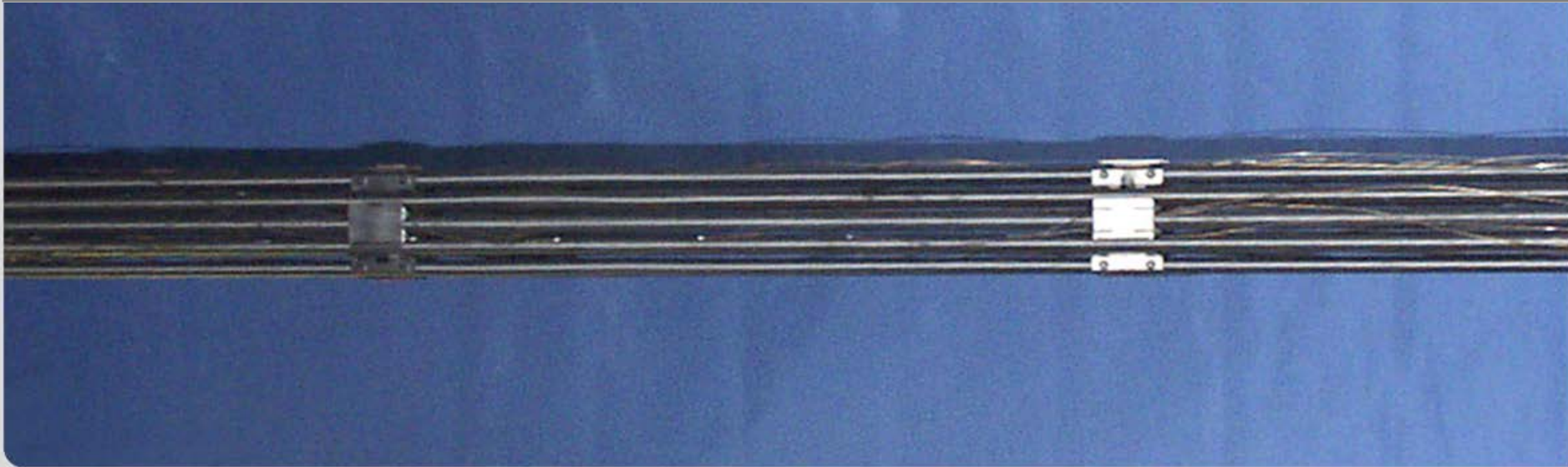


ASTEC modeling aspects of QUENCH bundle tests on air ingress

H. Muscher

*CESAM project 2nd periodic workshop
Feb 23rd – 26th 2015 ENEA Bologna*

Institute for Applied Materials
Materials Process Technology, Programme NUKLEAR



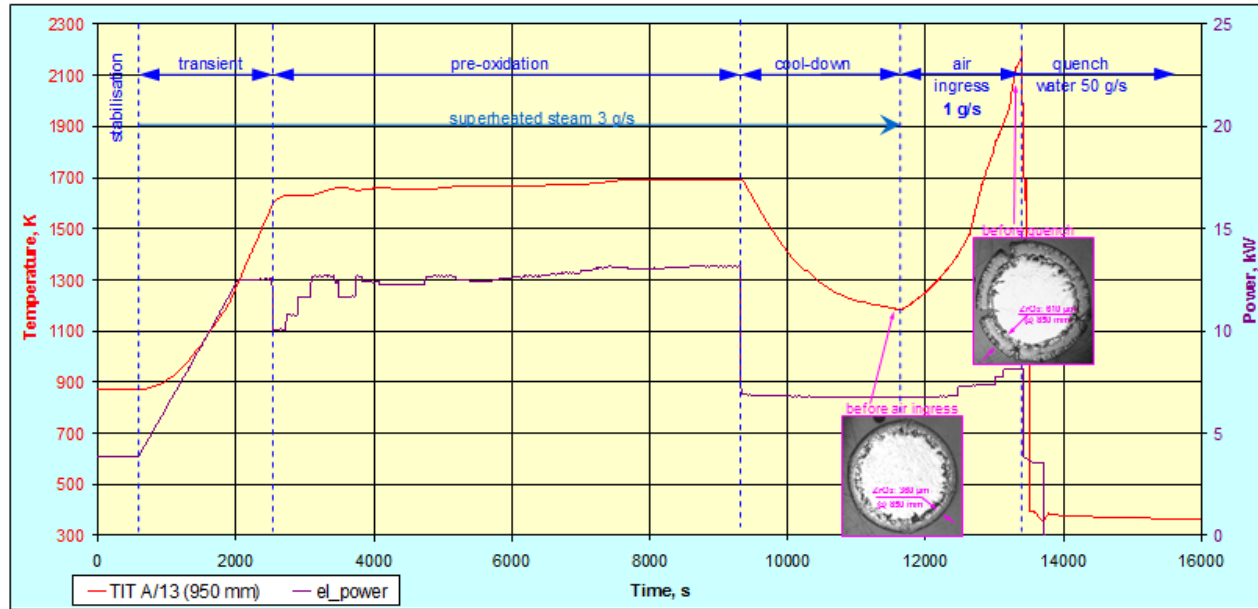
The aim is to present thermodynamic data for its further usage in ASTEC for investigating Q-10 effects on uncovered core under transient conditions.

- **ASTEC** principles and **general modeling features** – already known
- focus on the **ICARE** part
- 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 : **Q-14, Q-11 (LEE)**:
 Stabilization/ Heat up/ Pre-ox/ Transient heat up/ Quenching
- ➔ *QUENCH tests provide data for development of models & codes:*
- ➔ In former times: appl. of ASTEC on quench topics such as **mat.** studies Zry-4, M5[®], E110
- The CESAM-WP objectives /the scope of the work is outlined as:
- development of new ASTEC **IDs**, performing ASTEC runs with additional sensitivity analysis
- temp. histories & oxide axial profiles according to CESAM-needs
- the specific Q-facility **geometry, chronology of main events-** given in **quick look tables & KIT reports**
- **Q-10** to be further simulated; **work is underway** -progress still needed (parameter studies etc)
- *KIT-ASTEC 1.3 work done already by others (nodalization schemes, etc.)*
- *Now: ASTEC-V2.0 rev 3 p 3 (Dec 2014) used for several test cases*
 Further development of **air ingress Q-10/ Q-16 ASTEC IDs...**

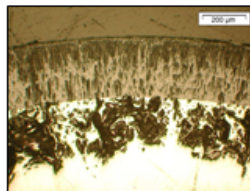


QUENCH-10 Experiment on Air Ingress

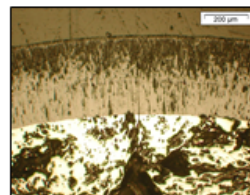
The main objectives: 1) examination of the oxidation and nitride formation of Zircaloy during air ingress, before flooding; 2) support understanding of the consequences of a possible failure of heat removal in a spent fuel pool.



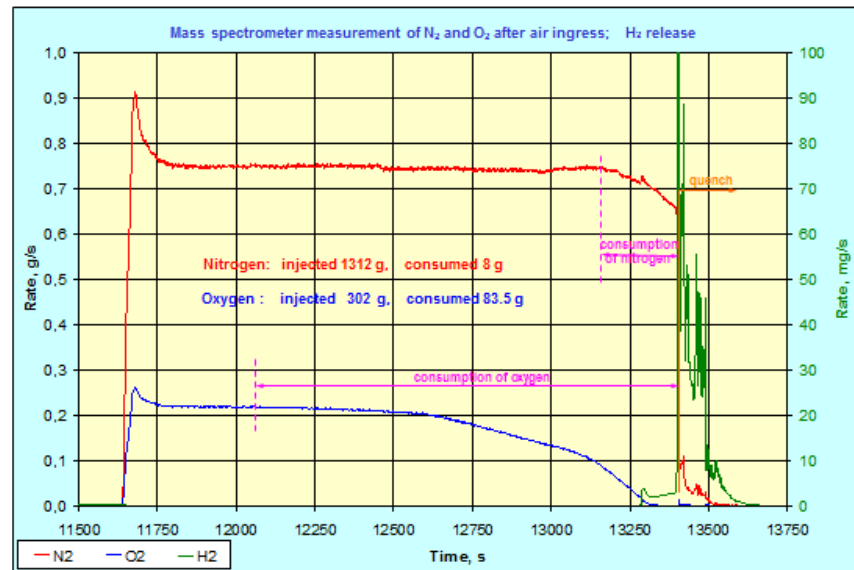
Structure of ZrO₂ scale on the surface of Zry-4 corner rod withdrawn before air ingress



