A mechanism of nitridation process in the Zr-O-N system during air oxidation

Sanggil Park[a], Leticia Fernandez-Moguel[a], Martin Steinbrück[b], Jonathan Birchley[a], Horst-Michael Prasser[a,c], Hans Jürgen Seifert[b]

[a]Paul Scherrer Institute, Switzerland
[b]Karlsruhe Institute of Technology, Germany
[c]ETH Zürich, Switzerland

NuMat 2014: The Nuclear materials Conference

27-30 October 2014, Hilton Clearwater, Florida

PAUL SCHERRER INSTITUT

Outline

- Motivation and Introduction of the air oxidation modeling
- Part I. Phases in the Zr-O-N system
- Part II. Conceptual nitridation process
- Part III. Mechanism of nitridation process
- Summary and Outlook

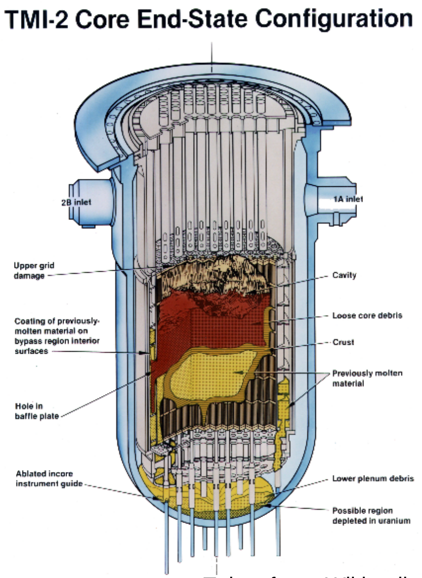
Motivation – Air Ingress scenarios

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

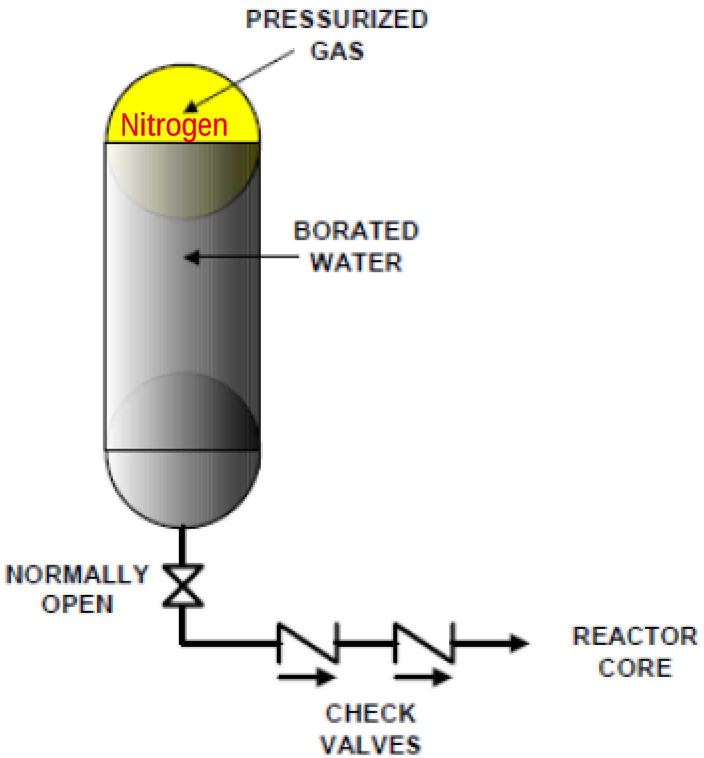
Refueling: RPV head removal

Taken from: www.power-eng.com

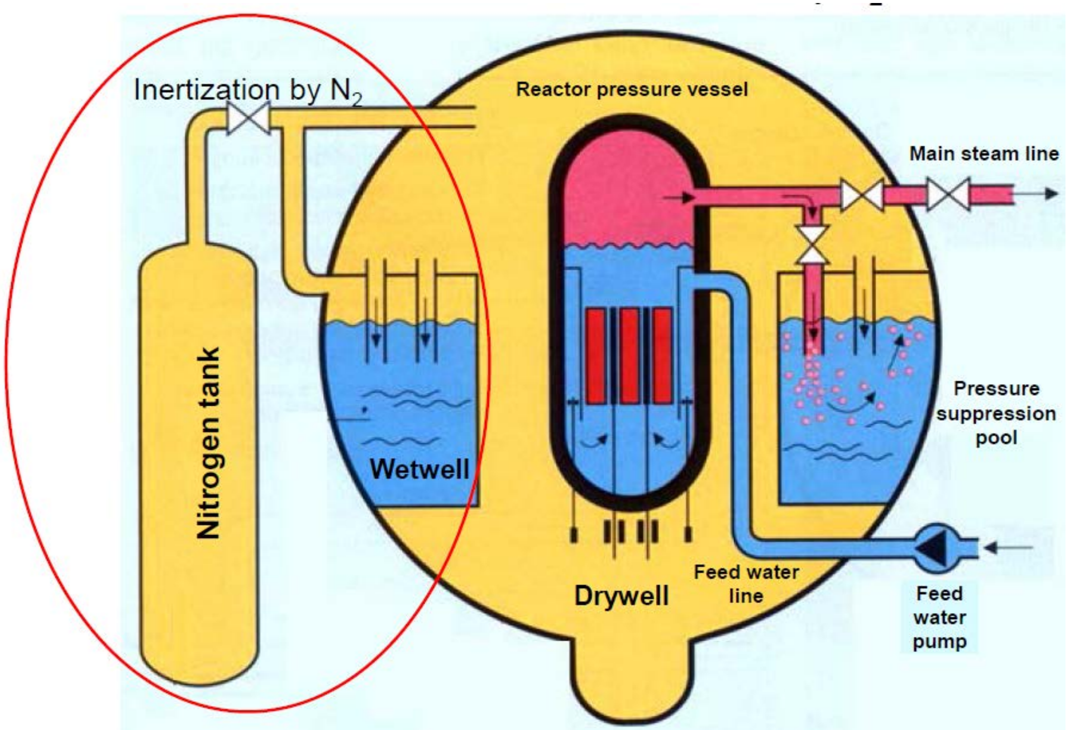
Dry storage cask drop during transport

Nitrogen reservoirs in reactors

- PWR
  - Hydroaccumulator filling by nitrogen
  - Passive high pressure injection
- BWR
  - Inerted containment by nitrogen
  - to prevent hydrogen combustion



