Overview of investigations on bulk distribution of hydrogen absorbed by zirconium alloys

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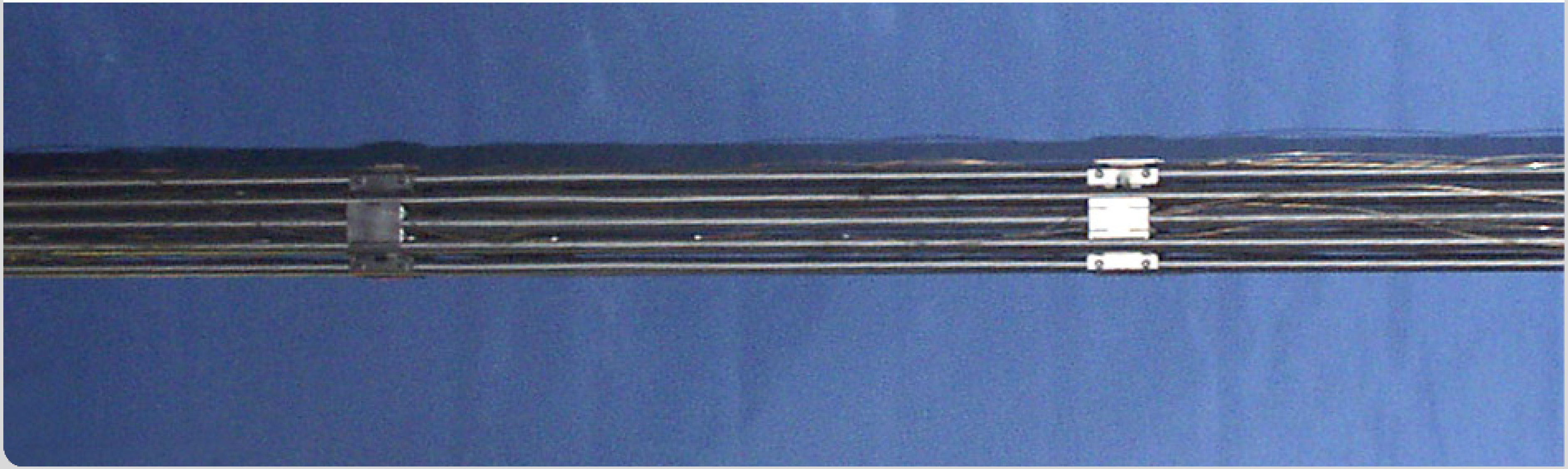
Institute for Applied Materials, IAM-WPT, Program NUKLEAR



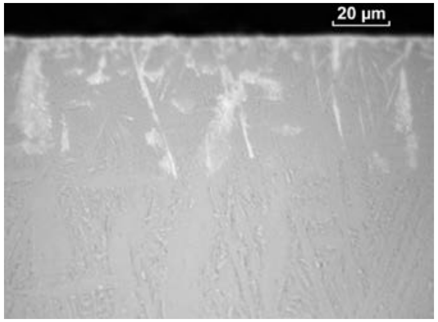
Objectives

- Hydride formation
- Mechanisms of hydrogen absorption
- Mechanisms of embrittlement
- Application to the results of QUENCH-LOCA tests

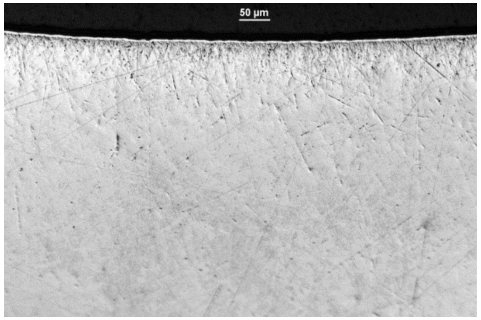
Embrittlement of hydrogenated cladding

M5 cladding pre-hydrided from outer side to 1700 wppm at 800°C: double rupture during tensile test

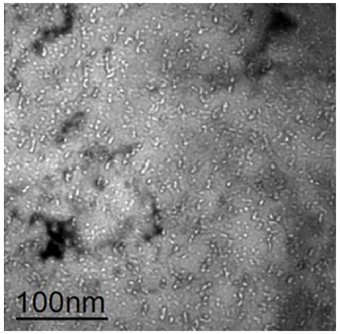
QUENCH-L0 (Zry-4), rod#2:
brittle double rupture during tensile tests,
fracture stress 400 MPa, elongation 1%;
to comparison rupture after necking: fract. elong. 10%



