Status of studies on high-temperature oxidation and quench behaviour of Zircaloy-4 and E110 cladding alloys

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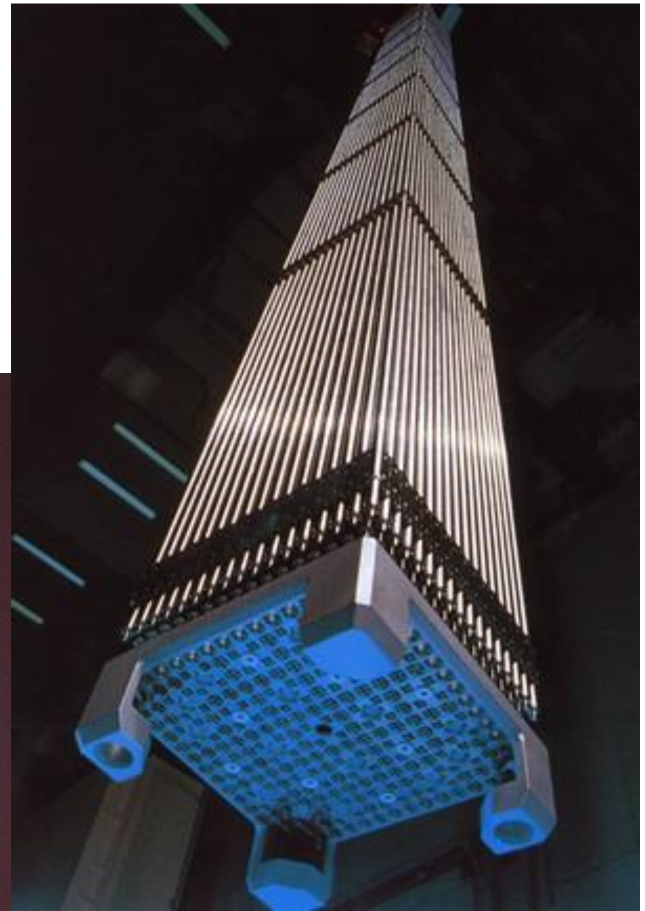
OUTLINE

- Introduction
- Separate-effects tests
- Bundle tests
- Modelling
- Future needs





Introduction – Oxidation of Zr alloys

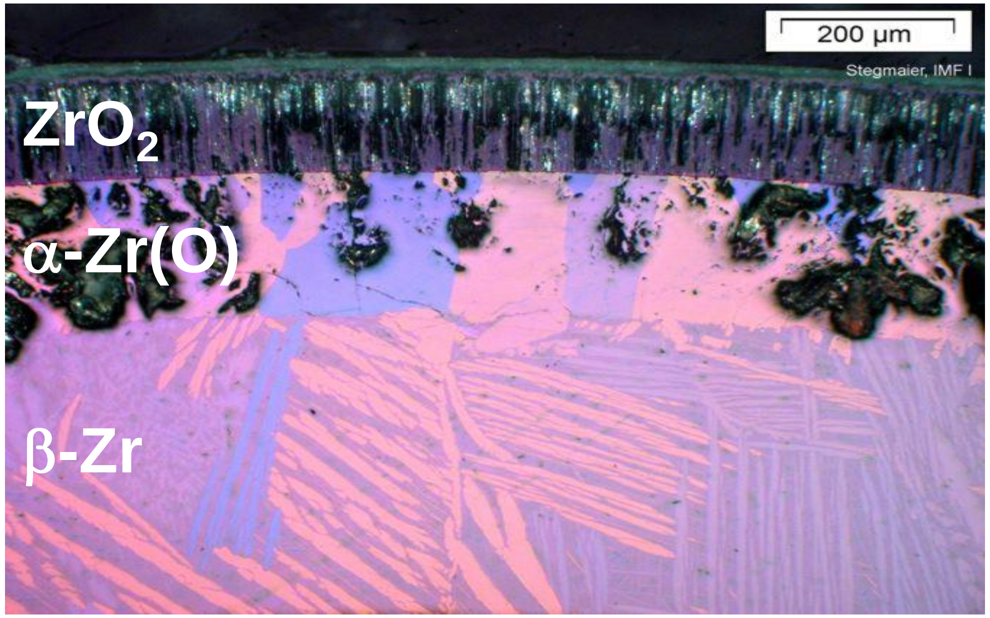
- **Chemical reactions**

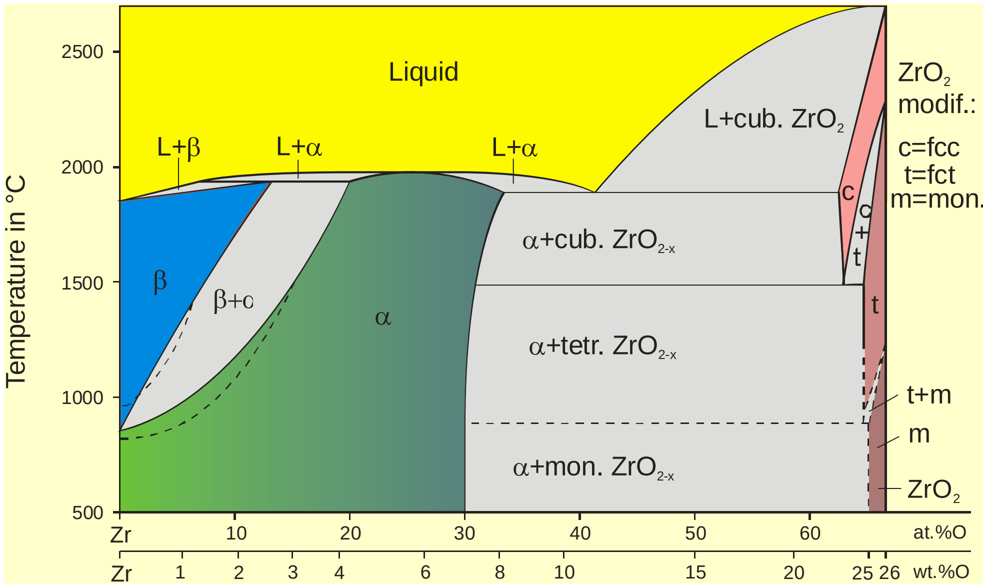
$$Zr + 2H_2O \rightarrow ZrO_2 + 2H_2 + energy$$

$$H_2 \Leftrightarrow 2H_{abs}$$

- **Diffusivity/solubility of gases**

	Oxide	Metal	
		α	β
Oxygen	+++	++	+
Hydrogen	-	+	++





Introduction – Oxidation of Zr alloys

- **Oxidation kinetics**

$$\frac{\Delta m}{S} = k_m \cdot t^n$$

Mass gain

$$d_{ZrO_2} = k_O \cdot t^n$$

Oxide thickness

$$k = A \cdot \exp\left(-\frac{E_A}{RT}\right)$$

Temperature dependence

n = 1/3 (cubic)	typical for low-temperature oxidation < 900 °C
n = 1/2 (parabolic)	**typical for high-temperature oxidation >1000 °C**
n = 1 (linear)	typical for breakaway oxidation at T< 1100 °C (after initial cubic or parabolic period)

Introduction – Zircaloy-4 and E110

Zircaloy-4:

- Used in western PWRs
- Zr production via chlorine chemistry and Kroll process

→ Sponge Zr

→ Impurities: Al, Mg, Ca

E110:

- Used in Russian VVER and RBMK reactors
- Zr production via fluorine chemistry and electrolysis

→ Impurity: F

Composition (wt-%):

	Nb	Sn	Fe	Cr	O
Zry-4	-	1.5	0.2	0.1	0.14
E110	1	-	0.008	0.002	0.05

Zr: balance

Recent experiments

Karlsruhe Institute of Technology

Separate-effects tests

- Isothermal tests (TG, furnace) in
  - oxygen ☞
  - steam ☞
  - air
- Transient tests (TG, furnace) in
  - oxygen
  - steam ☞
- Single rod quench tests with ☞
  - fresh samples
  - irradiated samples

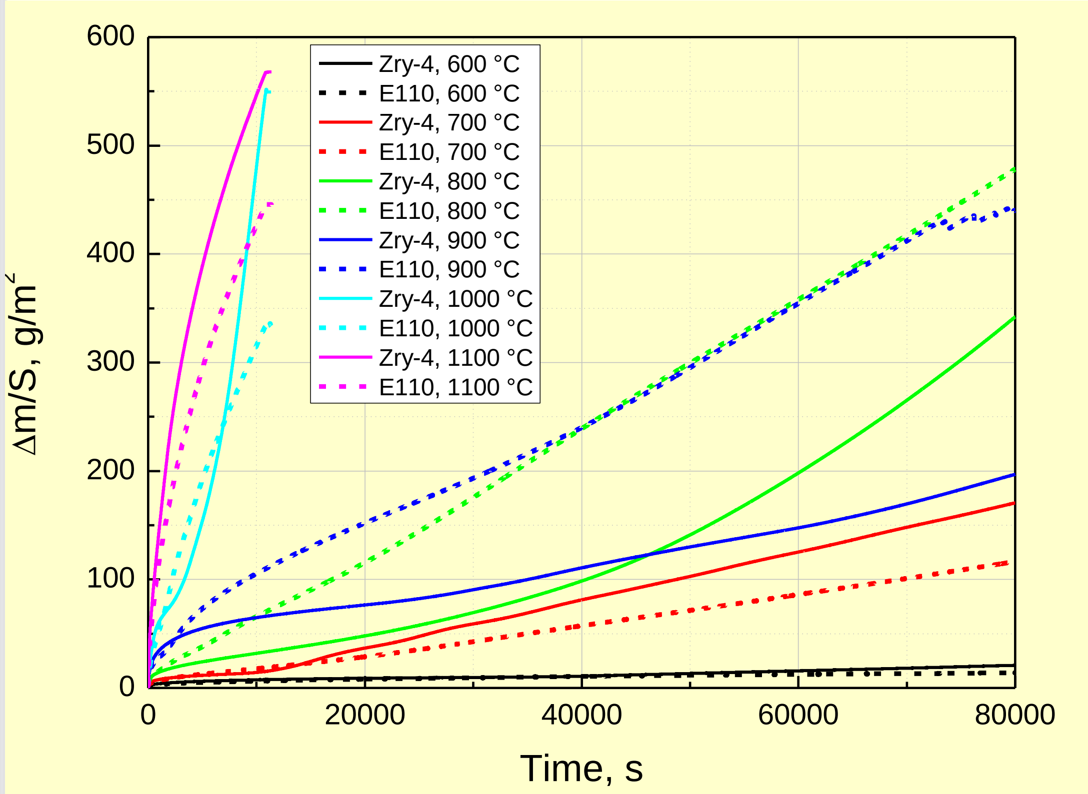
Bundle tests

- QUENCH-12 (vs. QUENCH-06) ☞
  - → 31 rods
- PARAMETER-SF
  - → 19 rods
- CODEX / CODEX-CT ☞
  - → 7 rods
- PAKS cleaning tank incident ☞
  - → 30 assemblies