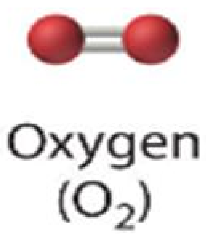
Taken from: www.lke.mavt.ethz.com



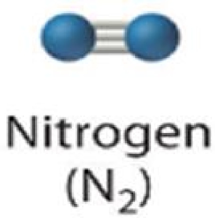
Taken from: www.lke.mavt.ethz.com

Introduction – Role of nitrogen during air oxidation

➢ Is nitrogen an inert gas?



- Dissociation of double bond = +497 kJ/mol
- Gibbs energy of formation ΔG_{ZrO_2} = -896 kJ/mol (1073.15K)



- Dissociation of triple bond = +945 kJ/mol
- Gibbs energy of formation ΔG_{ZrN} = -264 kJ/mol (1073.15K)

➢ After oxygen is sufficiently consumed, nitrogen plays an active role!

1st role of nitrogen: cladding degradation by volume mismatches between ZrO_2 and ZrN

- micro porous and macro cracked oxide forms due to ZrN formation and reoxidation

2nd role of nitrogen: exothermic heat release during ZrN formation and reoxidation

- accelerate the oxidation kinetics and enhance the heat release

Introduction – Purpose of the present study

➢ Limitations in current state of knowledge on the nitridation process

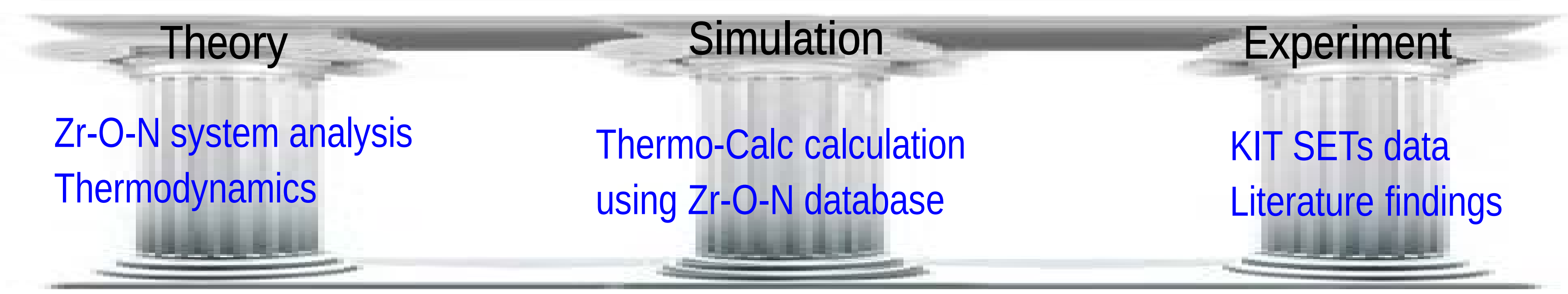
Post-test investigation

- The results of post-test investigations reveal no metastable state and phase transformations during the process
- The understanding of nitridation process is phenomenological
- Recently, Zr-O-N ternary compounds were detected by Raman investigation

Binary system analysis: Zr-O and Zr-N

- Only binary compounds, ZrO_2 and ZrN, are involved during the process

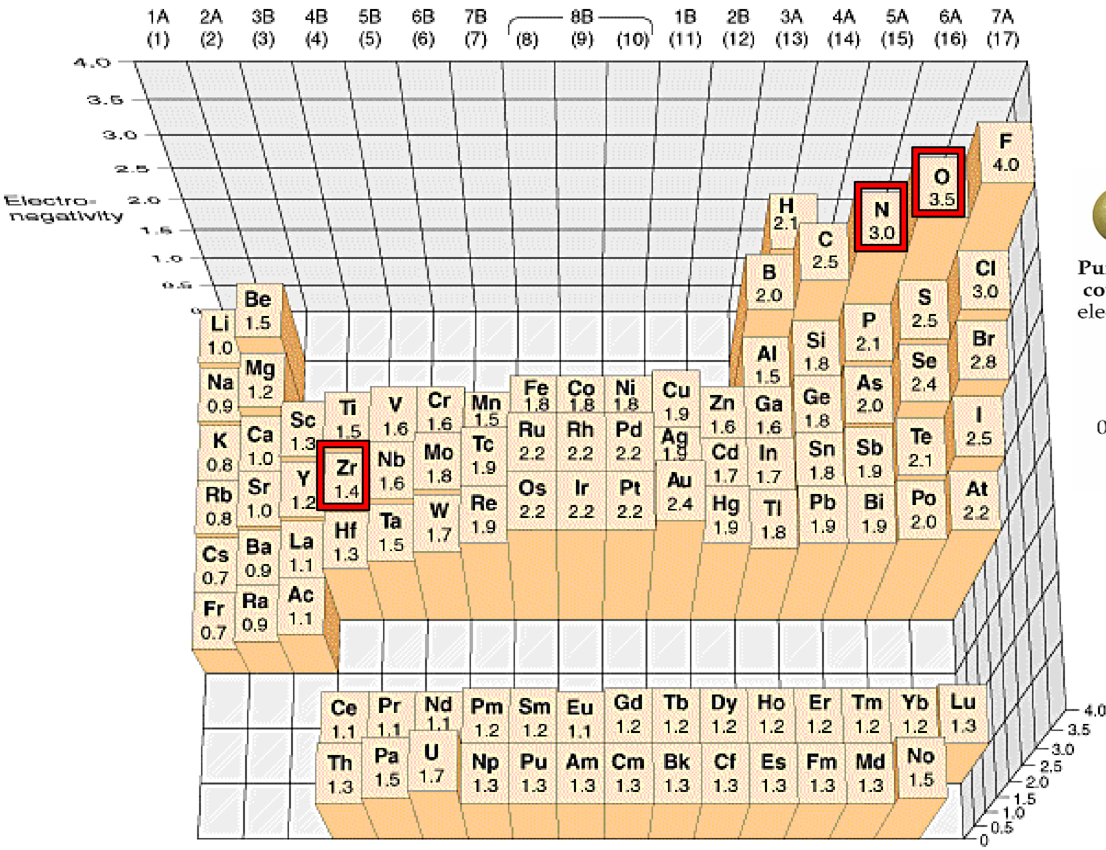
A mechanism of nitridation process in the Zr-O-N system during air oxidation



