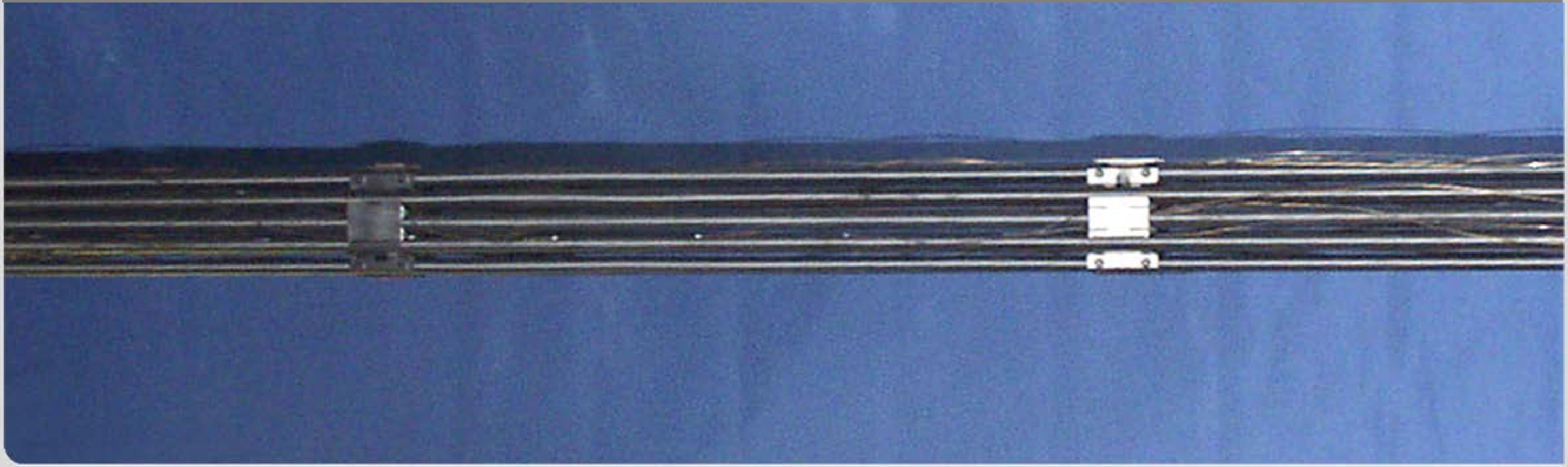
Air ingress modeling using ASTEC

-towards new activities at KIT-

H. Muscher

20th International QUENCH Workshop, Karlsruhe, 11.-13. Nov. 2014

Institute for Applied Materials
Materials Process Technology, Programme NUKLEAR



Introduction/ Motivation/ Outline

- Quench tests and the corresponding pre-/ post-test simulations- a success story:
- *QUENCH tests provide data for development of models & codes:*
- Code validation against experiments (many times successfully done for different bundle tests, although Q-10/ Q-16 not with ASTEC)
- In former times: Appl. of ASTEC on quench problems other than nitradation / e.g. Q-06/Q-14 comparative mat. studies Zry-4, M5®, E110

- Progress still needed in modeling of air ox. of Zr in SA-codes
- Adopting of ASTEC ICARE core degradation tool to describe kinetic transition from a diffusion-controlled process towards an accelerated ox -step

- The CESAM-WP general objectives /the scope of the work were outlined as follows :

  development concerning ASTEC IDs,
  performing ASTEC runs
  additional sensitivity analysis (parameter studies)

- Needed: temp. histories & oxide axial profiles according to CESAM-needs as well as the specific Q-facilities **geometry, chronology of main events of particular tests -** given in **quick look tables & KIT reports**

ASTEC v.2.0-QUENCH simulations presented in Ljubljana & Warsaw

The aim now is to present thermodynamic data for its further usage adopting ASTEC for additional investigating Q-10/Q-16, among others the H_2 source term resulting from the water injection into an uncovered core as well as the high temp. behavior of core materials under transient conditions.

- contract between GRS and KIT on ASTEC usage signed
- "Overview of the integral code ASTEC v2.0“
- "Evolution of ASTEC v2.0-rev1 with respect to the v2.0 source”
- **ASTEC** principles and **general** modeling **features**
- focus on the **ICARE** part within “ASTEC Training Course material“
- detailed ICARE user's manual; guidelines; **MARCUS usage** (web)
- At first: Understanding of "quench05.dat“ input deck

  in the context of the KIT- QUENCH facility **real design** (TCs, etc)
- **best-estimate** ASTEC- **input deck** for Q tests : **<u>Q-14</u>, Q-11;Q-08**

  Stabilization/ Heat up/ Pre-ox/ Transient heat up/ Quenching

- *activities: KIT Internal **Q-14** report published + available; NUKLEONIKA paper submitted*

- Q-**10**/-**16** to be further simulated **work is underway**
- *KIT-ASTEC **1.3** work done already 2006 by others (nodalization schemes, data fields, etc.*

Further development of **air ingress** Q-10/ Q-16 IDs

Q-10; Q-16 test conduct

The Q-10 test phases were as follows:

Heatup *and facility check.*

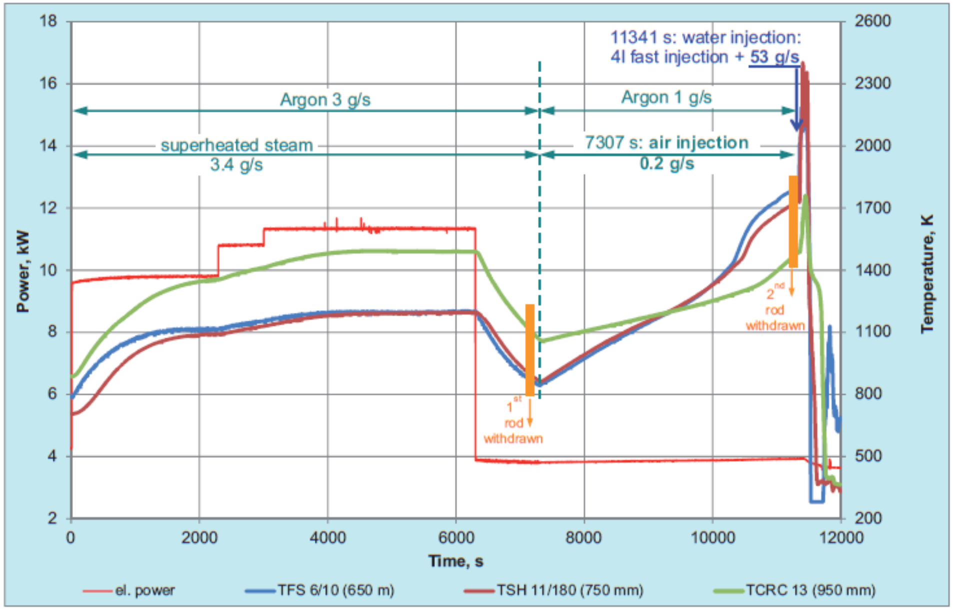
Phase I *Stabilization at a const. temp.*

Phase II *heat-up ~0.3-0.6 K/s*

Phase III *Long pre-ox of the test bundle in a flow of superheated* ***Ar /steam*** *at 1620-90K for ca. 113min, then cool-down lasting 38 min to 1190K*

Phase IV *steam flow replaced by 1/3 of he mass flow rate by air: duration 30 min*

Phase V *complete quenching of the bundle after 150s by a flow of water.*



QUENCH-16; Test conduct showing electric power input and selected temperatures.

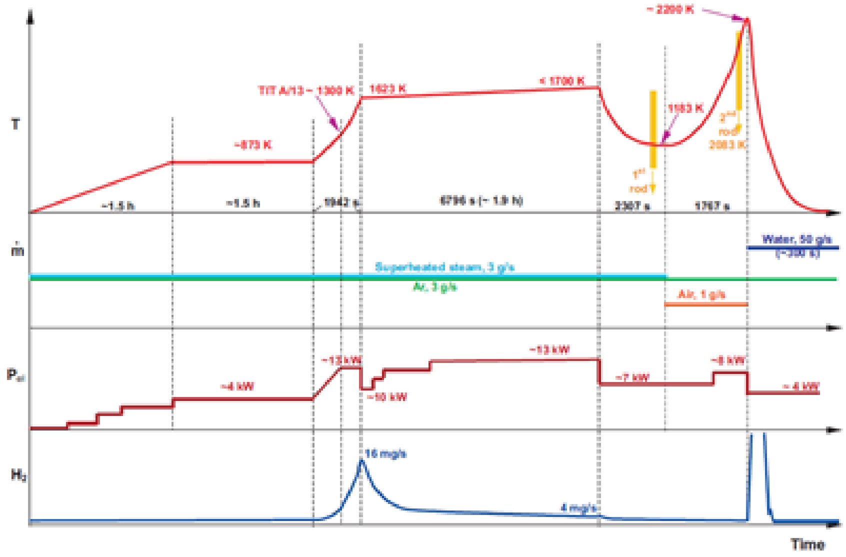
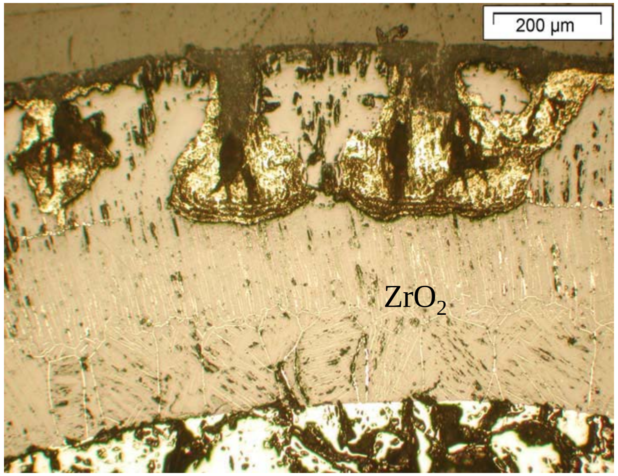
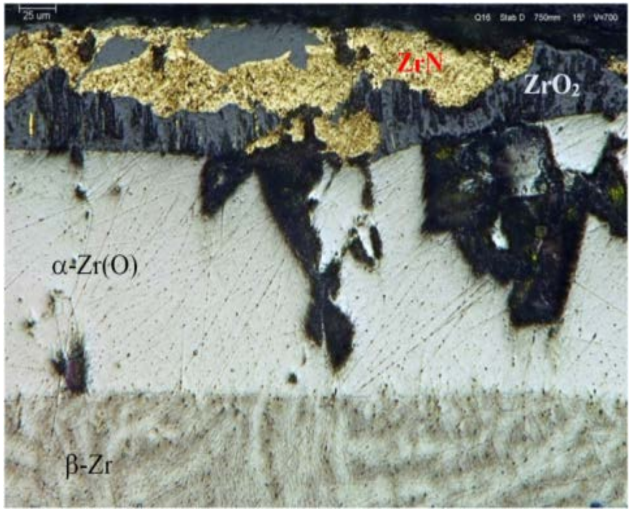