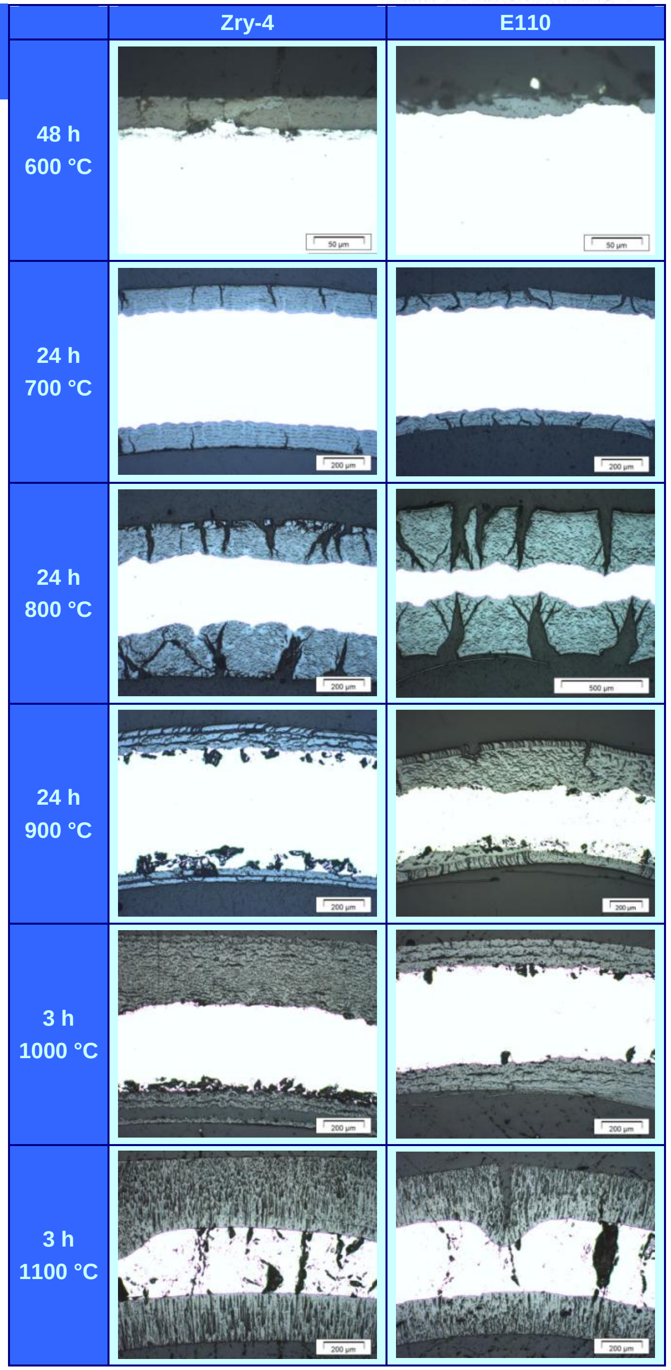
this presentation ☞

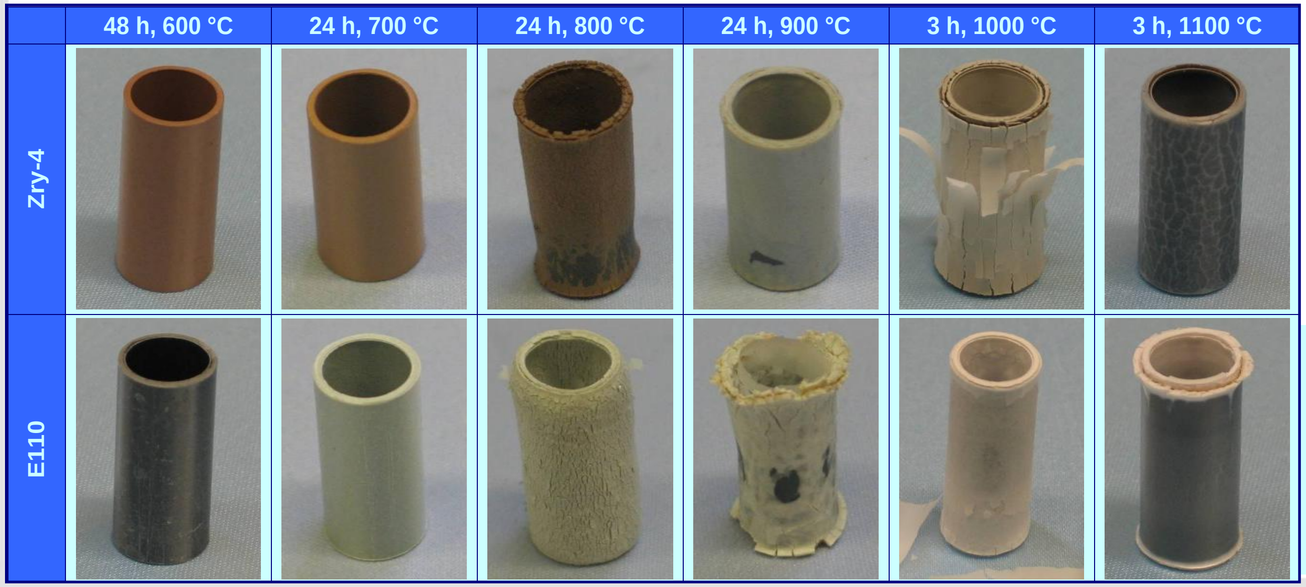
Isothermal tests in oxygen

TG



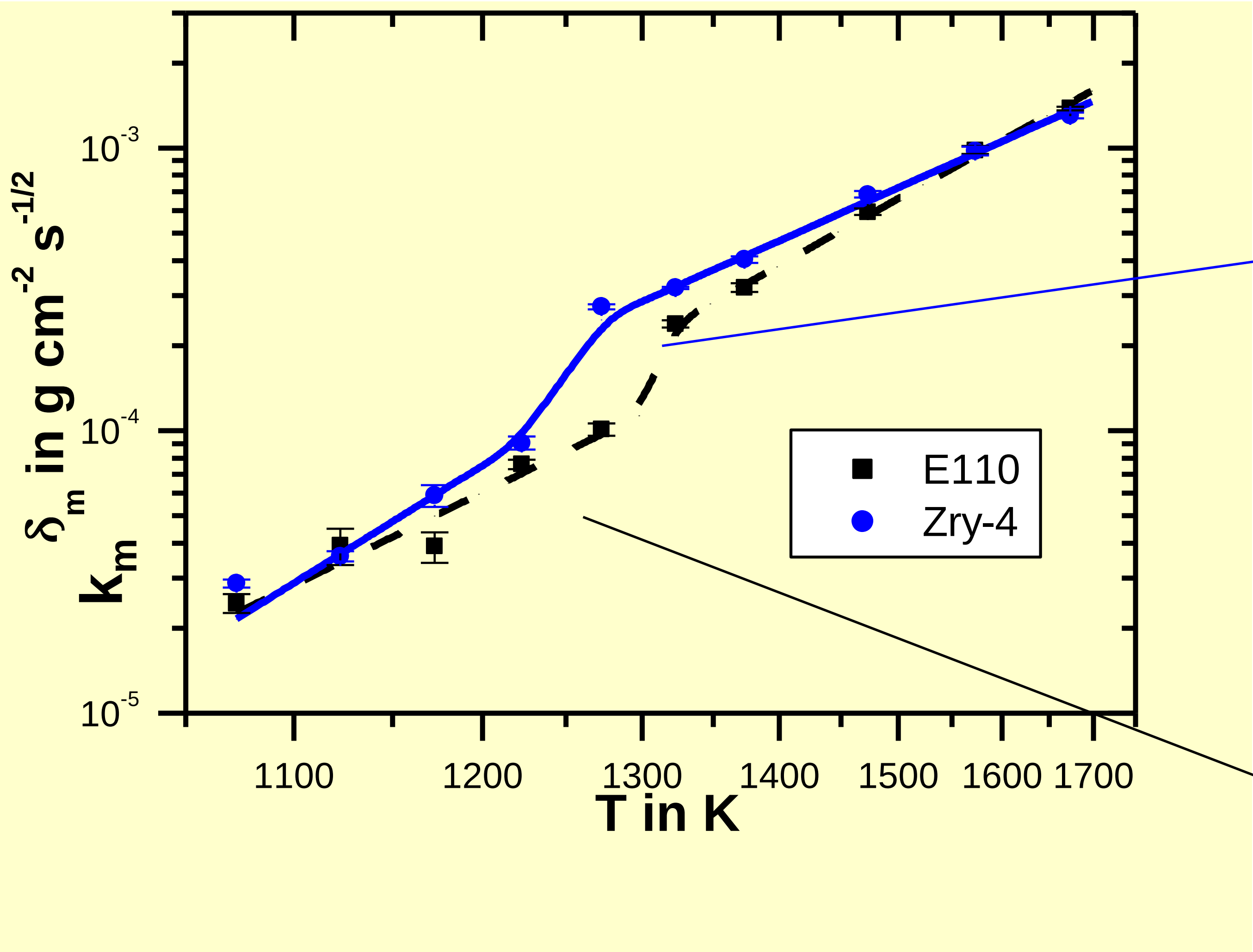
Microscopy

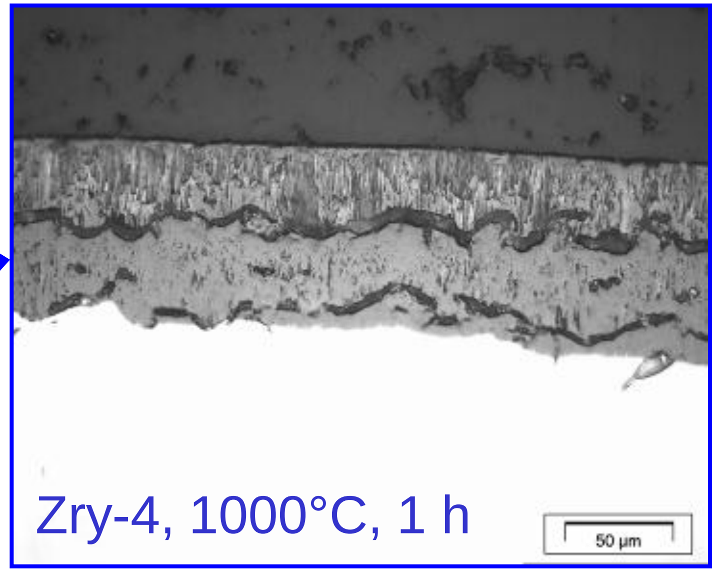


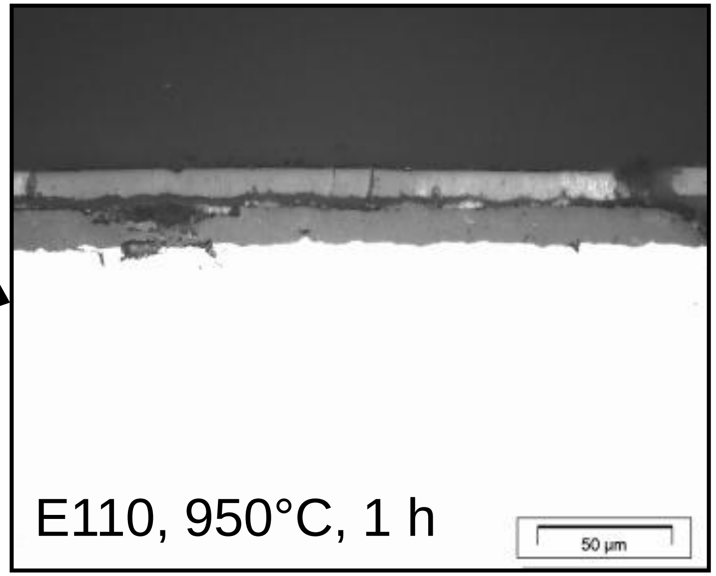


Post-test appear-ance

