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Wir schaffen Wissen – heute für morgen

The role of nitrogen in spent fuel pool accident scenarios

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7th EMUG, 17-18 March 2015, Brussels, Belgium

Outline

- Air ingress scenarios
- Overview of current knowledge
  - sources of data (Separate Effect Test & Integral experiment transient)
  - Air oxidation model development
    - Existing codes
      - PSI air oxidation model
    - Codes limitation (example: QUENCH-16 benchmark)
- PhD: Zirconium Nitride (ZrN) formation during oxidation of nuclear fuel cladding
  - possible mechanism for Zirconium nitride (ZrN) formation
- Additional Reactions?
- Summary and outlook

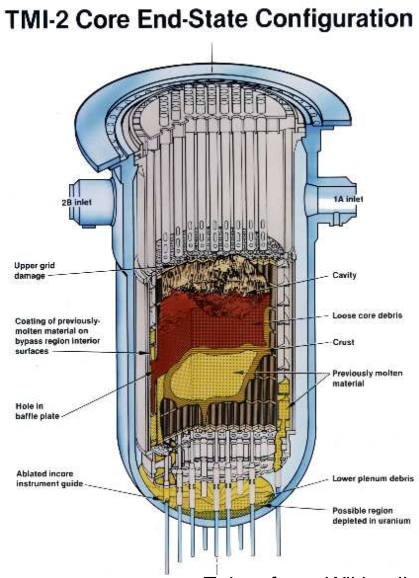
Air Ingress scenarios

Air Ingress scenarios

- Reactor sequences
  - Late phase after RPV failure
  - Mid loop operation: Refueling
- **Spent fuel sequences**
  - **Spent fuel pool draining**
  - **Dry storage cask drop**

Taken from: www.josephmiller.typepad.com

Spent fuel pool draining



Taken from: Wikipedia

Late phase after RPV failure

Taken from: www.cleanenergyinsight.org

Refueling: RPV head removal

Taken from: www.power-eng.com

Dry storage cask drop during transport

Sources of data

- **Numerous sources of Separate Effect Tests (SET's) data**
  - Argonne (ANL) USA,
  - Karlsruhe (KIT) Germany
  - Cadarache (IRSN) France
  - AEKI Hungary
  - INR Romania

- **Integral Experiment Transient (IET) data**
  - CODEX AIT (AEKI)
  - QUENCH-10, -16 (KIT)
  - PARAMETER-SF4 (LUTCH)
  - USNRC-sponsored SNL BWR SFP and OECD-sponsored SNL PWR SFP