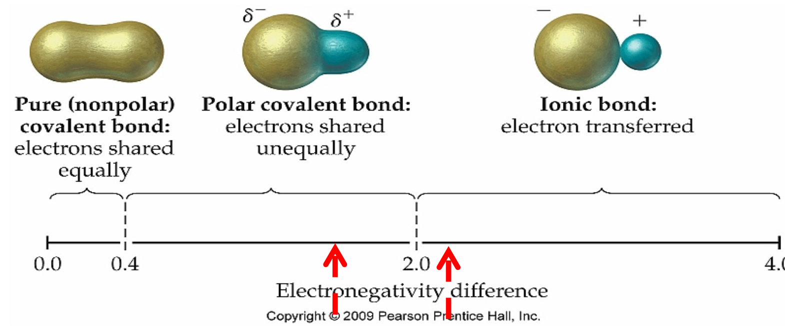
Part I – Phases in the Zr-O-N system

- Zr-O-N ternary system:
  ZrO_2-Zr_3N_4 pseudo binary system

Zr-O-N system	Electronegativity
Zr	1.33
O	3.44
N	3.04



Taken from: http://www.chem.ufl.edu/~itl/4411/lectures/lec_16.html



$\Delta E_n(Zr\text{-}O) = 2.11$

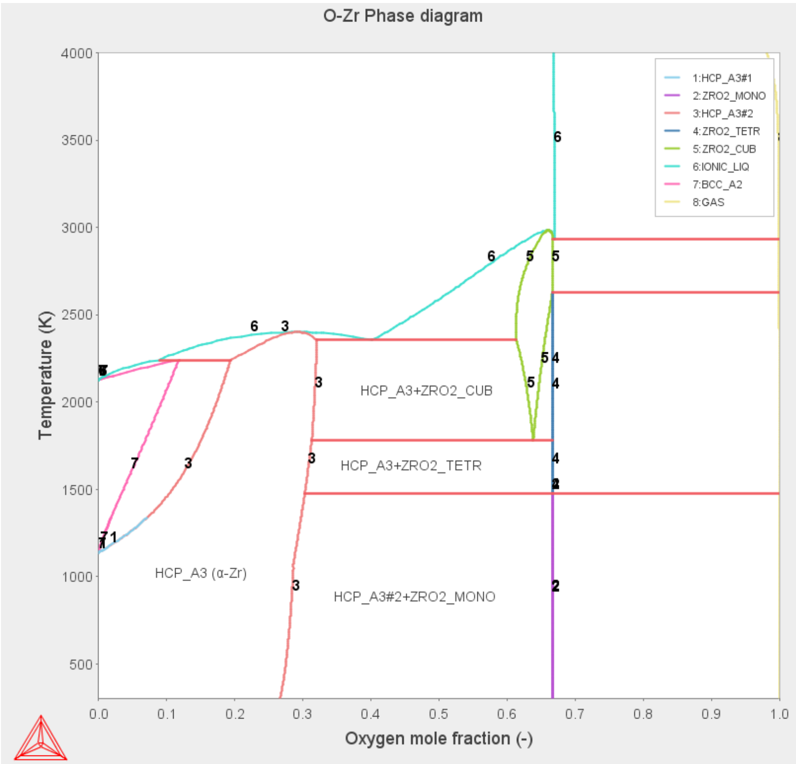
$\Delta E_n(Zr\text{-}N) = 1.71$

- ZrO_2: Ionic bond
- Zr_3N_4: Ionic-covalent bond (Polar bond)
- ZrN: Metallic bond

