Separate-effects tests on high-temperature oxidation of zirconium alloys in various atmospheres

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Workshop on Computational and Experimental Studies of the LWR fuel element behaviour under beyond design basis accidents and reflood conditions

(Formerly known as Workshop on Breakaway and its Consequences)

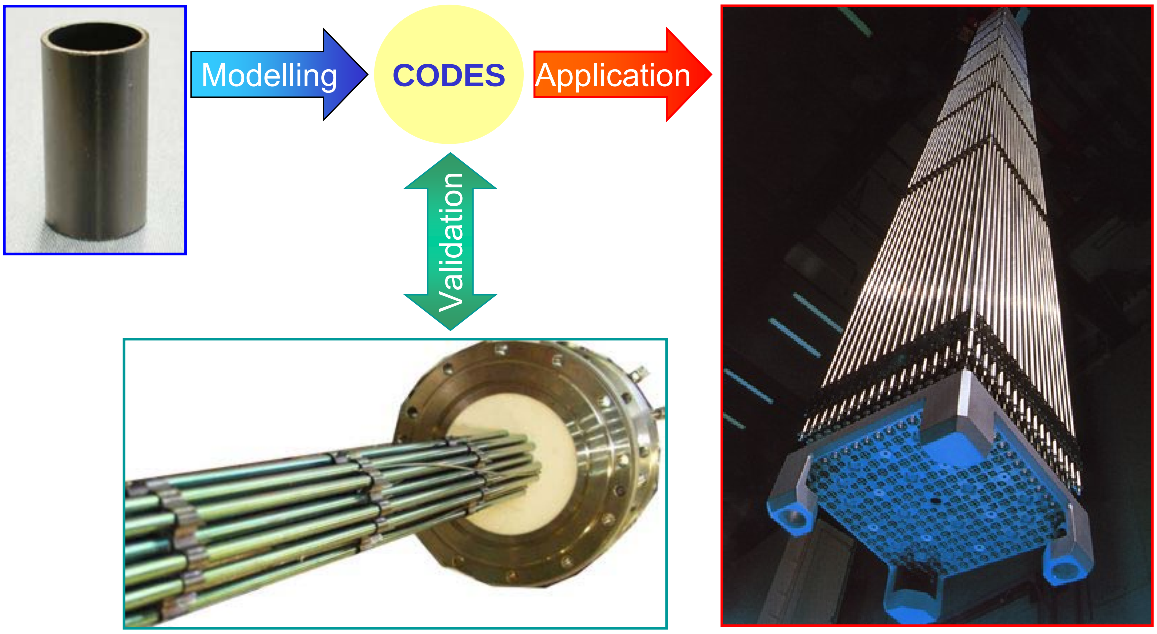
IBRAE, Moscow, 27-28 July 2009

Motivation

- A huge data base on oxidation kinetics is available for Zircaloy-4
- Most (if not all) models and correlations used in SFD code systems are based on these Zry-4 data
- Meanwhile, most Western NPPs use advanced cladding alloys, like M5® (AREVA) or ZIRLO™ (Westinghouse); E110 is used in Russian NPPs
- For these alloys, the publicly available data base on high-temperature oxidation was limited

→ **QUENCH-ACM Program**

Procedure



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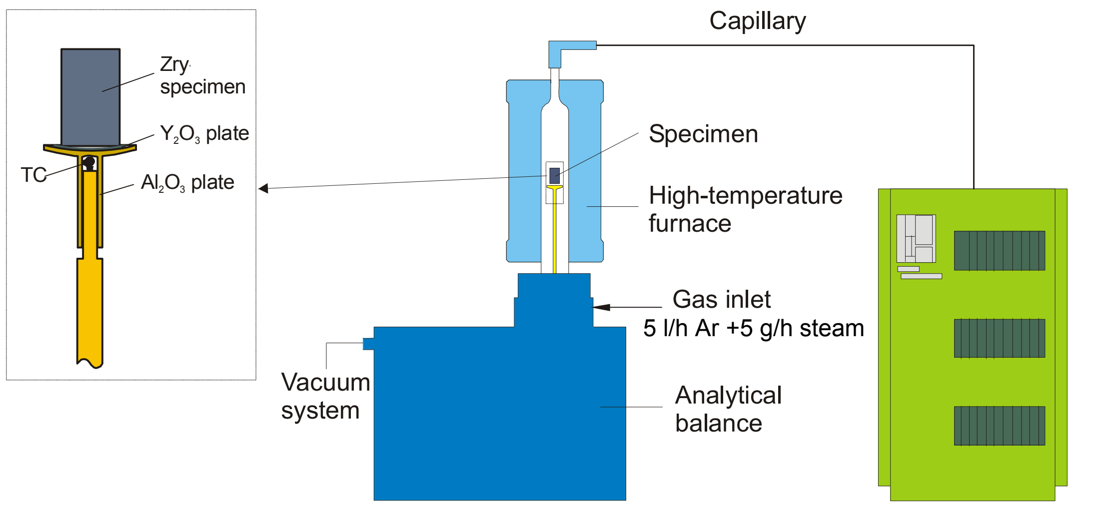
Test rig



TG measuring head **Thermobalance** **Mass spectrometer**

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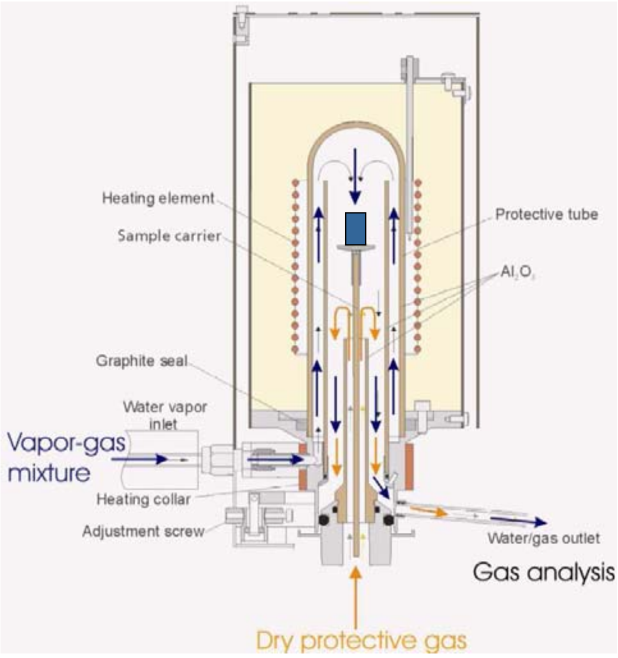
Test rig - steam furnace