General observations from SETs in air oxidation

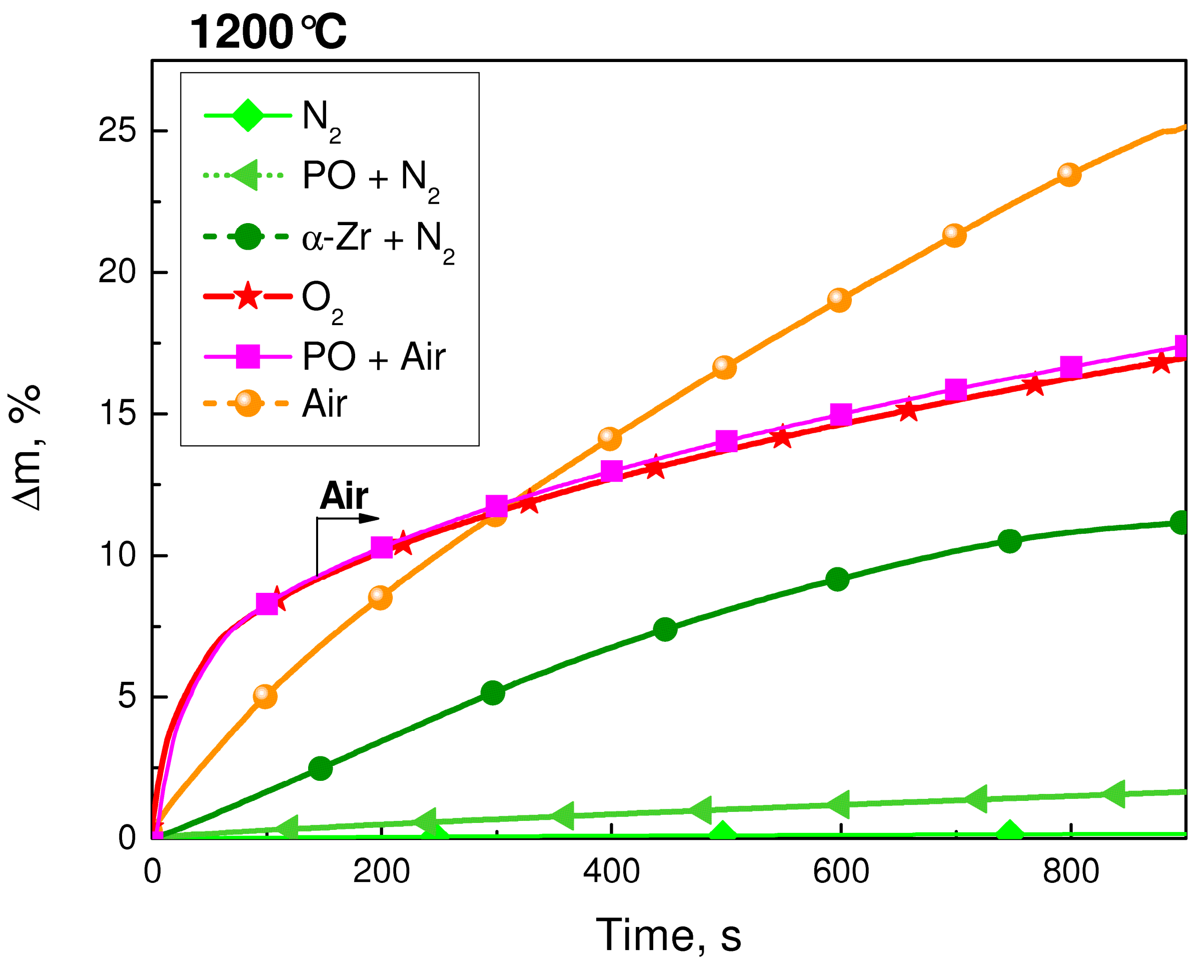
- **Zr exhibit faster mass gain during exposure to air than to steam alone**
  - attributed to the presence of nitrogen (not oxygen)
  - often interpreted as transition from parabolic to linear (breakaway) oxidation
  - the faster oxidation sometimes delayed and not always observed
    - may be inhibited by previous oxidation in steam (protective oxide layer)
    - pre-transition; the kinetics similar to steam or oxygen-argon
  - temperature dependence of the observed trends

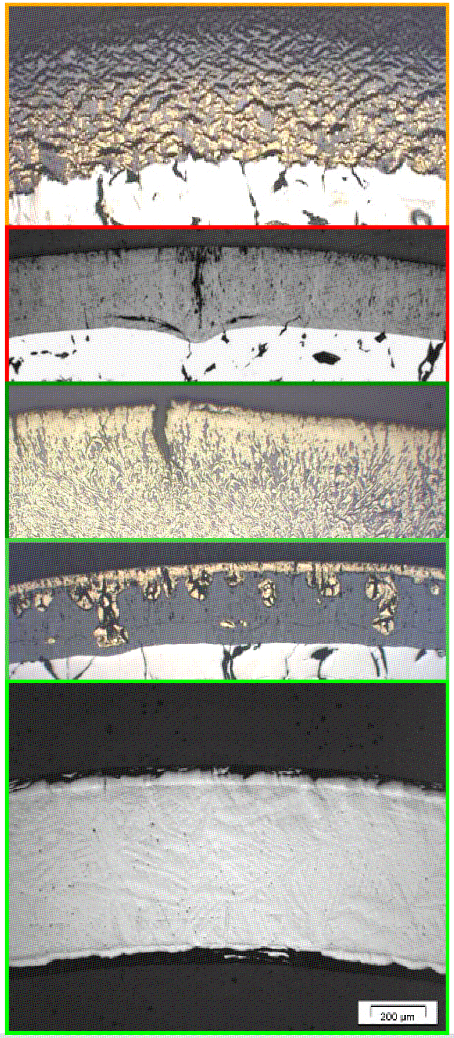
- **Frequently, but incorrectly regarded as purely oxidation**
  - nitrogen reaction very slow with pure Zr; often thought of as a catalyst for oxidation
    - composition not always examined to confirm oxide is the only product
  - trace presence of ZrN when gas is oxygen rich
    - ZrN readily forms from partially oxidised Zr in oxygen starved conditions