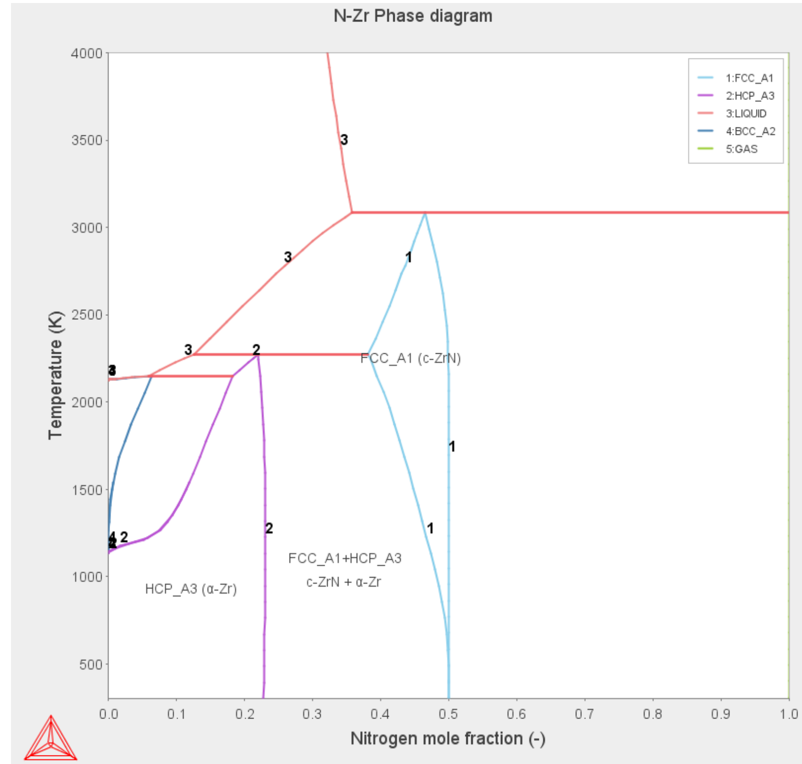
- Nitrogen rich Zr_3N_4 phase is a mestastable state and thus is decomposed to ZrN at high temperatures

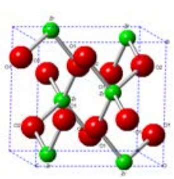
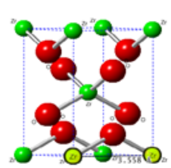
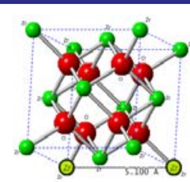
Part I – Phases in the Zr-O-N system

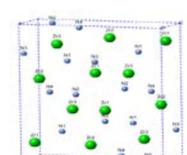
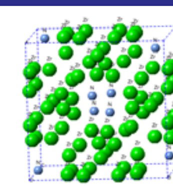
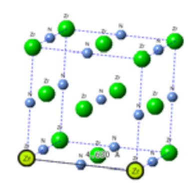
➢ Zr-O binary system



➢ Zr-N binary system



m-ZrO_2	t-ZrO_2	c-ZrO_2
		

o-Zr_3N_4	c-Zr_3N_4	c-ZrN
		

Part I – Phases in the Zr-O-N system

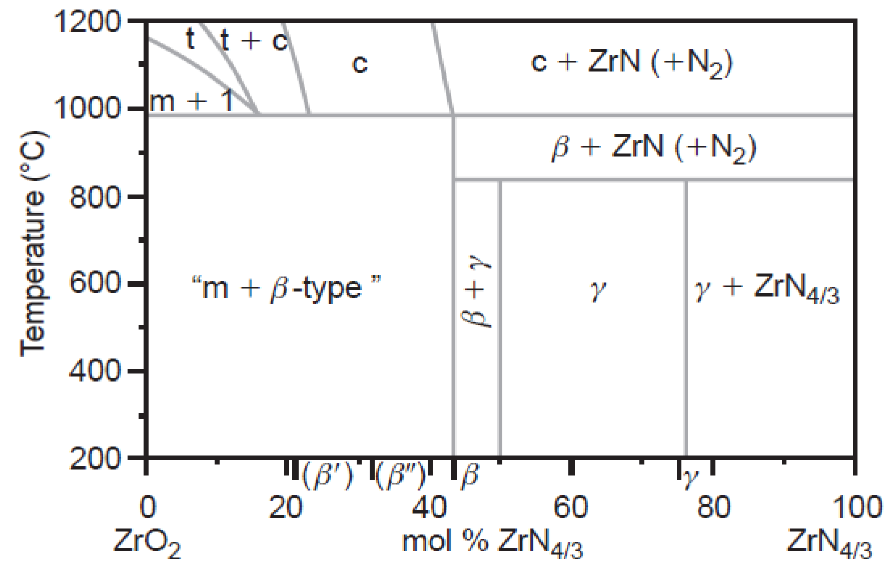
➢ Zirconium oxynitrides phases:

$\mathbf{ZrO_{2-2x}N_{\frac{4x}{3}}}$

Zr (+4)
O (-2)
N (-3)

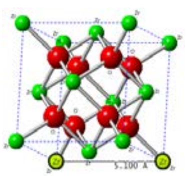
$+4*1 -2*(2-2x) -3*(4x/3) = 0$

$ZrO_{2-2x}N_{\frac{4x}{3}}$	Formula	Zr_3N_4 mol fraction (x)
β' $\left(x = \frac{3}{14}\right)$	$Zr_7O_{11}N_2$	0.214
β'' $\left(x \sim \frac{4.8}{14}\right)$	$\sim Zr_7O_{9.5}N_{3.0}$	~ 0.343
β $\left(x = \frac{6}{14}\right)$	$Zr_7O_8N_4$	0.418
γ $\left(x = \frac{3}{4}\right)$	Zr_2ON_2	0.75

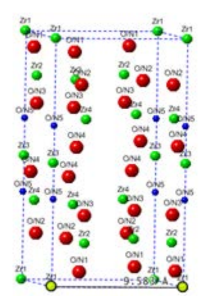


Taken from: (Lerch; 1998)

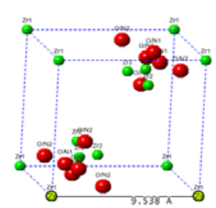
- Zriconium oxynitride phases retain the cubic fluorite structure of c-ZrO_2



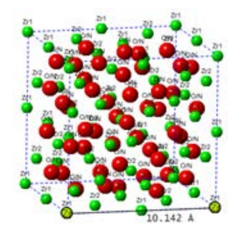
\- oxygen vacancies formed by the nitrogen incorporation, the original cubic lattice has been gradually distorted.