- T_{max} = 1250 °C
- Steam supply to the specimen from the top
- Ar as protective gas for the balance

⇨ Almost pure steam atmosphere at specimen

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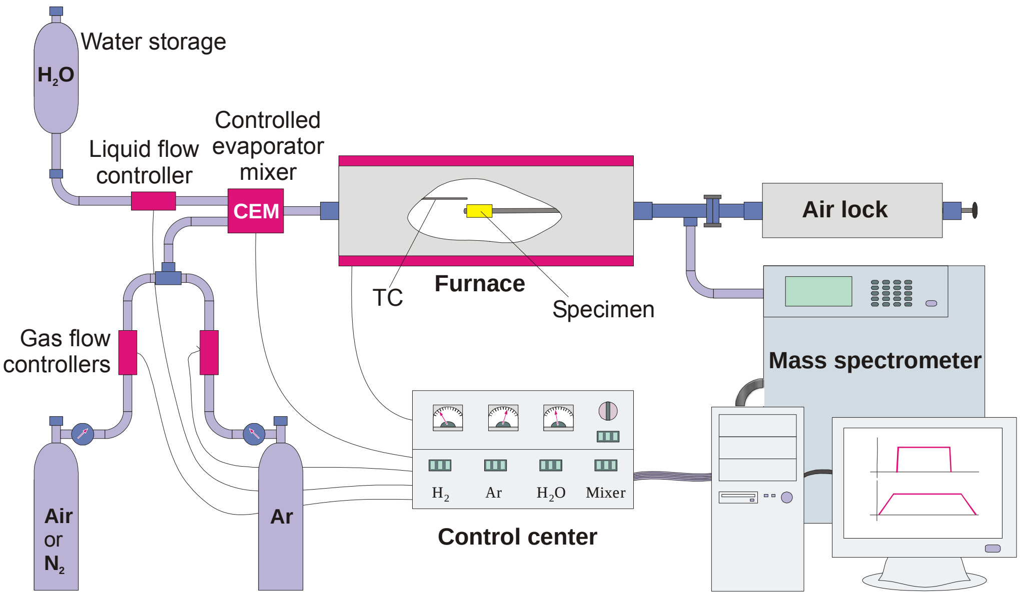
BOX Rig for oxidation experiments under controlled atmosphere



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Specimens

- 2-cm cladding segments
- Both side oxidation allowed

Composition (main alloying elements)

Element	Zry-4	D4	M5	E110	ZIRLO
Nb	**-**	**-**	**1**	**1**	**1**
Sn	**1.5**	**0.5**	0.01	< 0.01	**1**
Fe	0.2	**0.5**	0.05	0.008	~0.11

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Test matrix

Isothermal tests:

- 600-1100 °C in oxygen
- 600-1200 °C in steam
- 800-1500 °C in air, air-steam, and nitrogen-steam mixtures

- Test duration resulting in only partial oxidation and allow for metallographic post-test examination

Transient tests:

- Various tests 600 → 1200 °C in steam; 600 (1100) → 1600 °C in oxygen
- Heating rates 5 - 40 K/min

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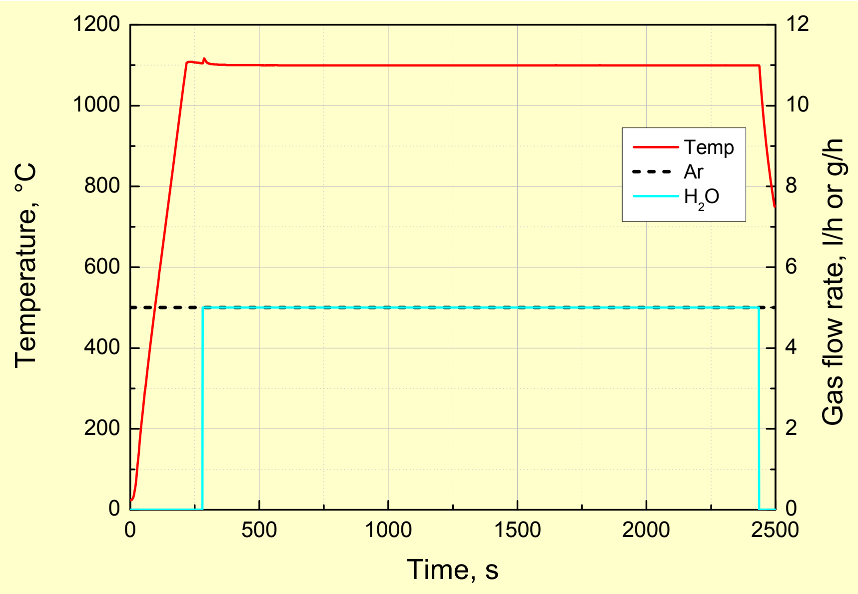
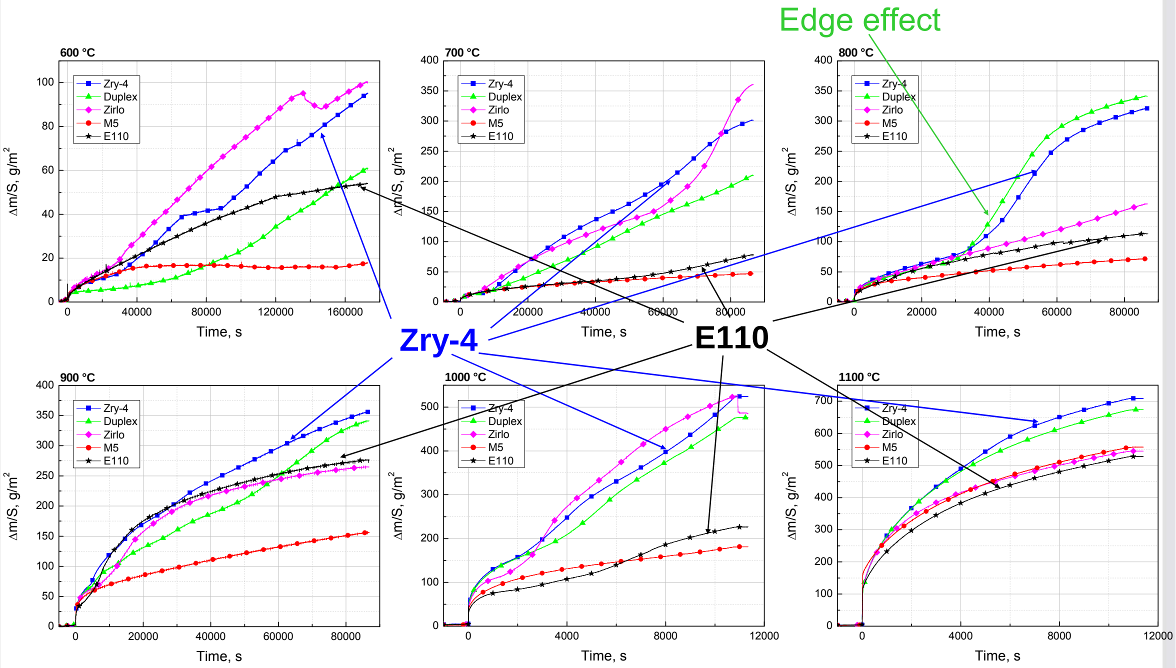
Tests in steam atmosphere