Isothermal tests in steam







Temperature dependence of mass gain rate

Transition to breakaway

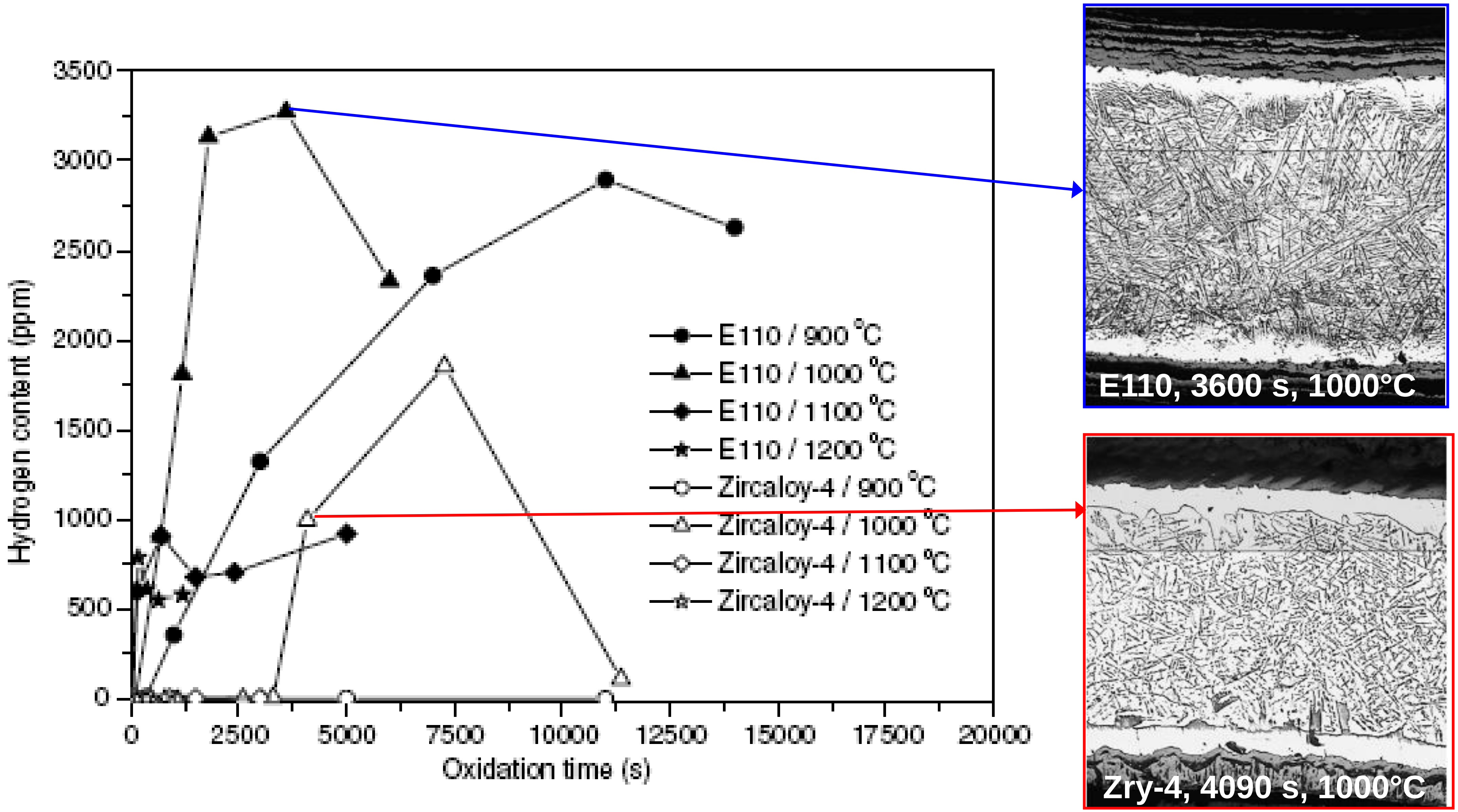
ZrO_2, µm	Zry-4		E110	
T, °C	O_2	Steam	O_2	Steam
600	6	6	na	na
700	9	7	14	17
800	33	37	na	11
900	50	29	19	18
1000	69	75	30	43
1100	nt		nt	