- Models for air oxidation generally based on SETs results

Example observations from SETs
Basis for PSI model

Oxidation of Zr alloys in various atmospheres





General observations from IETs

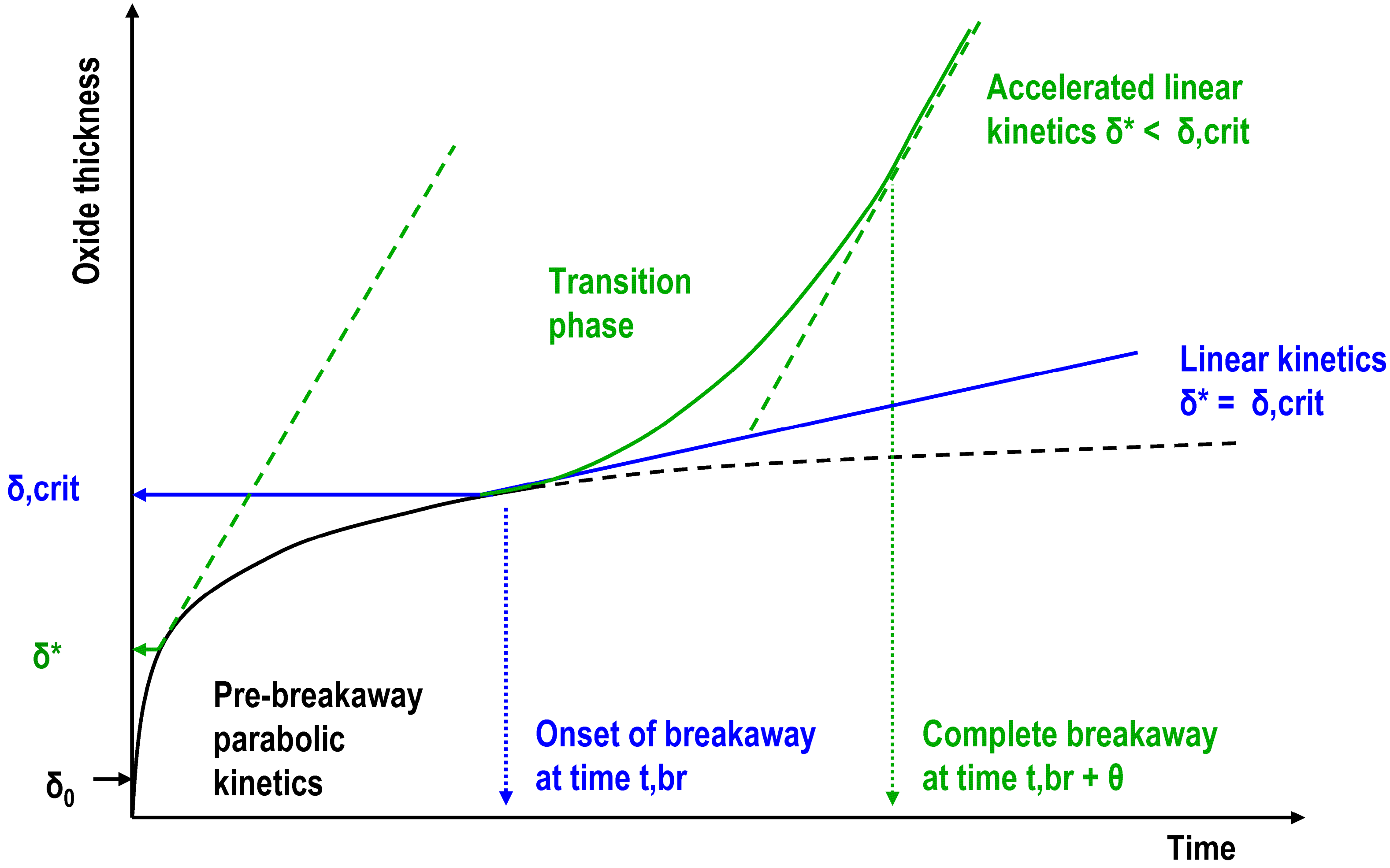
- Integral Experiment Transients show more complex behaviour than Separate Effect Tests
  - different behaviour in different parts of the test section
  - uncontrolled and changing conditions
  - history effects
  - other sources of incertitude