Isothermal tests conduct



Isothermal tests in steam – TG results



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Isothermal tests – Post-test appearance (1)

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Isothermal tests – Post-test appearance (2)

900 °C

1000 °C

1100 °C

Zircaloy-4 | Duplex | M5 | E110 | ZIRLO

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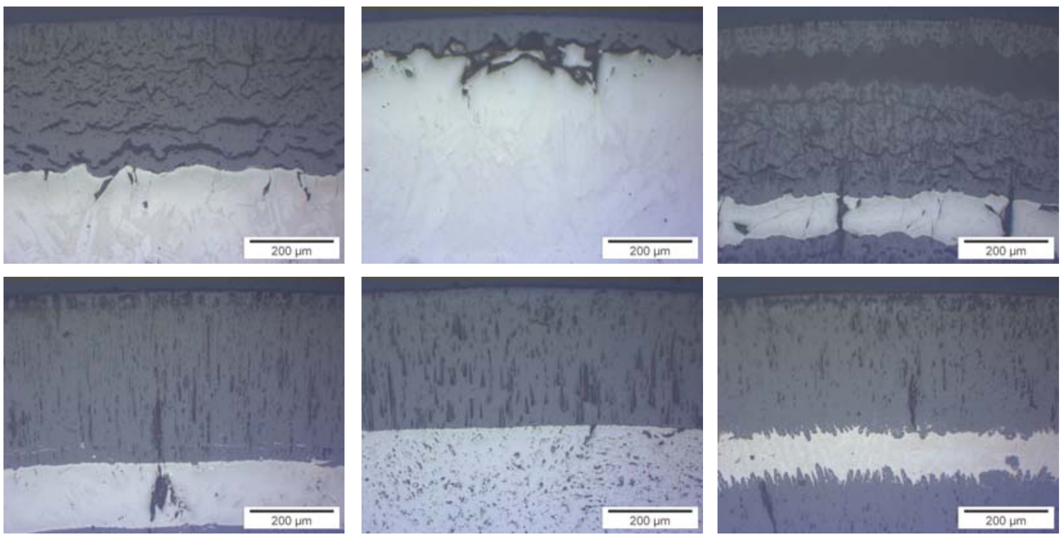
Isothermal tests – Metallographic images (1)

3 h, 1000 °C

3 h, 1100 °C



Zry-4 | M5 | ZIRLO

Typical oxide structures at 1000 and 1100 °C

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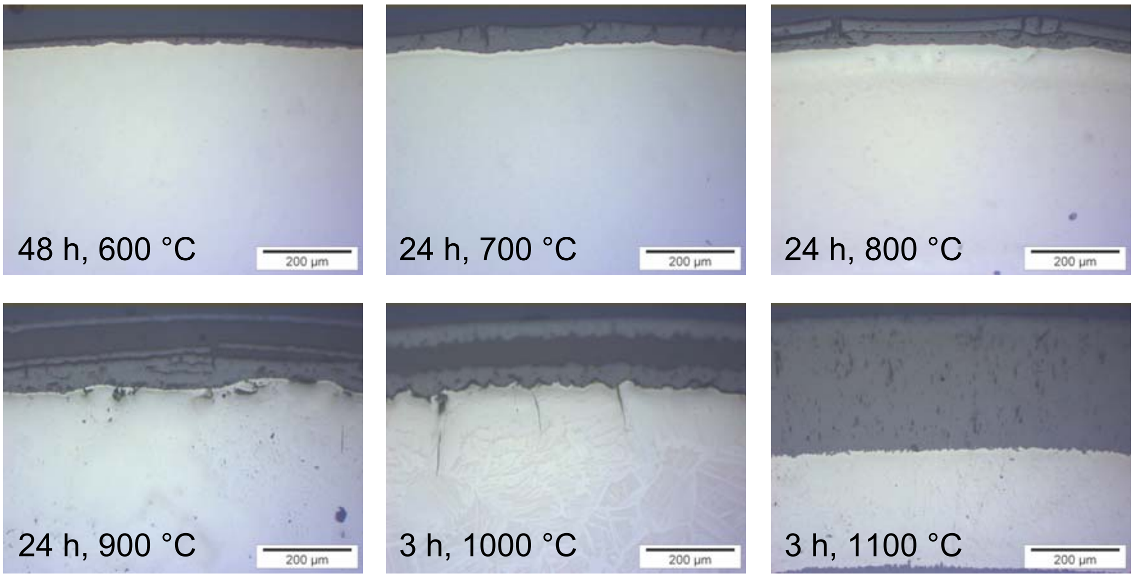
Isothermal tests – Metallographic images (2)