Fig 21 QUE10 test conduct.cdr
07.04.05 - IMF

QUENCH-10; test as conducted

Metallography of cladding cross sections





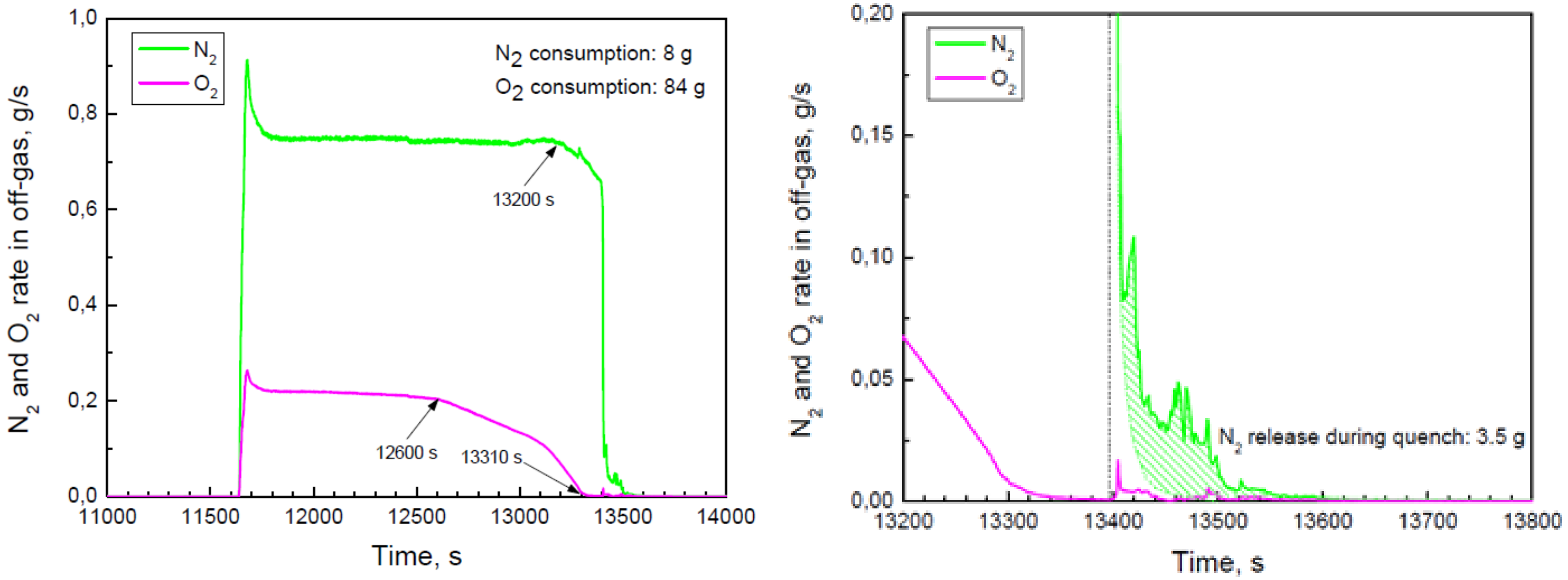
Stuckert *et.al.*

Q-10: only local presence of ZrN in ZrO$_2$ layer

Q-16: global presence of ZrN in ZrO$_2$ layer

Test	Quench medium and injection rate	Temp. at onset of flooding[1)]	Max. ZrO$_2$ before transient[2)]	Max. ZrO$_2$ (X s) before flooding[2)]	Posttest average ZrO$_2$ thickness[3)]	H$_2$ production before / during cooldown	Remarks, objectives
QUENCH-10 July 21, 2004	Water 50 g/s	≈ 2200 K	514 µm	613 µm (at 850 mm)	completely oxidized	48 / 5	LACOMERA Project; Air ingress.
QUENCH-16 July 27, 2011	Water 53 g/s	≈ 1870 K*	135 µm	130 µm at 450-950 mm, breakaway	1075 µm at 550-650 mm	144 / 128	LACOMECO Project; Air ingress.

Complete consumption of O_2 & partial consumption of N_2 during air ingress



N_2 & O_2 rates measured by MS in the off gas: Q-16 /*le*; Q-10/*ri*

Morphology of the phases after the air attack/ SRT; Q-16 test

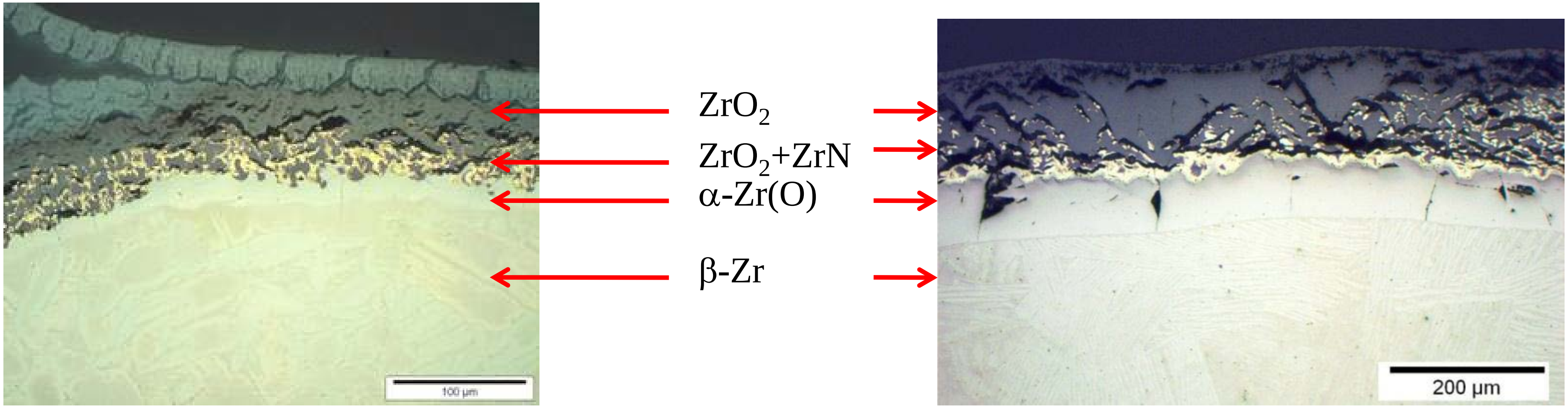
[ZrN] phases are formed in α-Zr(O)-phase, i.e. ZrO_x, as well as in nonstoichiometric ZrO_{2-x}. So, [ZrN] appeares in the vicinity of ZrO_2/α-Zr(O) interface.

The speed of [ZrN] formation is determined by the N_2 diff. in ZrO_2 layer, that is

1) by D_N coeff. taking into account its possible enhancement due to porosity as well as
2) by distance of the ZrO_2/α-Zr(O) interphase.