optical microscopy: no visible hydrides



optical microscopy of hydrogen enriched band: no visible hydrides

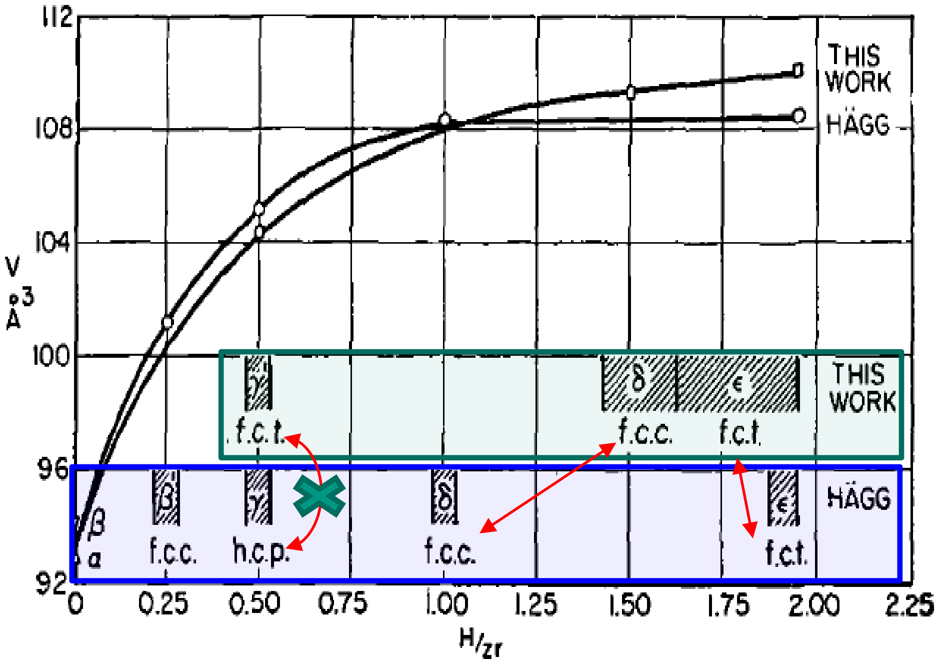


TEM image of inhomogeneities in the hydrogen enriched band

Known phases of Zr – H system

Zr – H phases

G. Hägg, Zeitschrift für Physikalische Chemie, 11, 439 (1930)



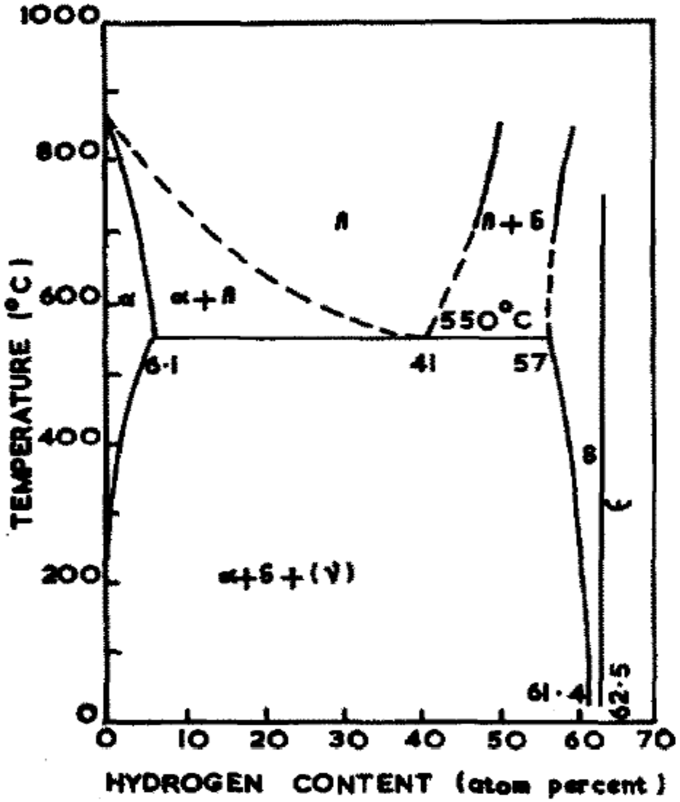
Volume of Zr and ZrH$_x$ structures after

E. A. Gulbransen and K. F. Andrew //

J. Electrochem. Soc. 1954, V.101(9), P. 474-480.

„γ – phase is metastable".

B. Nath // Journal of Nuclear Materials 58 (1975) 153-162.



Zirconium – hydrogen phase diagram

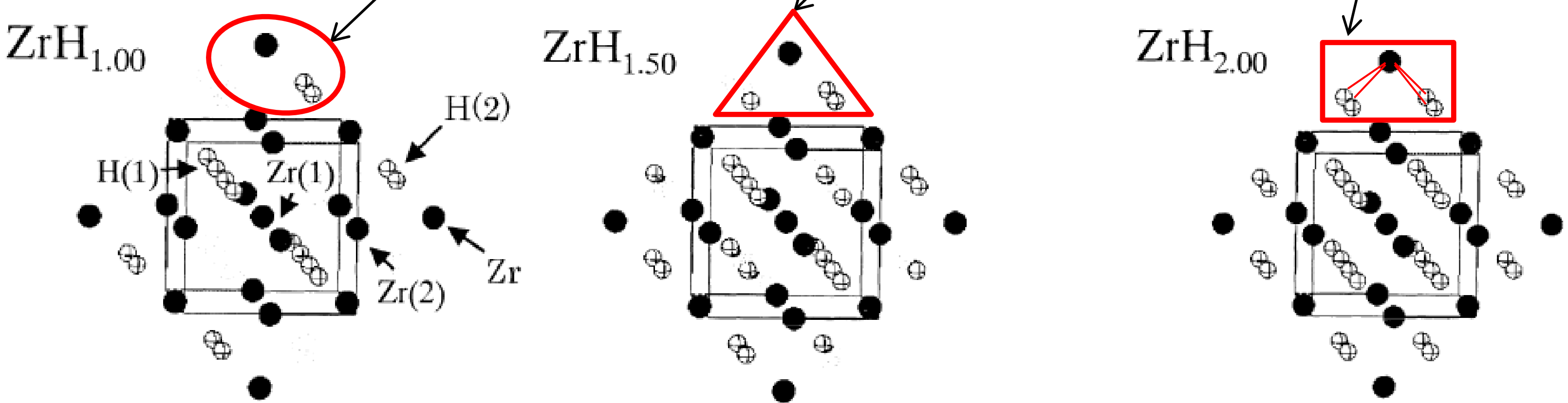
Beck R.L. // ASM Trans. Q.,55 (1962) 542-555.

"Hydrogen cannot be kept in supersaturated solution by quenching".

S.R. MacEwen et al., Acta Metal. 33 (1985) 753–757.

ZrH_x structures

	γ - phase	δ - phase	ε - phase
Stoichiometric ratio	x=1	x = 1.5–1.65	x = 1.75–2
atom positions in tetragonal cell occupied*	1/2	3/4	4/4
Stability	metastable (stable only in high purity Zr**)	equilibrium	equilibrium
Usually in presence of stabilizers**	β-stabilizers (Nb, H…)	α-stabilizers (Sn, Hf, O…)	-------



Cluster model of Zirconium hydride crystal structure

S. Yamanaka et al. // Journal of Alloys and Compounds 330 –332 (2002) 313 - 317.

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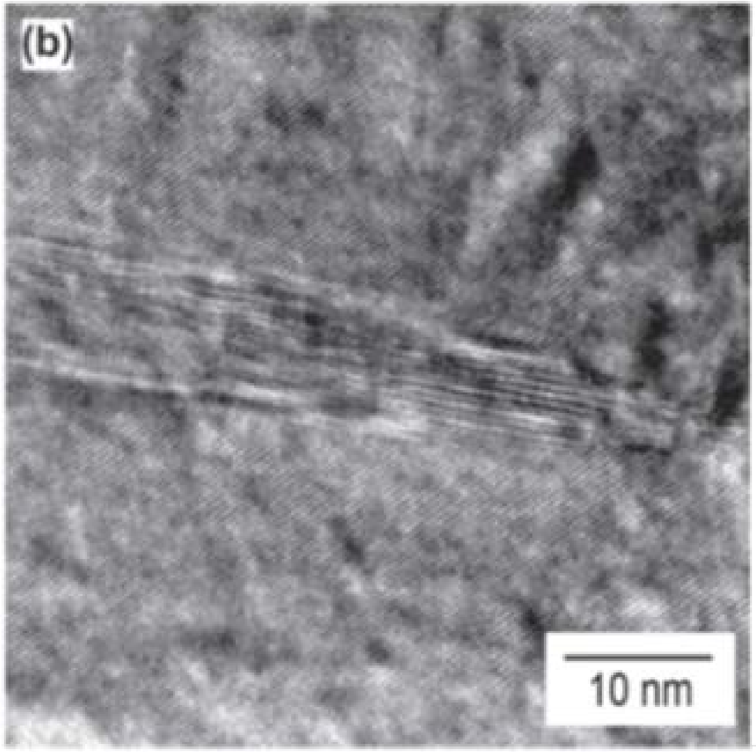
* *V. Perovic et al. // Acta metallurgica V.31, No.9 1381-1391.*