- Integral Experiments QUENCH-10, -16, PARAMETER-SF4, OECD SFP
  - Some unexpected behaviour (especially during **Q-16**)
    - importance of nitrogen as an active species
    - **re-oxidation of ZrN**
    - challenges for the simulation
  - QUENCH-air benchmark was important to test the code/model capability

Air oxidation Model development

	MELCOR and SCDAP (PSI)	MAAP	ICARE-CATHARE	ATHLET-CD	SOCRAT
	J. Birchley and L. Fernandez-Moguel (PSI)	Emillie Beuzet et al. (EdF)	O. Coindreau et al. (IRSN)	T. Hollands et al. (GRS)	Vasiliev A.D. (IBRAE)
Oxidation parameter	Oxide thickness	Oxide thickness	Weight gain	Weight gain	O_2 and N_2 diffusion
Oxidants in air	O_2	O_2	O_2	O_2	O_2 and N_2
Pre-transition	Parabolic kinetic rate	Parabolic kinetic rate	Parabolic kinetic rate	Parabolic kinetic rate	
Post-transition	Linear/accelerated kinetic rate	Linear/accelerated kinetic rate	Linear/accelerated kinetic rate	Linear	
Nitriding model	Nitrogen acts as a catalyst	Nitriding model and reoxidation (No degradation of cladding due to nitriding)	Nitrogen act as a catalyst	ZrN formation reaction rate under very low oxygen partial pressure	
On-going modeling	**PhD work: S. Park (since 2013)**	**PhD work: F. Haurais (since 2013)**	PhD work: M. Lasserre (finished 2014)		