Single rod test (Steinbrück)
T=1273K

QUENCH-16 test T=1800K



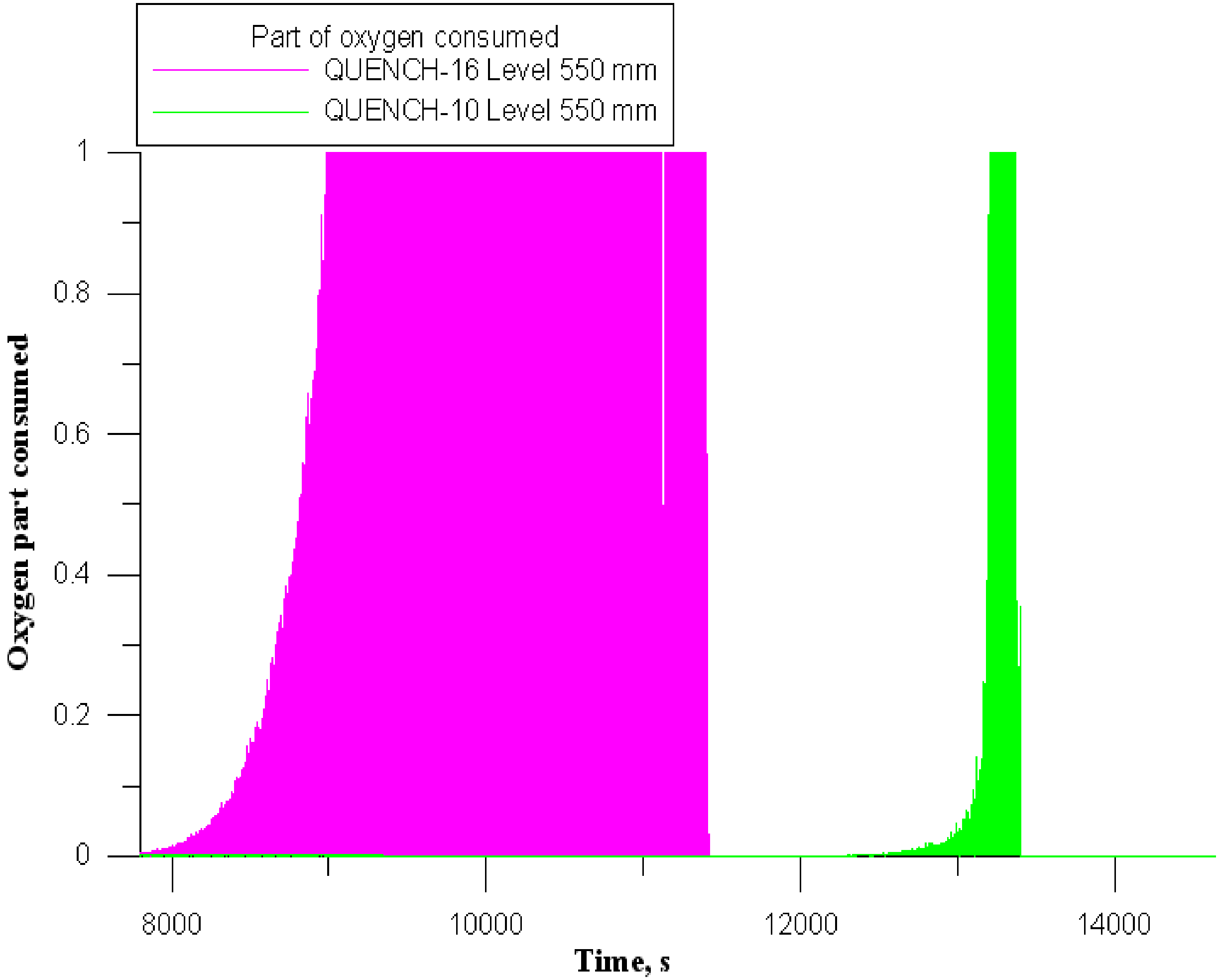
ZrO_2

ZrO_2+ZrN

α-Zr(O)

β-Zr

Local O_2 starvation in Q-10/Q-16 tests, given axially



Calc. local O_2 starvation in Q-16 & Q-10 at Level 550 mm

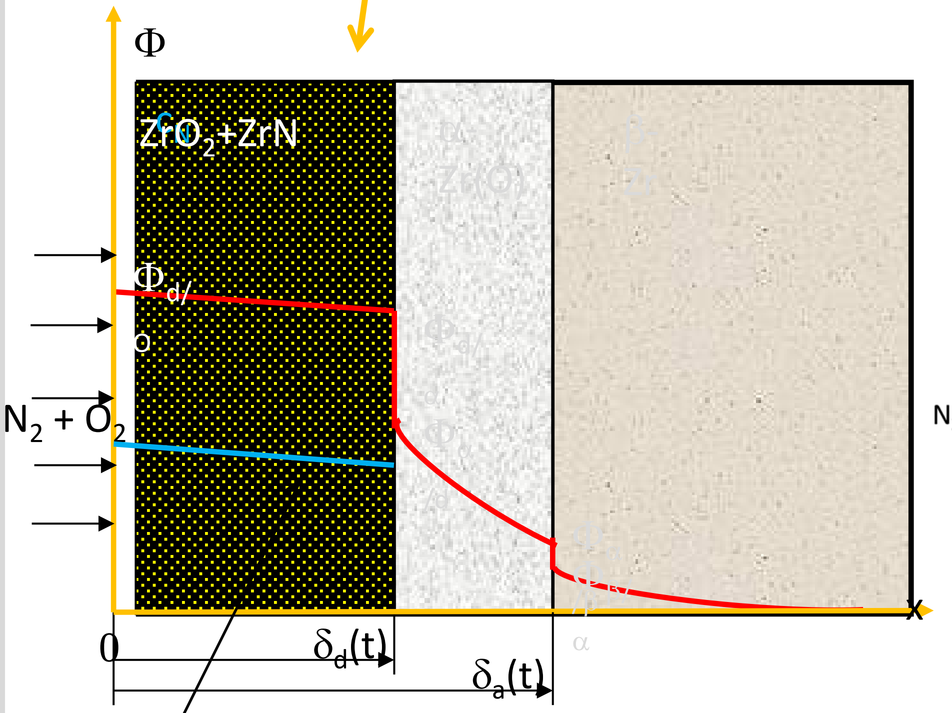
(A.Vasiliev; IBRAE)

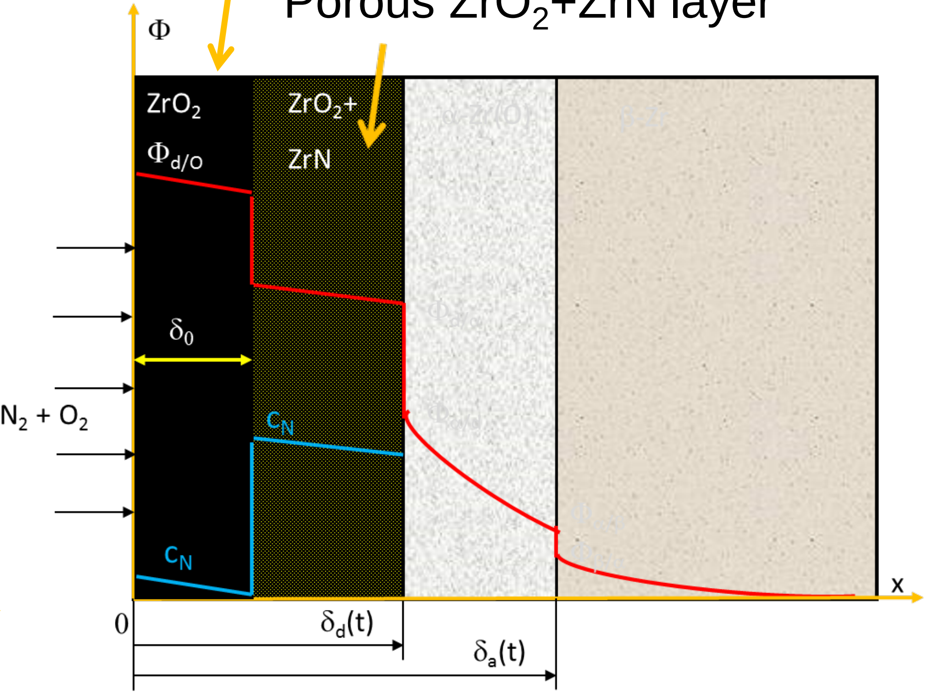
3- layer vs. 4- layer cladding oxidation in Air: diff. schemata

Porous ZrO_2+ZrN layer

Dense ZrO_2 layer

Porous ZrO_2+ZrN layer





nitrogen molar concentration

(A.Vasiliev; IBRAE)

Presentation of [ZrN] systems investigated *worldwide*

Substitution of oxygen by nitrogen

$$3(O^{2-})_O = 2(N^{3-})_O + (\mathrm{Vacancy})_O$$

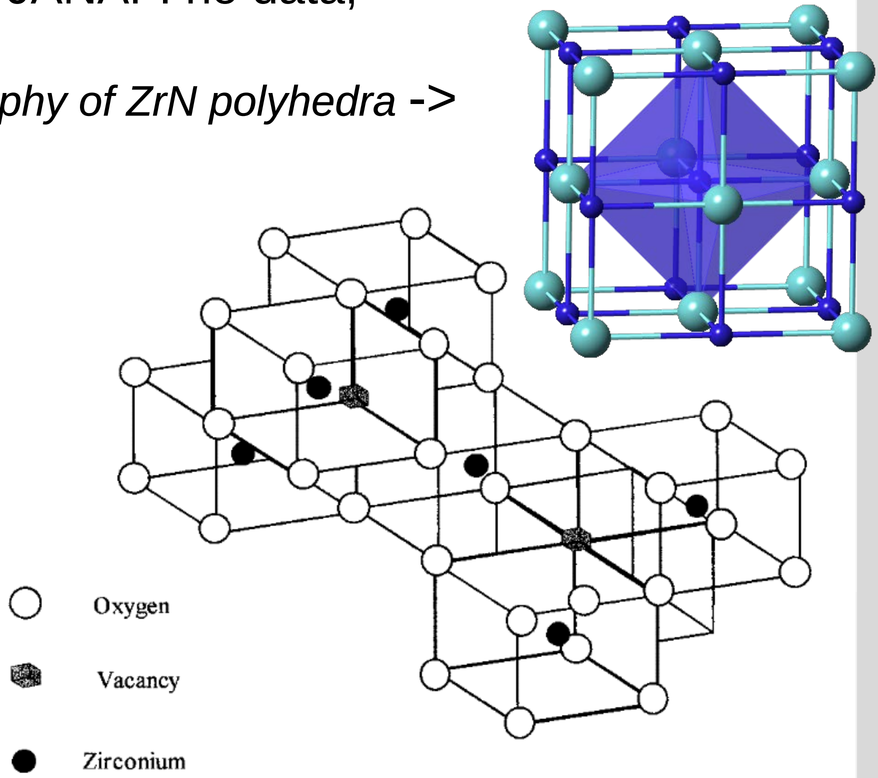
Goal: to develop systematic understanding of the O→N substitution in variety of nitride / oxynitride phases giving Δh_f and c_p (T) numerical values of Zr ternary oxynitrides: FactSage, HSC, Barin, Mils, JANAF: no data, elsewhere ThermoCalc (KIT), Glushko

A different crystalography of ZrN polyhedra ->

The results of recent studies in the system Zr–O–N include all zirconium oxynitride phases synthesized by direct nitridation of ZrO_2, belonging to the system ZrO_2–Zr_3N_4.