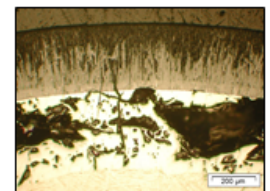
at elevation 800 mm



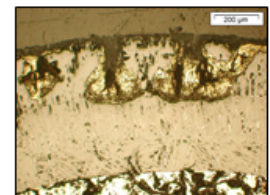
at elevation 850 mm



Structure of scale on the surface of Zry-4 corner rod withdrawn before quenching



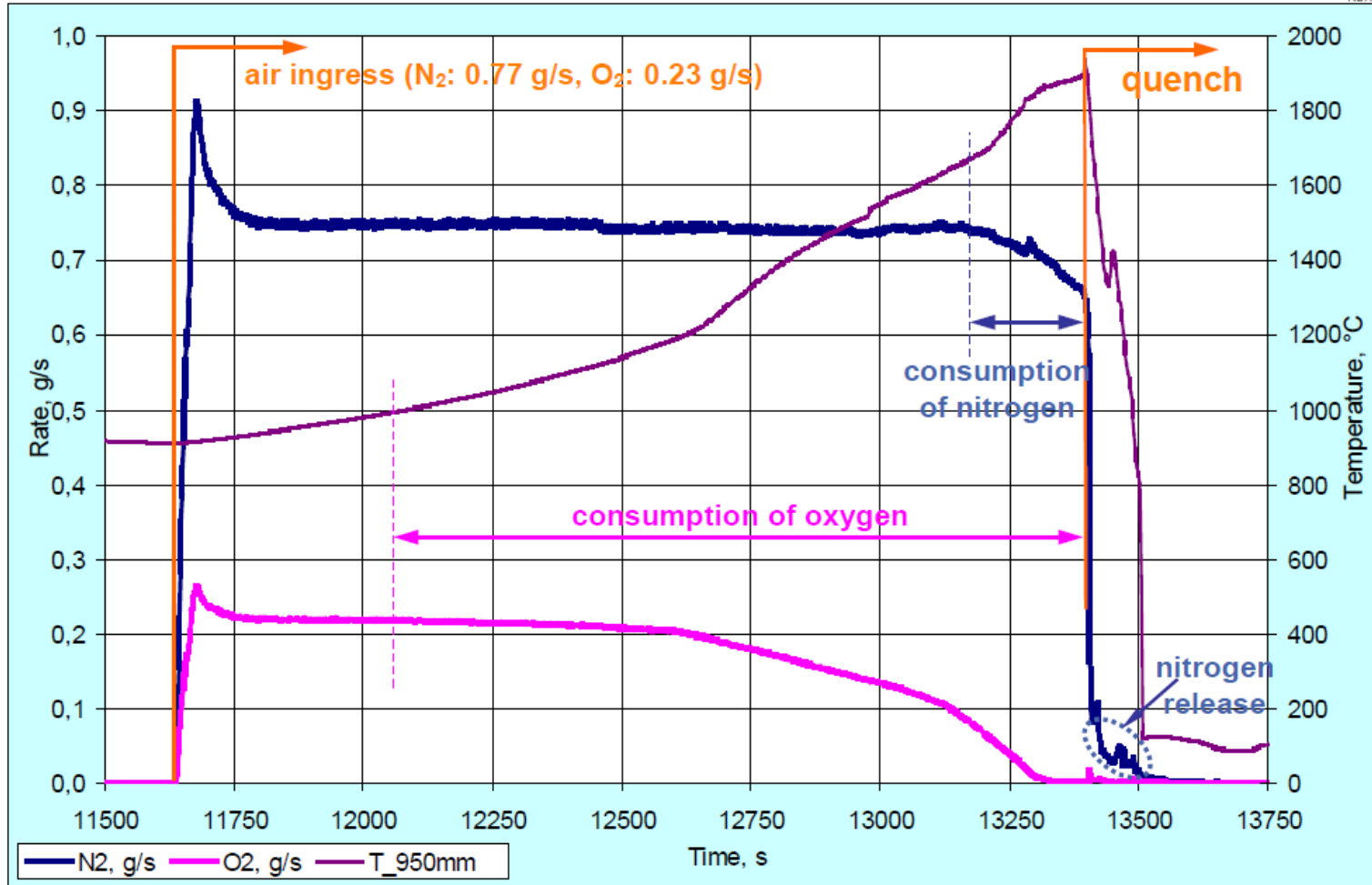
at elevation 800 mm



at elevation 850 mm, formation of nitrides

Influence of air ingress phase on the **final state** of oxide layer

QUENCH-10: Mass spectrometer measurement of N₂ and O₂ after air ingress

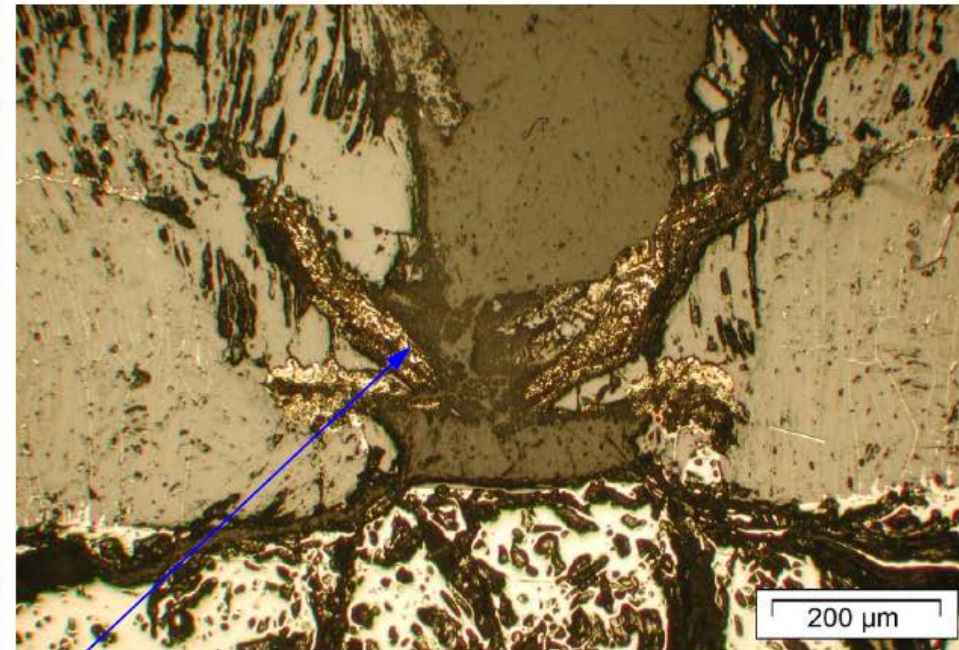
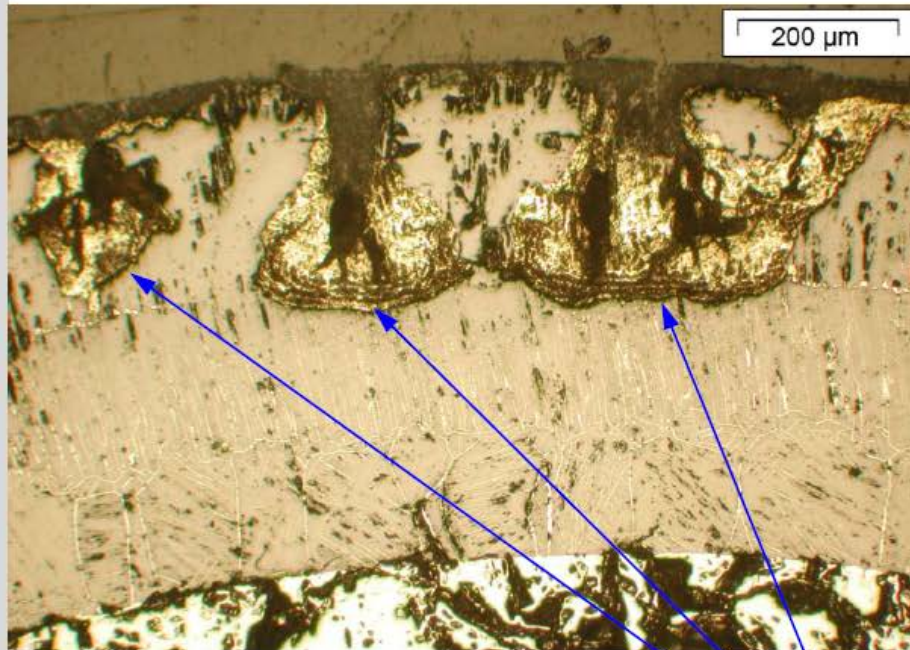


Oxygen : injected 302 g, consumed 83.5 g

Nitrogen: injected 1312 g, consumed 8 g, re-oxidised (quench) **3.5 g** ($2ZrN + 4H_2O = 2ZrO_2 + 4H_2 + N_2$)

Hydrogen (quench): 5 g, thereof **1 g** from nitride re-oxidation

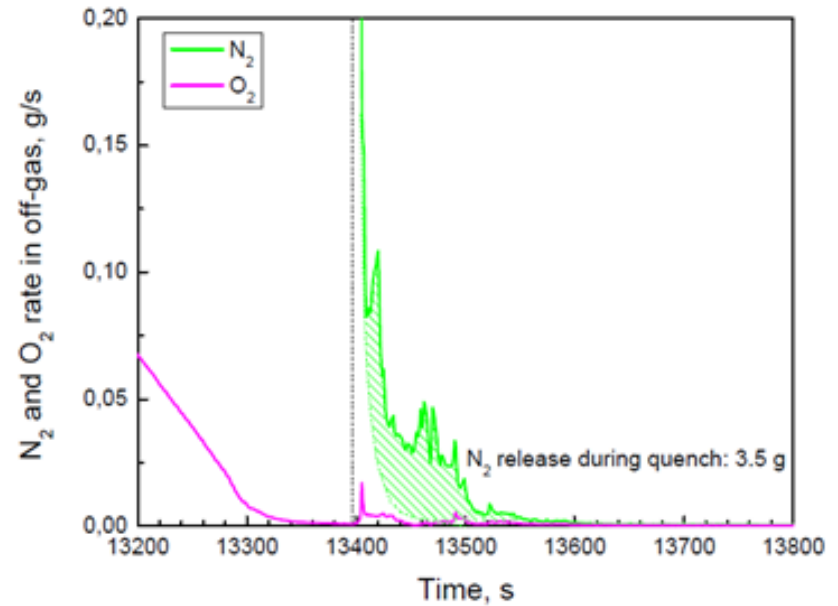
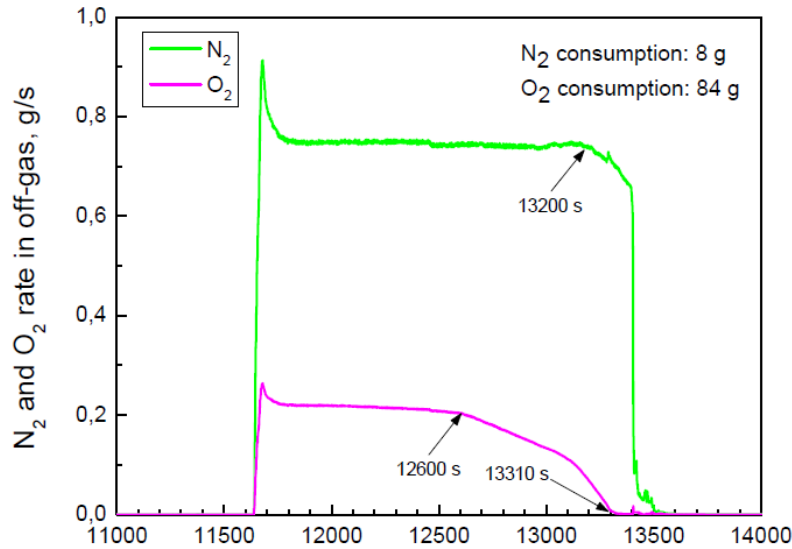
QUENCH-10: Nitride formation on the end of the air ingress phase (withdrawn Zry-4 corner rod)



T. Haste et al. / Nuclear Engineering and Design 283 (2015) 8–20

Nitride formation under oxygen starvation conditions
at the elevation 850 mm

-O₂ global starvation-



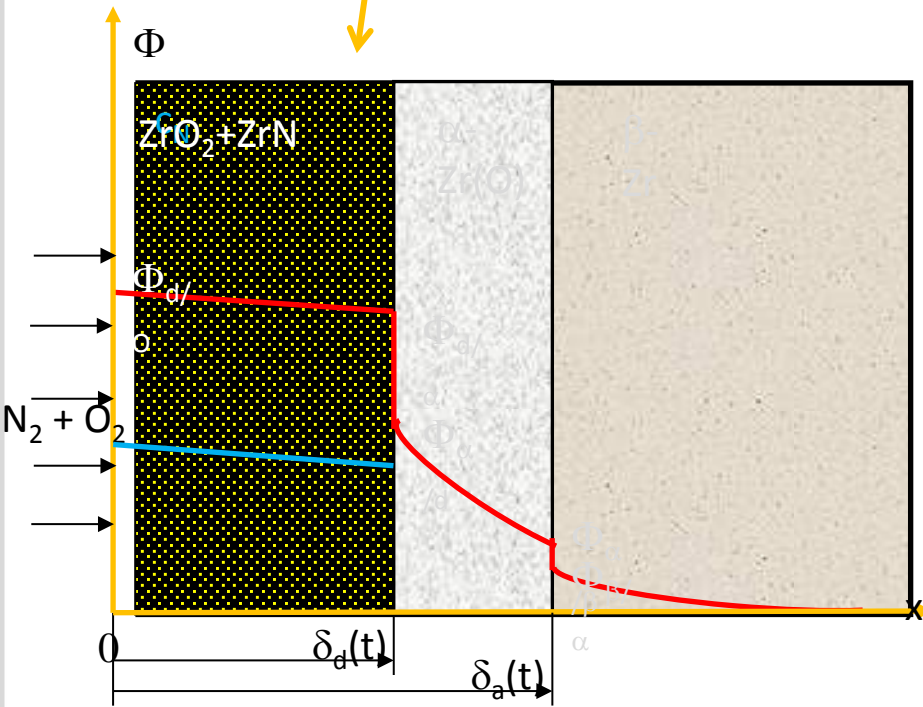
$$\mathcal{R}(\Phi) = \int_{\Phi_0}^{\Phi} d\Phi' \frac{D(\Phi')}{D(\Phi_0)}$$

-A. Vasiliev, IBRAE, Moscow- hint: **Kirchhoff transformation**-

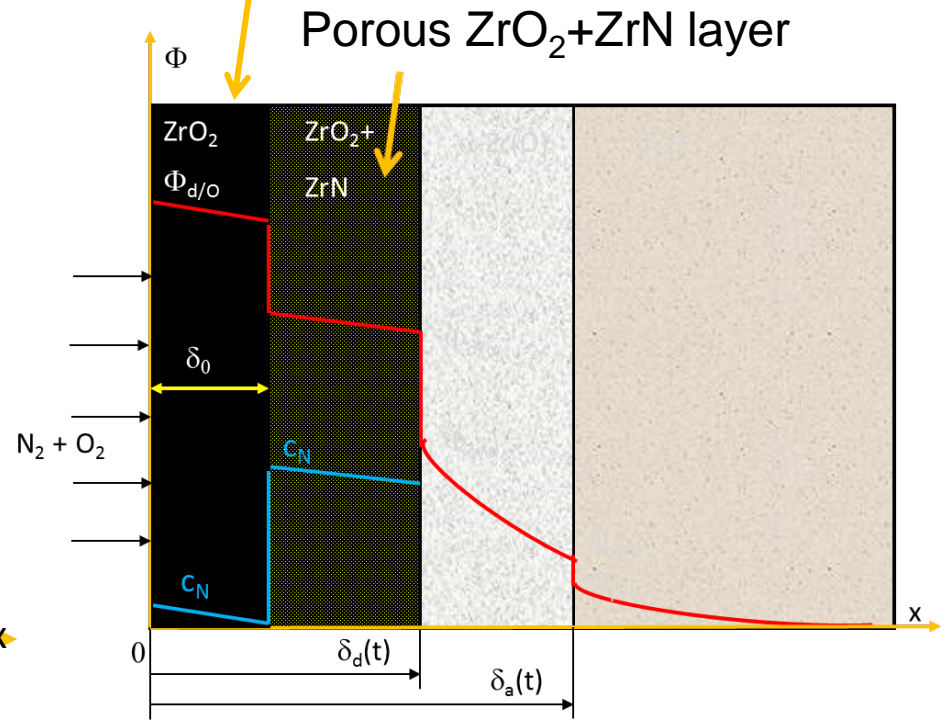
N₂ & O₂ rates measured via MS in the off gas: Q-16 //e; Q-10//ri