$Zr_7O_{11}N_2$



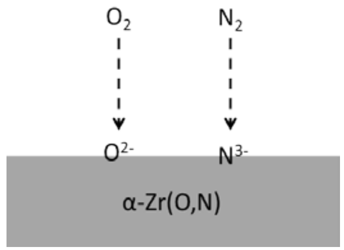
$Zr_7O_8N_4$



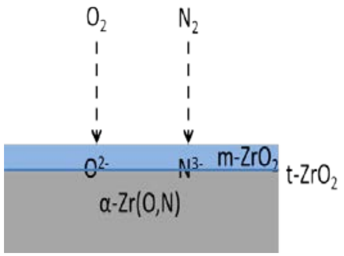
Zr_2ON_2

Part II – Conceptual nitridation process

- O_2/N_2 dissolution to **α**-Zr **and oxide formation after saturation of α**-Zr(O)



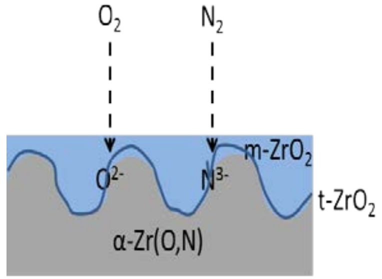
Oxygen and nitrogen dissolution



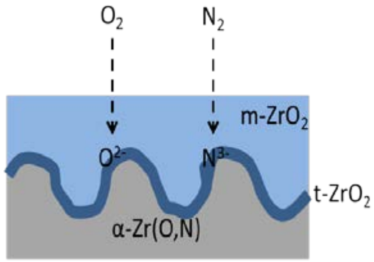
Oxide formation

- **Stabilization of t-ZrO_2 near the interface**

- High compressive stress, low grain size and sub-stoichiometry near the interface.

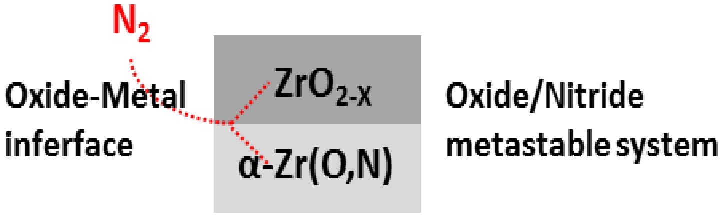


Undulation of the metal/oxide interface



t-ZrO2 thin layer formation

- O_2 **consumption by forming α**-Zr(O) and ZrO_{2-X}
- N_2 incorporation by stabilizing c-ZrO_2



Part II – Conceptual nitridation process

- Oxide/Nitride metastable system near the interface ($c\text{-}ZrO_2$ /$o\text{-}Zr_3N_4$)

– After solubility limit of the concentration of oxygen vacancies $(V_O^{\circ\circ})$

➡ $c\text{-}ZrO_2 + \frac{2}{3} N_2 \rightarrow \frac{1}{3}\, o\text{-}Zr_3N_4 + 2O$ (-14.34% molar volume shrinkage from $c\text{-}ZrO_2$)

– After solubility limit of $\alpha\text{-}Zr(O,N)$

➡ $Zr + \frac{2}{3} N_2 \rightarrow \frac{1}{3}\, o\text{-}Zr_3N_4$ (from $\alpha\text{-}Zr(O,N)$)

- Nitrogen rich part of Zr_3N_4/**γ**-Zr_2ON_2 system near the interface

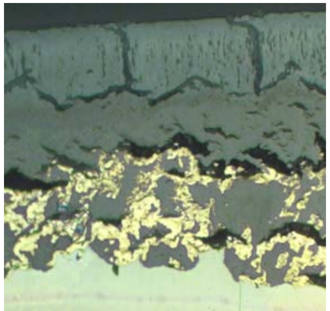
➡ $\frac{1}{2} ZrO_2 + \frac{1}{2} Zr_3N_4 \rightarrow Zr_2ON_2$

– Nitrogen rich Zr_3N_4 phase is a mestastable state and thus is decomposed to ZrN (and/or) $\gamma\text{-}Zr_2ON_2$ at high temperatures (above 800ºC)

$$Zr_3N_4 \rightarrow 3ZrN + \frac{1}{2} N_2$$

$$4\, Zr_3N_4 \xrightarrow{+3O_2-2N_2} 6\, \gamma\text{-}Zr_2ON_2 \xrightarrow{+9O_2-6N_2} 12\, m\text{-}ZrO_2$$

