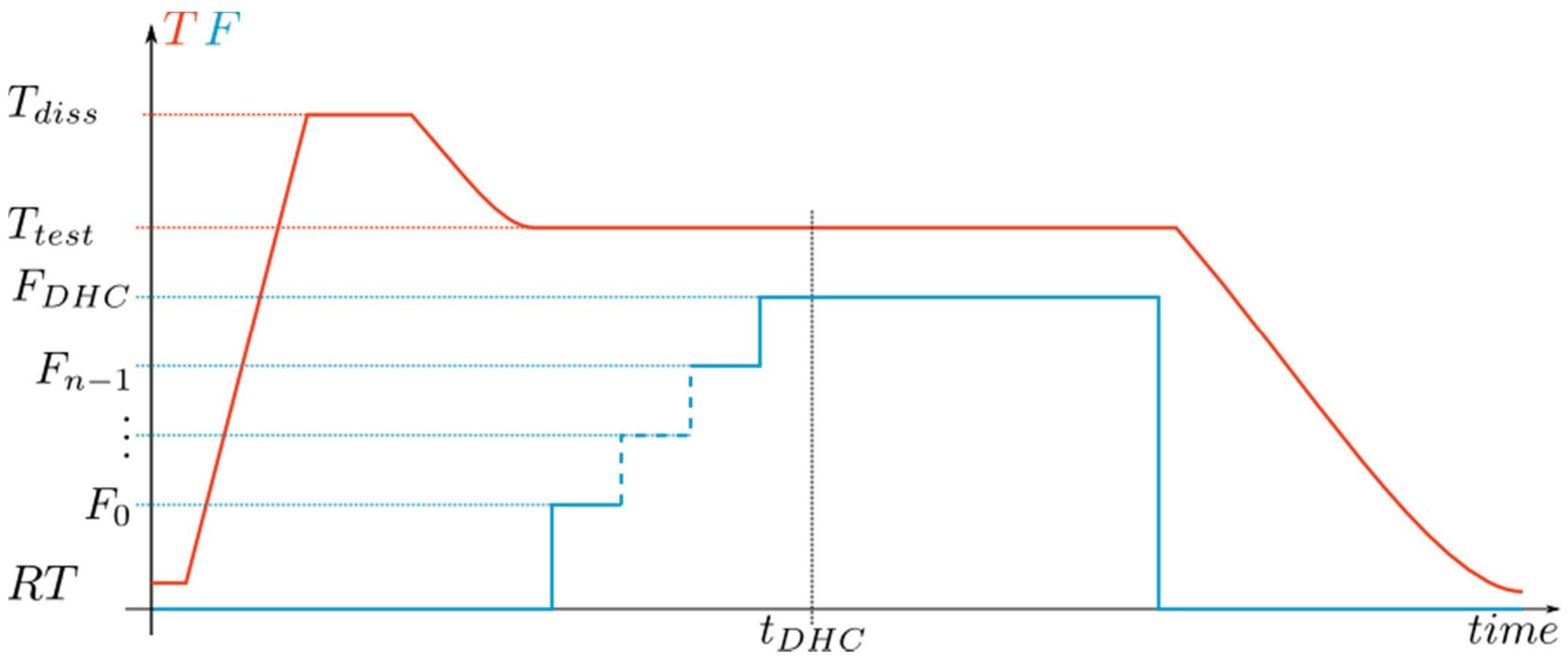
Theoretical approaches as well as standard tests can hardly give a non-questionable answer.

Cold neutron radiography is a suitable tool to tackle this subject.

Delayed Hydride Cracking

Thermo mechanical loading cycle:

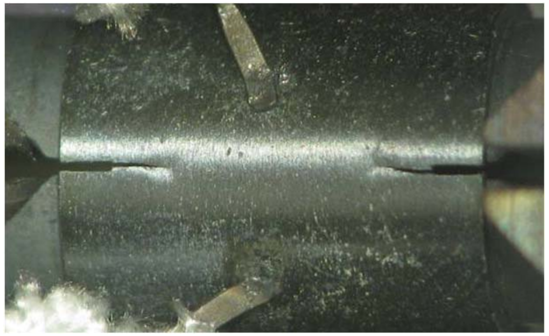
- dissolve hydrogen;
- go to test temperature;
- search for critical force;
- monitor thermo-mechanical loading;
- monitor crack propagation.