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

Porous ZrO_2+ZrN layer

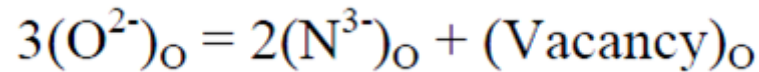


Dense ZrO_2 layer



-M. Vesthunov, A. Vasiliev schemes-

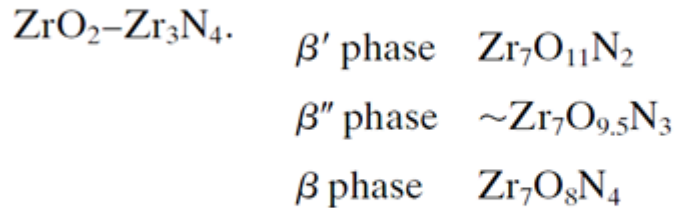
Substitution of oxygen by nitrogen



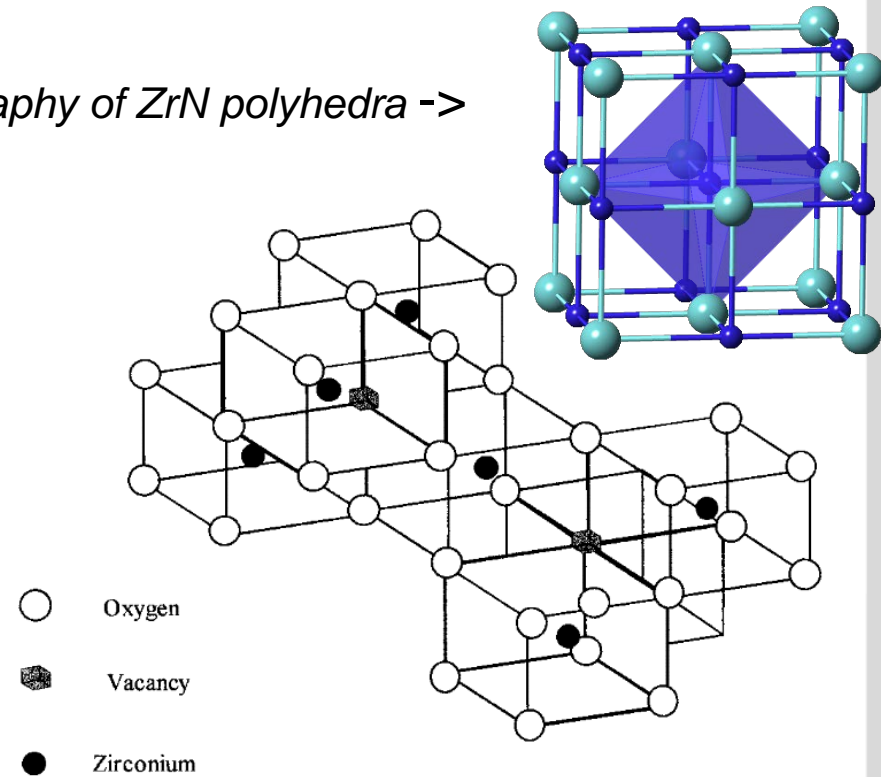
Goal: to develop systematic understanding of the O→N substitution in variety of nitride / oxynitride phases giving Δh_f and c_p (T) numerical values of Zr ternary oxynitrides: FactSage, HSC, Barin, Mils, JANAF: no data, elsewhere ThermoCalc (KIT), Glushko

A different crystallography of ZrN polyhedra ->

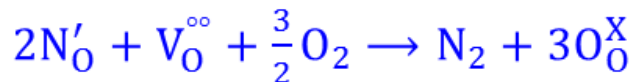
The results of recent studies in the system Zr–O–N include all zirconium oxynitride phases synthesized by direct nitridation of ZrO_2 , belonging to the system



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.



$$K_I = \frac{[V_0^{\circ\circ}]}{(1 - 3[V_0^{\circ\circ}])^3} p_{N_2}^{-1} p_{O_2}^{\frac{3}{2}}$$

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

$$[O_0^x] = [O_0^x]^* - 3[V_0^{\circ\circ}]_N$$

$[O_0^x]^*$ is the value in the case of pure ZrO_2 .

$$K P_{O_2}^{-3/2} P_{N_2} = \frac{4[V_0^{\circ\circ}]_N^3}{([O_0^x]^* - 3[V_0^{\circ\circ}]_N)^3}$$

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

$$[N'_0]^2 [V_0^{\circ\circ}] = K P_{O_2}^{-3/2} P_{N_2} [O_0^x]^3,$$

where

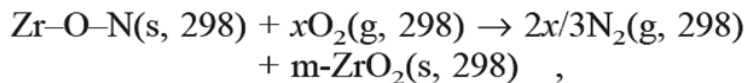
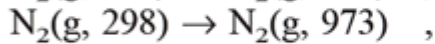
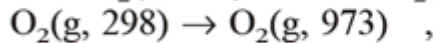
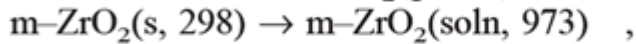
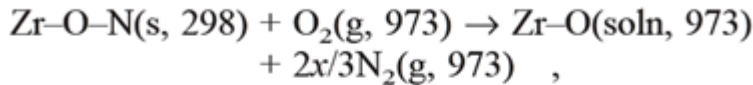
$$[V_0^{\circ\circ}] = [V_0^{\circ\circ}]_N$$

with

$$[V_0^{\circ\circ}]_N = \frac{1}{2}[N'_0]$$

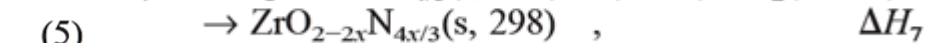
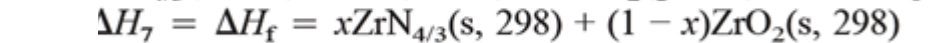
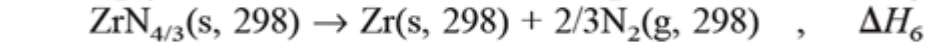
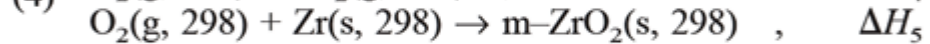
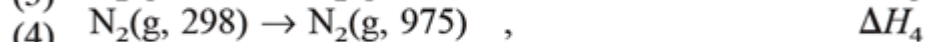
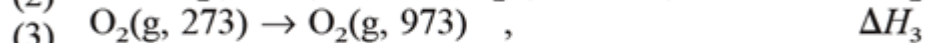
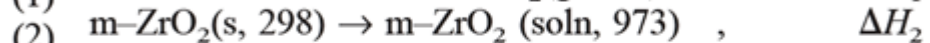
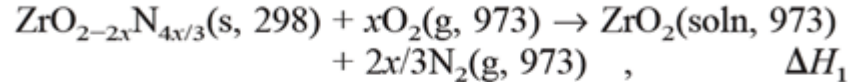
THERMOCHEMICAL CYCLES USED

C1. Enthalpy of oxidation of zirconium oxynitride



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

C5. Enthalpy of formation of zirconium oxynitrides relative to monoclinic ZrO₂ and ZrN_{4/3}



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

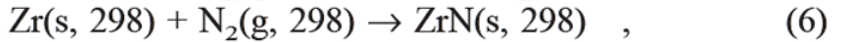
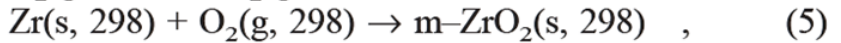
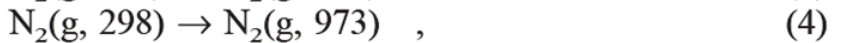
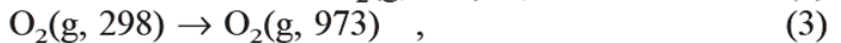
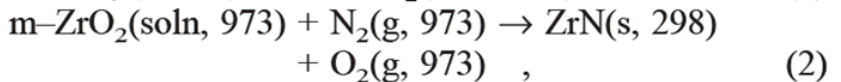
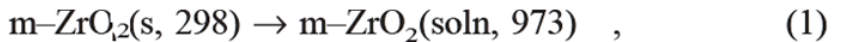
I. Molodetsky *et al.*: Energetics of oxidation of oxynitrides.

TABLE Thermochemical data for ZrN and estimated data for Zr₃N₄.

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 ₃ N ₄	-210	-354	-120

^aChase and Davies.

C2. Enthalpy of ZrN formation



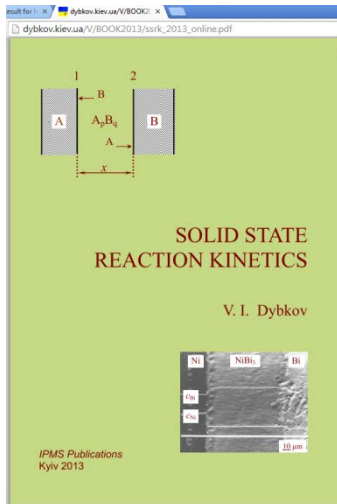
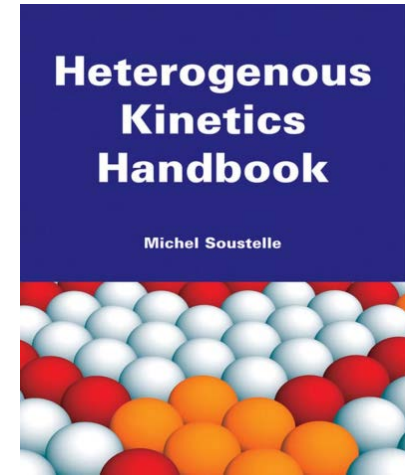
$$\Delta H_{f,\text{ZrN}} = \Delta H_6 = \Delta H_1 + \Delta H_2 - \Delta H_3 + 1/2\Delta H_4 + \Delta H_5$$

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

EDITED BY
C.H. BAMFORD
M.A., Ph.D., Sc.D. (Crested), F.R.I.C., F.R.S.
Formerly Campbell-Brown Professor of Industrial Chemistry,
University of Liverpool
The late C.F.H. TIPPER
Ph.D. (Bristol), D.Sc. (Edinburgh)
Senior Lecturer in Physical Chemistry,
University of Liverpool
AND
R.G. COMPTON
M.A., D.Phil. (Oxon.)
Lecturer in Physical Chemistry,
University of Liverpool.



Thermochemical data

	$H_{975} - H_{298}$
O ₂	21.8
N ₂	20.59

VOLUME 25
DIFFUSION-LIMITED REACTIONS
by
STEPHEN A. RICE
B.Sc. (London), D.Phil. (Oxon.), A.R.C.S., M.R.S.C.
ELSEVIER
AMSTERDAM-OXFORD-NEW YORK-TOKYO
1985

Jürgen Gegner

Komplexe Diffusionsprozesse in Metallen

Experimentelle Analyse und mathematische Simulation der Randentkohlung und Gasauflösung, 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)
0.63mZrO ₂ -0.37β'	ZrO _{1.76} N _{0.16}	-94.9 ± 3.0
0.46mZrO ₂ -0.54β"	ZrO _{1.39} N _{0.4}	-209.4 ± 9.7
0.56mZrO ₂ -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

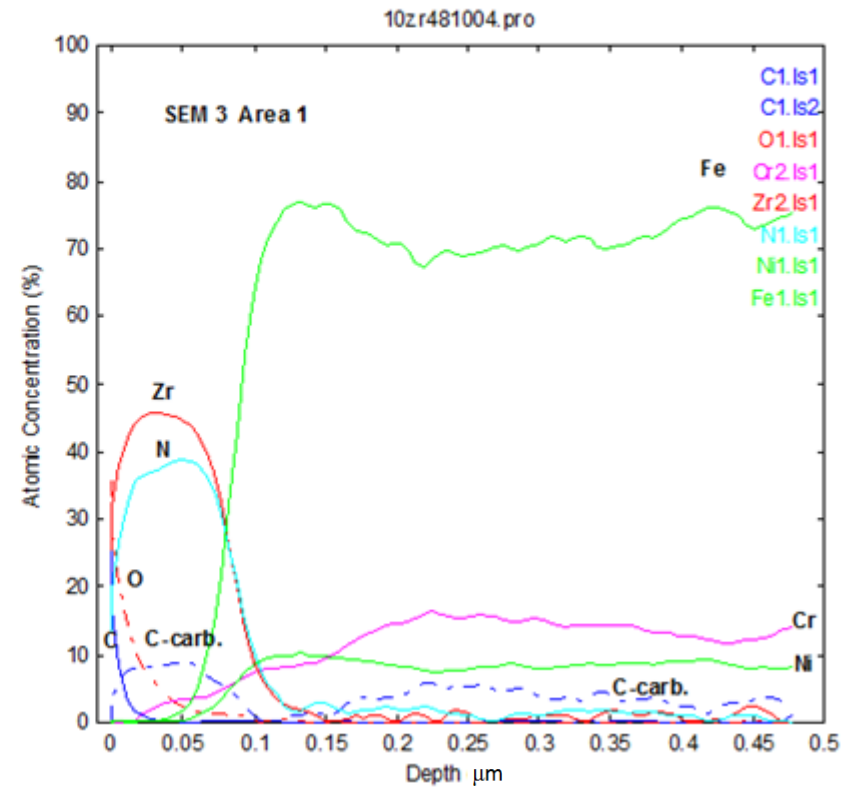
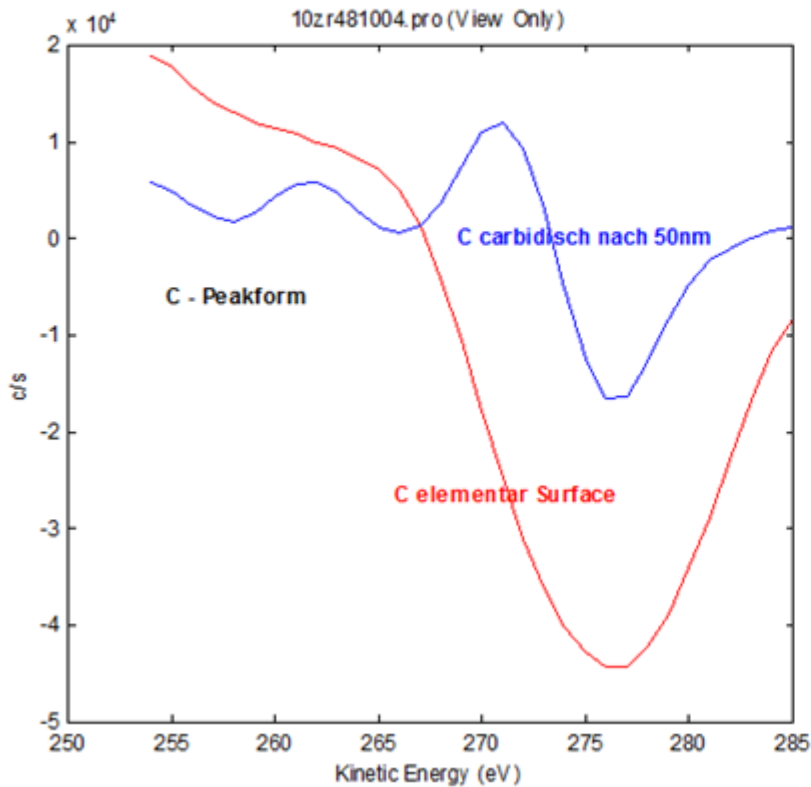
Hint of D. Powers: air incl. CO₂:- ZrC; (ZrOC)/ ZrN, ZrON ;