β' phase	$Zr_7O_{11}N_2$
β'' phase	$\sim Zr_7O_{9.5}N_3$
β phase	$Zr_7O_8N_4$

The β type phases are structurally derived from the fluorite-type structure of cubic zirconia. Anion vacancies are ordered in the lattice which leads to a trigonal distortion of the fluorite structure. Details of the crystal structures



Bevan cluster—a building unit in β-type phases.

Discussion of the Sanggil Park scheme; Gutzov´s statics: K_p (T)

Given at EDF, Paris, 20 May 2014

$$N_2 + 3O_O^X \longrightarrow 2N'_O + V_O^{\circ\circ} + \frac{3}{2}O_2$$

$$2N(ZrN) + 3O_O^X \longrightarrow 2N'_O + V_O^{\circ\circ} + 3O(ZrN)$$

$$2N'_O + V_O^{\circ\circ} + \frac{3}{2}O_2 \longrightarrow N_2 + 3O_O^X$$

$$K_I = \frac{[V_O^{\circ\circ}]}{(1 - 3[V_O^{\circ\circ}])^3} {p_{N_2}}^{-1} {p_{O_2}}^{\frac{3}{2}}$$

$$K_{II} = K_I p_{N_2} {p_{O_2}}^{-\frac{3}{2}} \times \frac{{a_O}^3}{{a_N}^2}$$

In the beginning: t-ZrO_2 and α-Zr(O,N)

Step I. Nitrogen incorporation (gas-solid reaction) near the oxide-metal interface:

Step III. Nitrogen rich part of Zr_3N_4/ γ-Zr_2ON_2 system near the interface

Step IV. Decomposition of Zr_3N_4/ γ-Zr_2ON_2 system to ZrN and m-ZrO_2 and β-type oxynitride phases from 800°C

Step V. Accelerated self-sustaining nitridation process (solid solution reaction and reoxidation)

In the end: m-ZrO_2

$$[N'_O]^2[V_O^{\circ\circ}] = KP_{O_2}^{-3/2}P_{N_2}[O_O^x]^3,$$

where

$$[O_O^x] = [O_O^x]^* - 3[V_O^{\circ\circ}]_N$$

$$[V_O^{\circ\circ}] = [V_O^{\circ\circ}]_N$$

$[O_O^x]^*$ is the value in the case of pure ZrO_2.

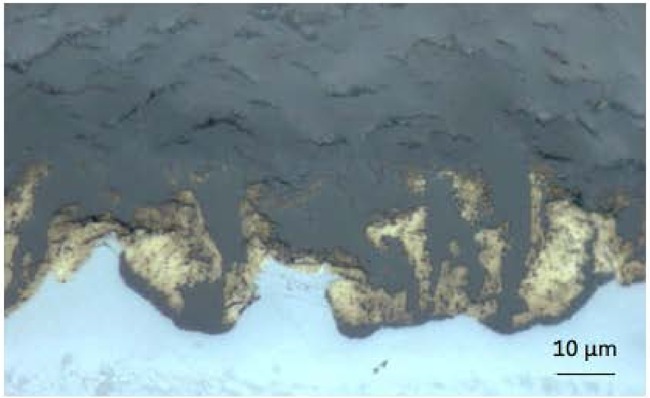
with

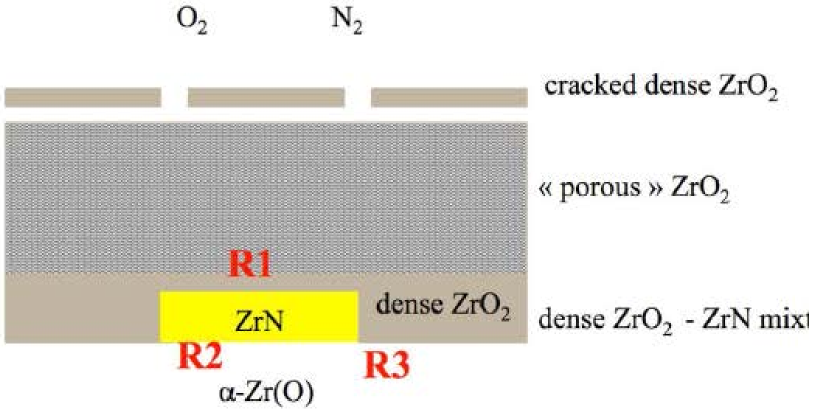
$$KP_{O_2}^{-3/2}P_{N_2} = \frac{4[V_O^{\circ\circ}]_N^3}{([O_O^x]^* - 3[V_O^{\circ\circ}]_N)^3}$$

$$[V_O^{\circ\circ}]_N = \tfrac{1}{2}[N'_O]$$

Discussion of reoxidation *(loops not excluded)*

Representation of the degradation process





Reaction 1 : oxidation of ZrN
$PBR_{ZrO2/ZrN}$= 1,47 → volume increase

$$O_2 + ZrN \rightarrow ZrO_2 + N^*$$

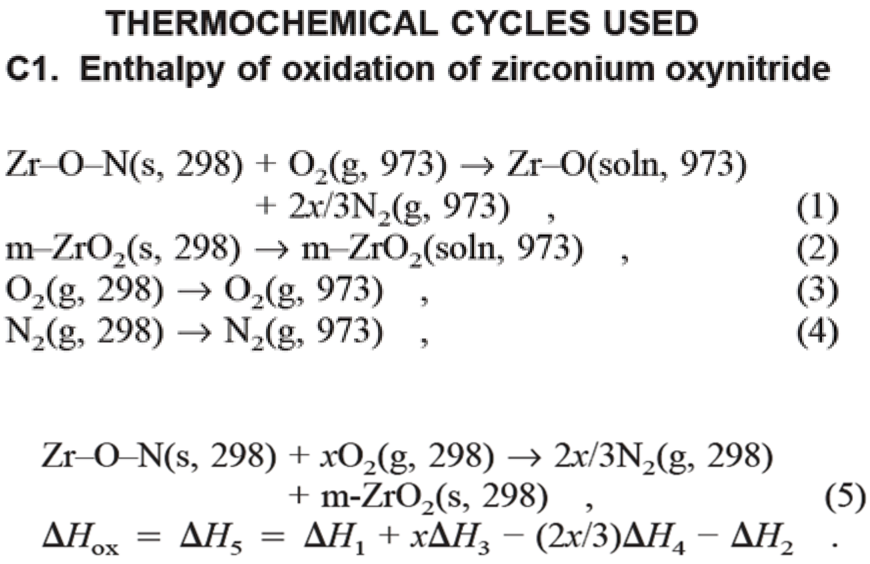
Reaction 2 : nitridation of metal
$PBR_{ZrN/Zr}$ =1,03 → no volume change

$$N^* + ZrO_x \rightarrow ZrN + x\,O^*$$

Reaction 3 : oxidation of metal
$PBR_{ZrO2/Zr}$ =1,51 → volume increase

$$(2 - x)O^* + ZrO_x \rightarrow ZrO_2$$

The according Hess–schemes (1^{st} law) *-Navrotsky, Malodetsky-*



THERMOCHEMICAL CYCLES USED

C1. Enthalpy of oxidation of zirconium oxynitride

$$\text{Zr–O–N}(s, 298) + O_2(g, 973) \rightarrow \text{Zr–O}(\text{soln}, 973) + 2x/3N_2(g, 973) \quad , \qquad (1)$$

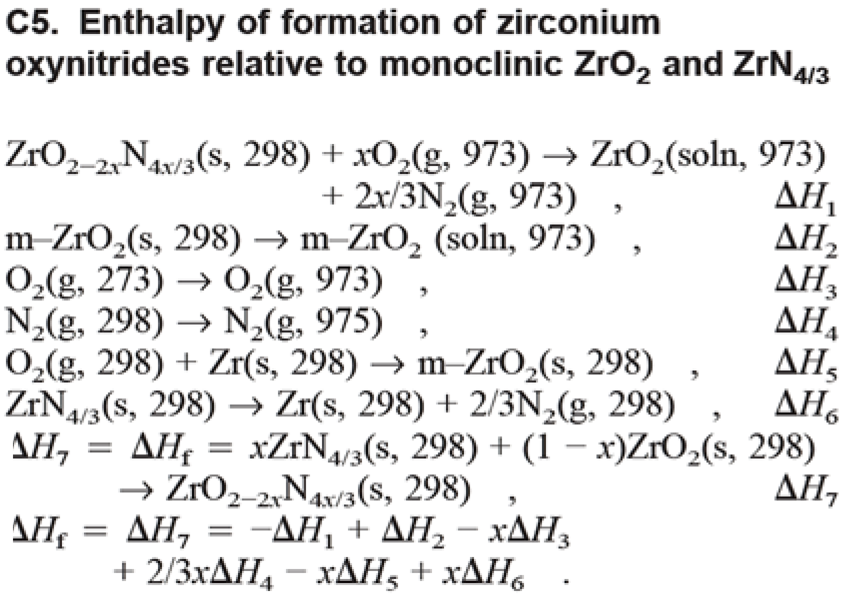
$$\text{m–ZrO}_2(s, 298) \rightarrow \text{m–ZrO}_2(\text{soln}, 973) \quad , \qquad (2)$$

$$O_2(g, 298) \rightarrow O_2(g, 973) \quad , \qquad (3)$$

$$N_2(g, 298) \rightarrow N_2(g, 973) \quad , \qquad (4)$$

$$\text{Zr–O–N}(s, 298) + xO_2(g, 298) \rightarrow 2x/3N_2(g, 298) + \text{m-ZrO}_2(s, 298) \quad , \qquad (5)$$

$$\Delta H_{ox} = \Delta H_5 = \Delta H_1 + x\Delta H_3 - (2x/3)\Delta H_4 - \Delta H_2 \quad .$$