Typical breakaway oxidation of E110

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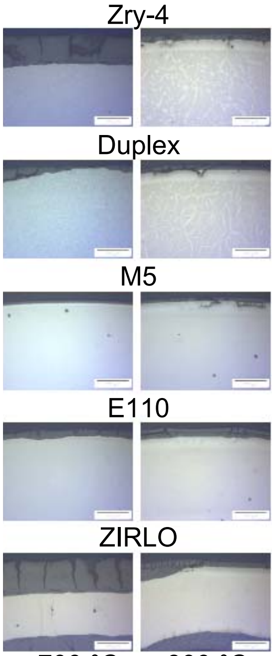
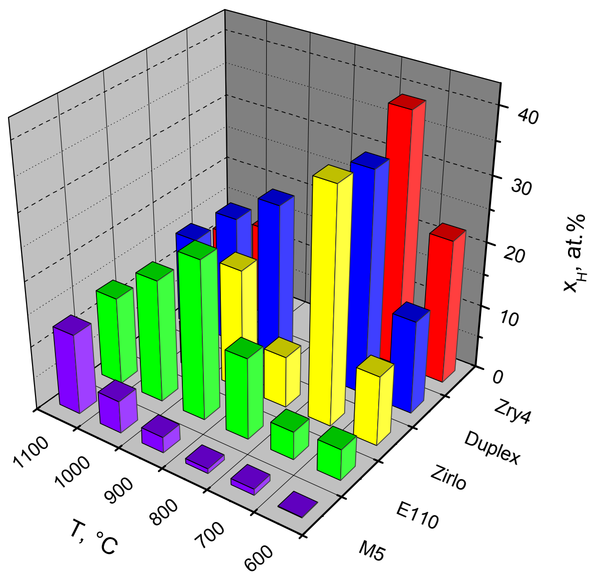
Determination of H in Zry samples by NR





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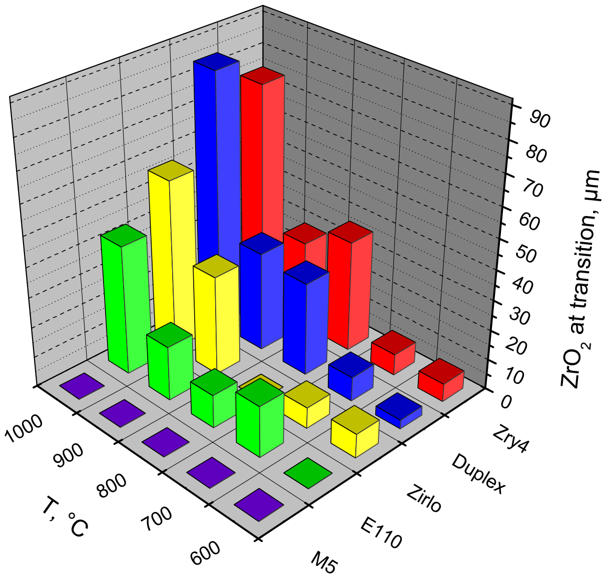
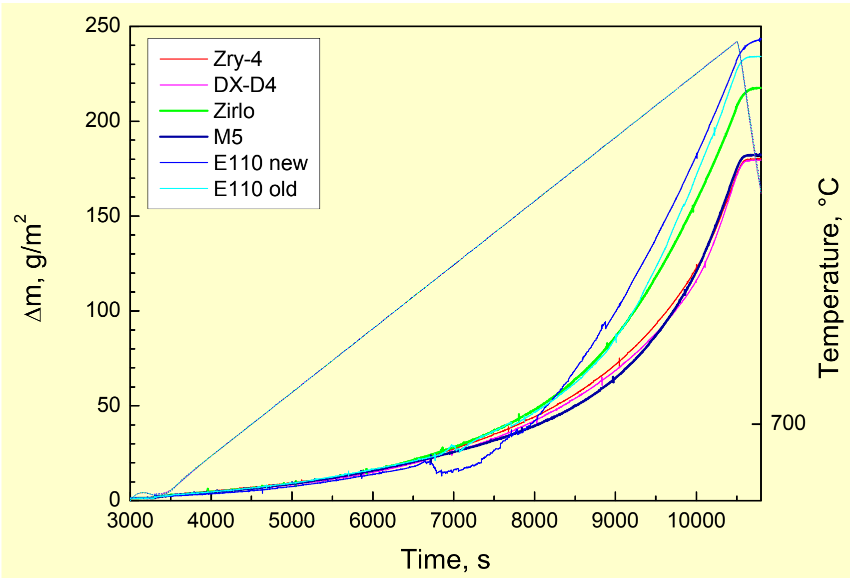
Transition to breakaway



Temperature °C	Time at transition h	Oxide at transition µm
600	6-8	3-8
700	1-10	7-17
800	1-7	11-37
900	0.6-1.5	18-33
1000	0.3-0.7	43-85

Oxidation under transient conditions



Mass gain at tests 600→1200°C with heating rate 5 K/min

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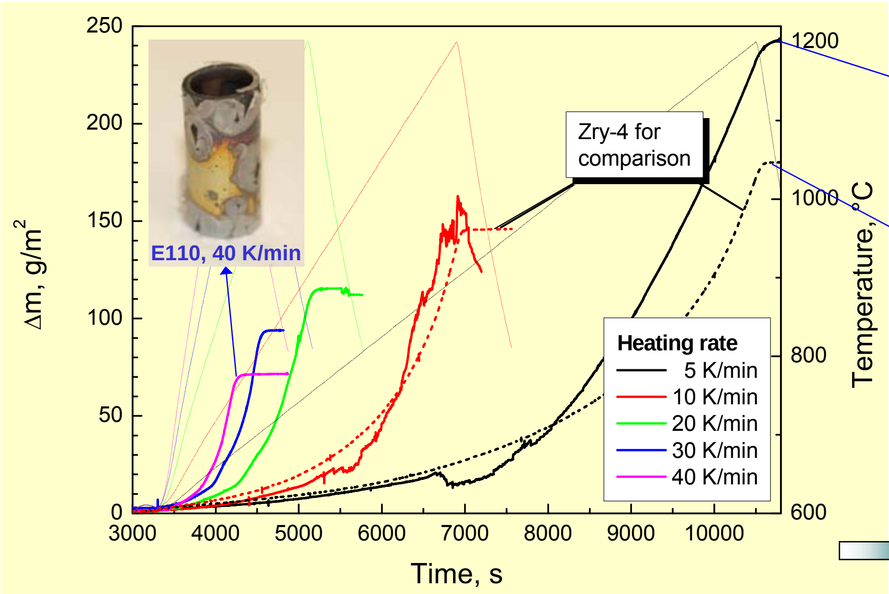
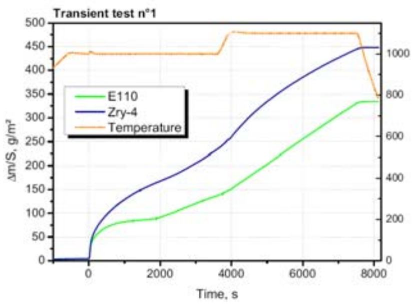
Oxidation under transient conditions