Oxide scale thickness (µm) at transition to breakaway

nt – no transition; na – not analysable

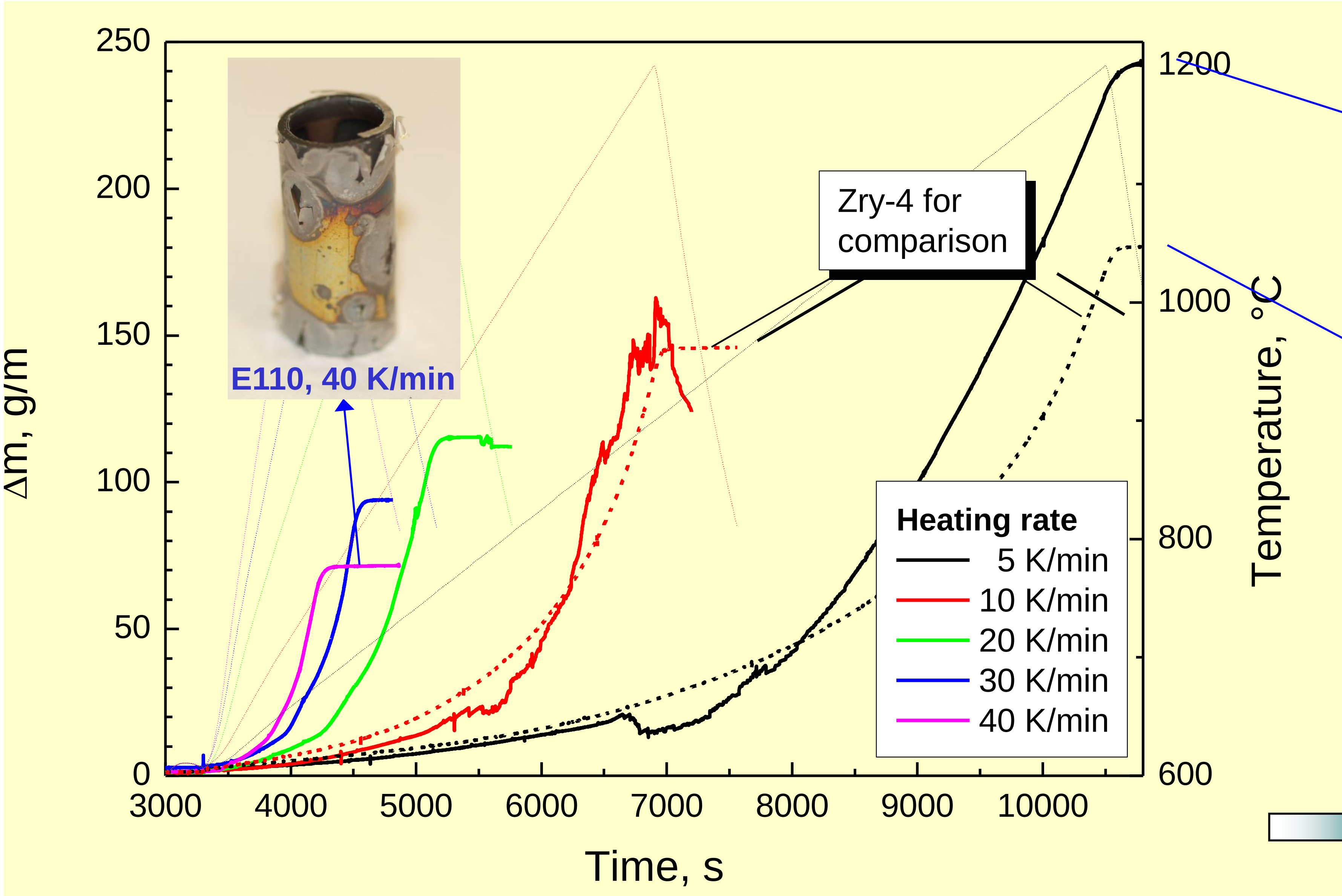
E110
24h, 800°C, steam

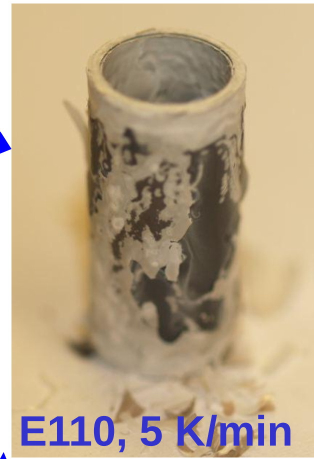
Hydrogen absorption during steam oxidation



Hózer et al., JNM373(2008) 415

Oxidation under transient conditions

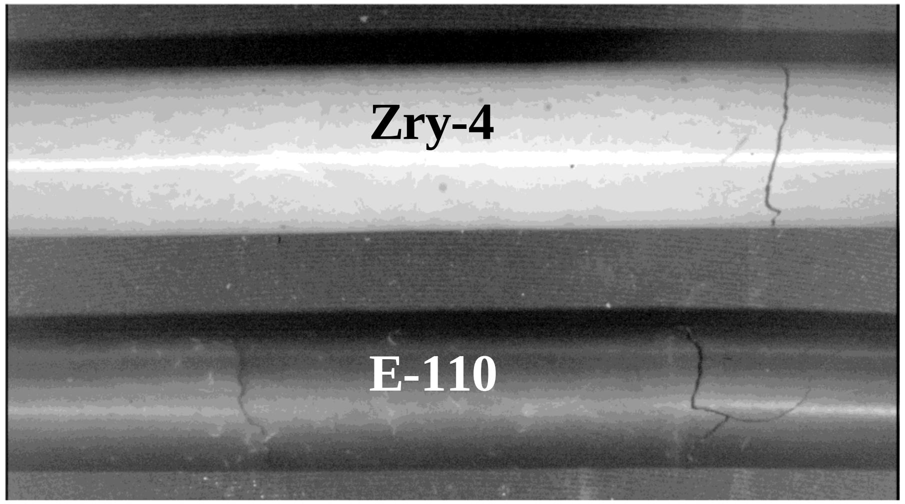


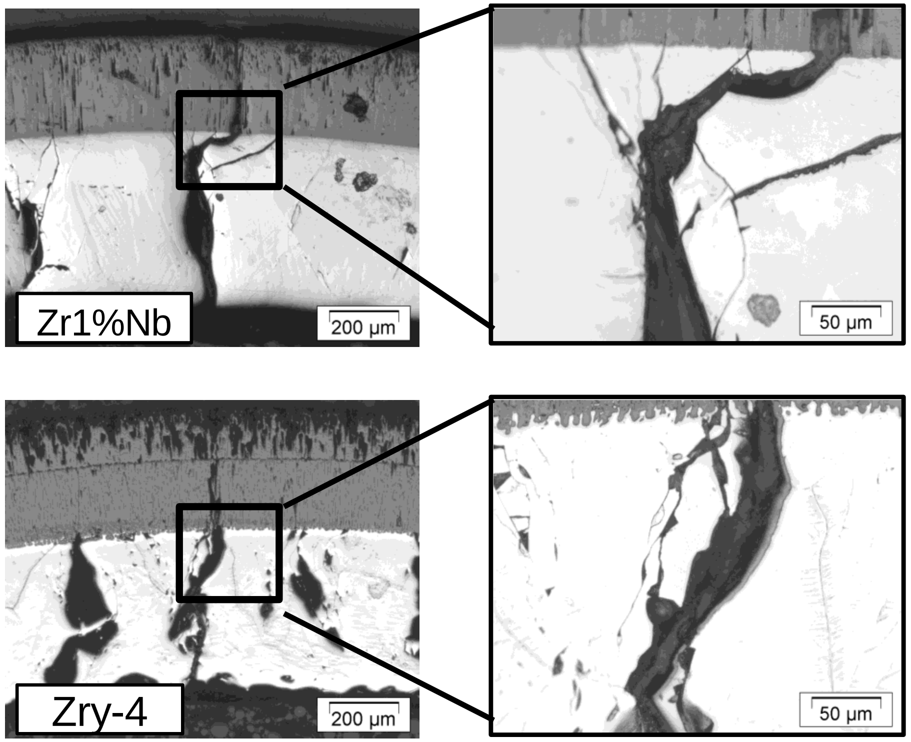


Breakaway only for E110

Transient oxidation of Zry-4 and E110 in steam in dependence on heating rate

Single rod quench tests





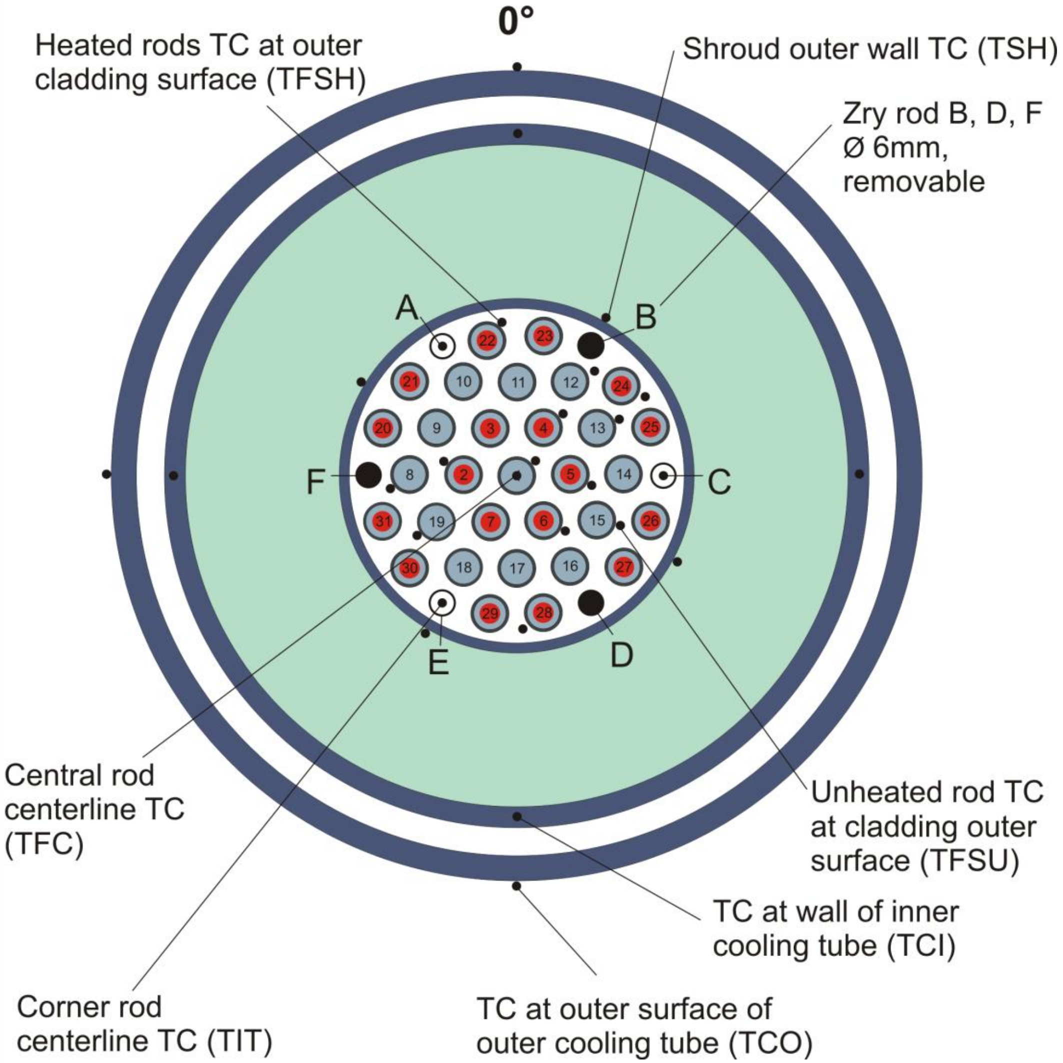
Oxidation and quenching from 1400°C

- Different colours and therefore emissivity
- Oxidation of through-wall cracks at Zry-4, but not at E110
- Increased hydrogen absorption during quenching for Zry-4