C5. Enthalpy of formation of zirconium oxynitrides relative to monoclinic ZrO_2 and $ZrN_{4/3}$

$$ZrO_{2-2x}N_{4x/3}(s, 298) + xO_2(g, 973) \rightarrow ZrO_2(\text{soln}, 973) + 2x/3N_2(g, 973) \quad , \qquad \Delta H_1$$

$$\text{m–ZrO}_2(s, 298) \rightarrow \text{m–ZrO}_2\ (\text{soln}, 973) \quad , \qquad \Delta H_2$$

$$O_2(g, 273) \rightarrow O_2(g, 973) \quad , \qquad \Delta H_3$$

$$N_2(g, 298) \rightarrow N_2(g, 975) \quad , \qquad \Delta H_4$$

$$O_2(g, 298) + Zr(s, 298) \rightarrow \text{m–ZrO}_2(s, 298) \quad , \qquad \Delta H_5$$

$$ZrN_{4/3}(s, 298) \rightarrow Zr(s, 298) + 2/3N_2(g, 298) \quad , \qquad \Delta H_6$$

$$\Delta H_7 = \Delta H_f = xZrN_{4/3}(s, 298) + (1 - x)ZrO_2(s, 298) \rightarrow ZrO_{2-2x}N_{4x/3}(s, 298) \quad , \qquad \Delta H_7$$

$$\Delta H_f = \Delta H_7 = -\Delta H_1 + \Delta H_2 - x\Delta H_3 + 2/3x\Delta H_4 - x\Delta H_5 + x\Delta H_6 \quad .$$

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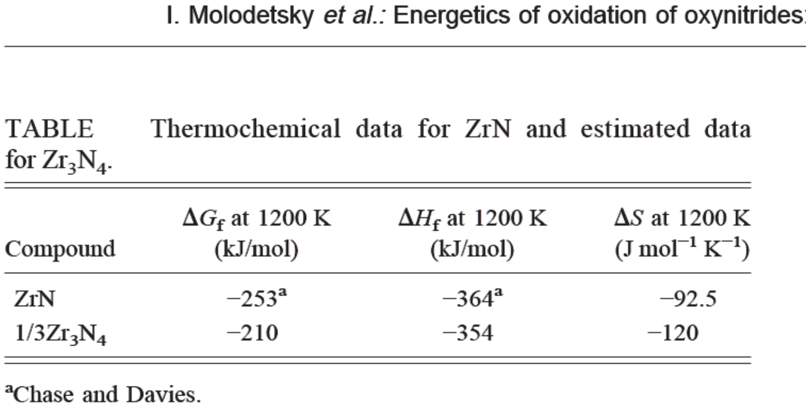
J. Mater. Res., Vol. 15, No. 11, Nov 2000

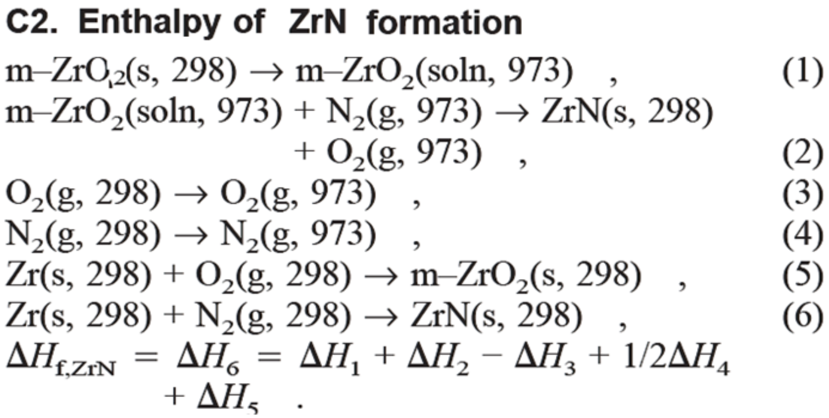


I. Molodetsky *et al.*: Energetics of oxidation of oxynitrides

TABLE Thermochemical data for ZrN and estimated data for Zr_3N_4.

Compound	ΔG_f at 1200 K (kJ/mol)	ΔH_f at 1200 K (kJ/mol)	ΔS at 1200 K (J mol^{-1} K^{-1})
ZrN	−253[a]	−364[a]	−92.5
$1/3Zr_3N_4$	−210	−354	−120

[a] Chase and Davies.



C2. Enthalpy of ZrN formation

$$\text{m–ZrO}_2(s, 298) \rightarrow \text{m–ZrO}_2(\text{soln}, 973) \quad , \qquad (1)$$

$$\text{m–ZrO}_2(\text{soln}, 973) + N_2(g, 973) \rightarrow ZrN(s, 298) + O_2(g, 973) \quad , \qquad (2)$$

$$O_2(g, 298) \rightarrow O_2(g, 973) \quad , \qquad (3)$$

$$N_2(g, 298) \rightarrow N_2(g, 973) \quad , \qquad (4)$$

$$Zr(s, 298) + O_2(g, 298) \rightarrow \text{m–ZrO}_2(s, 298) \quad , \qquad (5)$$

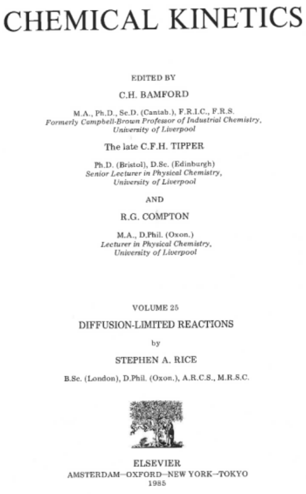
$$Zr(s, 298) + N_2(g, 298) \rightarrow ZrN(s, 298) \quad , \qquad (6)$$

$$\Delta H_{f,ZrN} = \Delta H_6 = \Delta H_1 + \Delta H_2 - \Delta H_3 + 1/2\Delta H_4 + \Delta H_5 \quad .$$

Thermochemistry of Zr- oxynitrides; Kinetics textbooks *recommended*

TABLE Enthalpy of oxidation per nitrogen atom in Zr–N–O

M	r_M/r_{Zr}	Phase	$\Delta H_{ox(N)}$ (kJ/mol of N)	No. of points (no. of compositions)
···	1	Cubic ordered	−468 ± 16	6
		β–Zr–N–O	−506 ± 16	4
		γ–Zr–N–O	−538 ± 3	2



CHEMICAL KINETICS

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VOLUME 25

DIFFUSION-LIMITED REACTIONS

by

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AMSTERDAM–OXFORD–NEW YORK–TOKYO
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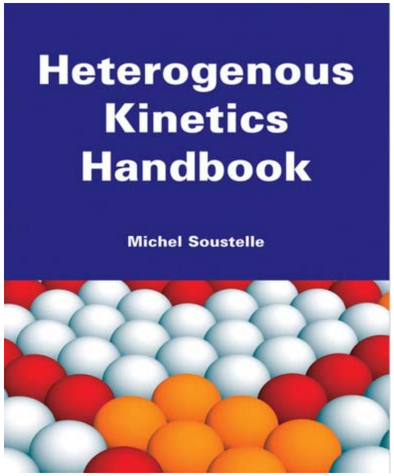
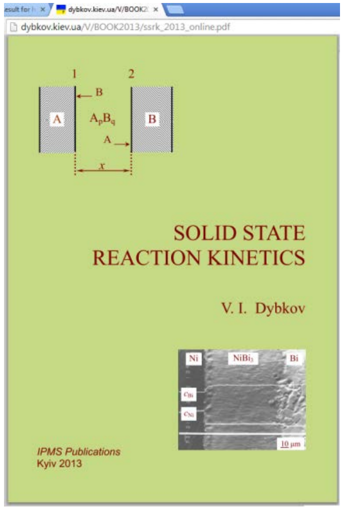


Heterogenous Kinetics Handbook

Michel Soustelle



dybkov.kiev.ua/V/BOOK2013/ssrk_2013_online.pdf

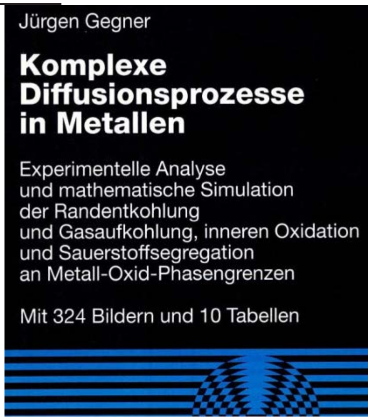
SOLID STATE
REACTION KINETICS

V. I. Dybkov

IPMS Publications
Kyiv 2013

Thermochemical data

	$H_{975} - H_{298}$
O_2	21.8
N_2	20.59



Jürgen Gegner

Komplexe Diffusionsprozesse in Metallen

Experimentelle Analyse
und mathematische Simulation
der Randentkohlung
und Gasaufkohlung, inneren Oxidation
und Sauerstoffsegregation
an Metall-Oxid-Phasengrenzen