Discussion point: LM Corr. inhibition on SS with ZrH₂

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

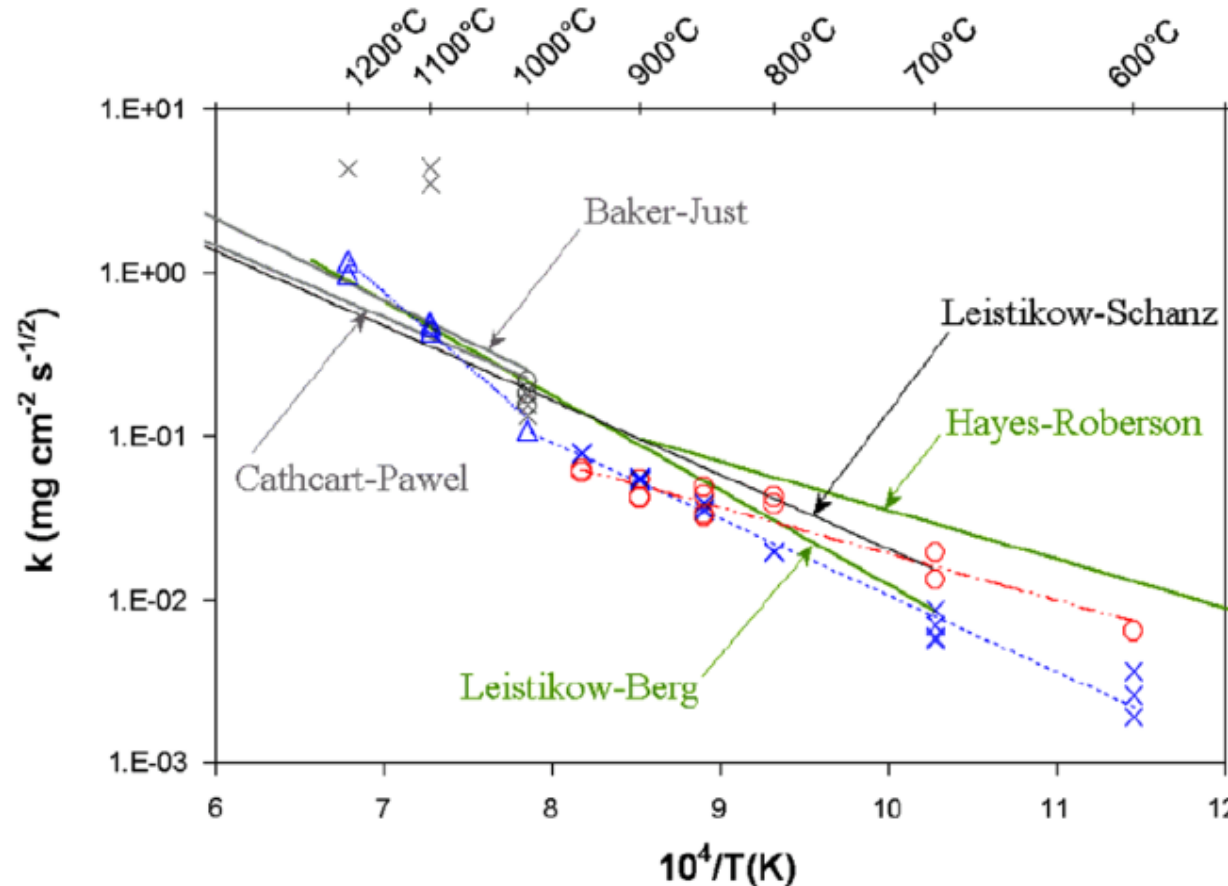
10zr481004.pro: SEM 2 Area 1 Profile1
03 Jul 25 10.0 keV 0 FRR
C1/Full/1
1.8878e+004 max
3.20 s
Company Name

10zr481004.pro: SEM 2 Area 1 Profile1
03 Jul 25 10.0 keV 0 FRR
Fe1/Full (Binom8 Binom3)
7.6923e+001 max
Company Name



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

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



and many others:

Steinbrück, LT
Steinbrück, HAT
Sokolov,
Berg,
Powers,
CODEX_AIT1,
AEKI Ar/O₂,
MOZART,
Best-fit, ICARE

for nitridation cases:

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

Parabolic rate constants from isothermal air oxidation tests on bare Zircaloy-4. 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).

Reactions with N₂ vs. O₂: concurrent processes that enhances ZrO₂ degradation

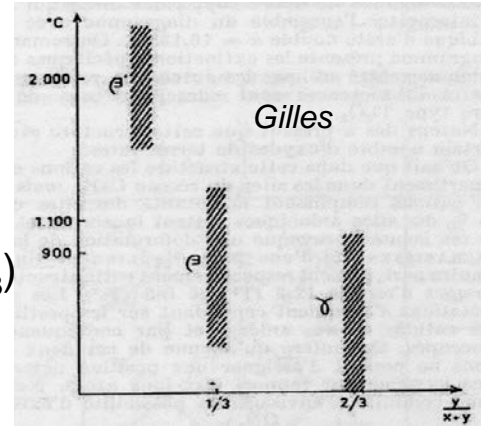
- Oxide end-phase: ZrO₂,
- Nitride end-phase: Zr₃N₄
- Oxynitride phases

(intermediate between ZrO₂ and ZrN_{4/3} i.e. ZrO_{2-2x}N_{4x/3})

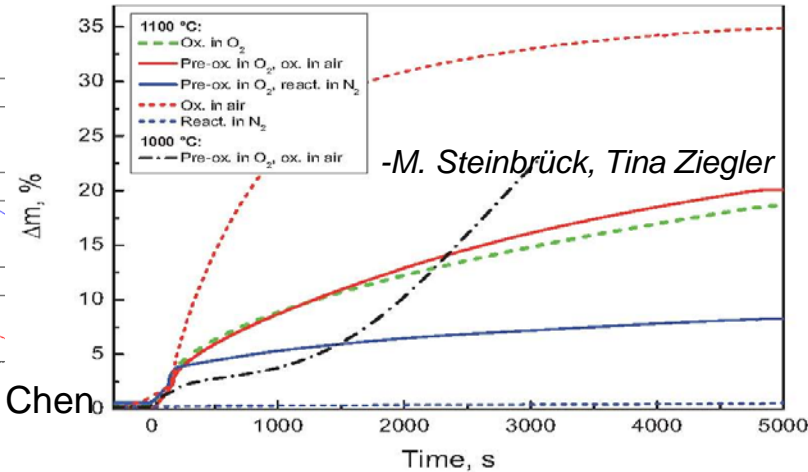
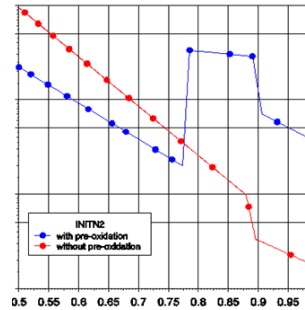
β': Zr₇O₁₁N₂: 21% mol ZrN_{4/3} i.e x= 3/14

β: Zr₇O₈N₄: 43% mol ZrN_{4/3} i.e x= 3/7

γ: Zr₂ON₂: 75% mol ZrN_{4/3} i.e x=3/4



Phase	Δ _r G [kJ/mol] at 2300K
ZrO ₂	-675 [THERMODATA]
ZrN	-151 [THERMODATA]
ZrON	1071 [Gutzov]; β''-phase discovered: Thompson, Chen



In case of simultaneous ox & nitriding of Zr [Powers]:

- **ZrO₂** being the most stable compound; if nitriding takes place, the product will react with O₂
- Nitride will be detected only if the O₂ reaction rate becomes too slow compared with nitride rate formation...i.e. in **starvation** case But lack of data above kinetics of O₂ 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;

➤ Φ modelling

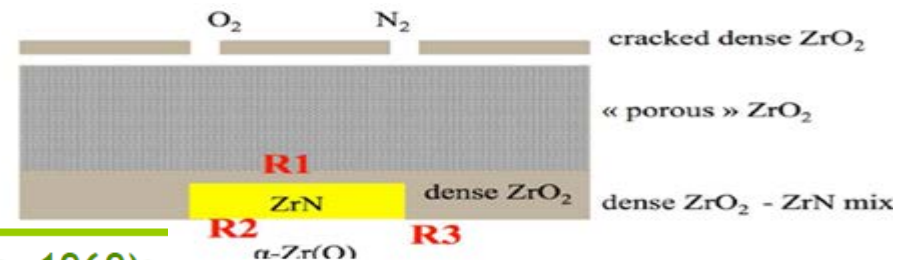
- study of variations of Φ with $p(\text{O}_2)$ and $p(\text{N}_2)$
- determination of a sequence of the three reactions involved during the process
- location and nature of the rate determining step : interfacial reaction step of the oxidation of ZrN precipitates mechanism

➤ $S_m(t)$ modelling

- analogy to nucleation and growth Mampel's model
- calculation of the kinetic rate versus time
- uncertainty of γ and Φ has been determined

$S_L(t)$: the free surface of nucleation (still in the pre-transition stage)
Depends of τ and A

Expression of Φ in function of partial pressures for each elementary step of the growth mechanism



Mampel's geometrical model (B. Delmon, 1969):

- well adapted for surface nucleation and growth
- competition between the nucleation γ and the growth Φ

Kolmogorov-Avrami(40)

Post-transition regions (B. Delmon, 1969):

$$\left(\frac{d\left(\frac{\Delta m}{S}\right)}{dt}\right)_{\text{post}} = \frac{n_0 \cdot M(\text{O}_2)}{S} \cdot \Phi_{\text{post}} \cdot S_m(t)_{\text{post}}$$

$$S_m(t)_{\text{post}} = \frac{V_m(\text{Zr})}{a_0} \cdot A \cdot \exp\left(-\frac{A}{3} \cdot \tau^3\right) \int_0^\tau \left[(\tau^2 - \xi^2) \cdot \exp\left[\frac{A}{3} \cdot \xi^2 \cdot (3\tau - 2\xi)\right]\right] d\xi$$

Parameters without dimension:

$A = f(\gamma, \Phi, a_0, V_m(\text{Zr}))$ and $\tau = f(\Phi, t, a_0, V_m(\text{Zr}))$

γ : the nucleation frequency in number $\cdot \text{m}^{-2} \cdot \text{s}^{-1}$

Φ : the areic rate of growth ($\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$)

a_0 : the mid-thickness of the plate (m)

$V_m(\text{Zr})$: the molar volume of zirconium ($\text{m}^3 \cdot \text{mol}^{-1}$)

$$\frac{d\alpha}{dt} = \Phi \cdot S_m(t)$$

α : the extent of reaction

Nitridation process

Volume change

In the beginning: t-ZrO₂ and α-Zr(O,N)

$$\Delta V_{t\text{-ZrO}_2 \rightarrow c\text{-ZrO}_2} = +0.15 \%$$

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

$$\Delta H_{O-N} = -500 \text{ kJ/mol N}$$

$$\Delta H_{V_{\infty}} = -190 \text{ kJ/mol } V_{O}^{\infty}$$

Step II. Oxide/Nitride metastable system near the oxide-metal interface Nitrogen rich part of Zr₃N₄/ γ-Zr₂ON₂ system

$$\Delta V_{c\text{-ZrO}_2 \rightarrow o\text{-Zr}_3\text{N}_4 / \gamma\text{-Zr}_2\text{ON}_2} = -11.49\%$$

Step IV. Decomposition of Zr₃N₄/ γ-Zr₂ON₂ system to ZrN and m-ZrO₂ and β-type oxynitride phases from 800°C

$$\Delta V_{ZrN \rightarrow m\text{-ZrO}_2} = +42.45\%$$

-S.Park, PSI-

reaction scheme

O dissolution by the metal: $Zr + xH_2O \rightarrow ZrO_x^{abs} + xH_2$

Oxide scale formation: $ZrO_x + (2-x)H_2O \rightarrow ZrO_2 + (2-x)H_2$

Nitride formation: $ZrO_x + \left(\frac{1-x/2}{2}\right)N_2 \rightarrow \frac{x}{2}ZrO_2 + (1-x/2)ZrN$

Nitride re-oxidation:

$(1-x/2)ZrN + (2-x)H_2O \rightarrow (1-x/2)ZrO_2 + \left(\frac{1-x/2}{2}\right)N_2 + (2-x)H_2$

Hydrogen absorption:

$H_2(g) \leftrightarrow 2H_{abs}$

Complete oxidation:

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

Stoichiometry coeff. only
(mass conservation law -
no info about molecularity,
reaction order, rds ...