Delayed Hydride Cracking

Test results for Zircaloy-2, 400ppm H:

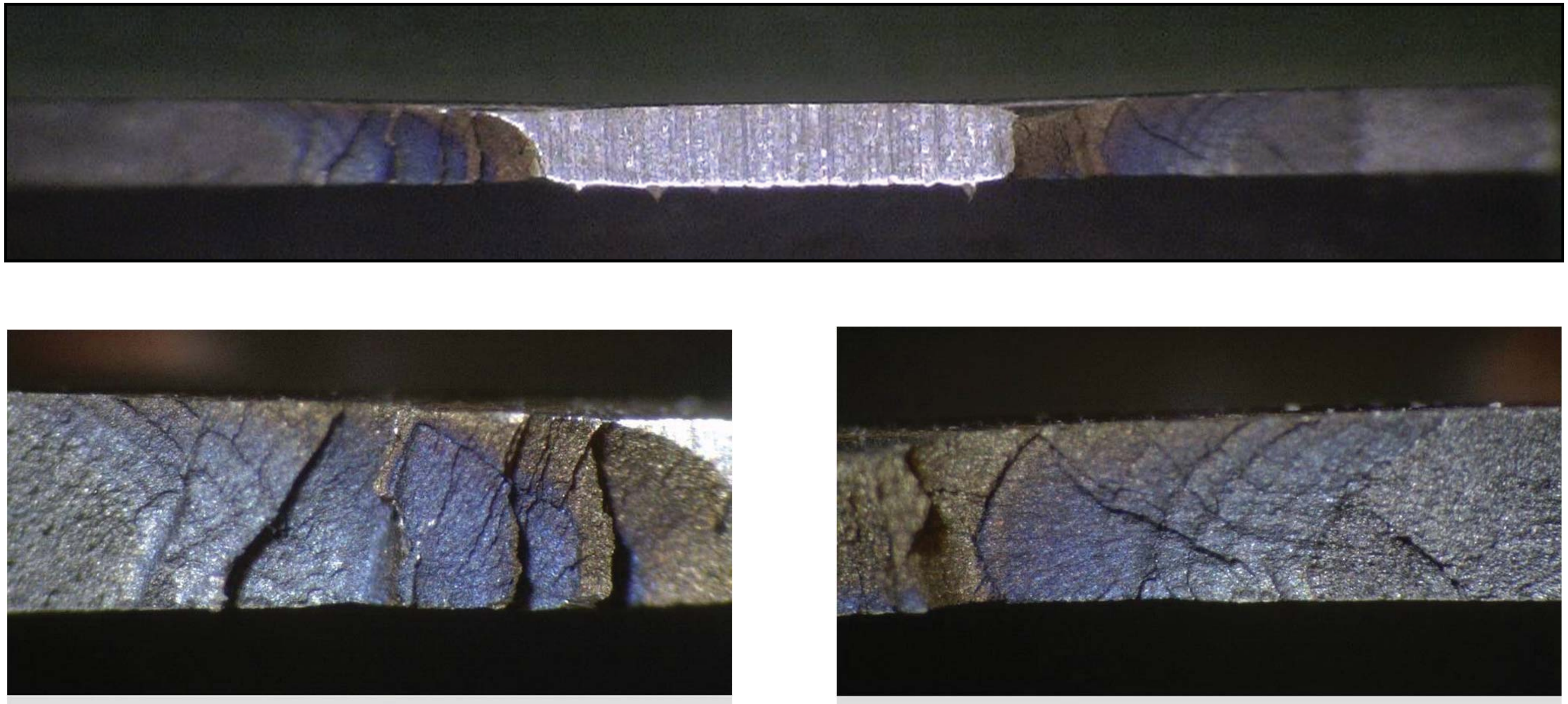
- propagation starts for F=2800N;
- incubation time 12~24 hours;
- KI around 25MPa.m$^{1/2}$ at start;
- velocity around 7.2 mm.day^{-1} at start.