** *L. Lanzani, M. Ruch // Journal of Nuclear Materials 324 (2004) 165-176.*

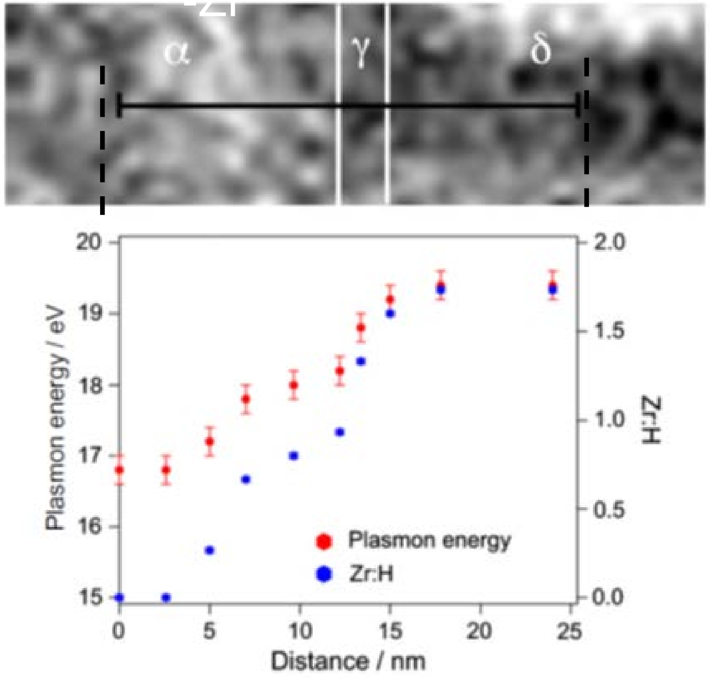
Recent investigation on Zr hydrides

A.T.W. Barrow, A. Korinek , M.R. Daymond // Journal of Nuclear Materials 432 (2013) 366–370.



HREM-image of zirconium hydride

Electron energy loss spectroscopy



Zr-matrix/hydride interface image with the diagramm of plasmon energy vs distance

Nano-beam electron diffraction results: the volume misfit associated with precipitation results in elastic strains that are 4 times greater in the matrix than the hydride.

How hydrogen penetrates into metal?

Penetration of H into Zr

Two opinions

Oxide is penetrable via lattice interstitial diffusion, crystallites boundaries and line defects.

Penetration $\sim \frac{P_{H2} * e^{T}}{d}$

Presence of water vapor will greatly reduce penetration of hydrogen because of reducing vacancy concentration.
T. Smith // Journal of nuclear materials 18 (1966) 323-336.

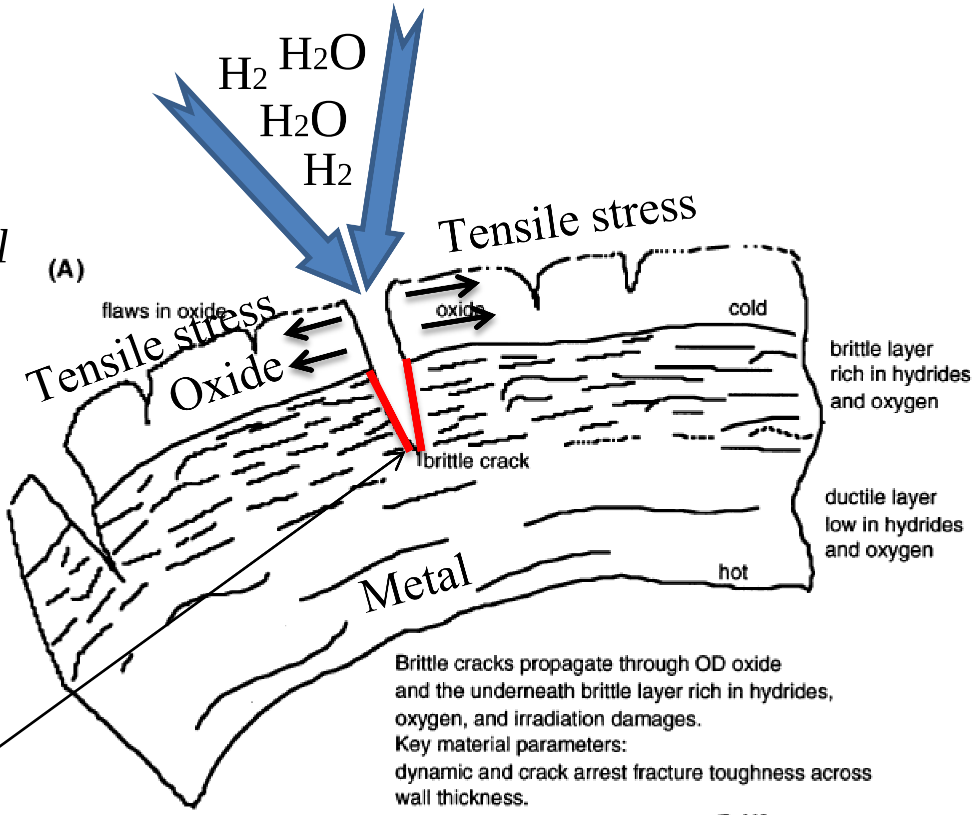
Hydrogen can permeate oxide layer in several days.
M.B. Elmoselhi // Journal of Alloys and Compounds 231 (1995) 716-721.

There is no evidence that hydrogen can pass trough oxide layer by those mechanisms. The only possibility is due to microcracks. He proposed the mechanism of „steam depletion“ on the bottom of the crack. Oxide layer cannot grow dick under this conditions. Such cracks become the way of hydrogen penetration.
B. Cox // Journal of Nuclear Materials 264 (1999) 283-294.

Oxide – induced stress is sufficient since the volume during Zr oxidation into ZrO_2 expands 1,56 times. Under these conditions cracks can easily pass through oxide layer and penetrate into metal, which is the perfect way for hydrogen uptake.
Chung H.M. // Proc. Of Intern. Meeting on LWR Fuel Performance, 2000, USA, 325-344.