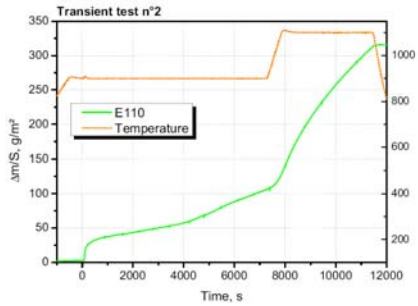


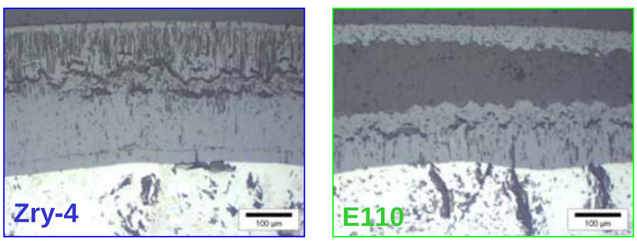
Breakaway only for E110

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

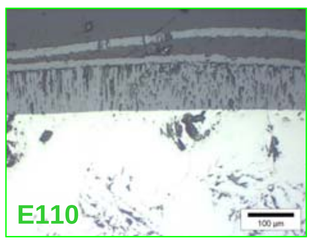
Transition from breakaway to “normal” oxidation







1h 1000°C, 1h 1100°C



2h 900°C, 1h 1100°C

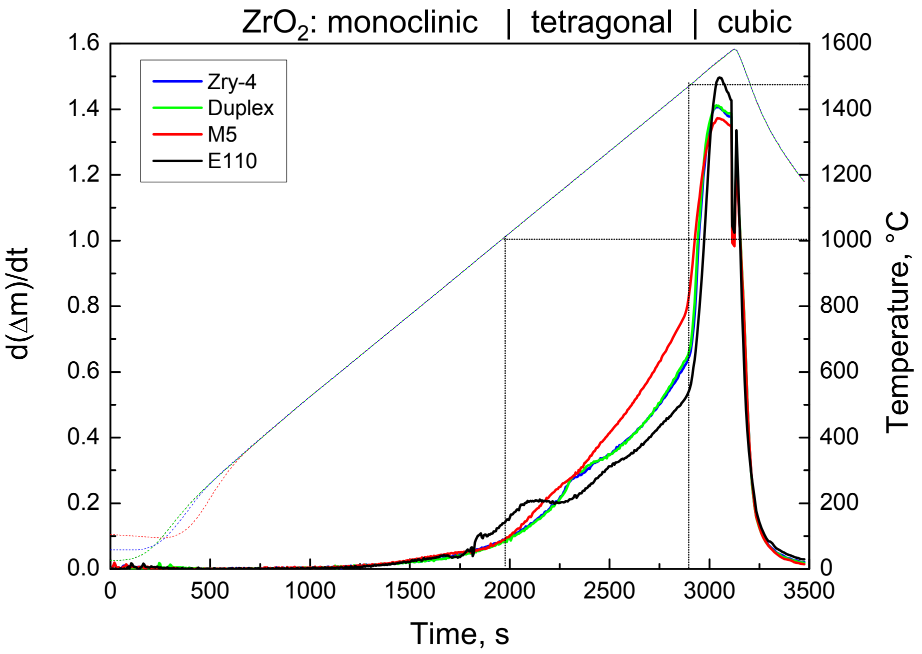
Dense and protective oxide scales after passing breakaway region

Summary of steam tests

- The oxidation kinetics of cladding alloys Zry-4, Duplex-D4, ZIRLO™, M5®, and E110 in steam have been investigated in the temperature range 600-1200 °C.
- Oxidation of Zr alloys with only slightly different composition is quite complex with strong differences up to 1050 °C (due to breakaway), and less, but significant variation at higher temperatures.
- The oxidation kinetics are mainly determined by the oxide scale (breakaway, crystallographic phase, degree of sub-stoichiometry).
- The strong correlation between breakaway oxidation and hydrogen uptake was confirmed.

Example of transient test in oxygen

Transient tests RT-1600 °C in oxygen



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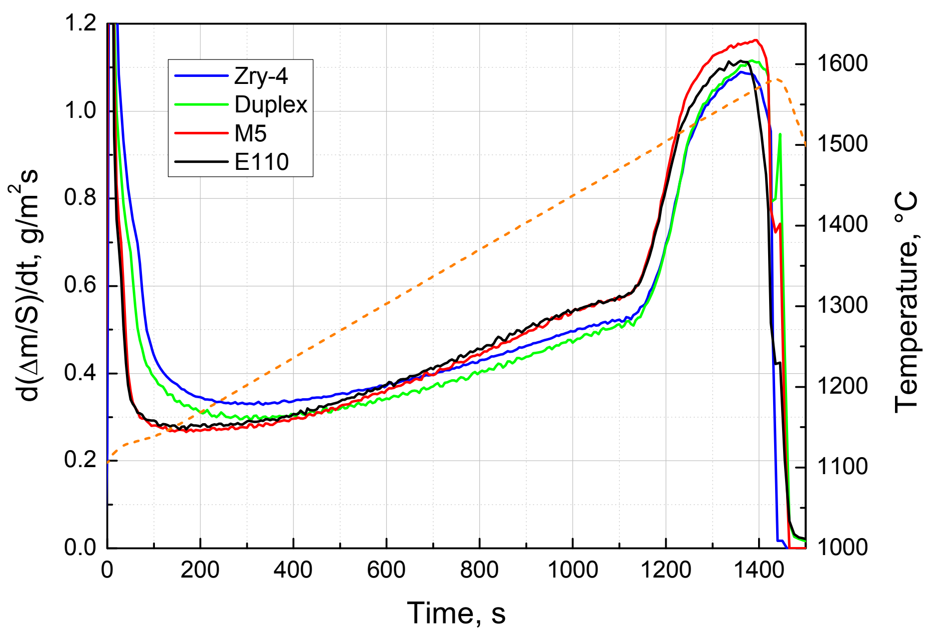
Transient tests 1100-1600 °C in oxygen