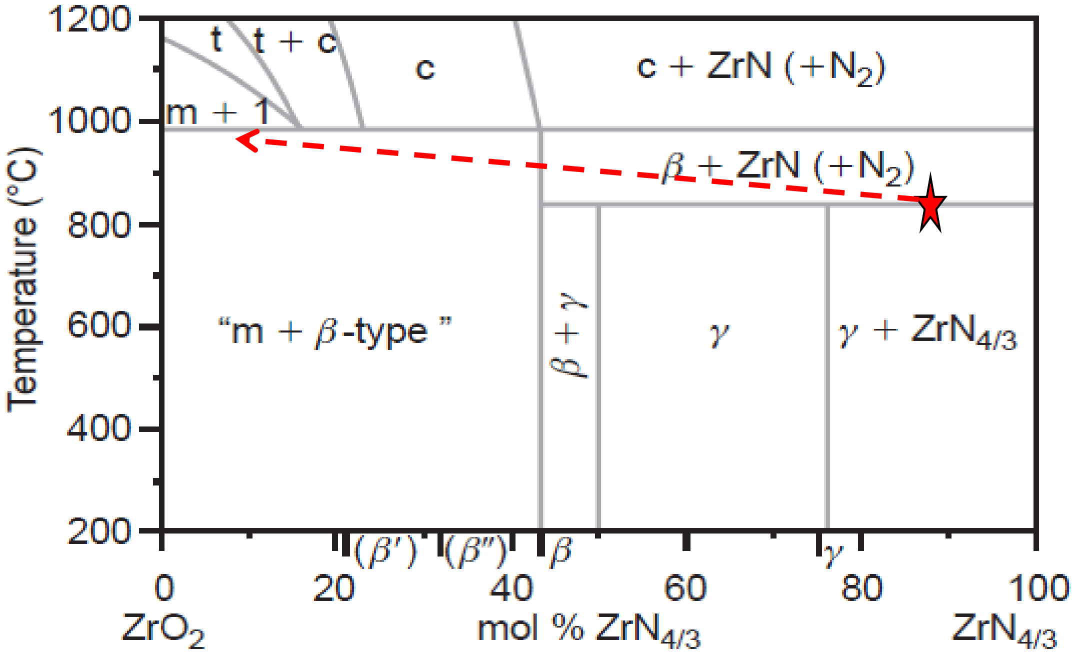
- <u>ZrN **and γ**-Zr_2ON_2</u> are optically golden-yellow color.



Part II – Conceptual nitridation process

- Decomposition of Zr_3N_4/**γ**-Zr_2ON_2 system to ZrN and m-ZrO_2 **and β**-type oxynitride phases from 800ºC

$ZrO_{2-2x}N_{\frac{4x}{3}}$	Formula	Zr_3N_4 mol fraction (x)
β' $\left(x = \frac{3}{14}\right)$	$Zr_7O_{11}N_2$	0.214
β'' $\left(x \sim \frac{4.8}{14}\right)$	$\sim Zr_7O_{9.5}N_{3.0}$	~ 0.343
β $\left(x = \frac{6}{14}\right)$	$Zr_7O_8N_4$	0.418
γ $\left(x = \frac{3}{4}\right)$	Zr_2ON_2	0.75



Taken from: (Lerch; 1998)

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

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

- Accelerated by low activation energy

$$2N_O' + V_O^{\circ\circ} + 3O \longrightarrow N_2 + 3O_O^X$$

- Self-sustained by newly generated nitrogen

Part III – Mechanism of nitridation process

➢ Reactions

I. Nitridation (solid-gas reaction): $N_2 + 3O_O^X \longrightarrow 2N'_O + V_O^{\circ\circ} + 3O$

(reducing condition; nitrogen activity and partial pressure are higher than oxygen's)

II. Nitridation (solid solution reaction): $2N(ZrN) + 3O_O^X \longrightarrow 2N'_O + V_O^{\circ\circ} + 3O(ZrN)$

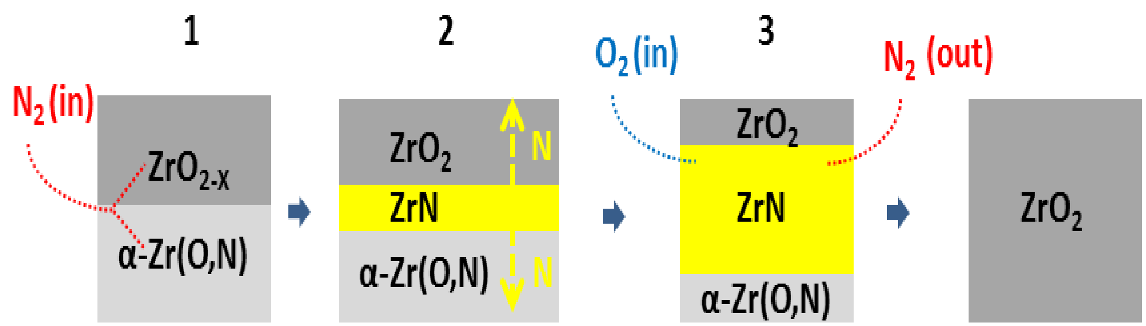
(reducing condition; nitrogen activity and partial pressure are higher than oxygen's)

III. Reoxidation: $2N'_O + V_O^{\circ\circ} + 3O \longrightarrow N_2 + 3O_O^X$

(oxidizing condition; nitrogen activity and partial pressure are lower than oxygen's)