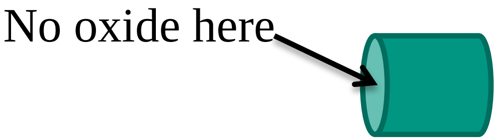
Oxide-induced stresses cause cracks

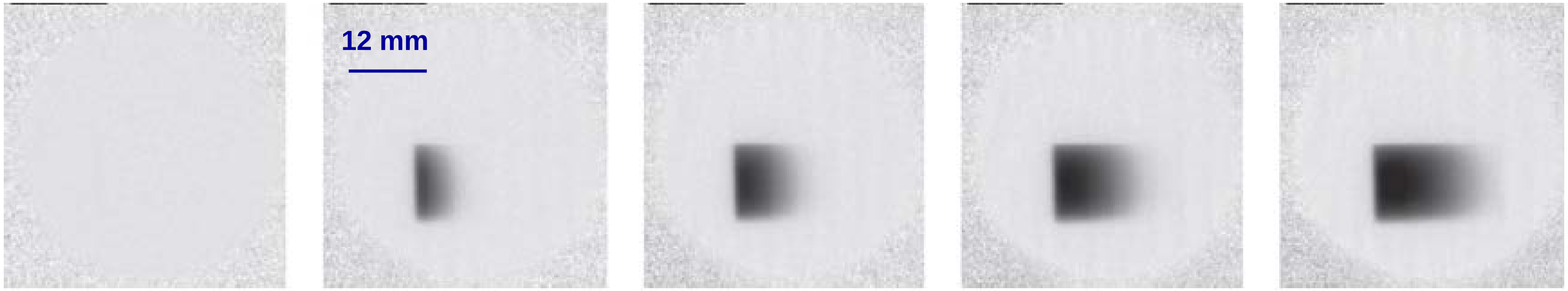
Scheme for
Chung H.M. // Proc. Of Intern. Meeting on LWR Fuel Performance, 2000, USA, 325-344.



Brittle cracks propagate through OD oxide and the underneath brittle layer rich in hydrides, oxygen, and irradiation damages.
Key material parameters:
dynamic and crack arrest fracture toughness across wall thickness.

In-situ diffusion experiments at 1173 K





0 s 600 s 1200 s 1800 s 2400 s

One-dimensional diffusion of the hydrogen in Zry-4 and the hydrogen uptake during steam oxidation by means of neutron radiography was studied. The authors found that when oxide scale at the left side of cylinder was removed a *rapid* hydrogen absorption took place at this site. Oxidised sides were not penetrable for hydrogen. *M. Grosse et al. // Nuclear Instruments and Methods in Physics Research A 651 (2011) 253–257.*

Hydride precipitation and dissolution.

Which factors influence hydride formation?

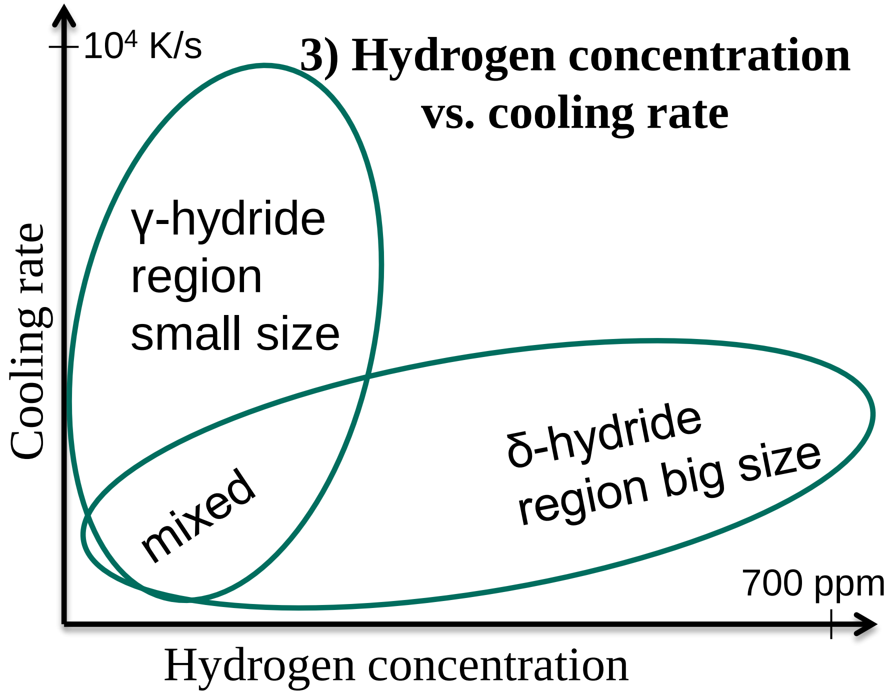
Effect of various factors

A. Akhtar // J. of Nucl. Mater. 64 (1977) 86-92. →

1) Stress gradient → inhomogeneous hydride precipitation

2) Tensile stress → improves easier hydride precipitation

3) Hydrogen concentration vs. cooling rate



B. Nath et. al // Journal of Nuclear Materials 58 (1975) 153-162.

J. E. Bailey // Acta Metallurgica, 11 (1963) 267-280.

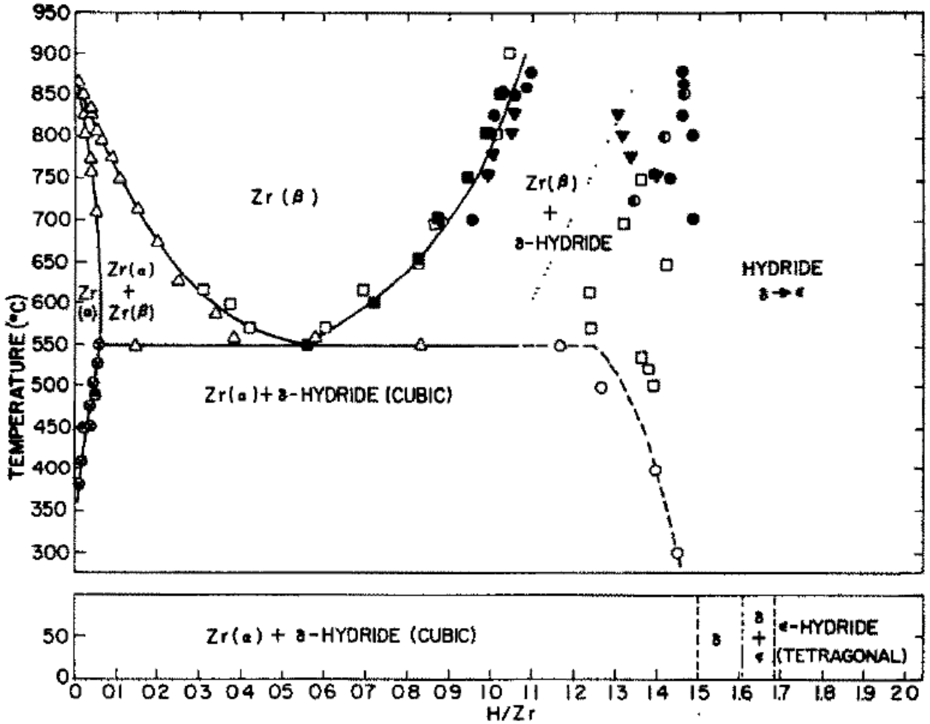
4) Secondary phase particles

Presence of the Ni containing phase causes an increase in the hydrogen uptake during the early period of oxidation.
B. Cox // Journal of Alloys and Compounds 256 (1997) 244-246.