12 hours	24 hours	36 hours
		
48 hours	60 hours	72 hours
		

Delayed Hydride Cracking

Post-mortem fractography:

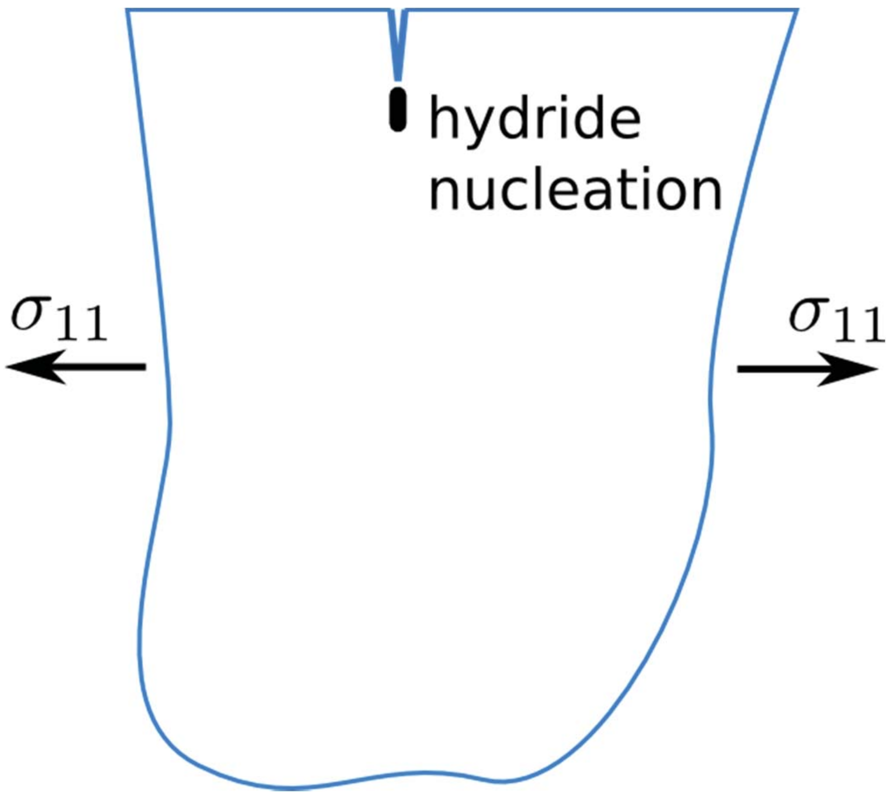
- striation typical from DHC;
- striations correpsonds to the stepwise crack propagation;
- striation spacing shows crack acceleration;
- crack front shape tends to be straighter.



Delayed Hydride Cracking

Phenomenological description:

- reoriented hydride nucleation;
- hydride growth to critical length;
- crack propagation;
- ...



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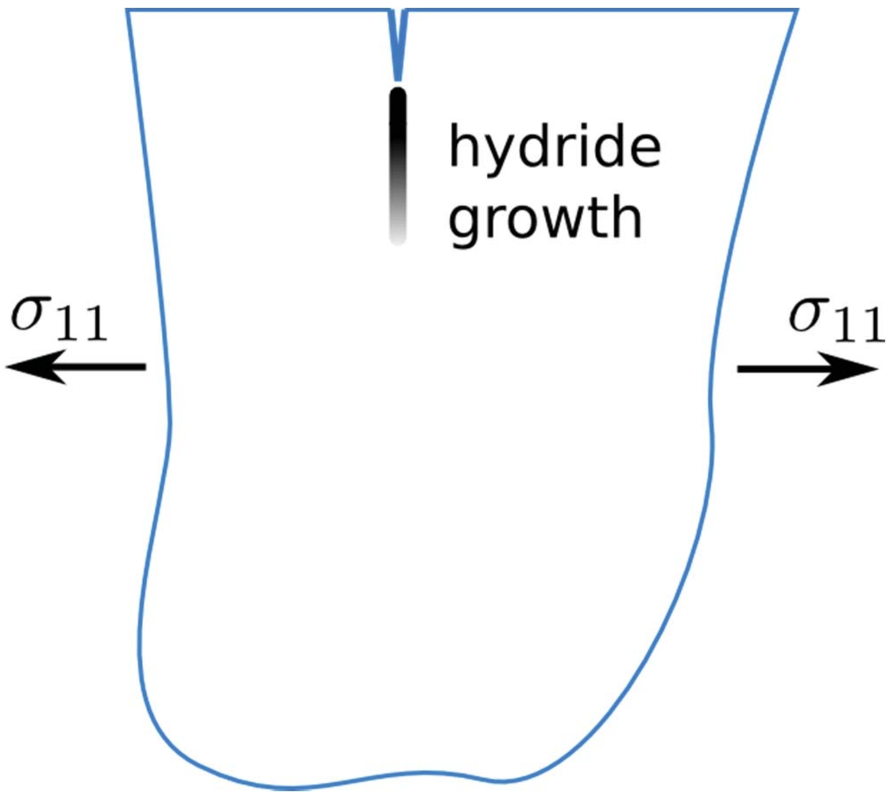