N₂ as catalyst, only if η reox = 100%

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

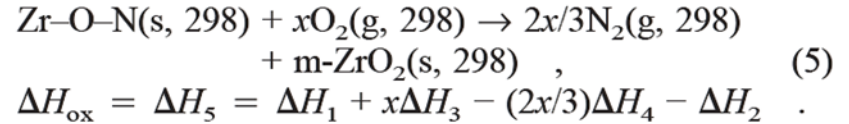


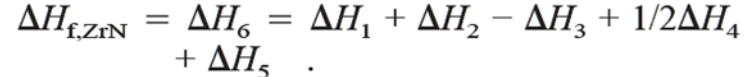
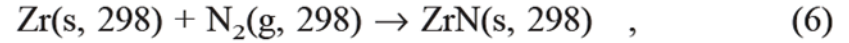
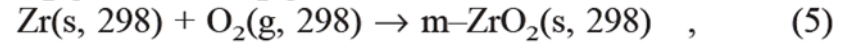
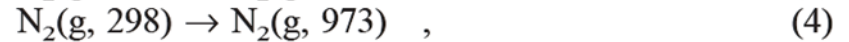
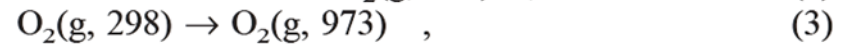
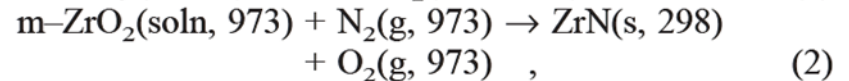
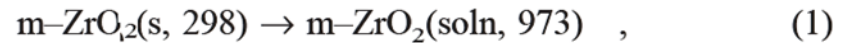
TABLE Thermochemical data for ZrN and estimated data for Zr₃N₄.

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 ₃ N ₄	-210	-354	-120

^aChase and Davies.

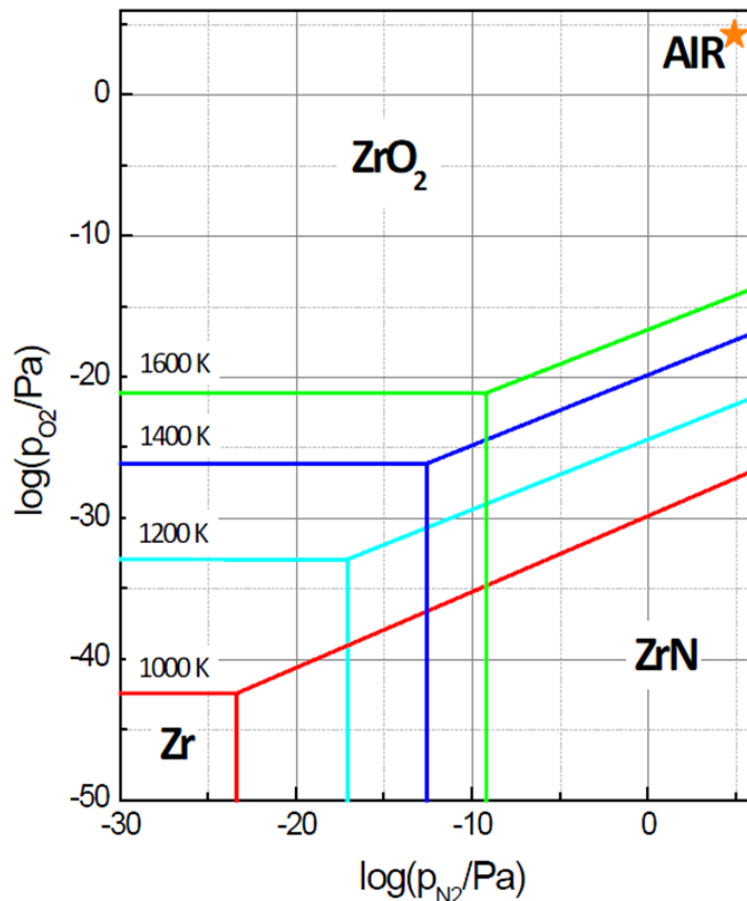
Q-10: only local presence of ZrN in the ZrO₂ layer

C2. Enthalpy of formation of zirconium nitride ZrN

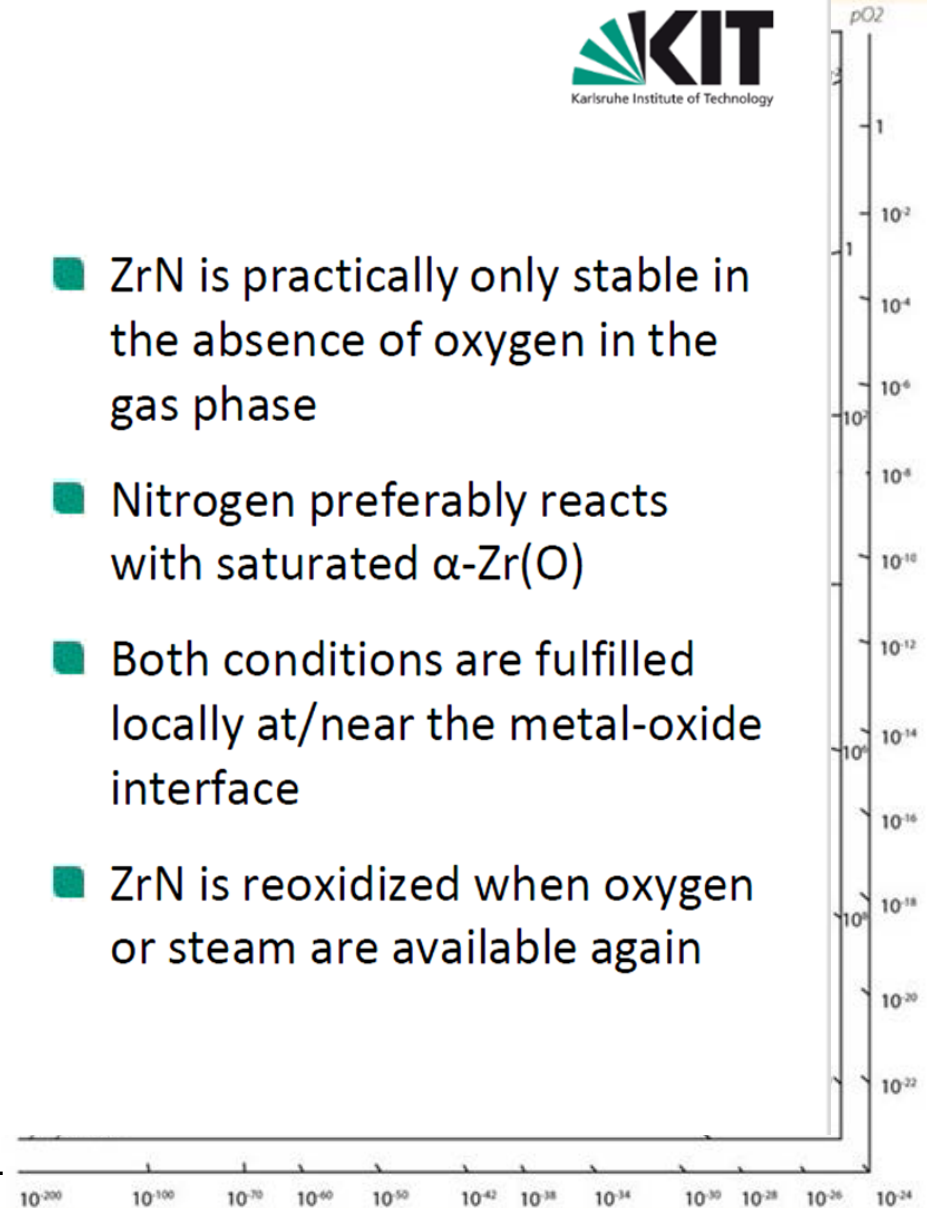


- Pre-oxidation in superheated steam during 6800 s at ~1700 K to a thick oxide of 514 μm;
- Intermediate cooling to 1183 K prior to air ingress;
- Moderate air ingress rate 1 g/s during ~30 min; 28 % of oxygen were consumed;
- Duration of oxygen starvation conditions about 80 s; nitrogen consumption (8 g from injected 1300 g); formation of zirconium nitrides inside the oxide layer;
- Quench: nitride re-oxidation, release of about 44 % of the nitrogen that was taken up during air ingress; hydrogen release 1 g (20%) due to nitride re-oxidation;
- Formation of **porous “pockets”** inside the oxide as result of re-oxidation of zirconium nitrides during reflow; hydrogen release 4 g (80%) due to clad metal oxidation under outer oxide scale.

ZrO₂-ZrN stability diagram



- ZrN is practically only stable in the absence of oxygen in the gas phase
- Nitrogen preferably reacts with saturated α -Zr(O)
- Both conditions are fulfilled locally at/near the metal-oxide interface
- ZrN is reoxidized when oxygen or steam are available again



Discussing reaction quotient, solubility limits, stability constants...

Look at the orders of magnitude! These are Δp -thresholds only! These numbers illustrate the following problem:

Derived from correct calculated **equilibrium constant K_p** nonsensical values of the “**equilibrium partial pressures**” (if any) are obtained,

even though the underlying **measurements of the relevant combustion enthalpies or $c_p(T)$ data are given with a relative error of only some %% (in the worst case).**

“Compositions in equilibrium” yield meaningless values for smallest systems.

These are numbers much less than the reciprocal Avogadro-number. Formally, it would mean here that one single particle have to be found in a very huge amount of solution (many km^3).

A chemist works in vessels of a smaller volume than these “many km^3 ”. Why is it so, that correct calculations based on real measured values result in such numbers?

What is the way leading to such extreme low values? What's wrong here? Is it the reaction quotient?

In the phenomenological thermodynamics it is assumed, that the functions of state and parameters such as $(\Delta p, V)$ can possess arbitrary low (but) positive values. (Implicit values could be arbitrarily small).

The point is- that matter has a molecular, corpuscular structure. One cannot change the small number of moles of a substance infinitesimally (at $V=\text{const.}$) since one single molecule is the smallest amount of a chemical substance. In thermodynamics, the concept of a mole means something entirely different than traditional chemical sense (as defined by IUPAC).

regarding a thermodynamic ensemble a MOLE it is a continuous, differentiable variable set for a given stoichiometry of the chemical reaction and from which the balance equations, rates etc. can be derived. At this point, the molecular structure of the matter is ignored.

The axiomatic of thermodynamics and the common thought patterns (a set of state variables assign a certain value of the thermodynamic functions of state such as S, U, H, G, F (all of which being continuous and totally differentiable). The (false) assumption about the continuity of matter, about the continuity of the state functions and first of all about the continuity of the thermodynamic Mole (as a “representation term”) can thus not be ignored for small systems.

Thermodynamics is true only in case if we are in the field of „allowed values “ (higher positive values of the parameters). For great ensembles the common thought patterns of thermodynamics are true and valid.

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{p,T,m_{j \neq i}}$$

But - to discuss the equilibrium constant describing a chemical equilibrium in a corpuscular world make only sense if a given mechanism of equilibration allows collisions between the

reactants. A balance -an equilibrium- set via appreciable reaction rates (forward/ backward), occurs only if these collisions are numerous. An experimental set of these threshold partial pressures should be in the order of about let's say $x=10^{-12}$ bar or higher, to allow measurable, sufficient high rate constants.

Otherwise, the reactions run with a decreasing speed until virtual standstill occurs due to low number of collisions.

A dynamic equilibrium in the classical sense (the same reaction rates from right to left and from left to right in reaction eqn.) will not be able to exist in extreme dilute systems.

Both the calorimetry and the **EMF method** are giving measurement data of **$mV(T)$ or $C_p(T)$ in J/mol** which can be used for calculating the **$\Delta G_f(T)$** . These analytical values have often nothing to do with reality at chemical equilibrium in very dilute systems.

Values according to the van't Hoff equation are purely formal here and cannot be used to create “ACCOUNTS” – i.e. to answer the question: „how is the composition of the system at the EQUILIBRIUM (in molar ratios).“ **Rather, there is not at all an equilibrium** set here. It would be advisable to use only in that case the values of **$\Delta G_f(T)$** – energy data in J/mol , since there are based on correct thermochemical values and not misleading.

(Dubious “**equilibrium**” partial pressures, derived from the **K_p**)

This expression is purely lexical suggesting the presence of equilibrium. In case of extreme low „values“ they do not provide any detailed info about the thermodynamic systems itself, giving only an **orientation about thermodynamic “thresholds”**. Which process is preferable?