Non-oxidized intermetallic particles allow hydrogen to penetrate easier into Zr matrix.
B. A. Kalin and A. A. Shmakov // Materialovedenie 10 (2005) 50-56.

5) Oxygen is the most important one for hydride precipitation at low hydrogen concentrations.
C. D. Cann, M.P. Puls //Journal of Nuclear Materials 126 (1984) 197-205.

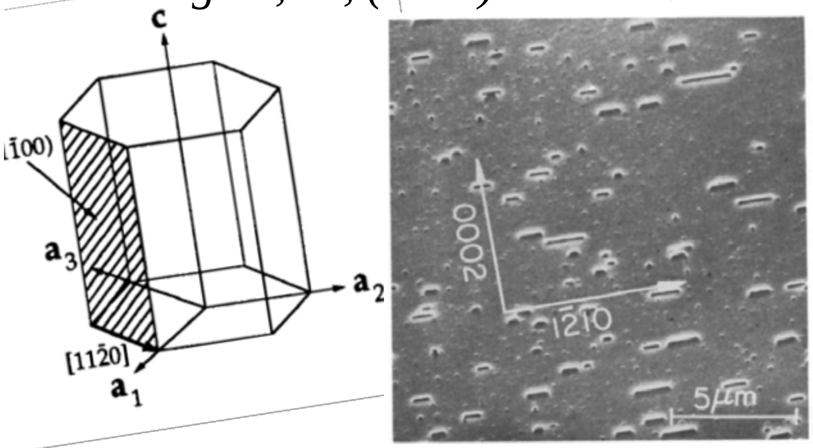
Hydrides precipitation and dissolution



Phase diagram from the paper of G. Libowitz // Journal of Nuclear Materials 5 (1962) 228-233.

The plane for hydride precipitation is prismatic $\{10\bar{1}0\}$.
J. P. Langeron and P. Lehr // Rev. Métall, 60 (1958) 901.

Prismatic plane $\{10\bar{1}0\}$ direction $[11\bar{2}0]$ *J. E. Bailey // Acta Metallurgica, 11, (1963) 267-280.*



A. Akhtar // Journal of Nuclear Materials 64 (1977) 86-92.

Transformation of Zr solid solution into hydride is believed to be a Bainitic type of reaction

J. S. Bradbrook // Journal of Nuclear Materials 42 (1972) 142-160.

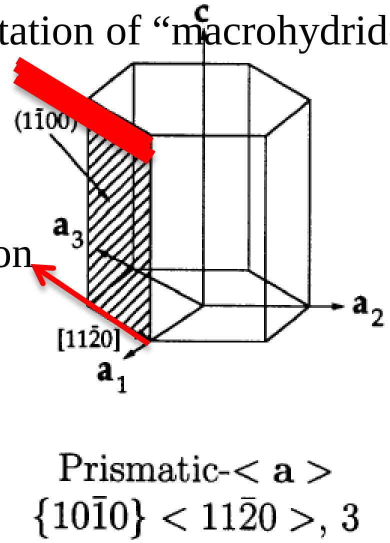
This mechanism was supported by G.J.C. *Carpenter, C.E. Ells, A. Akhtar, V. Perovic* in their works.

Size of hydrides

In 1968 it was established by Westlake D.G. that predominant habit of δ– and γ – zirconium hydrides in zirconium alloys is not prismatic but on the near-basal, hexagonal-close-packed (hcp) a-Zr $\{10\bar{1}7\}$ planes (14° from the {0001}). *Westlake D.G. // J. of Nucl. Mater. 26, 208 (1968).* Later it was supported by *Weatherly G.C. Acta Metall. 29, 501–512 (1981).*

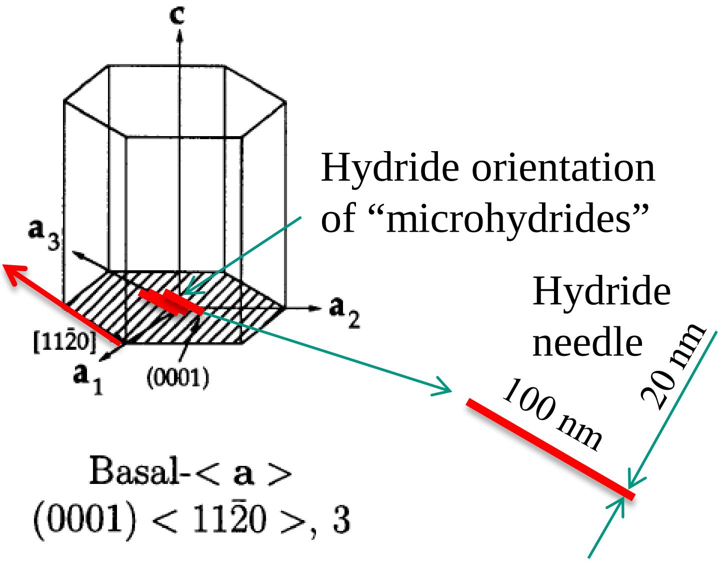
More details about orientation of hydrides in review of **D. L. Douglass**
D.L. Douglass The Metallurgy of Zirconium, Wien : IAEA, 1971.

Hydride orientation of “macrohydrides”



slip direction

Prismatic-$< \mathbf{a} >$
$\{10\bar{1}0\} < 11\bar{2}0 >$, 3



slip direction

Hydride orientation of “microhydrides”