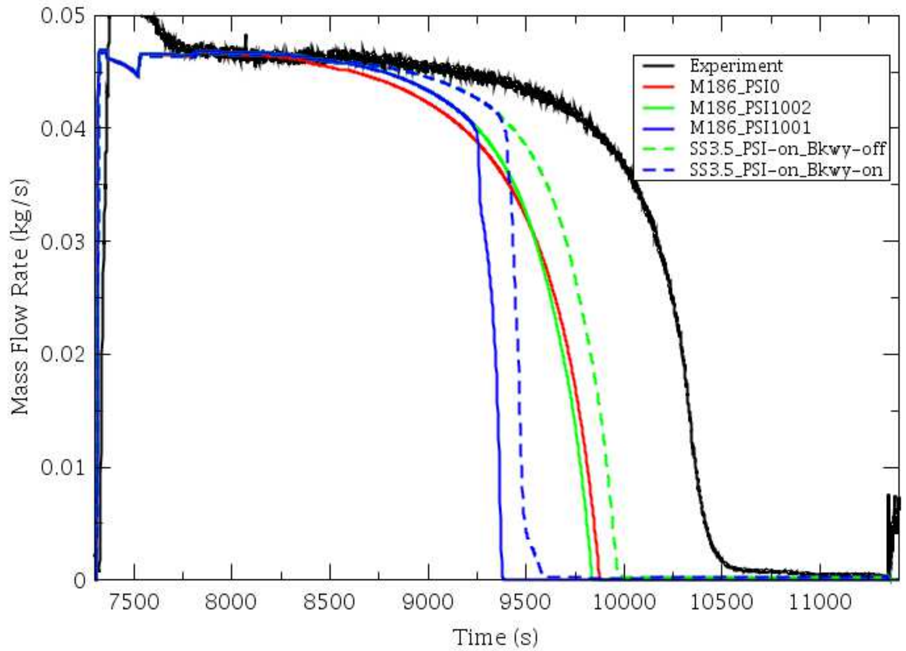
PSI air oxidation model concept



Nitrogen acts as a <u>catalyst</u> and not as an active species

No nitriding model

Q16: Air phase / Oxygen consumption

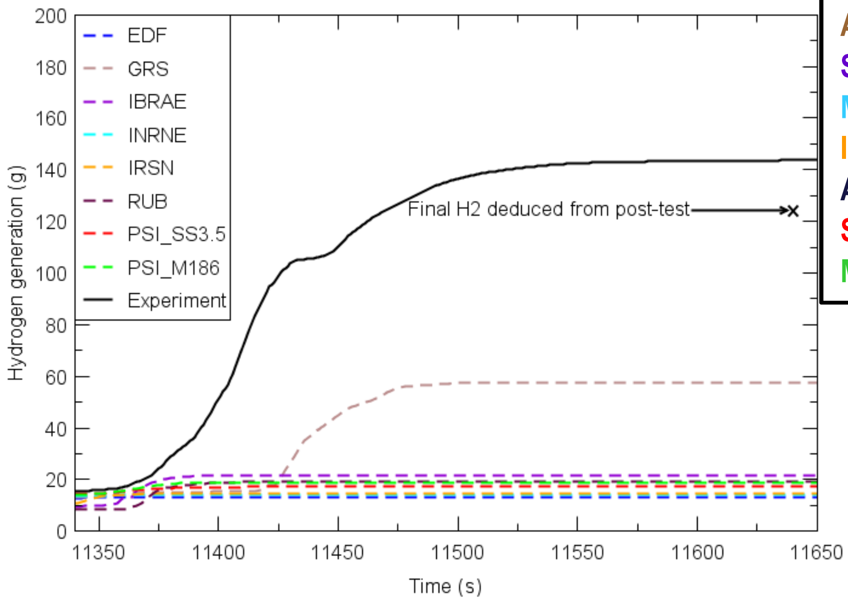


- M186_PSI0 and M186_PSI1002 calculated similar results as expected
  - small difference due to slight difference in oxidation kinetics
- Breakaway was expected during Q16 and it was calculated when breakaway was enabled (M186_PSI1001)

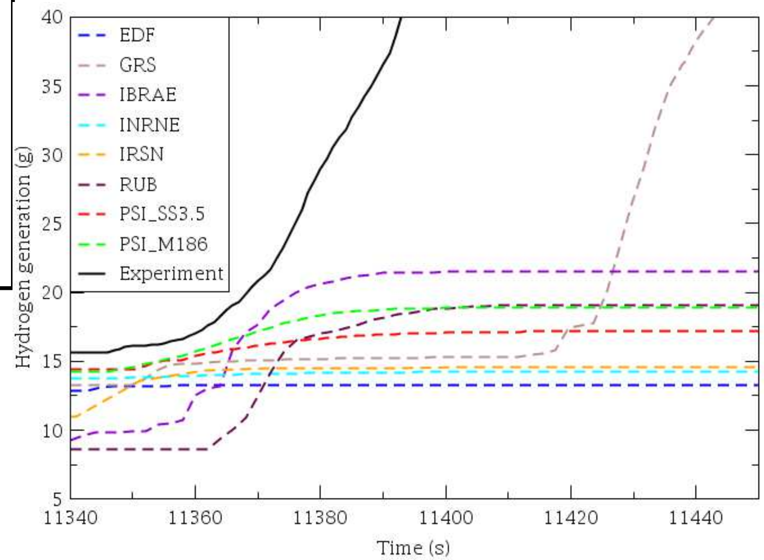
- There was no indication from thermal response or oxygen consumption that breakaway occurred in the experiment.
- This was consistent with the simulation where breakaway was disabled (M186_PSI1002).
- All cases predicted earlier oxygen starvation than observed in the experiment even with breakaway disabled.
  - Possible influence of the low oxygen concentration during the transient

Analysis of QUENCH-16 (benchmark)