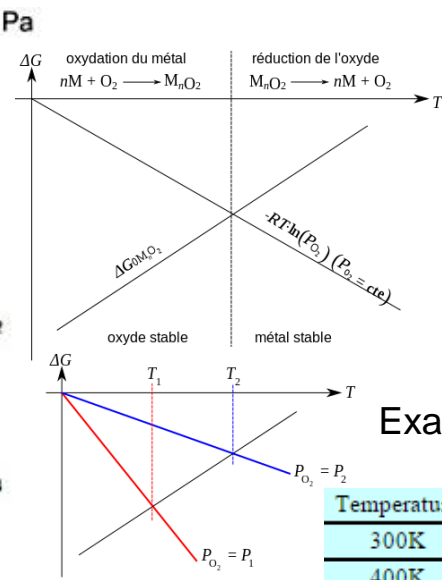
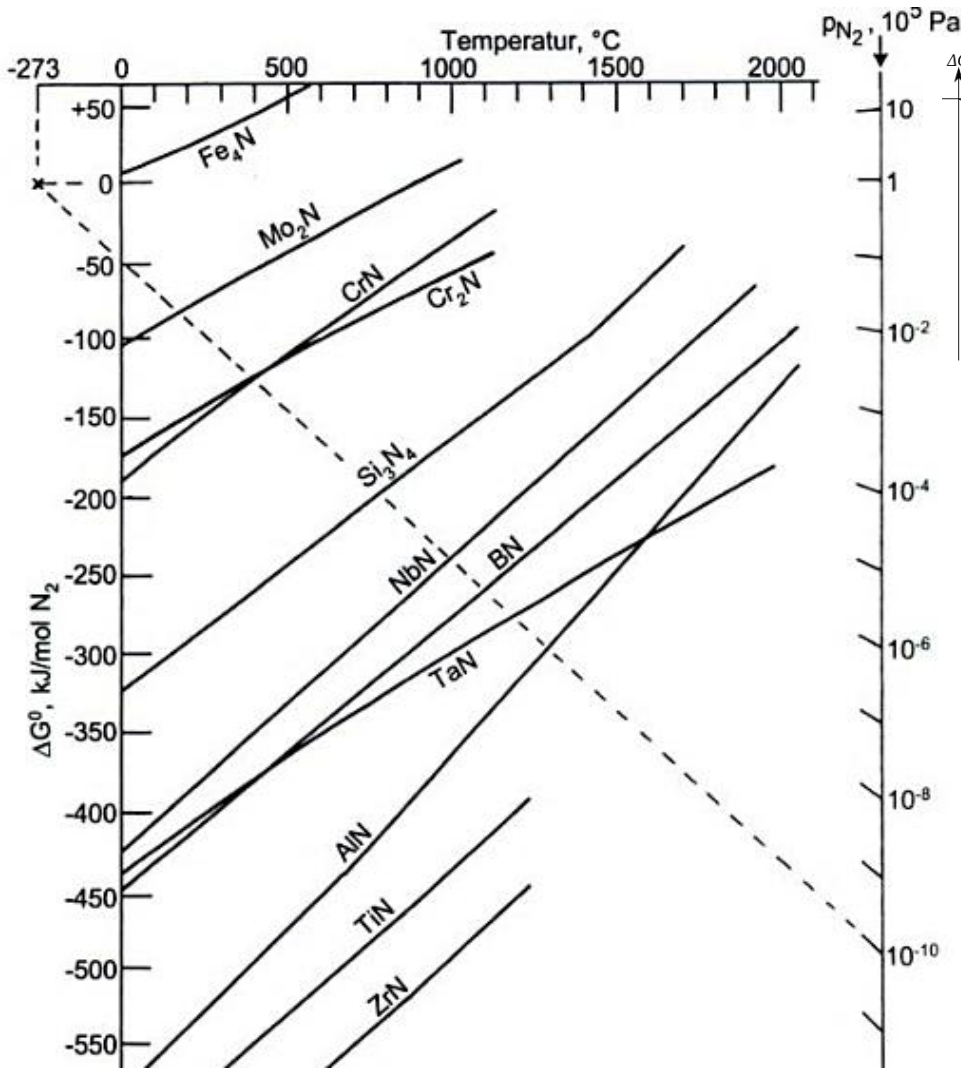
Let us conclude: in extreme small systems reactions are running slower and slower until it comes to a **standstill** due to rare collisions (a kind of a steady state, but being far from a state of dynamic chemical equilibrium).

The resulting smallest “Ellingham numbers” obtained using the **$\Delta G(T)$ “ansatz”** have little or nothing to do with reality at the equilibrium (analytical values of particular molar ratios x_i).

The same is true while analyzing other Darken-Gurry, Richardson-Kubaschewski-Evans-plots.

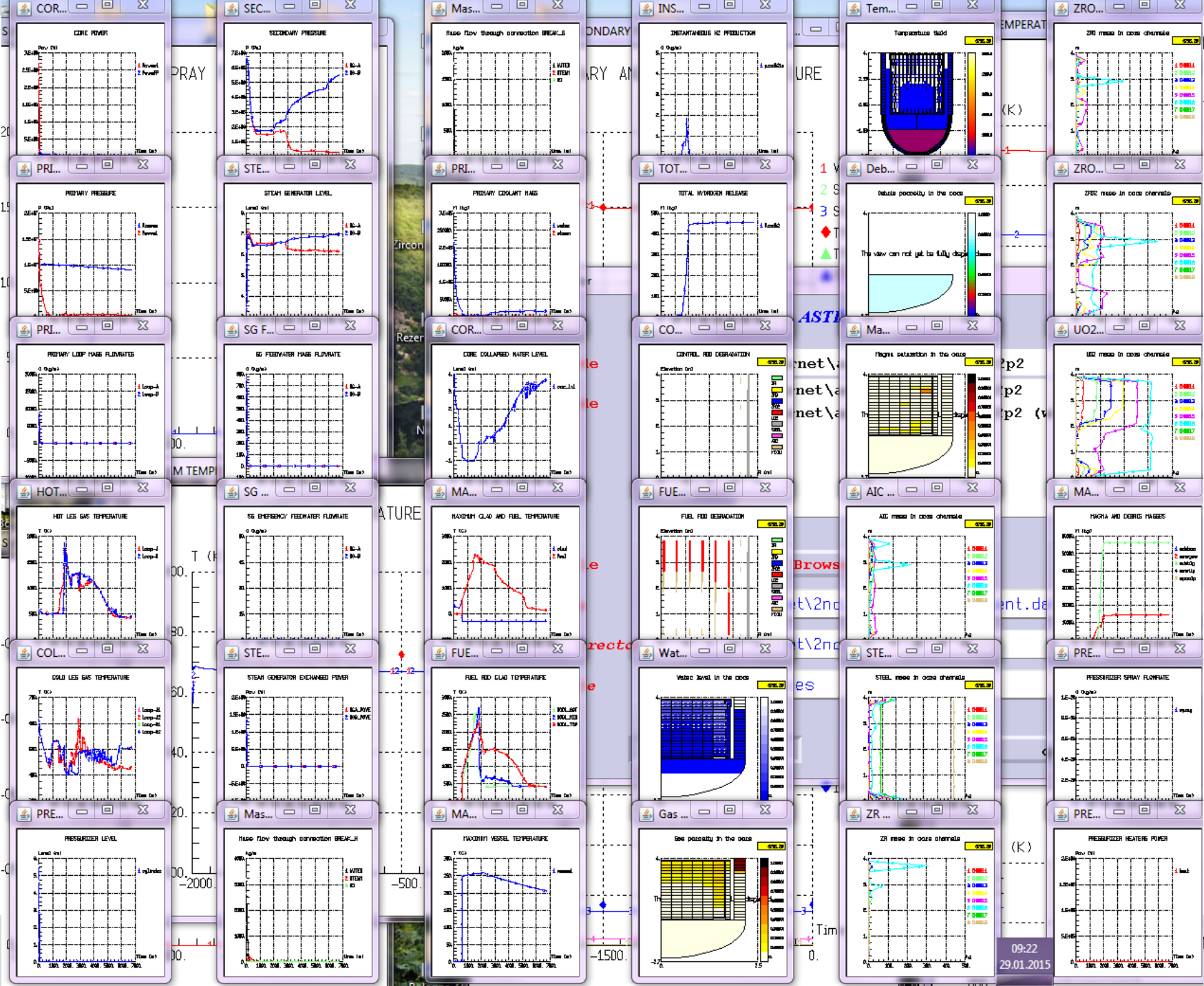
An extrapolation of the straight down to a scale with **10^{-200} bar** is meaningless in this context. The question about the analytical composition of a system in thermodynamic equilibrium (extracting dissociating rates etc.) has in all these cases little sense, since in fact there is no equilibrium here (a borderline to the phenomenological thermodynamics).

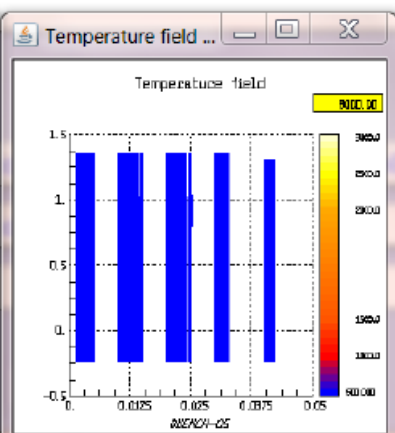
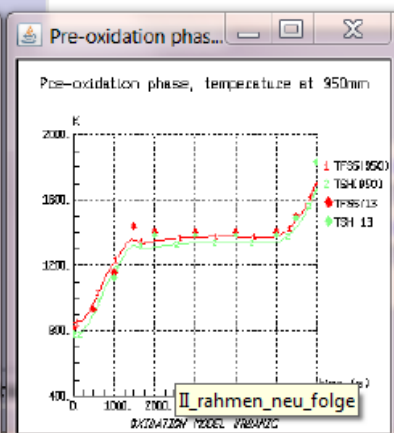
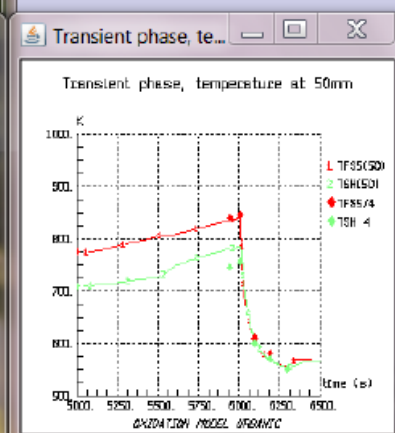
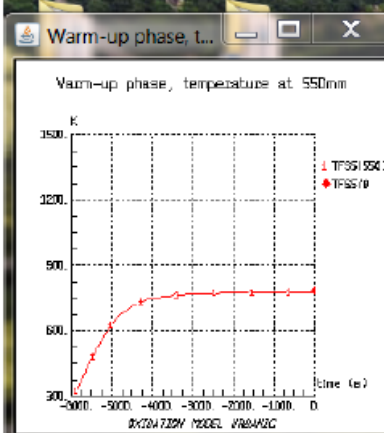
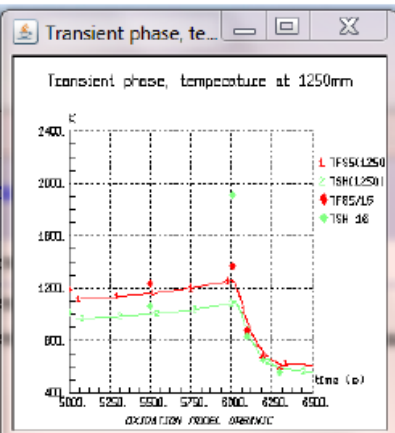
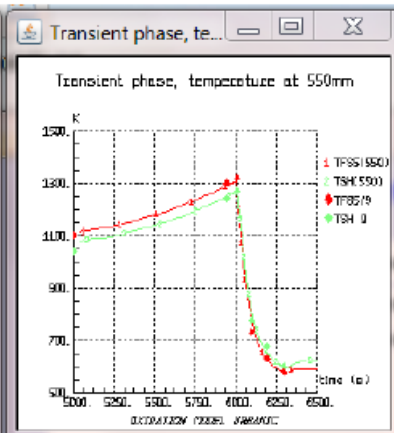
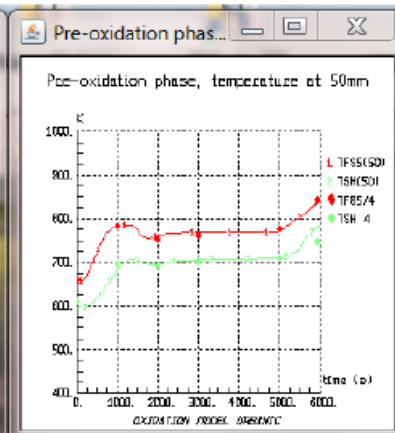
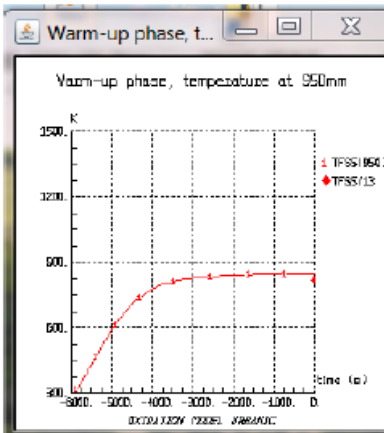
The “threshold values “above a given Δp in the particular reaction allow us to describe which reaction path is thermodynamically preferable, allowed, and the opposite being not”- This information has a qualitative, descriptive character only.