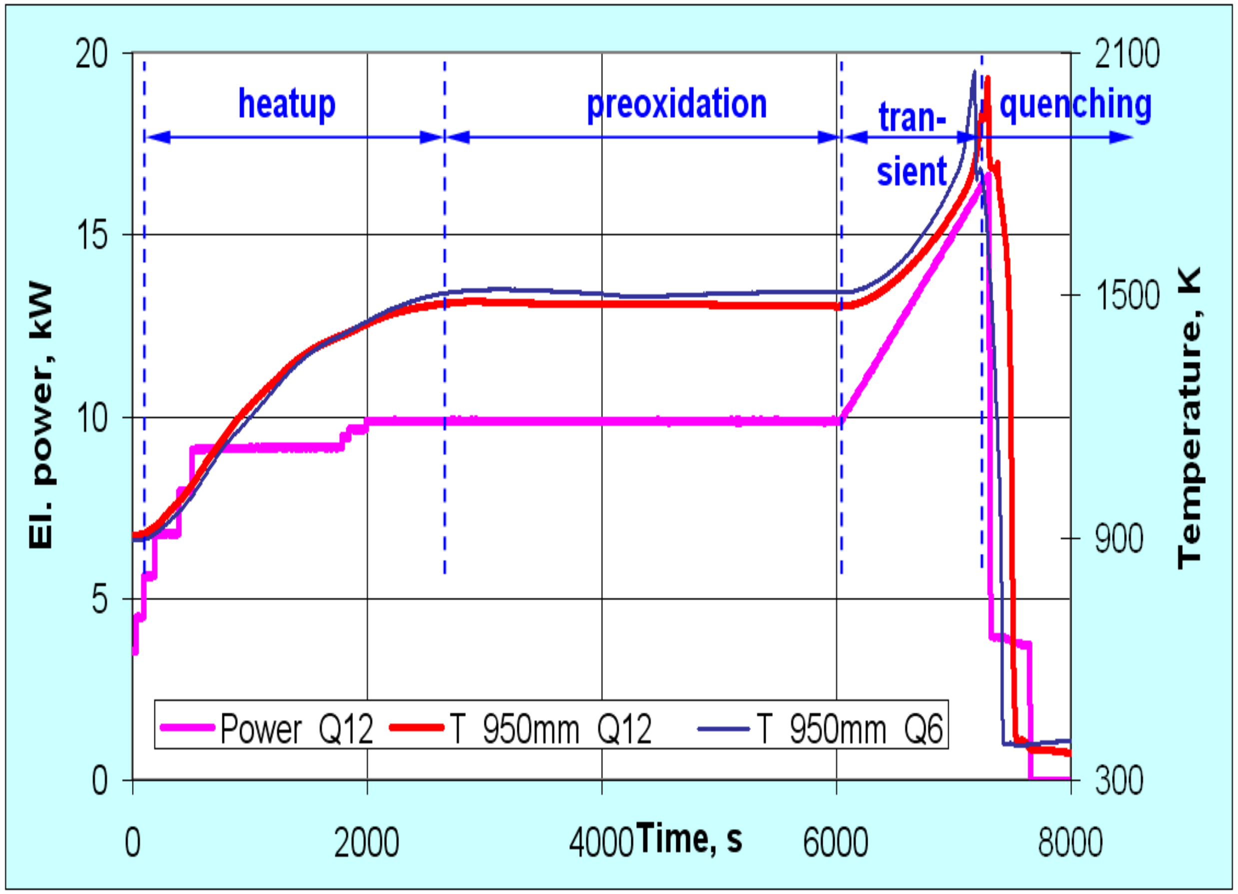
<u>Irradiated simulators (E110):</u>

- Earlier fragmentation and increased hydrogen release during oxidation
- Fuel swelling and clad creep causing contact between pellet and cladding lead to inner oxidation and embrittlement

VVER bundle test QUENCH-12



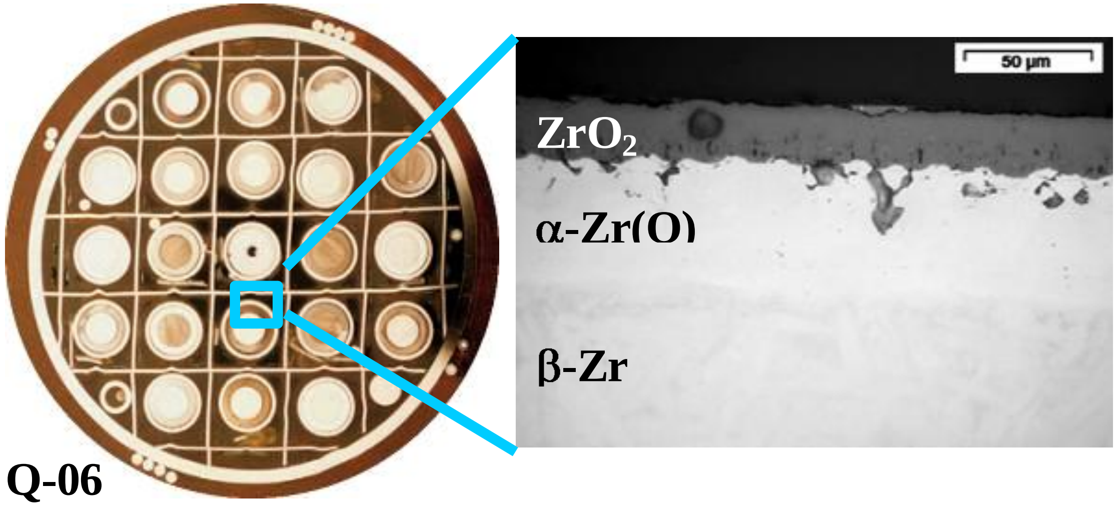
Bundle cross section



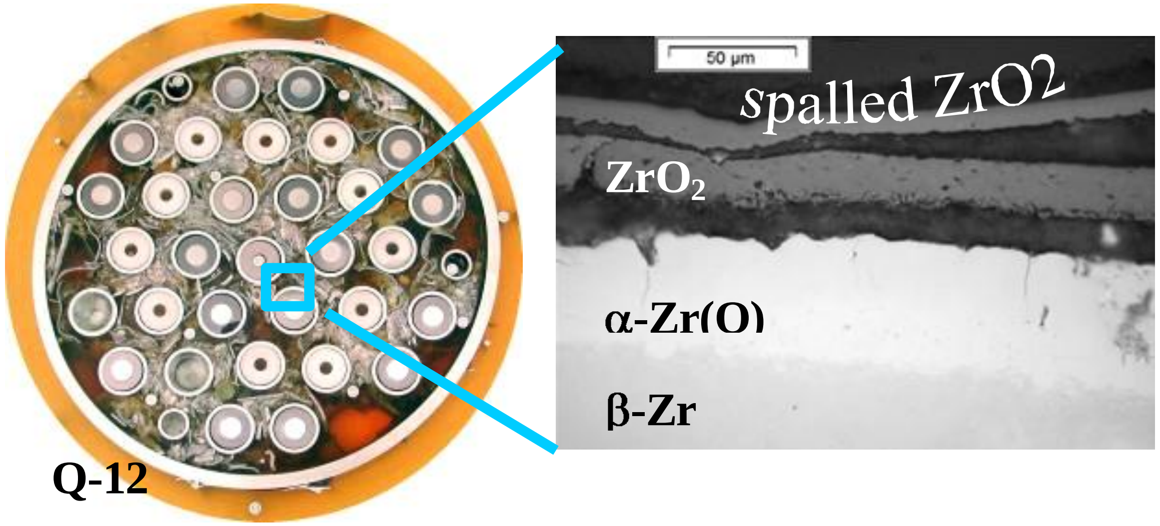
Power history and max. temperatures for QUENCH-12 and QUENCH-06