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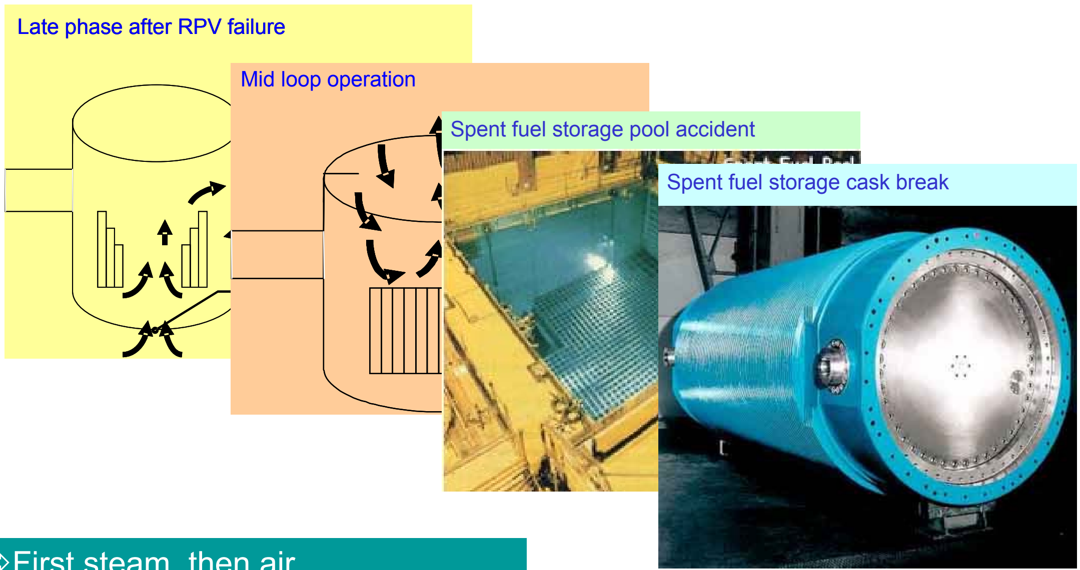
Summary of Tests

in nitrogen containing atmosphere

Scenarios for air ingress



⇨First steam, then air
⇨Mixed steam-air atmospheres

Consequences of air ingress

Strong exothermal reaction ($\Delta_R H^{air} >> \Delta_R H^{steam}$)

+ Less cooling effect

→ Temperature escalation

Detrimental effect of nitrogen on oxide scales

→ Enhanced cladding degradation

Higher oxygen activity in the core

→ Oxidation of fuel

FP release and transport

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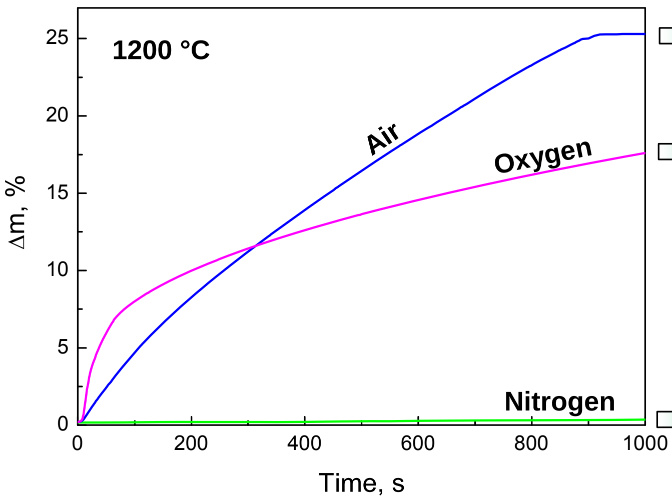
Oxidation of Zircaloy-4 in O_2, N_2, and air



→ ~ Linear oxidation kinetics (Air)

→ Parabolic oxidation kinetics (Oxygen)

→ Parabolic reaction kinetics (Nitrogen)

→ Oxidation rate in air is much higher than in oxygen or steam

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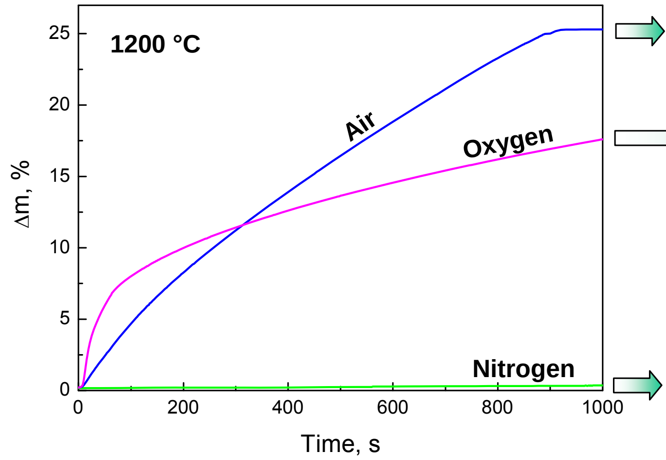
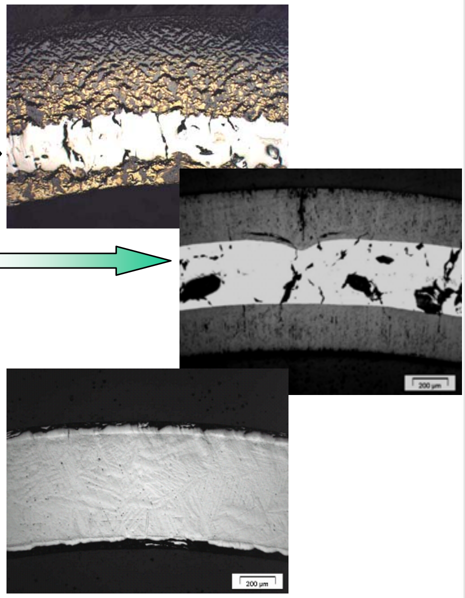
Oxidation of Zircaloy-4 in O_2, N_2, and air