Mit 324 Bildern und 10 Tabellen

TABLE Thermochemical data for Zr–N–O samples

XRD wt%	Oxynitride	ΔH_{ox} (kJ/mol)
0.63mZrO₂–0.37β′	$ZrO_{1.76}N_{0.16}$	−94.9 ± 3.0
0.46mZrO₂–0.54β″	$ZrO_{1.39}N_{0.4}$	−209.4 ± 9.7
0.56mZrO₂–0.44β	$ZrO_{1.34}N_{0.43}$	−266.4 ± 11.1
β		−220.3 ± 2.2
γ + β		−365.8 ± 4.0
γ + β		−348.3 ± 8.3

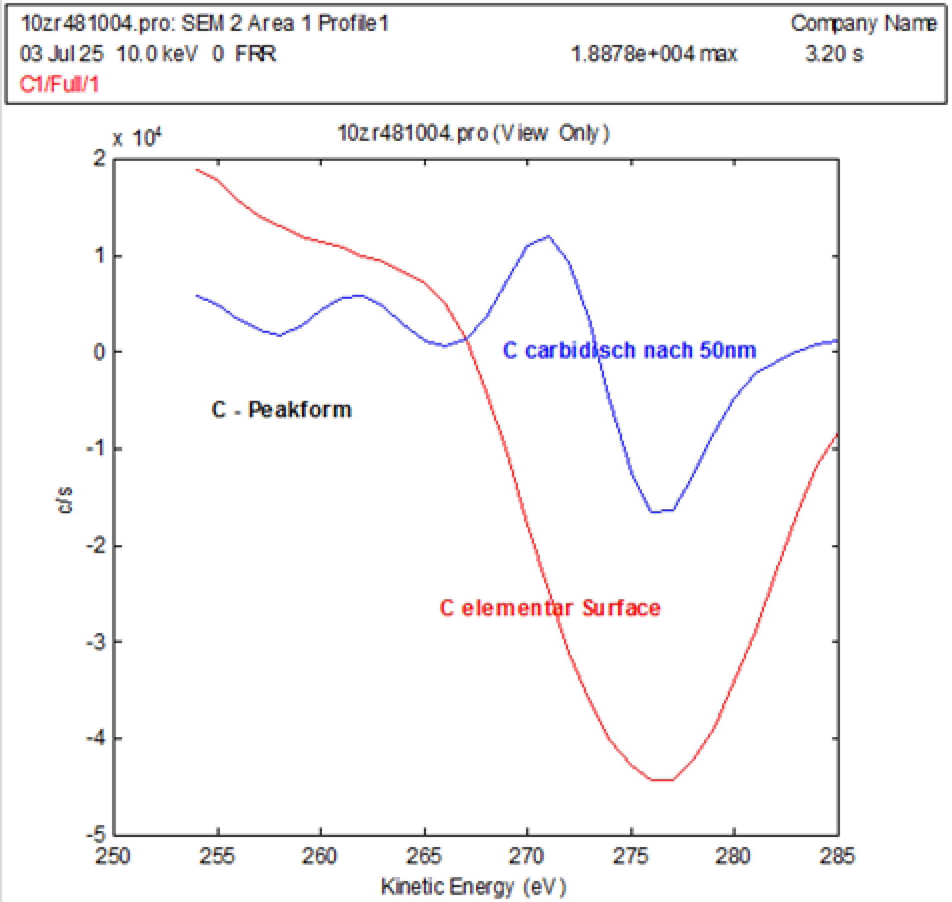
J. Mater. Res., Vol. 15, No. 11, Nov 2000

-O. Coindreau-

Hint of D. Powers: air incl. CO_2:- ZrC; (ZrOC)/ ZrN, ZrON ;

Discussion point: LM Corr. inhibition on SS with ZrH_2

E. Nold; H. Muscher (2003) ; Auger ES *PHI- nanoprobe: AES suitable for Q-metallography*



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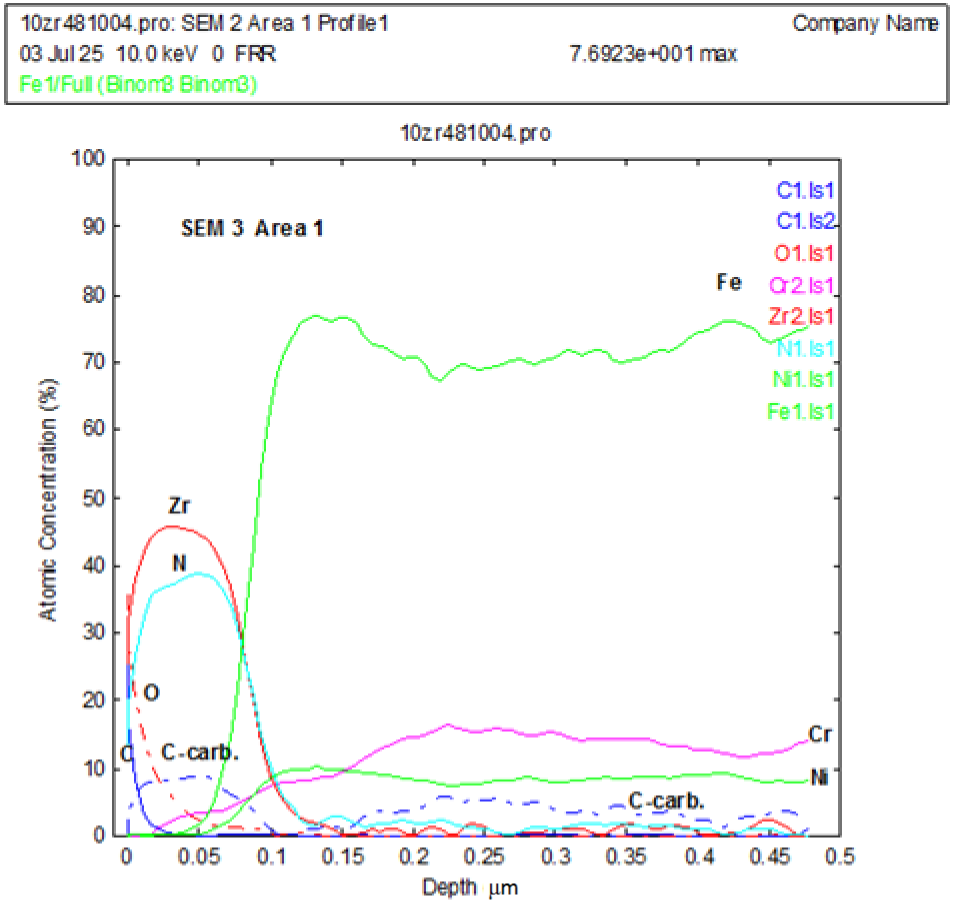
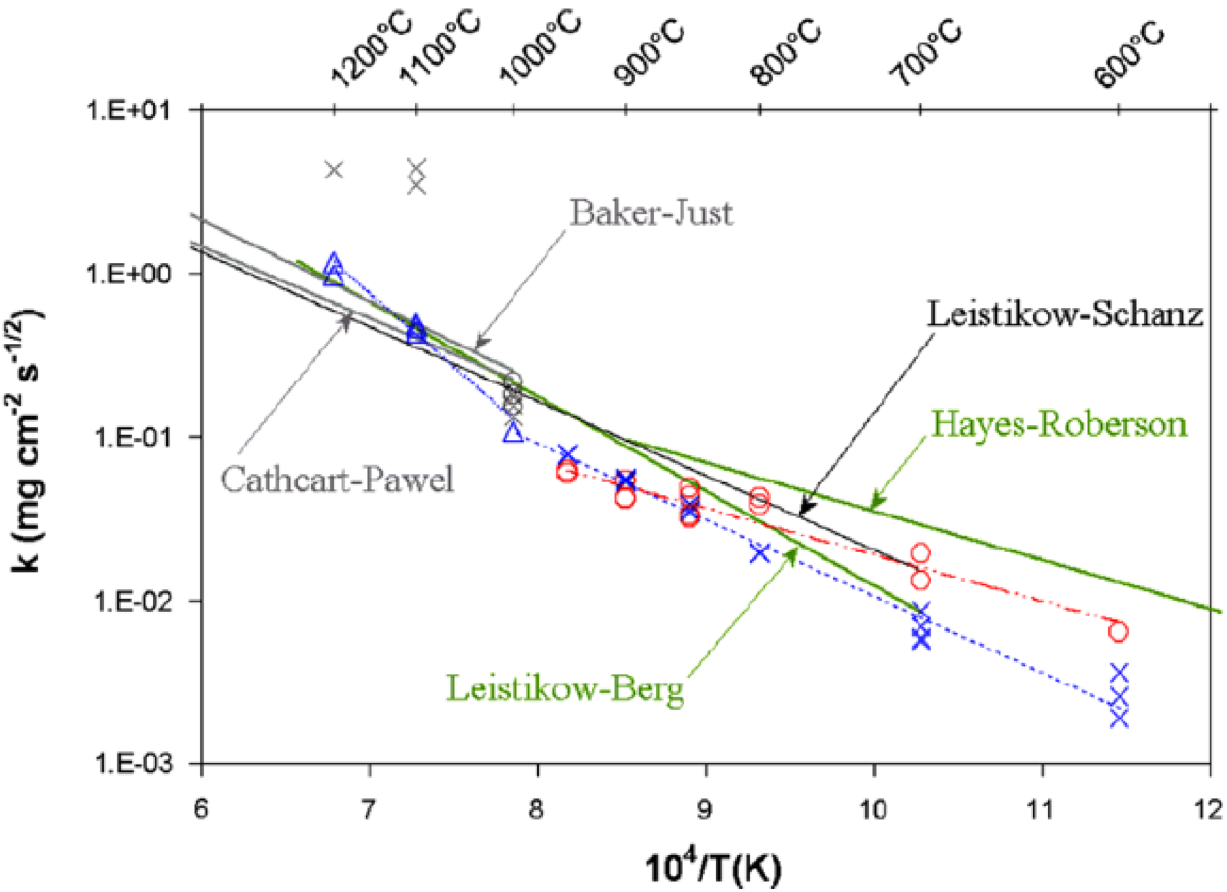
03 Jul 25 10.0 keV 0 FRR 1.8878e+004 max 3.20 s
C1/Full/1