⇨ Very similar boundary conditions

QUENCH-12 post-test appearance



QUENCH-06: Zry-4



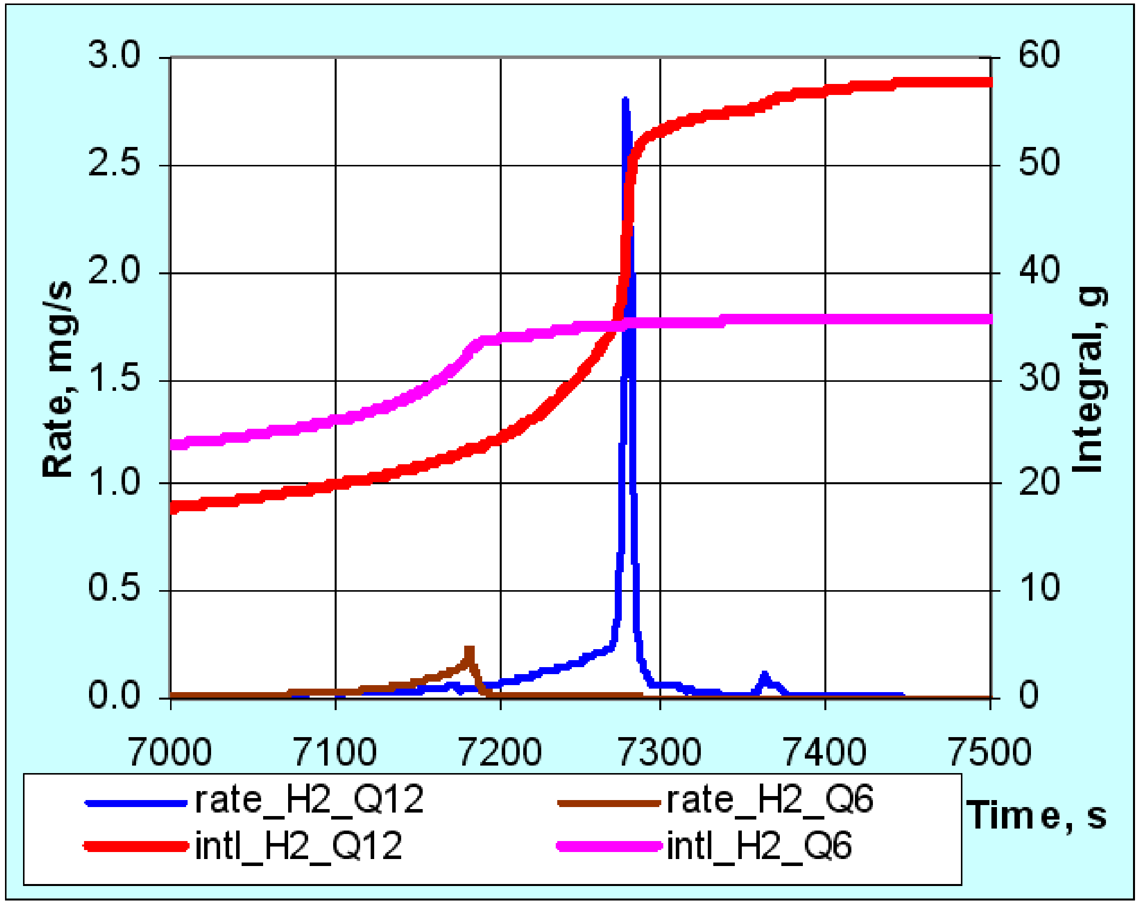
QUENCH-12: E110

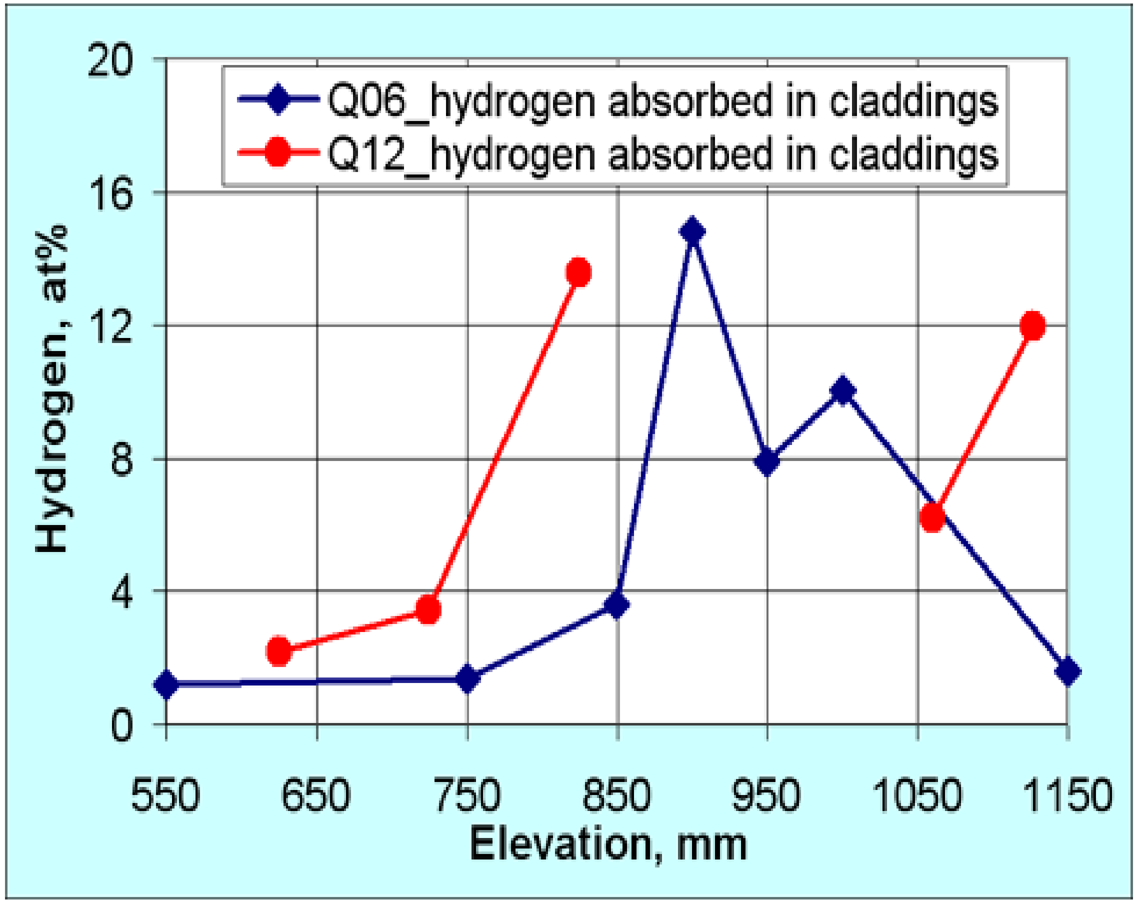
QUENCH-12:

- Intensive spalling of oxide scales
- Relocation of oxide debris to lower parts of the bundle

QUENCH-12 PT view

QUENCH-12 hydrogen (vs. QUENCH-06)





Hydrogen release

Hydrogen uptake

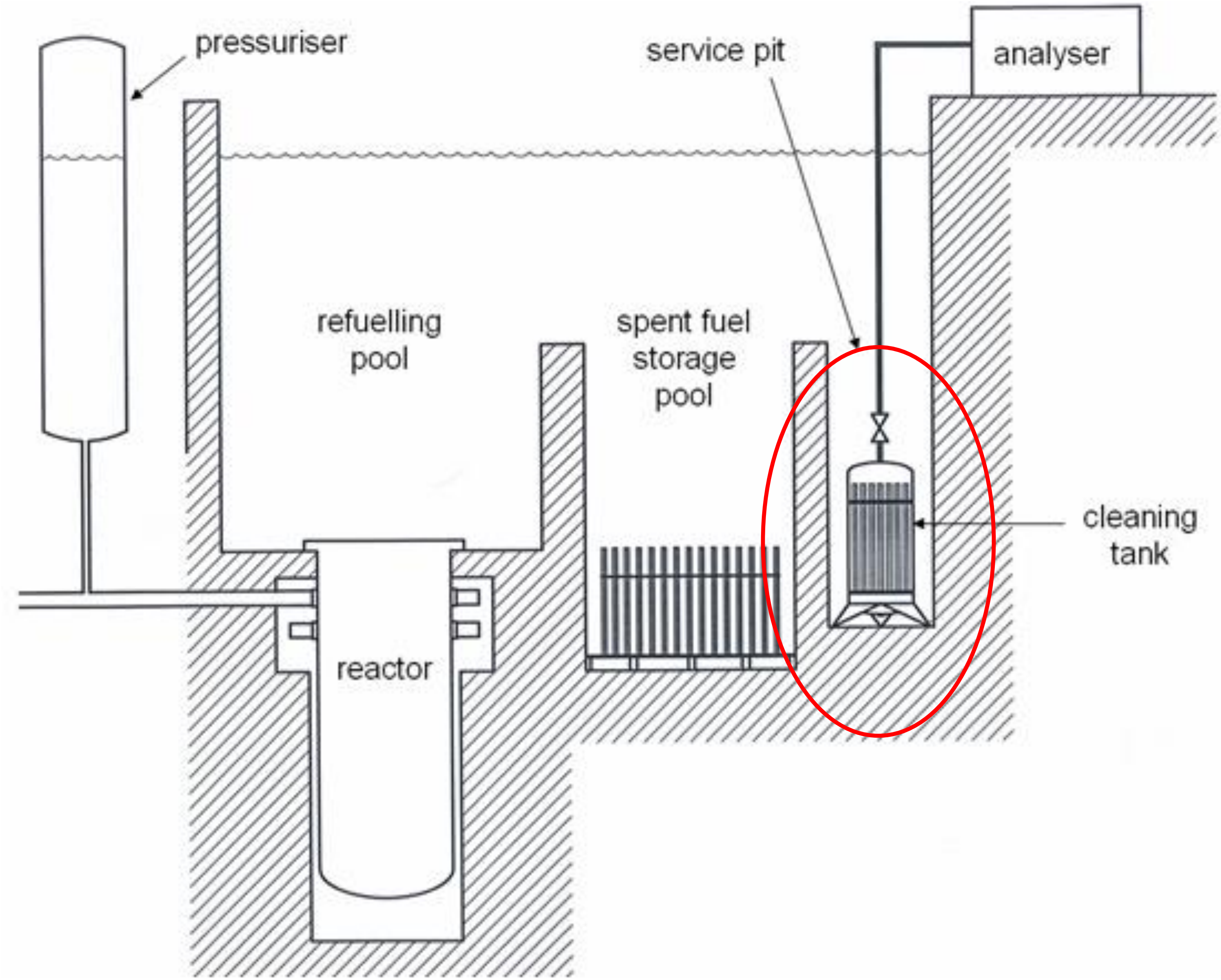
QUENCH-12:

- Higher hydrogen release during quench phase (24 g vs. 4 g in QUENCH-06)
- Increased hydrogen uptake by the remaining metallic cladding

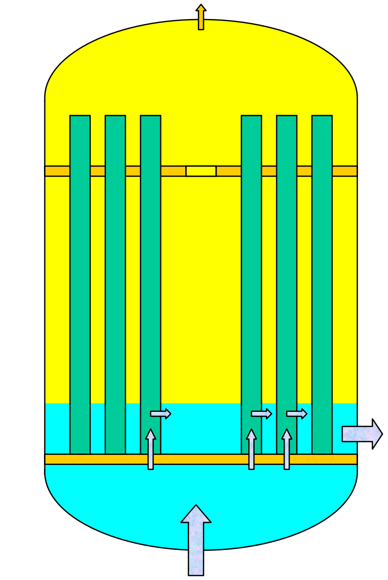
Paks-2 cleaning tank incident

High temperature oxidation of low power irradiated fuel assemblies for 7 hours in H rich steam

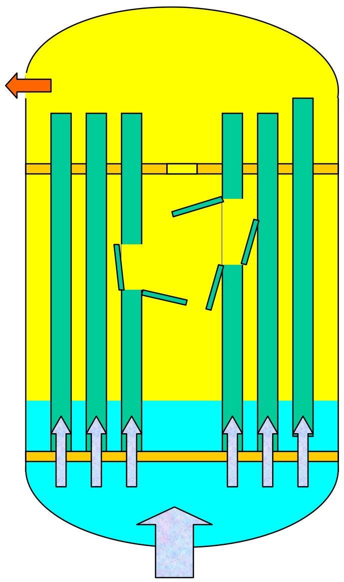
Fragmentation of fuel assemblies during opening of cleaning tank cover (quench by the water of pool)