Significant nitride formation in air but not in nitrogen

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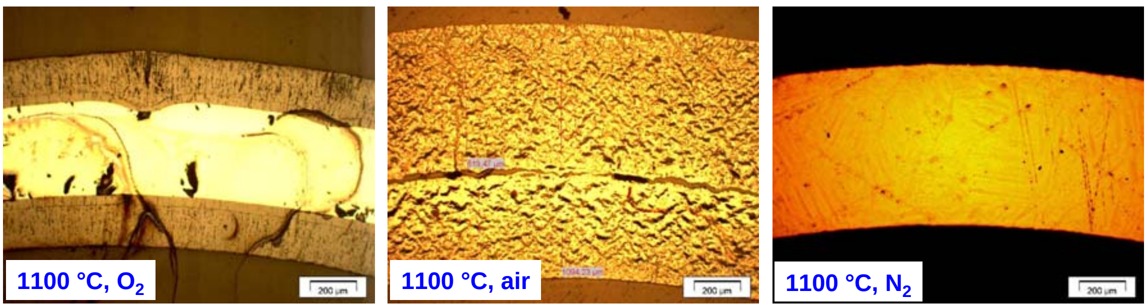
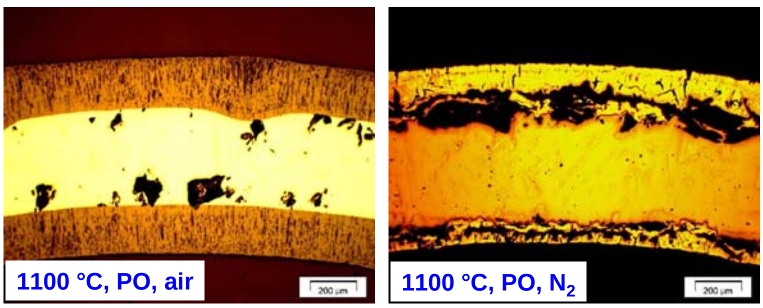
Influence of pre-oxidation



With pre-oxidation (PO) ⇨



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Oxidation in steam-air mixture

KIT Karlsruhe Institute of Technology

Air | 0.9 air / 0.1 H_2O | 0.7 air / 0.3 H_2O | 0.5 air / 0.5 H_2O | 0.3 air / 0.7 H_2O

0.1 air / 0.9 H_2O | 0.05 air / 0.95 H_2O | 0.03 air / 0.97 H_2O | H_2O

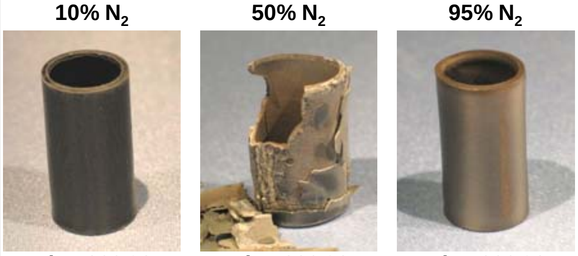
1h
1200 °C

Oxidation in steam-nitrogen mixture

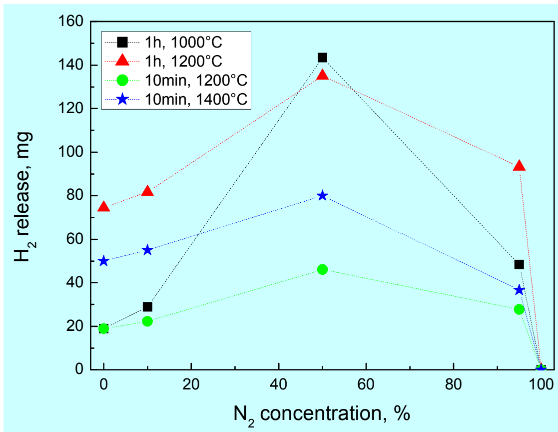
KIT Karlsruhe Institute of Technology

Post-test appearance of cladding segments

1 h, 1000 °C 10% N_2 | 1 h, 1000 °C 50% N_2 | 1 h, 1000 °C 95% N_2

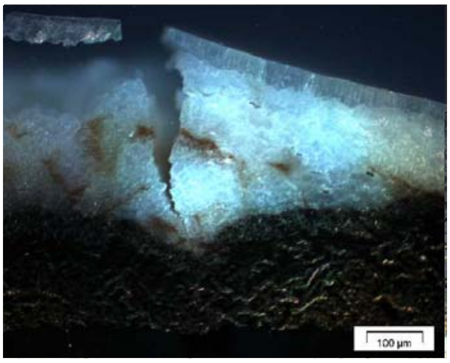


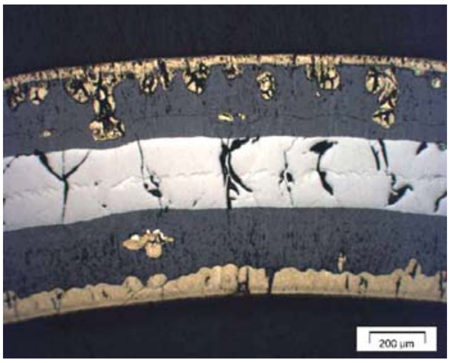
1 h, 1200 °C 10% N_2 | 1 h, 1200 °C 50% N_2 | 1 h, 1200 °C 95% N_2



Hydrogen release in dependence on composition of atmosphere

Mechanism of nitrogen attack





Local oxygen starvation:
Formation and re-oxidation of nitride phase at metal-oxide phase boundary

Global oxygen starvation:
Pre-oxidation in steam and subsequent reaction in pure nitrogen

→ Nitride formation only in the absence of oxygen in the gas phase and in the presence of oxygen in the solid phase!