10zr481004.pro: SEM 2 Area 1 Profile1 Company Name
03 Jul 25 10.0 keV 0 FRR 7.6923e+001 max
Fe1/Full (Binom3 Binom3)

Discussion of the ox-correlations for the pre-transition regime

C. Duriez et al. / Journal of Nuclear Materials 380 (2008) 30–45



Parabolic rate constants from isothermal air oxidation tests on bare Zircaloy-
Dotted lines are Arrhenius fits of the data, in the 600–1000 and 1000–1200 °C temperature ranges. Full lines: Leistikow–Schanz correlation (Zircaloy-4 steam oxidation, 600 °C < T < 1500 °C) (Volchek et al., 2004) and NUREG-1-2 recommendations for Zircaloy air oxidation (Powers et al., 1994).

and many others:

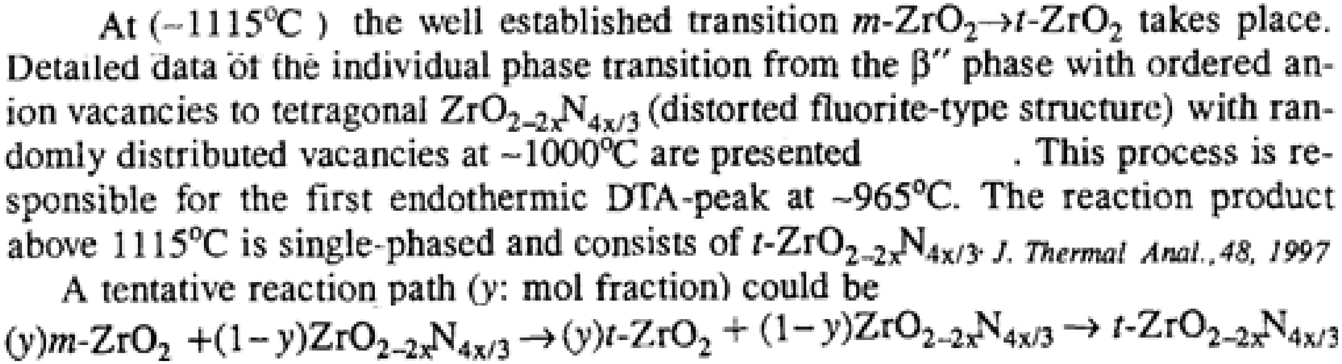
Steinbrück, LT
Steinbrück, HAT
Sokolov,
Berg,
Powers,
CODEX_AIT1,
AEKI Ar/O_2,
MOZART,
Best-fit, ICARE

for nitridation cases:

only 2 sets of A,E,n:
„Hollands w/o pre-ox“
„Hollands with pre-ox“

Zr ox. by steam/ a lit. overview/ AIT /Q-10 simulations / IRSN *et al.*

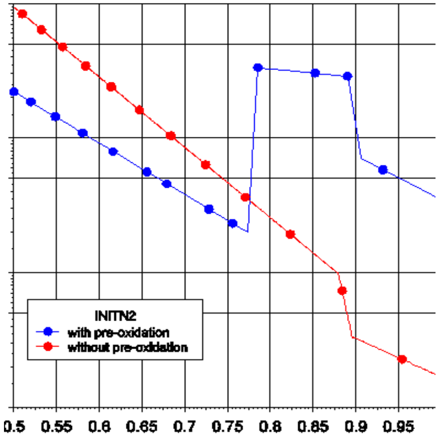
- [ZrN] formation: 2 correlations from Th. Hollands diss. can be used
  2 different reaction rates with & w/o pre-ox (PO)
  E_{act} of [ZrN] formation model for cases, where $p_{O2}/p < 1.0 \cdot 10^{-2}$;
  full rate could be calc`d if $p_{O2}/p < 1.0 \cdot 10^{-3}$ but no oxynitride modeling !



At (~1115°C) the well established transition $m\text{-}ZrO_2 \rightarrow t\text{-}ZrO_2$ takes place. Detailed data of the individual phase transition from the β″ phase with ordered anion vacancies to tetragonal $ZrO_{2-2x}N_{4x/3}$ (distorted fluorite-type structure) with randomly distributed vacancies at ~1000°C are presented . This process is responsible for the first endothermic DTA-peak at ~965°C. The reaction product above 1115°C is single-phased and consists of $t\text{-}ZrO_{2-2x}N_{4x/3}$. *J. Thermal Anal., 48, 1997*

A tentative reaction path (*y*: mol fraction) could be

$$(y)m\text{-}ZrO_2 + (1-y)ZrO_{2-2x}N_{4x/3} \rightarrow (y)t\text{-}ZrO_2 + (1-y)ZrO_{2-2x}N_{4x/3} \rightarrow t\text{-}ZrO_{2-2x}N_{4x/3}$$



- ➢ *The τ-dependency of the O_2 consumption could be calc`d in agreement with measured data with the correlation of Steinbrück with a shift in the interpolation region is adopted*
- ➢ *The O-starvation condition reaches also lower bundle elevations (→350 mm) :*

The τ-dependence of the N_2 consumption can be calc`d in good agreement with measured data with the correlation of Hollands (derived from SETs, Ziegler, KIT), when the case "w/o pre-ox" was taken;

<u>The ox of Zr-based claddings in the air behaves in a different way compared to ox. in steam</u>

- The ΔH_r **of Zr ox in air** is approx. 2 times larger than in **steam**.
- The kinetics of Zr ox **in air is non-parabolic** (approx**. linear, that is more strong**) in contrast to parabolic kinetics of Zr ox in steam.
- important is the diff of O atoms through porous ZrNx layers formed in α-Zr(O) layer. The role of **ZrNx formation in the O_2 starvation phase** is crucial for understanding the air ingress phenomena

-lit. partially taken from: O Coindreau-

Reactions with N_2 vs. O_2: concurrent processes that enhances ZrO_2 degradation

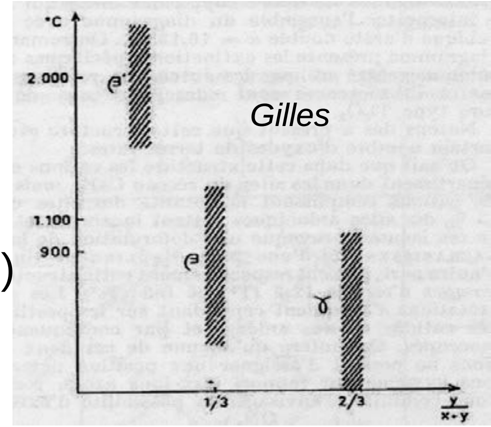
- Oxide end-phase: ZrO_2,
- Nitride **end-phase: Zr_3N_4**
- Oxynitride phases

(intermediate between ZrO_2 and $ZrN_{4/3}$ i.e. $ZrO_{2-2x}N_{4x/3}$)

β':$Zr_7O_{11}N_2$: 21% mol $ZrN_{4/3}$ i.e x= 3/14

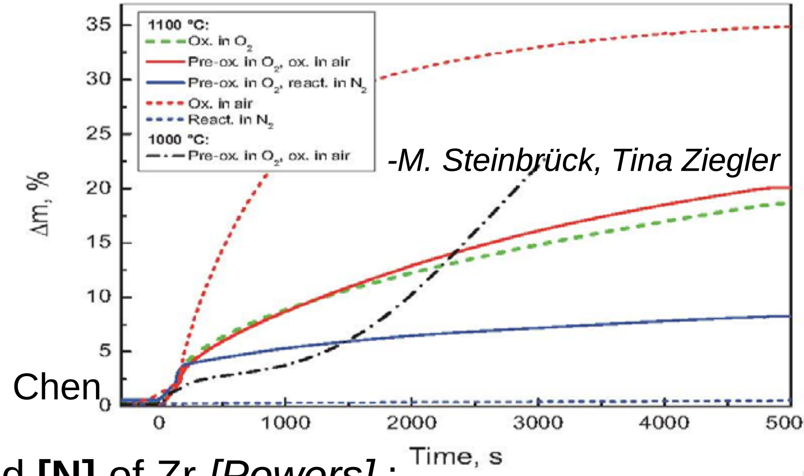
β: $Zr_7O_8N_4$: 43% mol $ZrN_{4/3}$ i.e x= 3/7