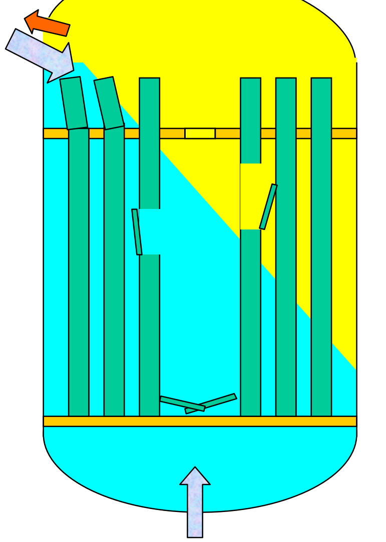
Paks-2 cleaning tank incident



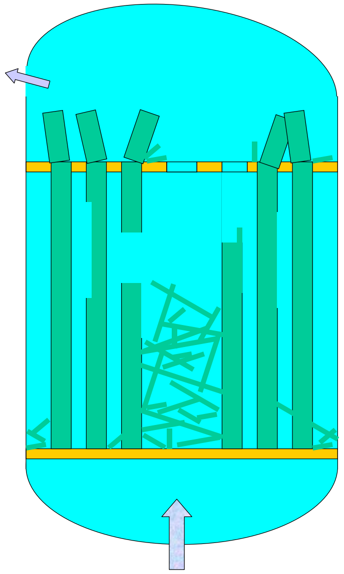
1) Insufficient cooling



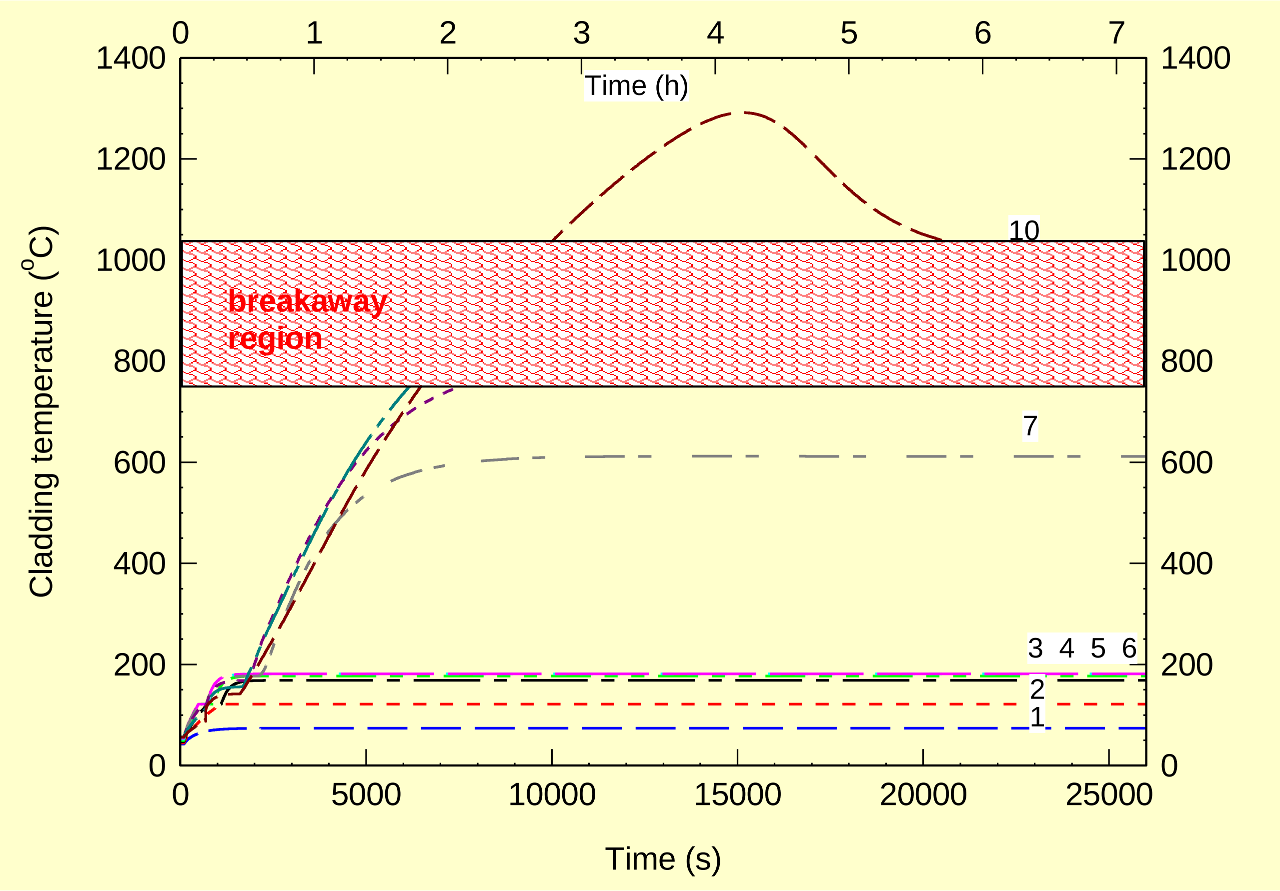
2) Ox. in steam/H_2



3) Flooding



4) Collapse of FRs



Calculated temperature history

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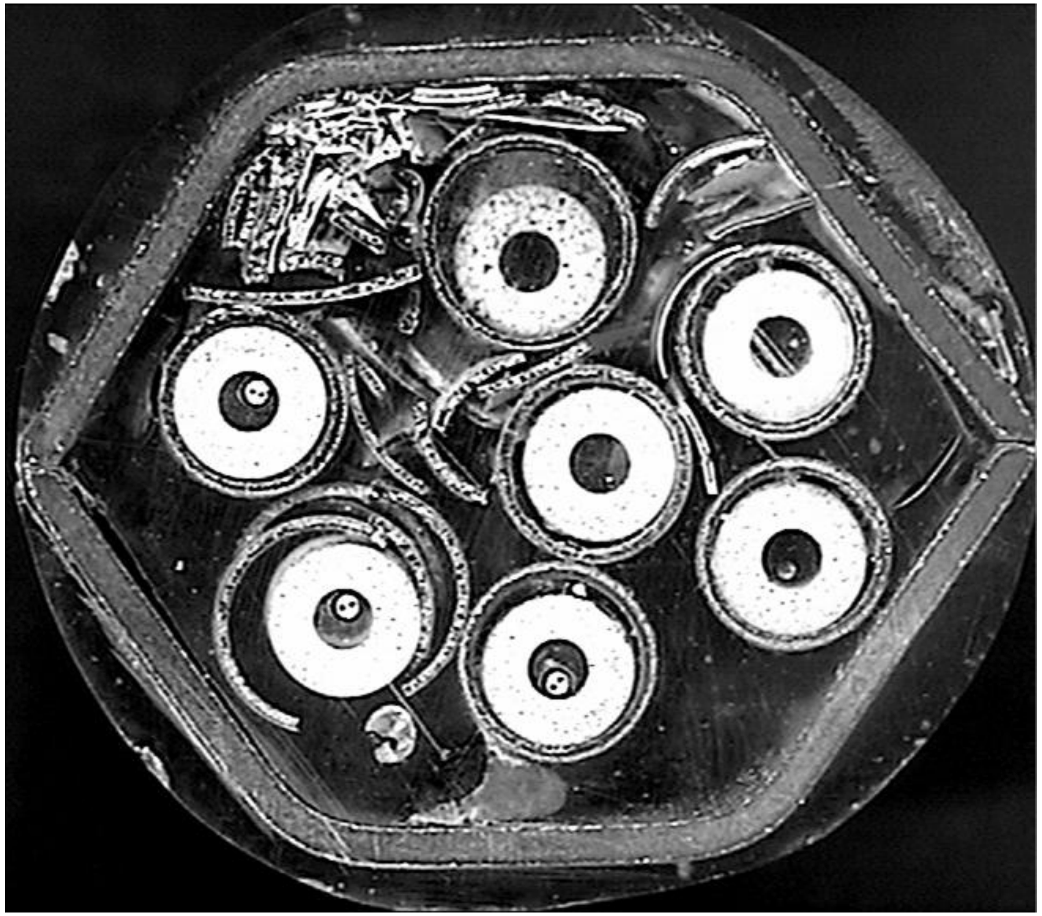
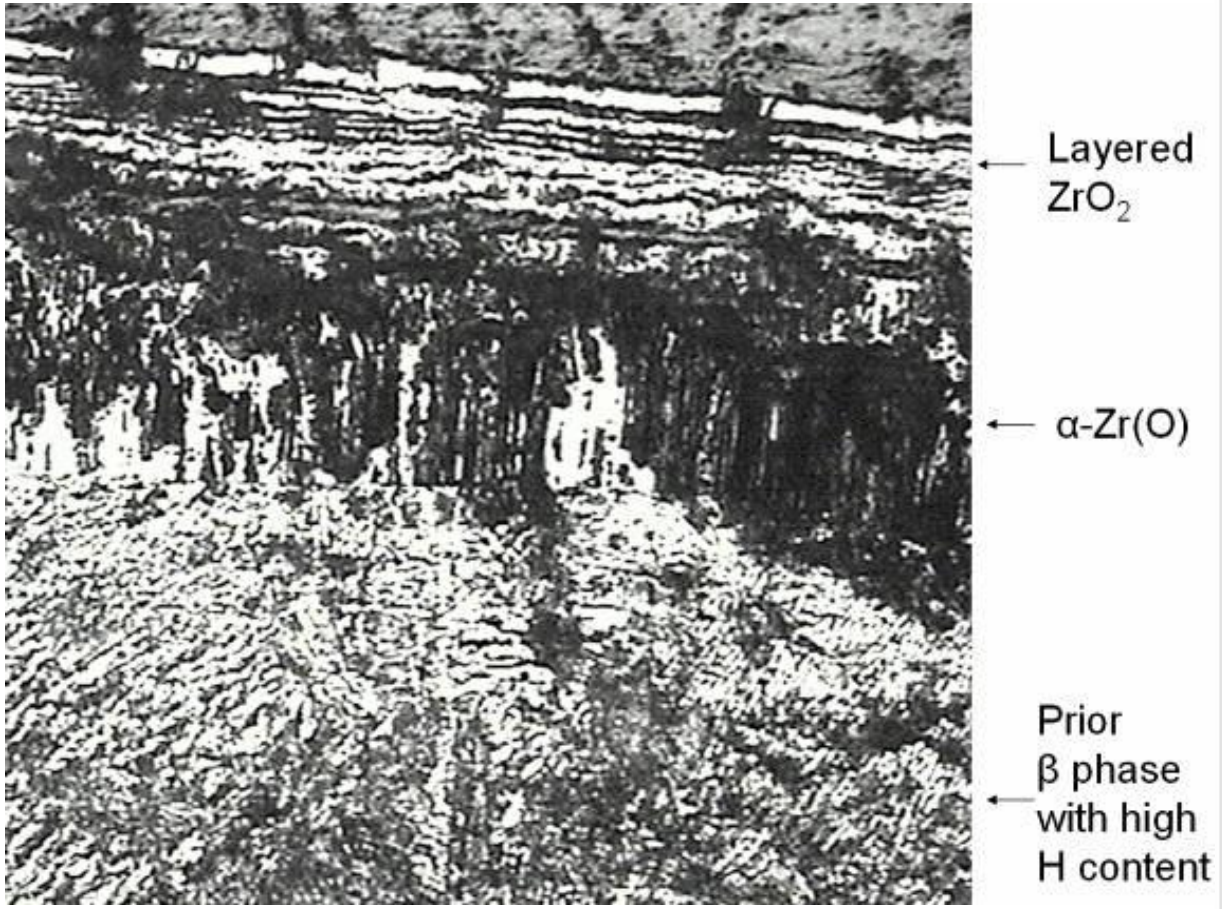
CODEX-CT PT appearance (Paks-2 simulation)