Nitridation process 1→2→3

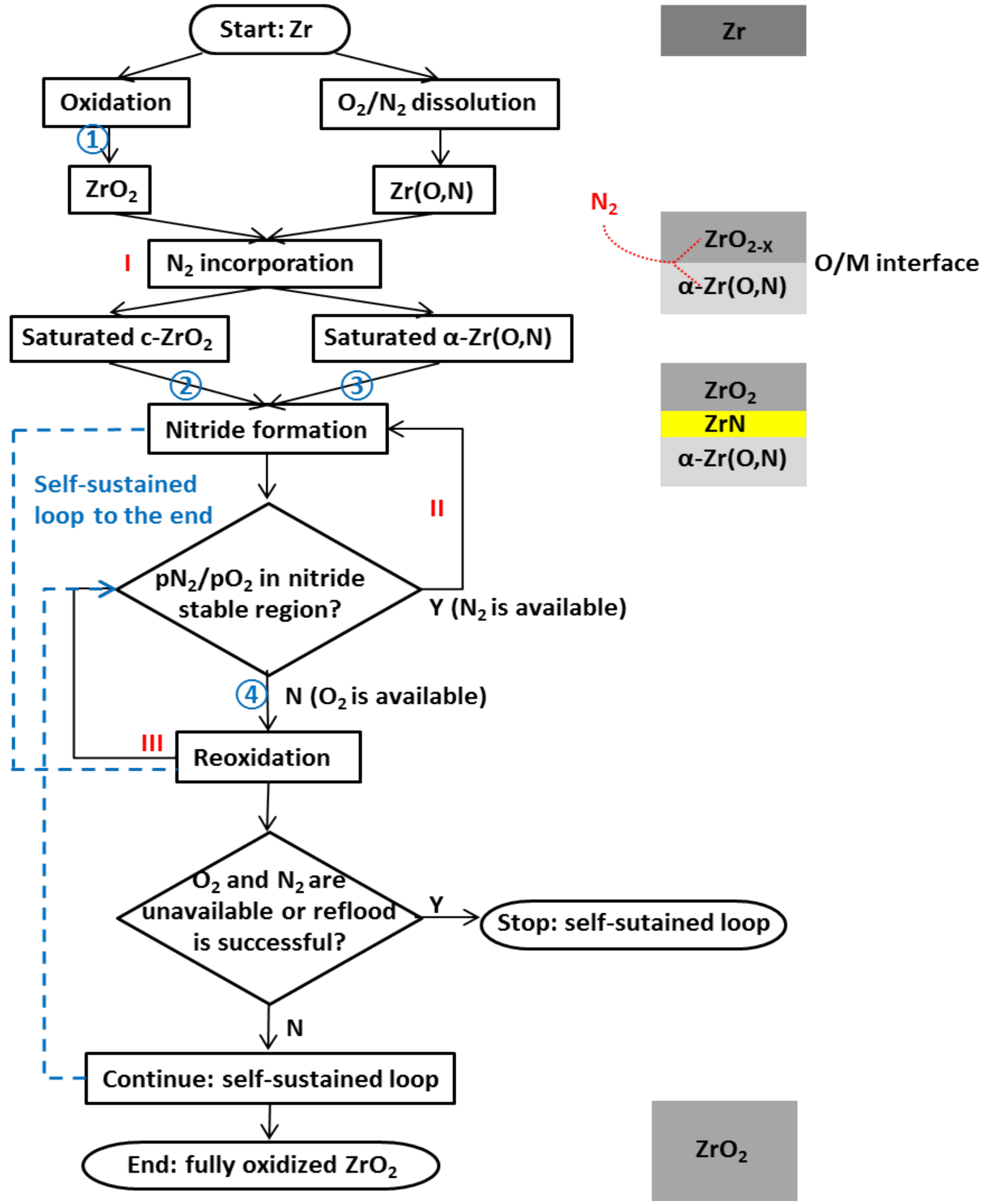
1. $N_2 + 3O_O^X \rightarrow 2N'_O + V_O^{\circ\circ} + 3O$
2. $2N(ZrN) + 3O_O^X \rightarrow 2N'_O + V_O^{\circ\circ} + 3O(ZrN)$
3. $2N'_O + V_O^{\circ\circ} + 3O \rightarrow N_2 + 3O_O^X$

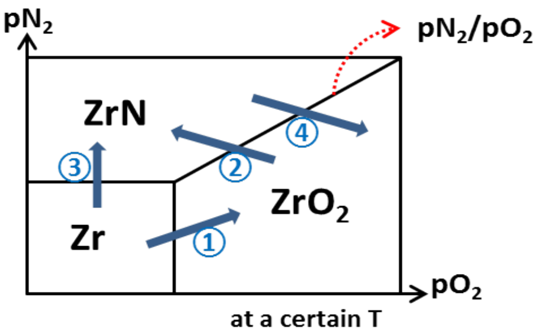


N accelerates the nitridation

- At 1 N_2 comes in and then comes out at 3
- N_2 acts as a catalyst by accelerating the whole reaction.
- Nitrogen solution (N) accelerates the whole reaction.

Part III – Mechanism of nitridation process





Simple reaction equations

① $Zr + O_2 = ZrO_2$

② $ZrO_2 + ½ N_2 = ZrN + O_2$

③ $Zr + ½ N_2 = ZrN$*

④ $ZrN + O_2 = ZrO_2 + ½ N_2$

*Reaction ③, nitridation of Zr, is not with fresh Zr but with saturated α-Zr(O,N).

Nitridation process (defect equations)

I. Nitridation (solid-gas reaction):

$$N_2 + 3O_O^X \longrightarrow 2N_O' + V_O^{\circ\circ} + 3O$$

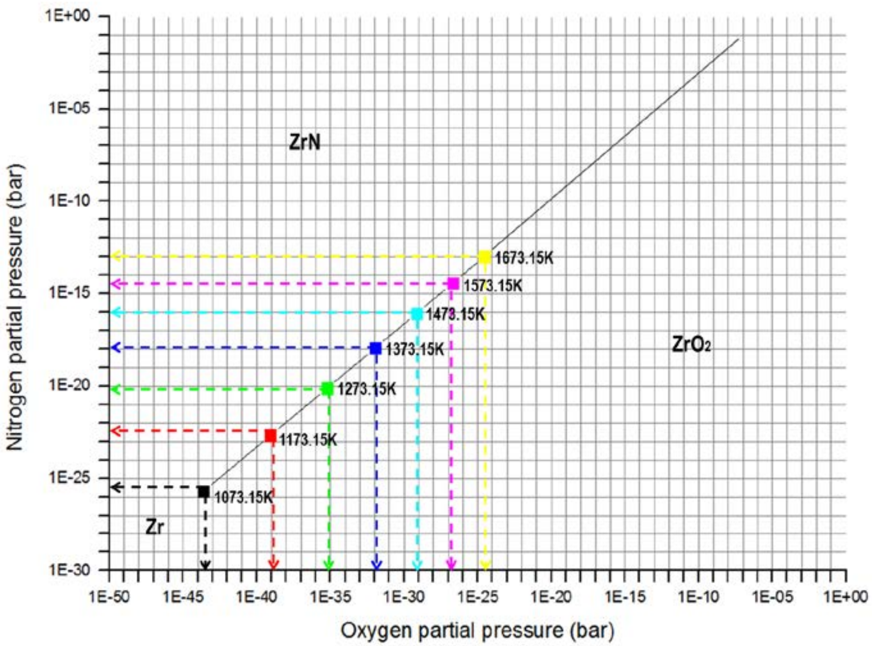
II. Nitridation (solid solution reaction):