γ: Zr_2ON_2: 75% mol $ZrN_{4/3}$ i.e x=3/4



Gilles

Phase	Δ_r**G** [kJ/mol] at 2300K- data scarce
ZrO_2	-675 *[THERMODATA]*
ZrN	-151 *[THERMODATA]*
ZrON	1071*[Gutzov]*;**β''-phase** discovered:Thompson, Chen



-M. Steinbrück, Tina Ziegler

In case of **simultaneous** reaction of **Zr** with both **[O]** and **[N]** of Zr *[Powers]* :

- **ZrO_2** being the most stable compound; if nitriding takes place, the product will react with O_2
- Nitride will be detected only if the O_2 reaction speed becomes slower compared with nitride one

…i.e. in **starvation** case But lack of data above kinetics of O_2 reaction with [ZrN] products

- Me creep ⇒ ↑ area exposed to air/ further propagation to the whole sample
- Spatial non uniformity of the ox process ⇒ local init. of the breakaway transition (pores!);

Lessons learned from nitridation tests of ZrO_2 *(SET at IAM/ KIT)*

It has been shown *[Lerch et al.]* that ZrO_2 can be nitrided directly at temp. above 1400°C in a N_2 The kinetics follows a lin law K_O=128 m/s

$$ZrO_2 + \frac{2x}{3}N_2 \leftrightarrow ZrO_{2-2x}N_{4x/3} + xO_2$$

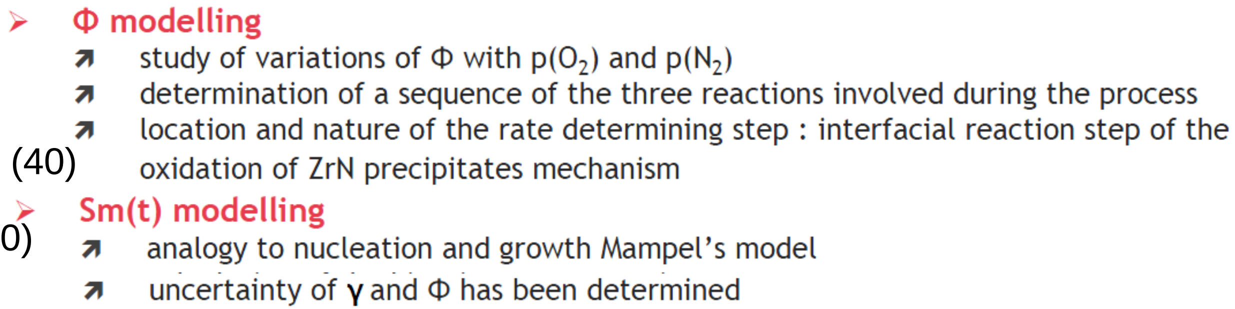
„pure N_2 not aggressive, air very aggressive vs. Zr"

Delmon kinetics (69)

Surface of nucleation

Kurt Mampel kinetics (40)

Kolmogorov-Avrami(40)



- **Φ modelling**
  - study of variations of Φ with $p(O_2)$ and $p(N_2)$
  - determination of a sequence of the three reactions involved during the process
  - location and nature of the rate determining step : interfacial reaction step of the oxidation of ZrN precipitates mechanism
- **Sm(t) modelling**
  - analogy to nucleation and growth Mampel's model
  - uncertainty of γ and Φ has been determined

description of the air ox model in ASTEC for validation on the QUENCH tests

- *in air ingress simulations, modeling of the pre-breakaway by a **sub-parabolic** law was required*
- ***k_p (T)** coeff. (rate) exhibits a strong dependence !*
- *at low **T(τ)** modeling of the post-breakaway **by an accelerated** law whereas lin kinetics observed at 850°C*
- *kinetic transition : determining of **τ_{break}** difficult, due to the non-uniformity of the ox-n process*
- *QUENCH-Inhomogeneities: oxide layer is thicker close to air inlet, where breakaway occurs at first*

T rises too quickly in the simulations of the air ingress done by the Q-community so far:
- Protective oxide layer not thick enough,
*- **T(τ)** correlations used up till now (for **non PO** cladding) overestimate the **Δm** (and so ΔHr) for **PO cladding***
Not enough N_2 taken from the gas phase:
Criterion to switch from ox. to nitridation based on adequate "critical starvation coeff."→ developped by Christa Bals
Not enough H_2 generated during reflood

ASTEC- ICARE nitriding- simulation work: a lit. summary

- It is reported in one ref.: - *JNM, 403 (2010) p.212* -, that an 1D-ASTEC simulation according to Olivia´s C. proposed kinetic model was already performed with 10 axial meshes+1 fluid CH.
- Double face oxidation is calc`d for the cylindrical Zry sample.
- To simulate the quasi-isothermal phase, the external wall temp is set as a BC. Temp., mass flow rate, non-condensable mass & void fractions were imposed as inlet BCs, too. Additionally a Δp outlet BC was used.
- Heat exchanges by conduction, convection, radiation were modeled. Convective HT coeff. between the gas and the walls is computed via Nu Nr.
- The radiation heat was computed between the cladding & the gas based on net radiation enclosure (surface to surface interactions); the reflection anisotropic factor was accordingly set for cladding, fuel rod simulators & shroud.
- The gray gas properties, the view factor between heating source & cladding were automatically updated while the core degradation proceeded.
- A still more accurate model describing oxy-nitriding responsible for formation of pores and fast cladding degradation, resulting in a SA is needed.
- While implementing the older & newer models in ASTEC, assistance of colleagues of IRSN /GRS will be needed in near future.

Conclusions/1

- we believe, that ASTEC has the potential to simulate QUENCH simple air ingress tests (some evidence was given by *Olivia C., JNM 405-2010,207ff*), nevertheless incorporating right $\boldsymbol{\Delta H_f}$ values of **[ZrON] (ternary)** phases– still a problem; as well as parts of the nitradation process itself

Dynamic behavior (τ dependences; evolution)/ profiles developed should evaluated …

- Reference ASTEC- ID with Gaëtan Guillards implementation of Olivia`s models – still to be adopted.

- Tables, figures & **standardized** spread sheets with the for **Q-10/ Q-16** material should be submitted to the CESAM at the next stage
- **Q-10/ Q-16 work is ongoing**/ not completed yet

✓ ASTEC **Ox models at the current State of the Art**/ *(but not nitriding!)*

✓ best fit (Schanz` recommendation) kinetics of **Zry ox by steam** /sensitivity studies possible

✓ **base case CESAM Q-10/Q-16 work** regarding temp- transients (work will be done similar to *A. Palagins* output presented at the 12th QWS, but now not for a SVECHA-single rod, but for complete bundle test)

Get detailed ox kinetics data /understanding of the Zr alloys ox mechanisms- important for SA !

Conclusions/2 - using the KIT-SET & Q-10 / Q-16 knowledge-

Air ox. in pre-breakaway regime - according to the parabolic law
Breakaway" or "pore-building" "transition: correlation between a critical Δm at transition point & crit. temp. → a hyperbolic law.
➢Assumption: breakaway transition is linked with transformation of t- ZrO_2 to m- ZrO_2 (B. Cox)

➢Post-breakaway: modeled by an accelerated law, scaling rate increasing linearly

➢Above 800°C, the kinetic transition is associated with **nitriding**. The ZrN formation begins because of a relative high N_2 thermodynamic activity in the gas mix due to O_2 **starvation**

➢Once nitriding begins, a porous oxide grows under the influence of a **self-sustained** reaction
➢Sequence **$ZrN + O_2 \rightarrow ZrO_2 + 1/2N_2$** ($N_2$ is trapped in the clad). It leads to fast degradation.

Perspectives (*future prospects)* further **validation of the models on Q-10/ Q-16**

- It is also needed to take into account the interdiff. of O_2 & N_2 in the mix containing possibly steam, H_2 & non-condensables ("real" SA-case, traces of that gases) (*according to A. Vasiliev)*
- At final phase of **Q-16** (quenching at water reflood or slow cooling) **reox.** of [ZrN] takes place.
- During this process N_2 & H_2 (in steam) is released and additional Δ**H** is generated It is important to incorporate in the models the Δ**H** values of both nitriding & re-ox, which are large.

Outlook/ next stages *(in the framework of CESAM, together with IRSN)*

✓ further ASTEC work: (sensitivities..) ; continuing with **new ASTEC v2.1 since 01/15**

✓ Nitradation: further modeling an obvious need– preliminary / lit. study done, also for ZrON–

✓ pointing out the key parameters in order to evaluate their impact on air ingress, bundle coolability, H_2 prod…. (especially for **Q-10/ Q-16**) – to be done

✓ Mandatory further work **still to be continued (CESAM/ Bologna 2/15)** : further developing of modified ASTEC IDs (Q-10, Q-16) modelling transients at first w/o nitradation effect, later fulfilling the complete set of recommendations…)

- both the instantaneous or cumulated (integral) $\mathbf{H_2}$ prod rates [kg/s]/ [kg] during the Q- phase
- both the instantaneous or cumulated (integral) $\mathbf{N_2}$ prod rates [kg/s]/ [kg] during reoxidation

- *N_2 Lacks in ICARE modeling identified, to be consulted with Gaëtan Guillard, Stéphane Bertusi, IRSN CS-SI (**development currently underway: ASTEC source code changes still needed**):*
- *suitable criterion to switch from oxidizing to nitration and vice versa (influence of the th-H)- according the technique of Christa Bals*
- *model for **reox of ZrN**/ oxide thicknesses at the end of the pre-ox phase, where reox. is quite low – to be developed. Specific models for reflood should be used including re- ox. after nitradation*

Acknowledgement: **thank you, J. Stuckert.**

Thank you all.