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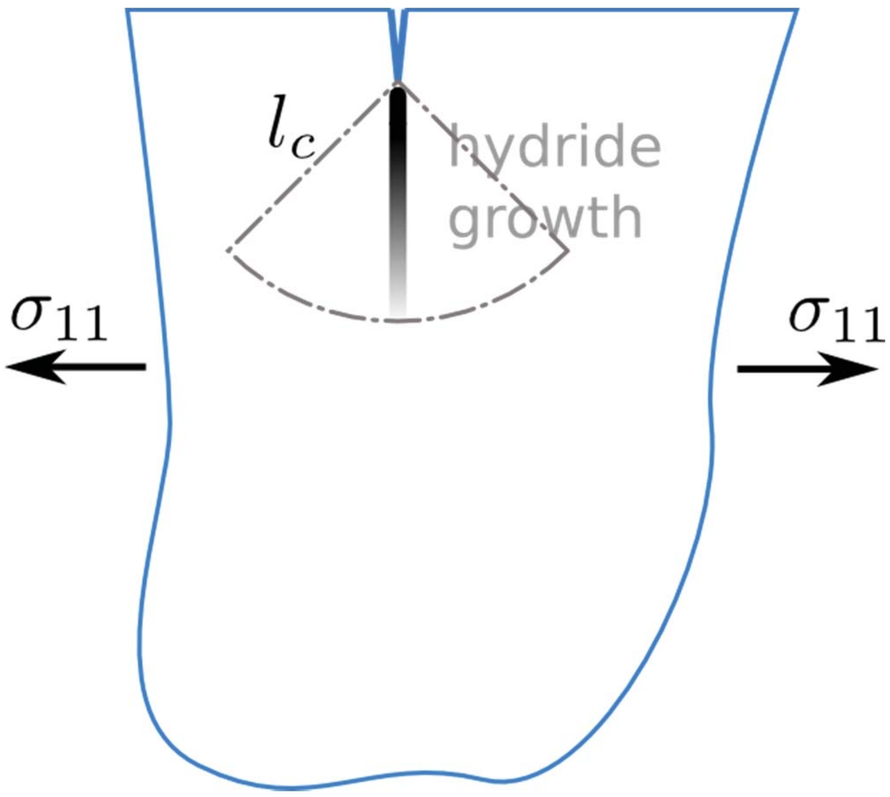