Hydrogen generation

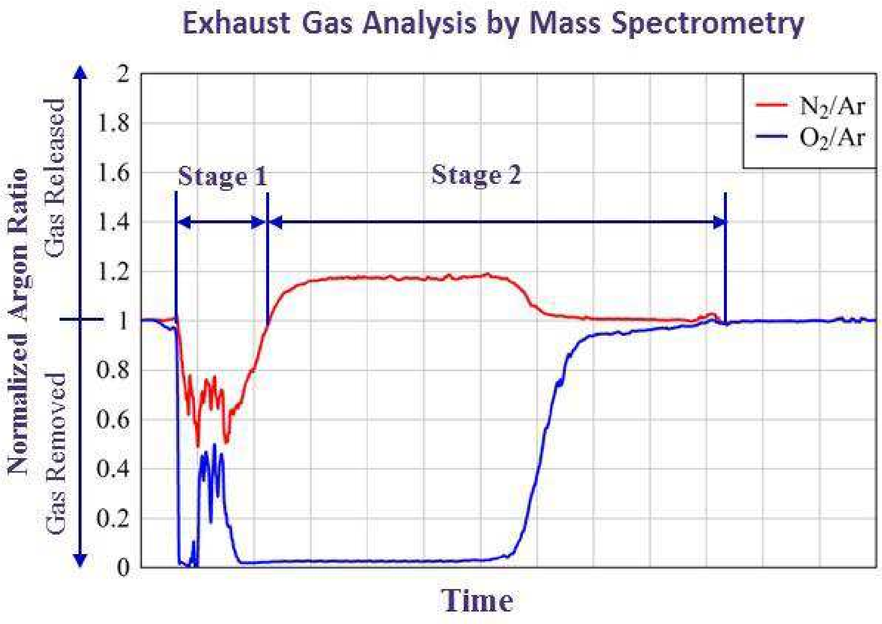


MAAP
ATHLET-CD (with ZrN)
SOCRAT
MELCOR 185
ICARE
ATHLET-CD (no ZrN)
SCDAPSim
MELCOR 186



- Most of the codes under-predicted by far the H_2 generation during the reflood.
  - Only GRS calculated an excursion and a large amount of H_2 generation, but it was still under-predicted.
  - The reason might be that GRS calculation had higher temperatures at the start of reflood than the others
    → **nitriding / re-oxidation may contribute to the cladding degradation (core limitation)**
- It is noted that most of the codes do not model rapid oxidation of metallic melt.

Analysis of OECD SFP Phase II



Stage 1 Oxidation

$Zr + O_2 \rightarrow ZrO_2$

$Zr + \frac{1}{2}N_2 \rightarrow ZrN$

Stage 2 Oxidation

$ZrN + O_2 \rightarrow ZrO_2 + \frac{1}{2}N_2$

During fire downward propagation (Stage 1) the Nitrogen is up to 1/3 consumed

The observation of Oxygen in this stage indicates that counter current flow from above to the sampling line input could even lead to a higher consumption of Nitrogen during Stage 1.

During fire upward propagation (Stage 2) more nitrogen came out of the test section indicating reoxidation of ZrN.

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PhD: Zirconium nitride (ZrN) formation during oxidation of nuclear fuel cladding

1st: Understanding of the role of N_2 during air oxidation

1st year PhD:

19th QWS: The role of nitrogen during air oxidation

NuMat 2014: A mechanism of nitriding process in the Zr-O-N system during air oxidation (submitted to JNM)

2nd: Experimental data review, further SETs and preliminary model development

2nd year PhD:

20th QWS: Overview of the air oxidation kinetic modeling

SETs and Raman: Nov.-Dec. 2014 at KIT

3rd: Mathematical model and formulate for the code model

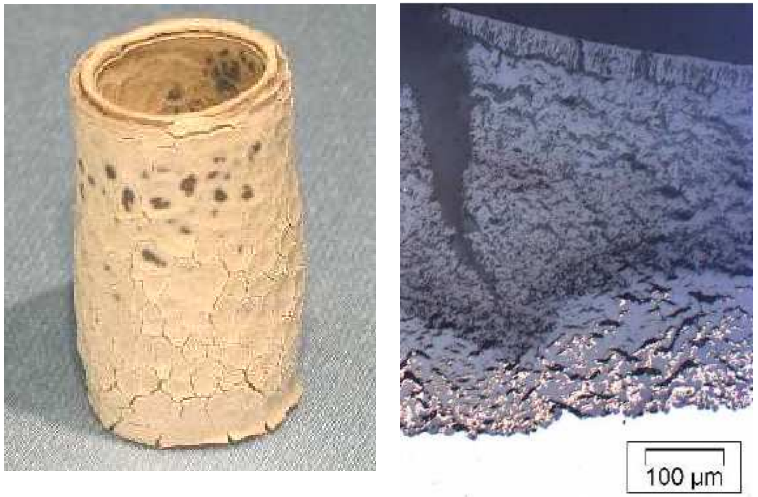
2nd and 3rd year PhD:

PSI-KIT air oxidation model

PSI-KIT joint PhD project

Literature review: Oxidation of Zr in presence of N_2

- No significant nitriding in pure nitrogen environment with fresh Zr
- Nitrogen will react in:
  - Nitrogen/oxygen enviroment
  - nitrogen/steam environment
  - Pure nitrogen environment with pre-oxidized Zr
    oxide or dissolved oxygen in Zr is needed for nitriding
    → Pre-transition
- Three possible mechanism has been identified:
  - Self-sustained nitriding-reoxidation process
  - Sudden kinetic transition (breakaway like process)
  - Gradual kinetic transition (porosity development)



Zry-4 cladding oxidation for 1 hour at 1000°C in air

M. Steinbrück et al., Prototypical Experiments on Air Oxidation of Zircaloy-4 at High Temperatures, Forschungszentrum Karlsruhe, FZKA 7257, January 2007

Ongoing research…

Accelerated kinetics

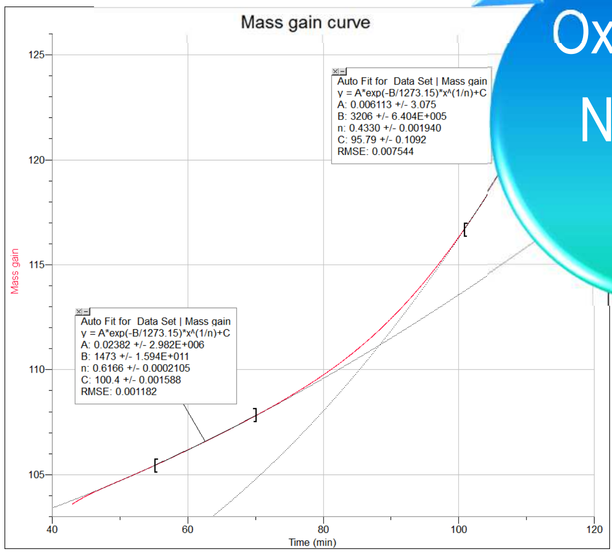
Heat generation

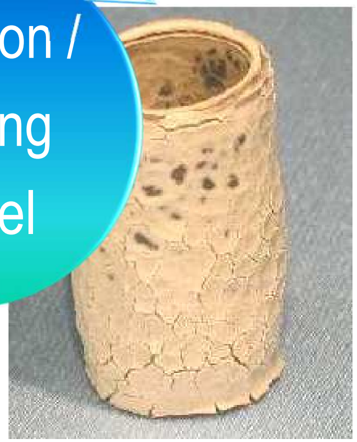
Chemical effects ⟷ **Mechanical effects**

Porosity development

Macro cracks formation

Oxidation / Nitriding model





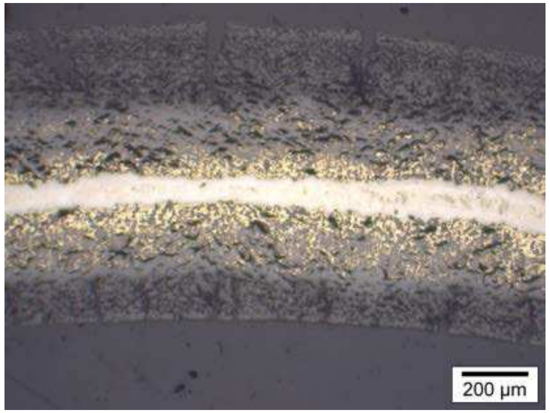
Zry-4 cladding oxidation for 1 hour at 1000ºC in air