⇨ Ballooning and fragmentation of fuel rods

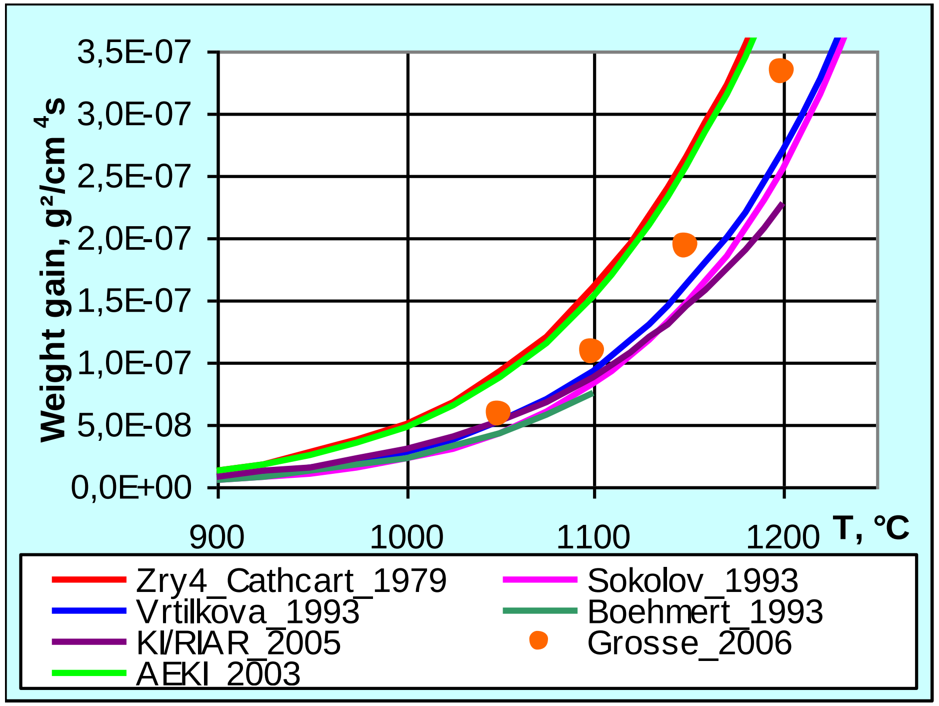
⇨ Formation of layered oxide scale on the cladding

⇨ High H absorption by Zr

Modelling of oxidation kinetics

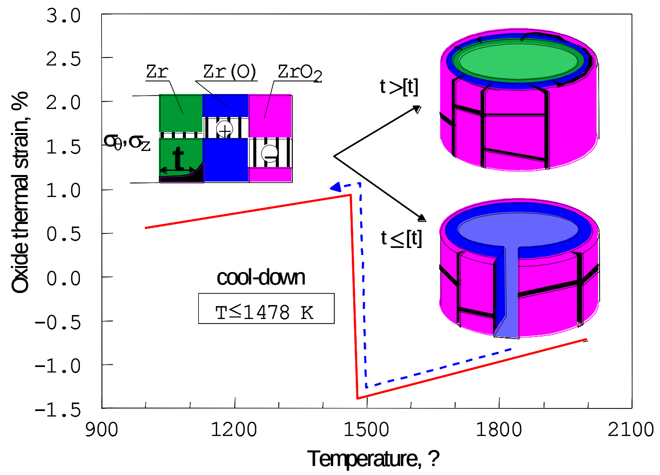
- Parabolic oxidation kinetics applied in all codes
- Critical assessment of all experimental data and best-fitted correlations available for Zircaloy-4 (Schanz, Veshchunov):
  - Cathcart-Pawel (or Leistikow-Schanz) in low-temperature range
  - Prater-Courtright in high-temperature range
- For E110 many data available, but comprehensive analysis still missing

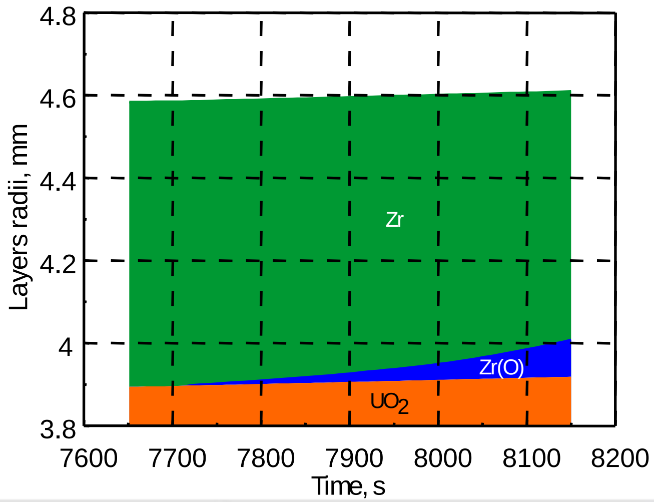
Alloy	Kinetic	Temperature range, °C	Oxidation degree, µm	K_{0w}, (g^2/cm^4s)	T_{ew}, K
Zry-4	*UH (AECL, 1978)*	*1580-1850*	*δ_{ox}>200*	***0.879***	***16610***
Zry-4	PC (PNNL, 1986)	1630-2000	100<δ_{ox}<600	***32.95***	***26440***
Zry-4	CP (ORNL, 1979)	1000-1500	δ_{ox}<75	**0.3622**	**20100**
Zry-4	LS (FZK, 1983) [38]	900-1500	δ_{ox}<600	**0.52418**	**20962**
Zry-4	FZK, 2006	1050-1400	50<δ_{ox}<550	**0.0888**	**18067**
E110	VNIINM, 1988 [4]	550-1200	δ_{ox}<400	**0.8464**	**20820**
E110	VNIINM, 1993 [29]	1200-1500	δ_{ox}<100	**1.59**	**23040**
E110	*VNIINM, 1993* [29]	*1500-1600*	*δ_{ox}<150*	***0.9825***	***20800***
E110	VV, 1993 [42]	600-1450	δ_{ox}<250	**0.561**	**21426**
E110	BDL (FZR) [3]	700-1100	δ_{ox}<100	**0.2375**	**20522**
E110	KI/RIAR, 2005 [5]	800-1200	δ_{ox}<100	**0.09772**	**19105**
E110	AEKI, 2003 [47]	500-1200	δ_{ox}<150	**0.4330**	**20400**
E110	FZK, 2006	1050-1400	50<δ_{ox}<350	**1.5952**	**22664**



Further modelling activities

- Mainly in the frame of SVECHA/Q code development
- Thermo-mechanical behaviour of cladding during quenching
  - ⇨ Prediction of local (tensile and compressive) stresses causing deformation and rupture
- Influence of irradiation
  - ⇨ Successful application to RIAR SR quench tests with irradiated fuel rods (ISTC-1648.2)





Summary

- HT oxidation data of Zircaloy-4 and E110 have been compiled including SETs and integral bundle tests
- Oxidation is strongly dependent on temperature and atmosphere
- Integral and transient tests indicate a higher susceptibility of E110 to breakaway connected with less protective oxide scales, increased hydrogen absorption, and earlier embrittlement
- New data for model improvement are available

Conclusions and outlook

- Comprehensive analysis of high-temperature oxidation data of E110 is needed
- New development of E110 production procedure in Russia (change from “electrolytic” to “metal sponge” raw material) should be followed and the new material should be considered for HT investigations
- Advanced cladding alloys must be investigated carefully and oxidation model parameters have to be revised if necessary

Finally…

You are invited to the

14^{th} International QUENCH Workshop

Forschungszentrum Karlsruhe (FZK)

November 4-6, 2008

www.fzk.de/quench

Thank you for your attention!