Example: (here Al_2O_3 data)

Temperature	Threshold partial pressure for formation
300K	3.04E-103atm
400K	3.51E-75atm
500K	2.41E-58atm
600K	4.05E-47atm
700K	4.21E-39atm
800K	4.34E-33atm
900K	2.06E-28atm
1000K	1.14E-24atm
1100K	1.31E-21atm
1200K	4.66E-19atm
1300K	6.72E-17atm
1400K	4.76E-15atm
1500K	1.91E-13atm
1600K	4.83E-12atm
1700K	8.36E-11atm
1800K	1.05E-09atm
1900K	1.02E-08atm

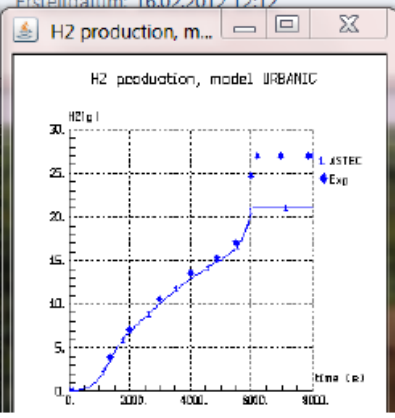
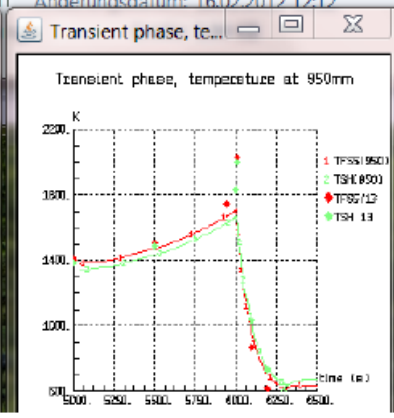
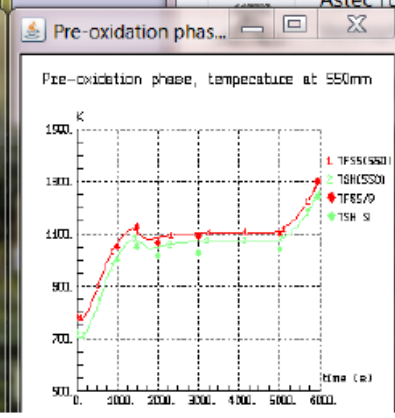
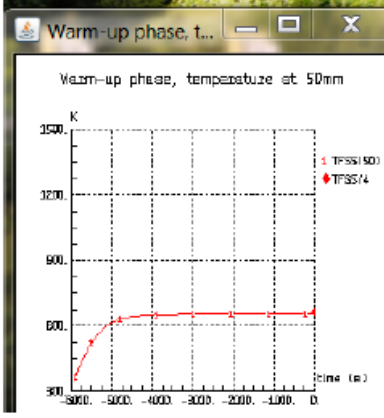




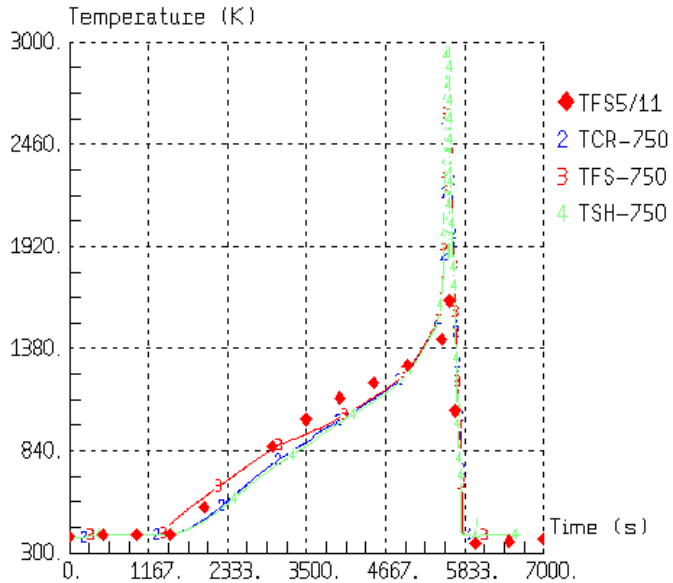
output :

Astec run Änderungsdatum: 16.02.2012 12:12

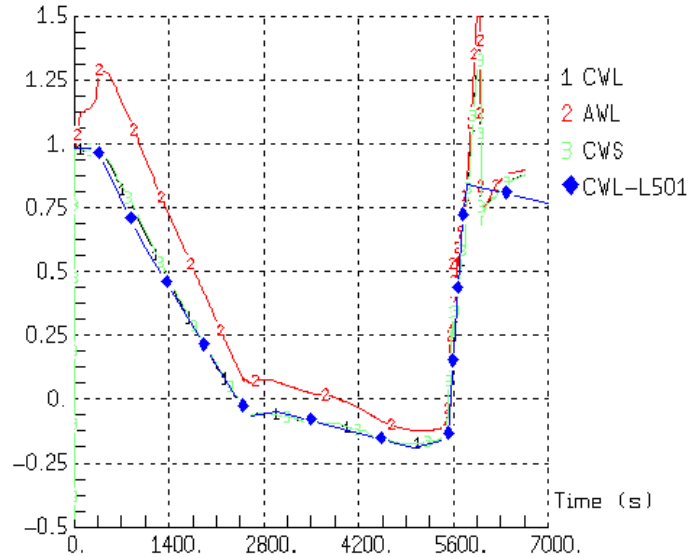
Erstelldatum: 16.02.2012 12:12



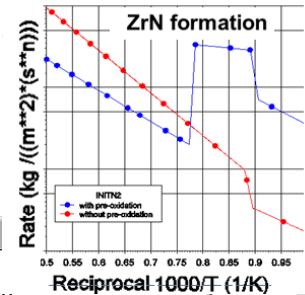
Heat-up phase



Water level (m)



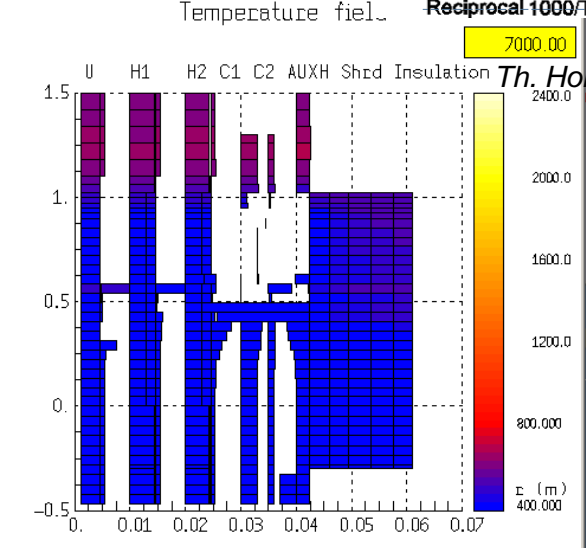
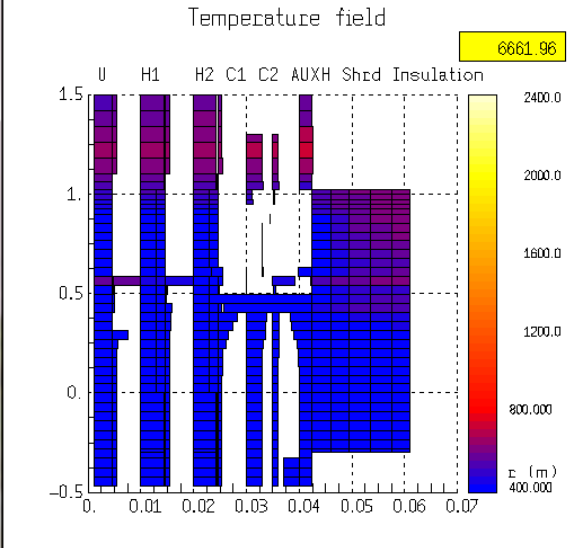
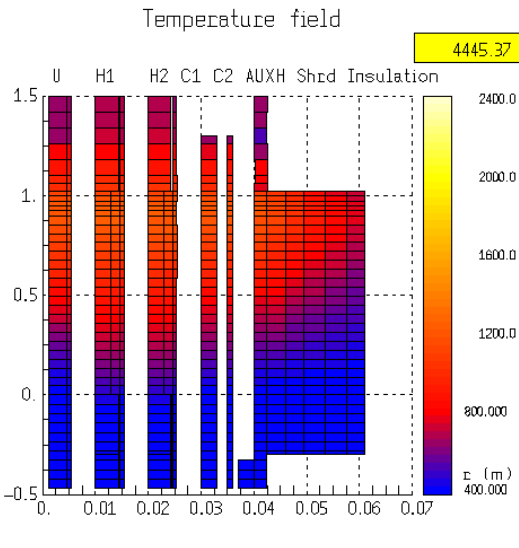
Q-11
ID: LEE
ASTECv2r1
C1/2: rods
degradation
clear visible!