Summary of air tests

- The formation and oxidation of ZrN is the main reason for the enhanced degradation of the cladding in nitrogen containing atmospheres (due to the strongly different densities of Zr, ZrO_2, and ZrN)
- Nitriding occurs under local (microscopic) or global (macroscopic) oxygen starvation conditions and in the presence of oxygen in the solid phase
- Nitrogen attack starts at imperfections in the oxide scale, e.g. at breakaway oxide and accelerates the degradation of the cladding
- Nitrogen is not an inert gas under the conditions of a nuclear accident!

Influence of inert gas on oxidation

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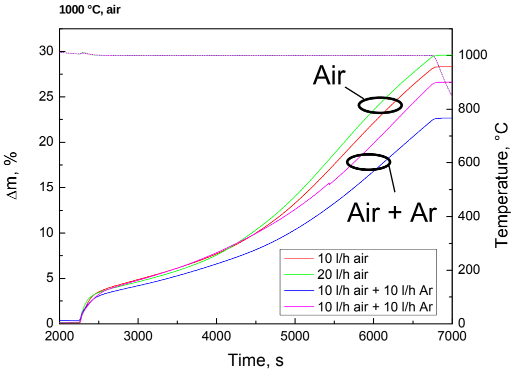
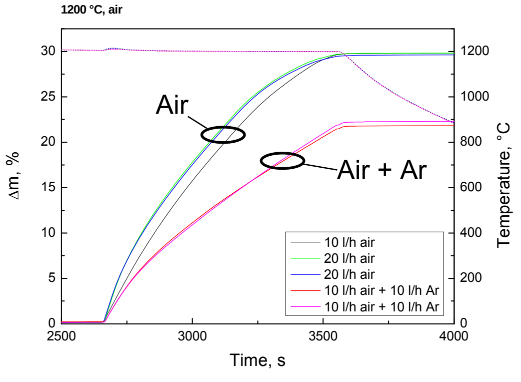
Influence of argon during air oxidation





Significant influence of inert gas on oxidation in air

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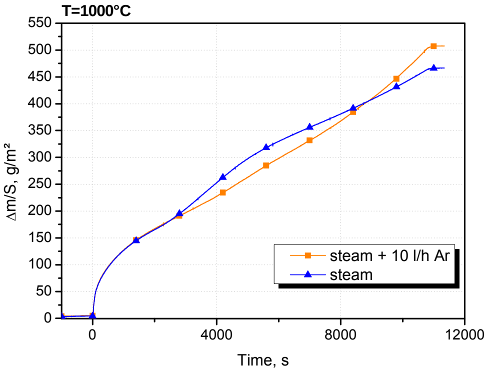
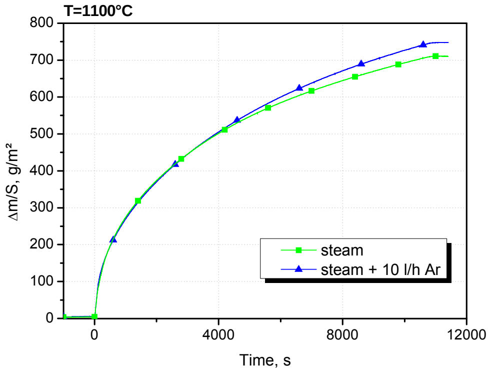
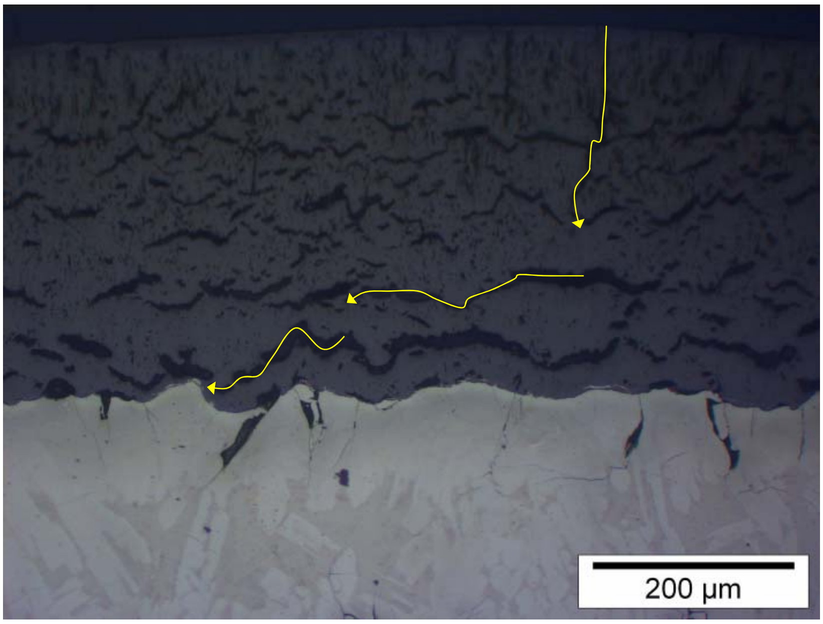
Influence of argon during steam oxidation





Small influence of inert gas on oxidation in air at 1000 °C after transition to breakaway and insignificant effect at 1100 °C

Influence of argon during steam oxidation



Inert gas may influence the gas phase transport through cracks and pores in the oxide.

This effect should be more pronounced in case of oxidation by oxygen or air because the reaction gas is completely consumed.

General summary on breakaway effect

- Breakaway occurs at most Zr cladding alloys at temperatures below 1050 °C.
- Breakaway causes a change in oxidation kinetics from parabolic (or cubic) to faster, rather linear kinetics.
- Transition to breakaway occurs after about 20 min at 1000 °C and after several hours at lower temperatures, according to a few tens of µm and a few µm oxide thickness, respectively.
- During LOCA and fast BDB accident scenarios, breakaway should not play a role because the breakaway temperature range is passed too fast.
- Breakaway plays a role during slow transients at lower temperatures as they may occur during spent fuel pool or storage tank accidents.
- During transient oxidation, kinetics changes again to parabolic after passing through the breakaway temperature range (as was e.g. seen in the PARAMETER-SF2 PTE).

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