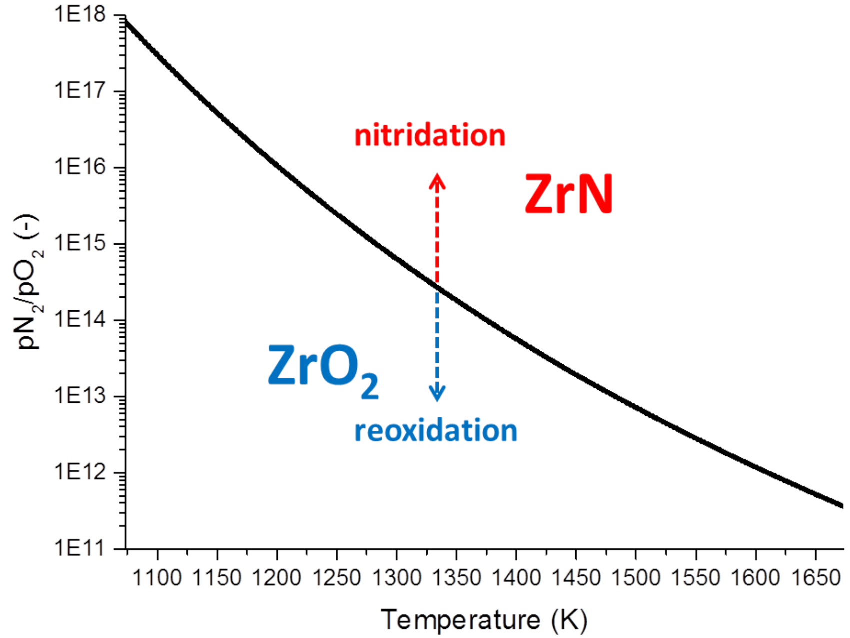
$$2N(ZrN) + 3O_O^X \longrightarrow 2N_O' + V_O^{\circ\circ} + 3O(ZrN)$$

III. Reoxidation: $2N_O' + V_O^{\circ\circ} + 3O \longrightarrow N_2 + 3O_O^X$

Part III – Mechanism of nitridation process

- p_{O_2}/p_{N_2} stability diagram (from Thermo-Calc. calculation)

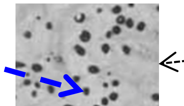




- Cladding degradation by self-sustained nitridation-reoxidation

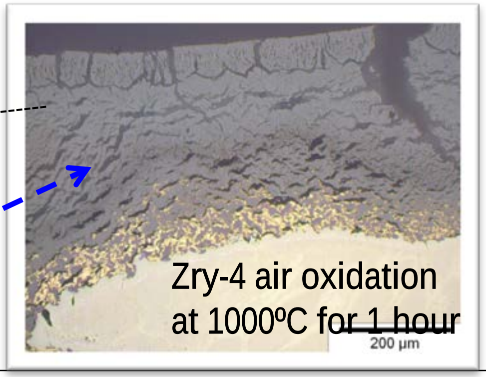
Nitridation: $\Delta V_{c-ZrO_2 \rightarrow o-Zr_3N_4/\,\gamma-Zr_2ON_2} = -11.49\%$

- micro porous media



Reoxidation: $\Delta V_{ZrN \rightarrow m-ZrO_2} = +42.45\%$

- micro cracked media (mainly circumferential cracks)



Part III – Mechanism of nitridation process

Nitridation process	Volume change and heat generation
In the beginning: t-ZrO_2 and α-Zr(O,N)	$\Delta V_{t-ZrO_2 \rightarrow c-ZrO_2} = +0.15\ \%$ $\Delta H_{O-N} = -500\ kJ/mol\ N$ $\Delta H_{V_O^{\circ\circ}} = -190\ kJ/mol\ V_O^{\circ\circ}$
Step I. Nitrogen incorporation (gas-solid reaction) near the oxide-metal interface:	
Step II. Oxide/Nitride metastable system near the oxide-metal interface	$\Delta V_{c-ZrO_2 \rightarrow o-Zr_3N_4/\ \gamma-Zr_2ON_2} = -11.49\%$
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	$\Delta V_{ZrN \rightarrow m-ZrO_2} = +42.45\%$ $O_2(g) + ZrN \rightarrow m - ZrO_2 + N_2(g)$ $\Delta H_{Reoxidation} = -732\ kJ/mol\ ZrN$
Step V. Accelerated self-sustaining nitridation process (solid solution reaction and reoxidation)	
In the end: ZrO_2	

Summary and Outlook

Limitations in current state of knowledge on nitridation process

- Post-test investigations and binary system analysis

Different approach to develop a detailed conceptual model

- Theory: Zr-O-N ternary system analysis from different fields and thermodynamics
- Simulation: Thermo-Calc calculation (using TTZR1 and ALCHYMY databases)
- Experiment data: KIT SETs data and literature findings

A mechanism of nitridation process in the Zr-O-N system

I. Solid-gas nitridation

II. Solid solution nitridation

III. Reoxidation

Thank you for your attention.

Questions ?