Hydride needle

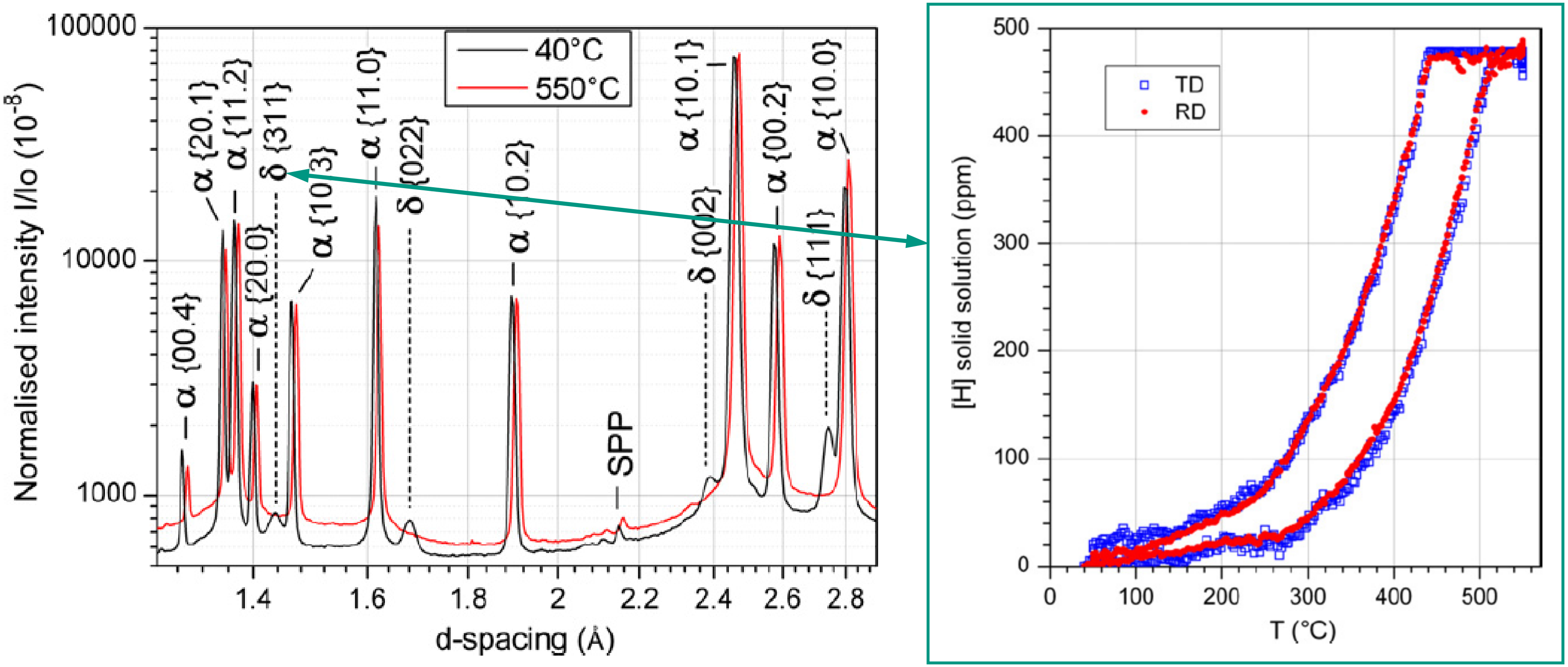
100 nm

20 nm

Basal-$< \mathbf{a} >$
$(0001) < 11\bar{2}0 >$, 3

The microscopic hydrides in the material is of 20-80 nm thick and 100-500 nm long.
Usual macroscopic hydrides are not less than 100-200 nm thick and 2,000- 10,000 nm long.
Chung H.M. // Proc. Of Intern. Meeting on LWR Fuel Performance, 2000, USA, 325-344.

Hydride precipitation and dissolution in Zry-4

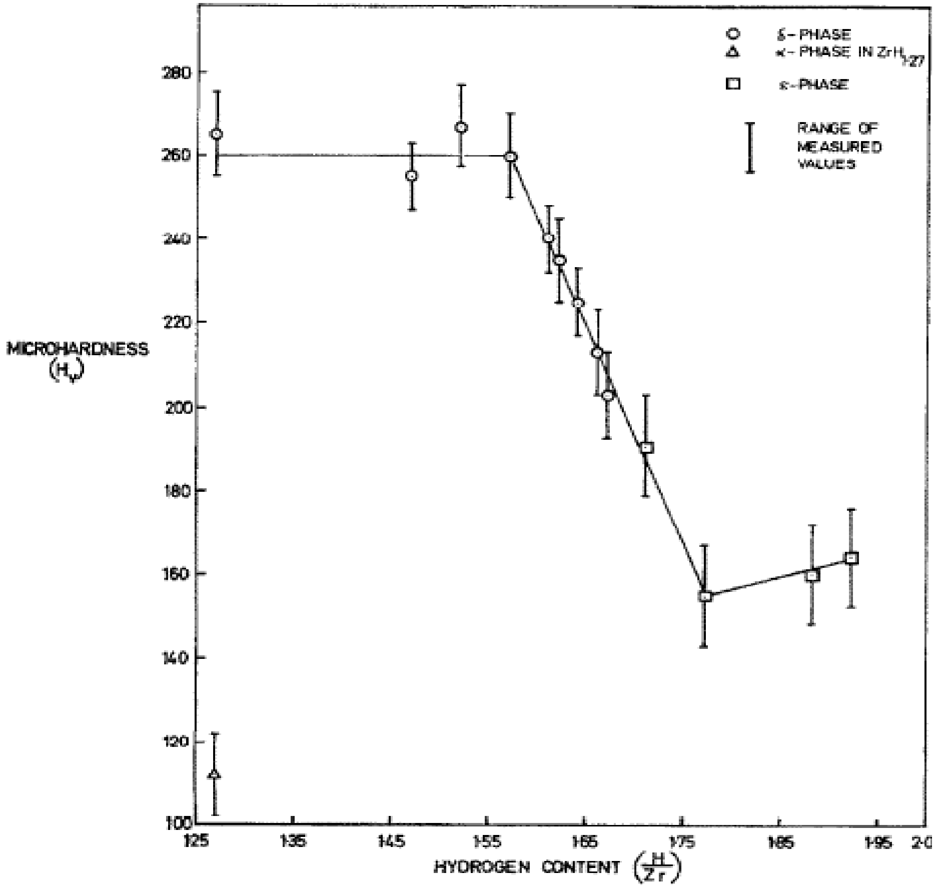


In situ synchrotron diffraction study supports the theory of B.W. Leitch and S.-Q. Shi (*Modelling Simul. Mater. Sci. Eng. 4 (1996) 281–292*) that the combination of surface energy, elastic and plastic strains generated around the hydrides during their formation are responsible for the irreversible behavior and the supersaturation of the solid solution.
O. Zanellato et al. // Journal of Nuclear Materials 420 (2012) 537–547.

Thermal history of a sample has an effect on Terminal Solid Solubility during precipitation.
Z.L. Pan et al. // Journal of Nuclear Materials 228 (1990) 227-237.