Temperature field

Temperature field

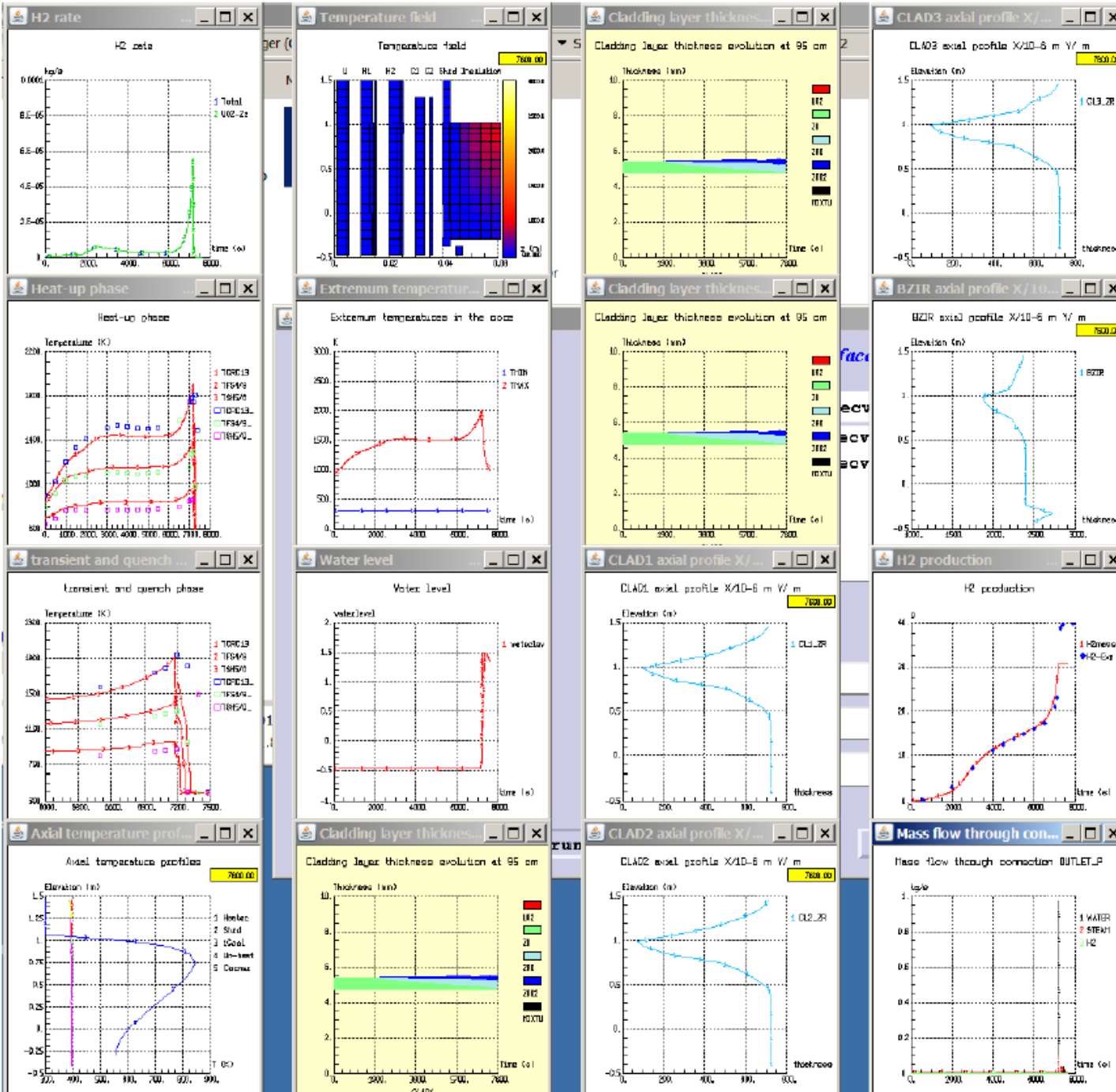
Temperature field

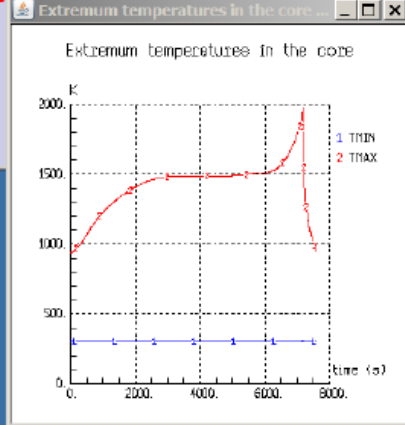
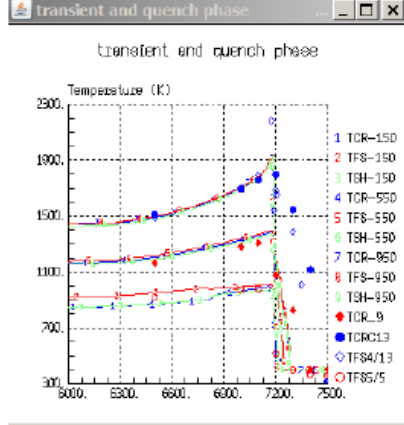
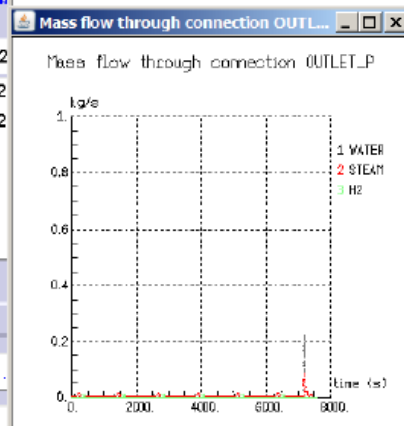
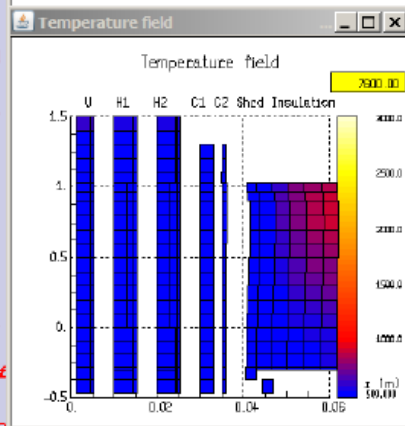
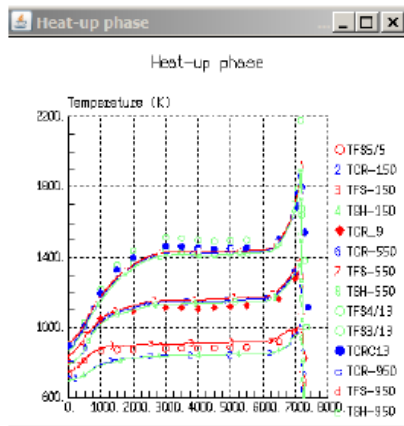
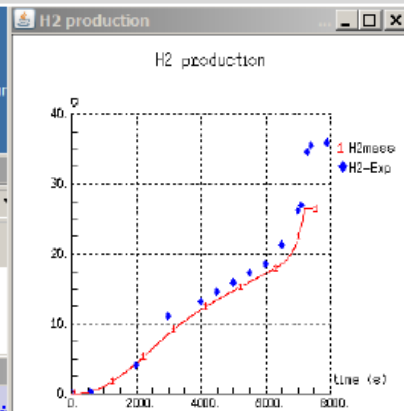
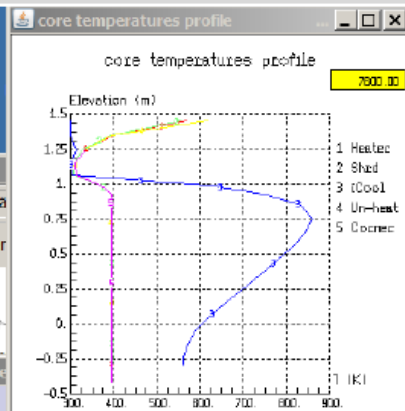
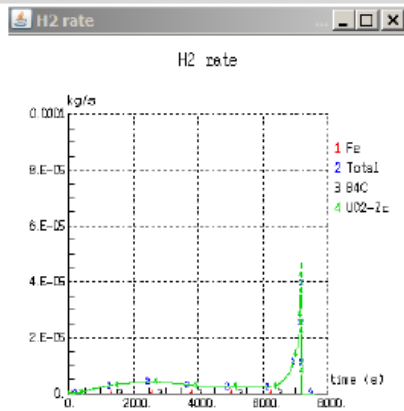


Interner Bericht

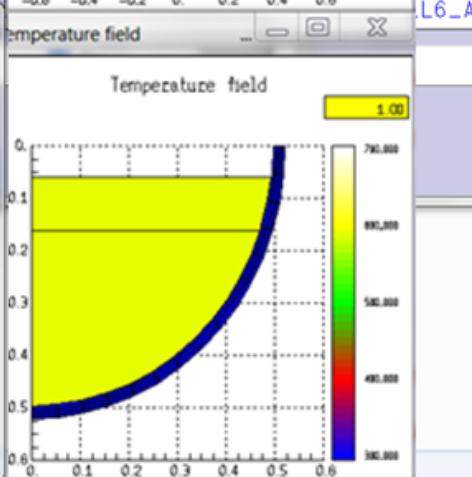
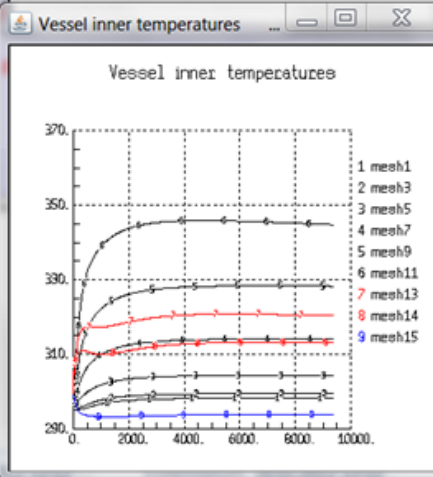
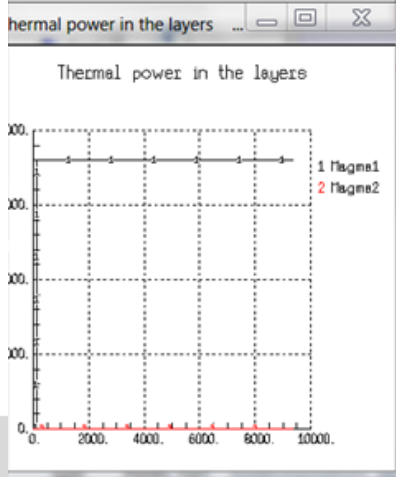
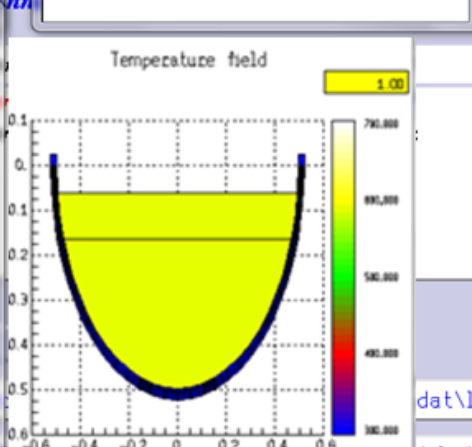
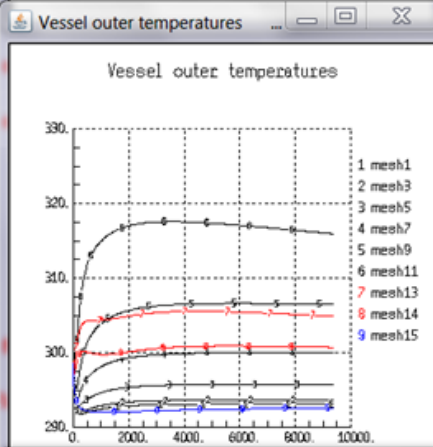
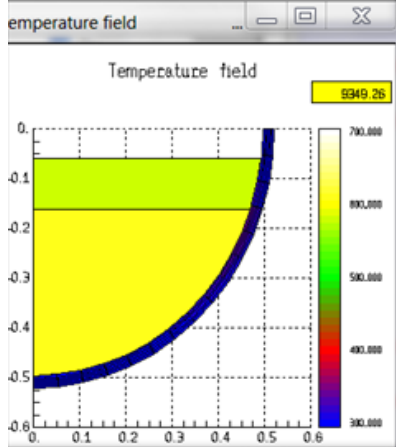
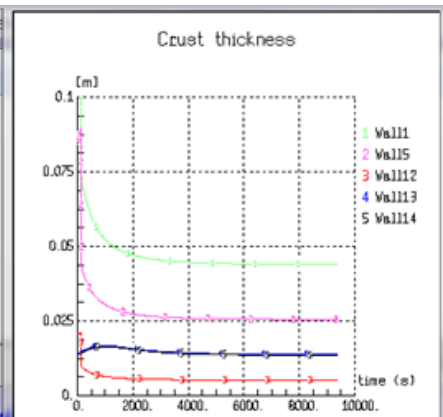
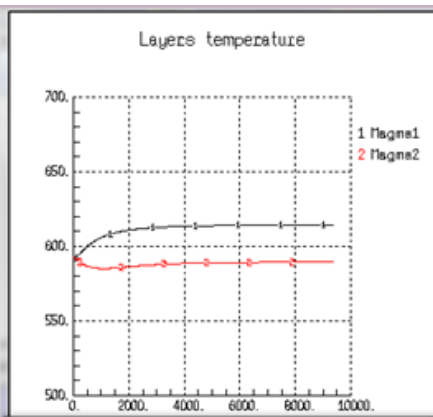
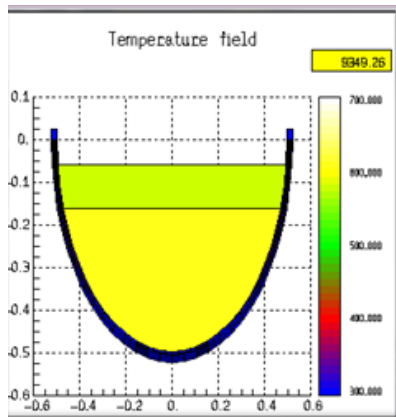
32.22.11 - P. Kaleychev
3452 NUKLEAR
November 2012

Q-14





Q-06



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 it is still a problem; especially parts of the nitradation process itself
- Dynamic behavior (time dependences; histories, τ -evolution)/ profiles developed should be visualized online air phase/ steam phase/ O₂/ N₂ consumptions, H₂ gen rate, $T(\tau)$ as well as $\delta(OZ)$
- A reference ID with Gaëtan Guillard implementation of Olivia`s C. models to be adopted...

- Tables, figures & **standardized** spread sheets with the for **Q-10/ Q-16** material should be submitted to the CESAM team at the next stage (→ Pascal G., EU, Holger N., GRS)
- **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 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 a complete bundle test)
- ✓ ASTEC produced in former times somehow conflicting results because of an extrapolation of ss models to the processes in the liq. phase. The modeling of Zr-O **melt oxidation**, being independent of ss-processes, needs more consideration

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

- Above 800°C, the transition is associated with **nitriding**.
- Once nitriding has begun, a **porous oxide grows** under the influence of a self-sustained
- $\text{ZrN} + \text{O}_2 \rightarrow \text{ZrO}_2 + 1/2\text{N}_2$ sequence (N_2 is trapped in the clad). It leads to fast degradation

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

both the instantaneous & cumulated (integral) H_2 / N_2 prod rate [kg/s]/ [kg] during the Q- phase

- suitable criterion to switch from ox to nitradation (influence of the th-H)- according the technique adopted by Christa Bals, ATHLET-CD,
- ASTEC has the potential to simulate different Q- exp.-s giving good results for Q-5, Q-6, Q-11, Q-14.
- ...Reference IDs being adopted..
- → sim. evidence was given for ex. in our reports to **Zry-4/ E110/ M5[®]** mat. comparison/ **Q-14**
- **Q-5/ Q-6/ Q-11** & especially **Q-14** ASTEC **outputs** (such as T_{pct} , H_2 prod., FRS τ -behavior of **CR(U)**, **IRR(H1,H2)**; **ORR(C1,C2)**; **SH**; **CJ**; insulation, axial oxide δ 's are ok –
- results (transients, distributions) were dependent on the imposed BC/IC in the right manner:
ASTEC description of our q-facility (nodes) & q-tests conducted as specified **scenarios**—done (IDs)
Q-10 trends/profiles must also have been consistent with the (intuitive) expectation,
as it was the case of all visualized **Q-14** τ - dependences.

- ✓ further ASTEC work: (sensitivities..) ; continuing with **new ASTEC v2.1 since 2015**
- ✓ 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, H₂ prod....
- ✓ Mandatory further work **still to be continued (CESAM)** : further developing of modified ASTEC IDs (Q-10 later Q-16) modeling transients at first w/o nitradation effect, later fulfilling the complete set of recommendations...)
- *N₂ -Lacks in ICARE modeling identified, to be consulted with Gaëtan Guillard, Stéphane Bertusi, IRSN CS-SI (development currently underway: ASTEC code changes needed):*
- *model for reox of ZrN: specific models for reflood to be developed.*

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

Thank you all.

<http://www.iam.kit.edu/wpt/english/471.php/>

<http://quench.forschung.kit.edu>