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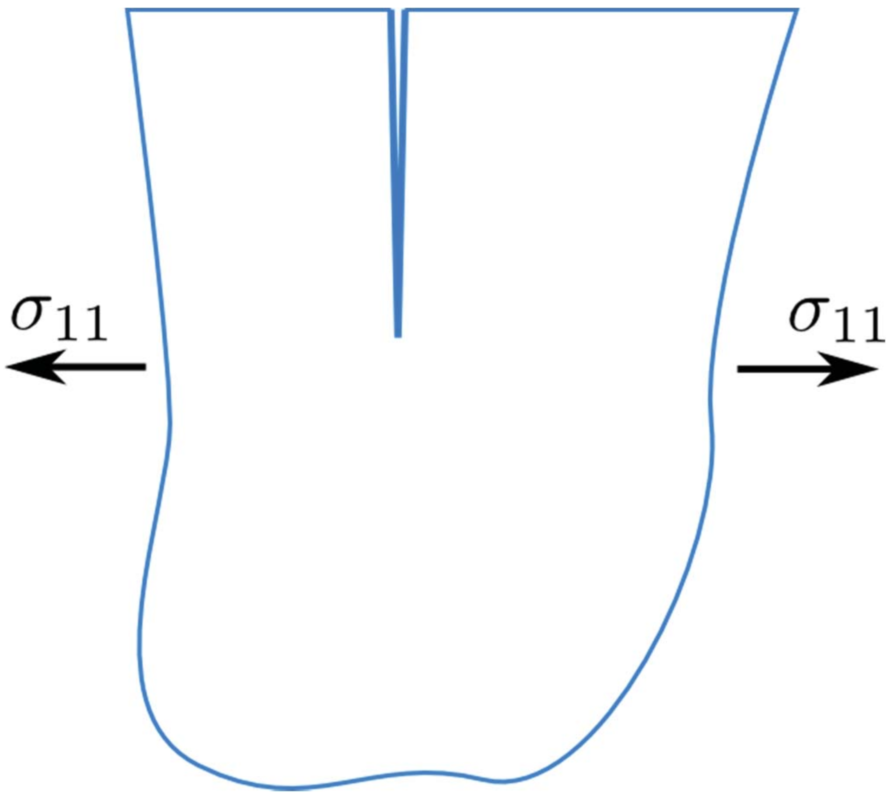

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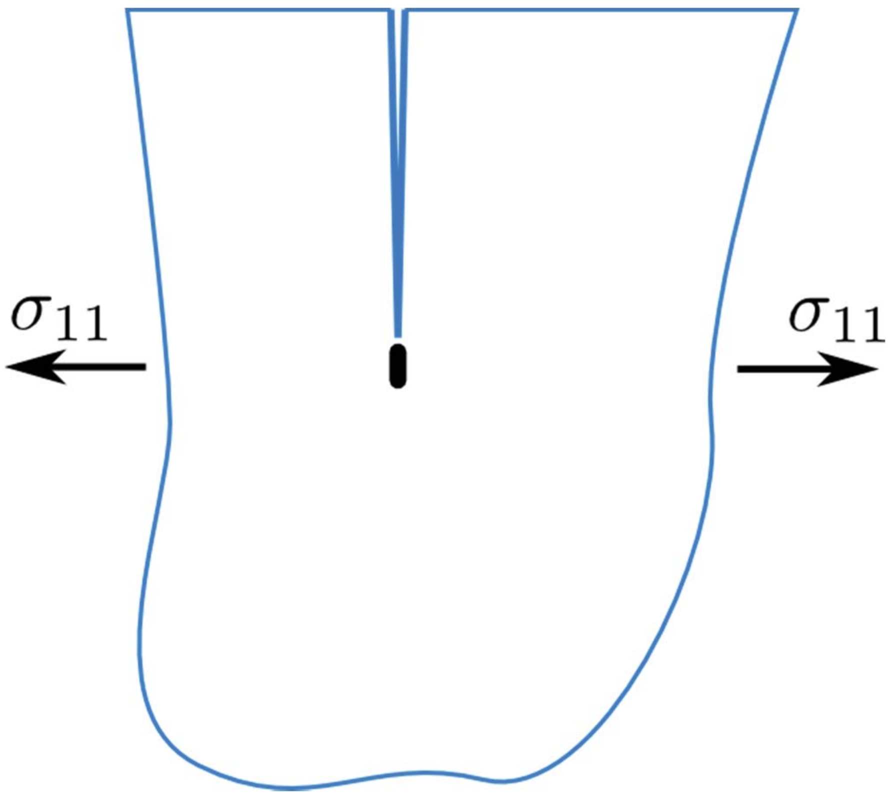

Neutron radiography and hydrogen diffusion

Sample #3:

- notched specimen, fatigue pre-crack;
- tensile loading around 80MPa;

- temperature 350° C
- Ar+H2 atmosphere at partial pressure 4kPa.