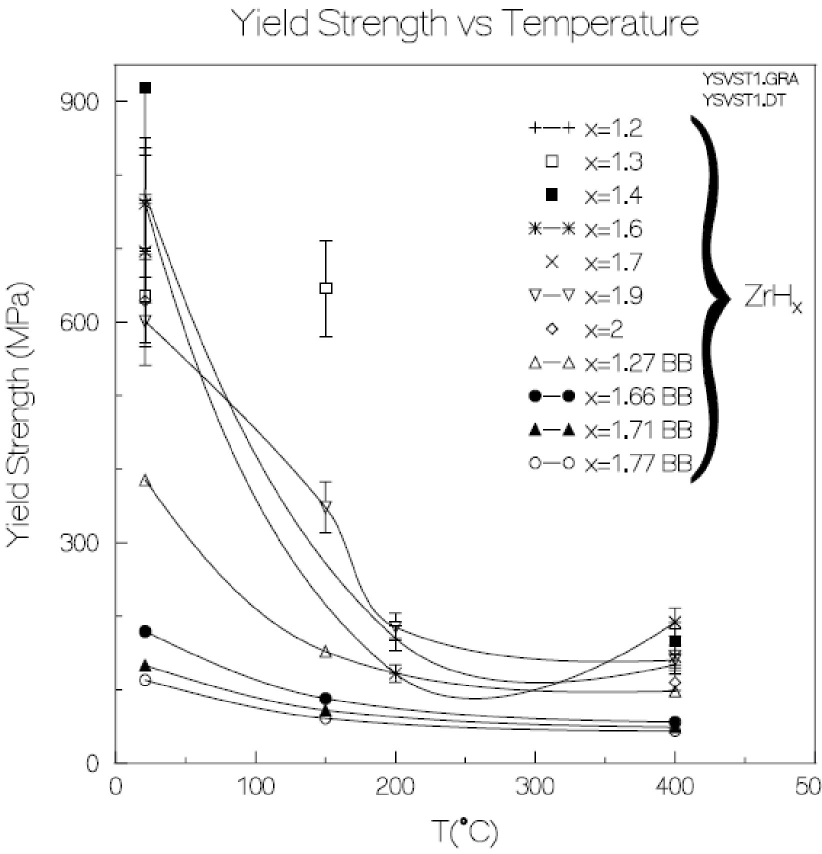
Mechanical properties of hydrides

Mechanical properties of hydrides



The microhardness of zirconium hydrides

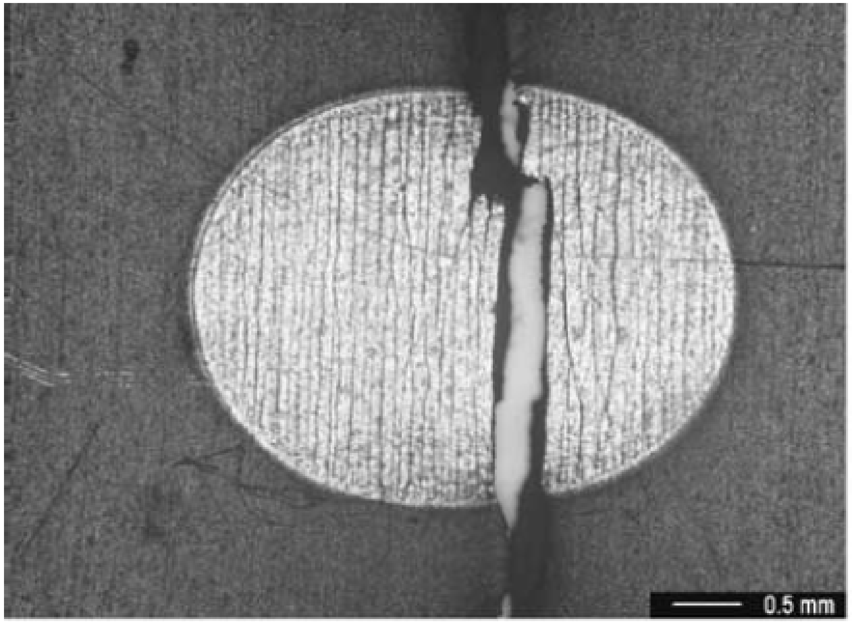
K.G. Barraclough and C.J. Beevers //
J. of Nucl. Mater. 34 (1970) 125-134.



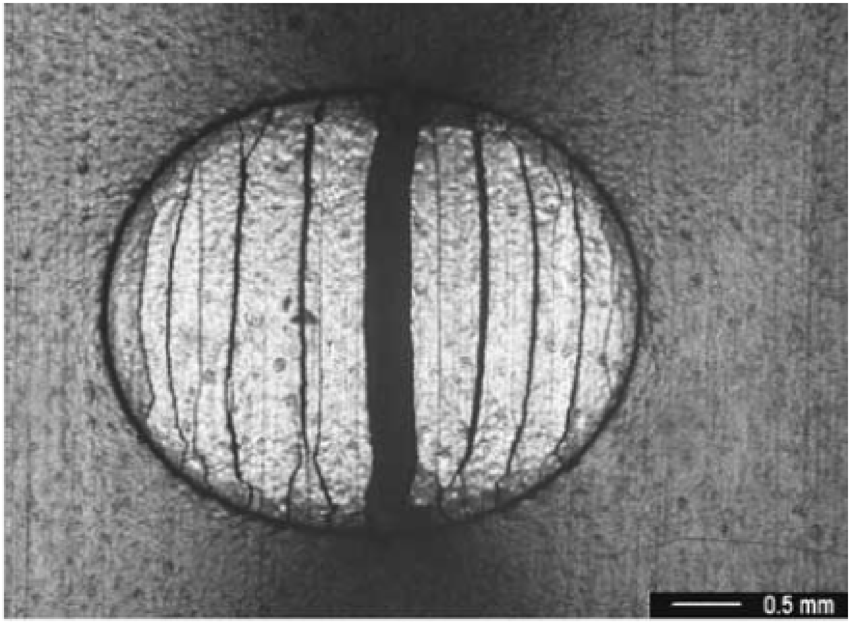
E(25°C) = 90 GPa (δ-phase); 50 Gpa (ε-phase)

M.P. Puls et al. // Journal of Nuclear Materials 336 (2005) 73–80.

Hydride blisters under tension: brittle rupture



50 mkm depth blister fractured at 25 °C



100 mkm depth blister fractured at 300 °C

O.N. Pierron et al. // Journal of Nuclear Materials 322 (2003) 21–35.

Mechanisms of embrittlement

In general for the loss of ductility the following factors are necessary:

Hydrogen concentration, temperature, size and morphology of hydrides and their orientation with respect to applied stress.

B. A. Kalin and A. A. Shmakov // Materialovedenie 10 (2005) 50-56.

1) Mechanism was proposed by Beevers C. J. (*Beevers C. J. On the fracture of zirconium containing zirconum hydride precipitates.— Electrochem. Technol., 1966, v. 4, p. 222.*):

- Stage 1: Crack starts in brittle hydride phase;
- Stage 2: From brittle phase crack propagates into metal;
- Stage 3: Crack continues to grow in metal.