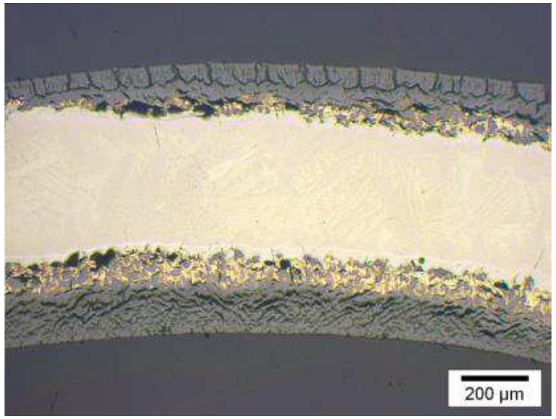
Other Reactions?

KIT seperate effect tests to examine differences between air and steam/nitrogen mixtures.

Hydrogen may be absorbed by the metal or released to the environment.

1000°C, 1 hour





M. Steinbrueck et al, NUGENIA TA 2.1 meeting, Jandia, Spain 2015

Other Reactions?

KIT seperate effect tests to examine differences between air and steam/nitrogen mixtures.

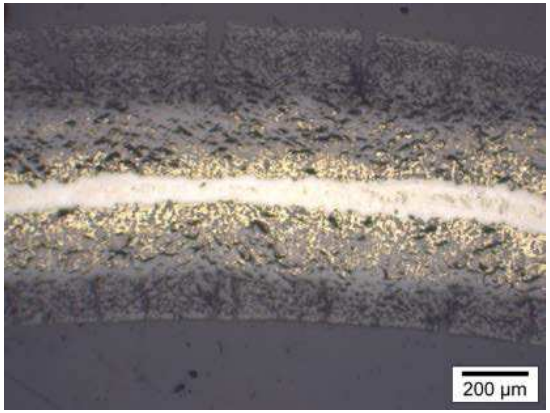
Hydrogen may be absorbed by the metal or released to the environment.

Hydrogen reduces locally the O_2 concentration and stabilizes the ZrN and Hydrogen affects the stability of the remaining metal due to Hydrogen uptake.

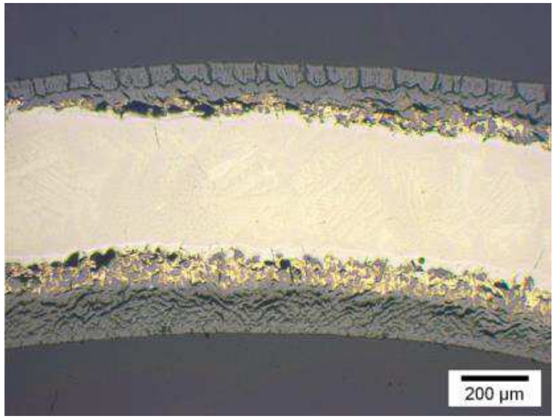
Hydrogen/Steam mixtures reacts more aggresive than air with Zircaloy cladding.

1000°C, 1 hour

N_2/H_2O 80/20



N_2/O_2 80/20



M. Steinbrueck et al, NUGENIA TA 2.1 meeting, Jandia, Spain 2015

Other phenomena at SFP calculations

SFP policies of countries are different in case of loss of cooling accidents.

Some countries use the feed and boil strategy.

Questions:

- What happens with crud at heatup and boiling?
- What happened with fission products during feed and boil?
- What is the atmospheric composition during feed and boil?

- Is there a plan to include models for SFP accidents?

Summary and Outlook

- Literature review for oxidation of Zr in the presence of nitrogen have been performed

- Weakness of the current code models have been identified
  - Not all the models take nitrogen as an active specie
  - No reoxidation of nitrides are currently modeled
  - Mechanical changes (porosity development) not taken into account

- Three possible mechanism have been identified for the nitriding process
  - Self-sustained nitriding-reoxidation process
  - Sudden kinetic transition (breakaway like process)
  - Gradual kinetic transition (porosity development)

- Next step for the air oxidation modeling
  I. Support the identified mechanisms for the modeling with Separate Effect Tests and Raman experiments (running)
  II. Further SET's for specific cases
  III. Formulate the model
  IV. Validate with independent experimental data

Thank you for your attention