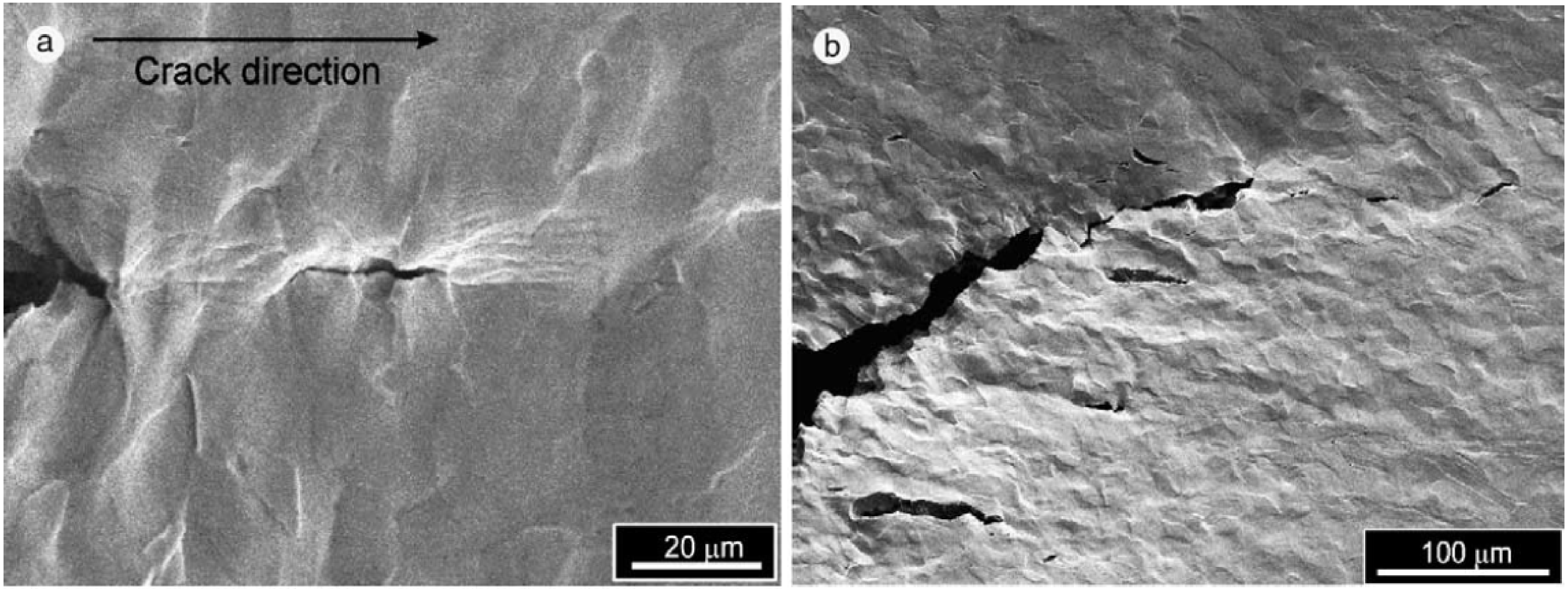
2) In 2000 Hee M. Chung had proposed another mechanism (*Chung H.M. // Proc. Of Intern. Meeting on LWR Fuel Performance, 2000, USA, 325-344*).

The main idea is that hydrides are ductile during operation temperatures of nuclear reactor. He had observed many dislocations around the hydride region. Plastic deformation that occurs at the hydride/metal interface is the key factor for the degradation of mechanical properties.

But anyway the fracture can be either brittle or ductile in this case.

Mechanisms of embrittlement

The mechanism of Beevers C. J. was clearly in situ demonstrated by G. Bertolino (*G. Bertolino et al. / Journal of Nuclear Materials 322 (2003) 57–65*). Under tensile stress the crack at first occurs in hydride phase and then easily penetrates to the metal matrix. If hydrides are oriented normal to tensile stress (parallel to crack direction) the process goes much easier. Hydrides themselves prepare the future path for the crack before it comes. That is why one needs much lower stress to destroy material.

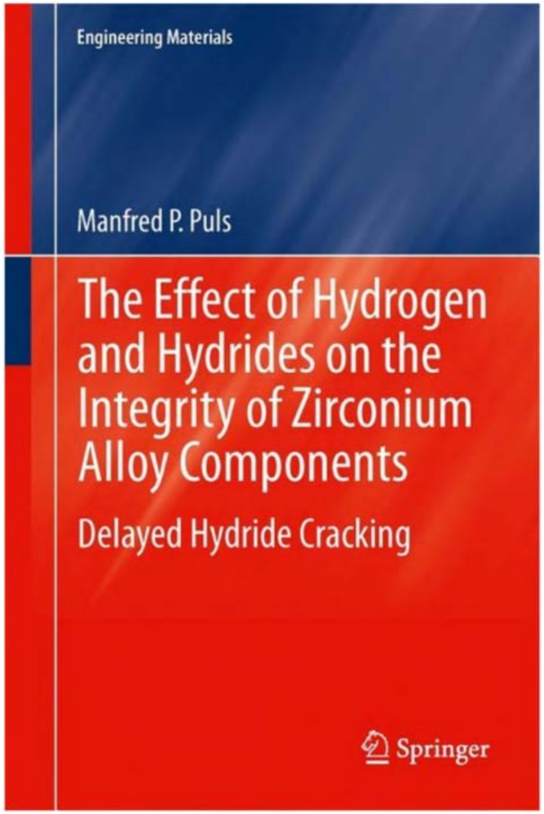


Recent studies on the problem of DHC

The book of Manfred P. Puls (Atomic Energy of Canada Limited).
The Effect of Hydrogen and Hydrides on the Integrity of Zirconium Alloy Components. Delayed Hydride Cracking.
Springer-Verlag London 2012.

The book provides more detailed descriptions of the current theoretical and experimental foundations of the properties and behavior of hydrogen, hydrides, and DHC in zirconium and its alloys than is usually found in individual papers in the literature.

M.P. Puls mentioned however, that: “*Even in this seemingly obvious case it is not entirely clear why and how fracture of a localized hydrided region under high tensile stresses occurs since the hydrides have positive transformation strains that create large compressive stresses inside them that could potentially shield them from any externally applied high local tensile stresses*”.
He actually asks the previous authors why their mechanism works!!!



Engineering Materials

Manfred P. Puls

The Effect of Hydrogen and Hydrides on the Integrity of Zirconium Alloy Components

Delayed Hydride Cracking

Springer

Conclusion

- Zr-H system has δ and ε stable phases. γ – phase is metastable.
- Oxide scale is not permeable by hydrogen during short-time periods such as 1 hour. It seems to be penetrable during several days period. Because of this there are two controversal opinions on the penetration mechanism.
- External stresses, heat treatment, intermetallic particles and oxygen have very strong effect on the hydrogen uptake and hydride formation.
- Hydrides precipitate in the direction of primary slip plane in the main slip direction, which can obstruct the plastic deformation of zirconium alloy and should be the main cause of embrittlement.
- The mechanical parameters (E module, micro harness, yield strength) of the solid hydride specimens remain almost the same as those of the original tube material for hydrogen compositions up to about $ZrH_{1.6}$. The value of these parameters starts to drop when δ - hydride becomes the major phase and reaches minimum levels for ε - hydrides. Specimens consisting mostly or only of the δ - hydride phase have the highest yield strength and lowest ductility. With the increase of temperature the ductility of hydrided alloy can partly recover.
- Two mechanisms of embrittlement due to hydrogen were described in literature (1. crack initiation inside hydride; 2. plastic deformation of matrix surrounding hydride) but the nature of embrittlement remains unclear.

Thank you for your attention!