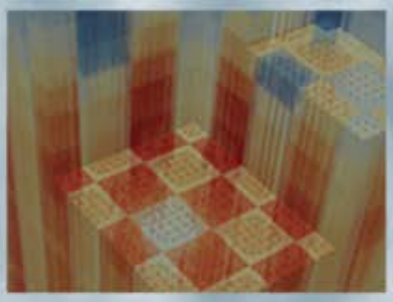
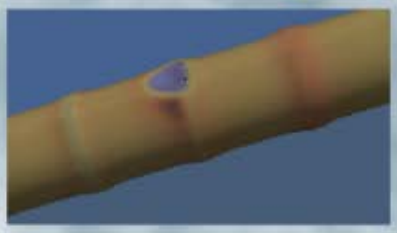
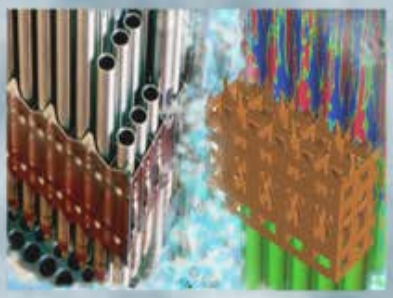
CASL-U-2015-0109-000

Finding the Cure for CRUD: Combined Simulations & Experiments at CASL & MIT







Michael P. Short
Massachusetts Institute of Technology

July 9, 2013

CASL-U-2015-0109-000

Finding the Cure for CRUD: Combined Simulations & Experiments at CASL & MIT

Prof. Michael P. Short (MIT)

With Thanks To:
D. Hussey (EPRI)
D. Gaston, C. Permann (INL)
D. Andersson, B. Kendrick, C. Stanek (LANL)
I. Dumnernchanvanit, A. Dykhuis, W. Li, E. Paramonova,
X. Qian, Y. Yang, J. Buongiorno, J. Li, B. Yildiz, S. Yip (MIT)
D. Brenner, C. O'Brien (NCSU)
T. Besmann, D. Shin (ORNL)
B. Collins, A. Manera, V. Petrov (Univ. Michigan)

CASL Summer Student Workshop
Oak Ridge National Laboratory
2013-07-09

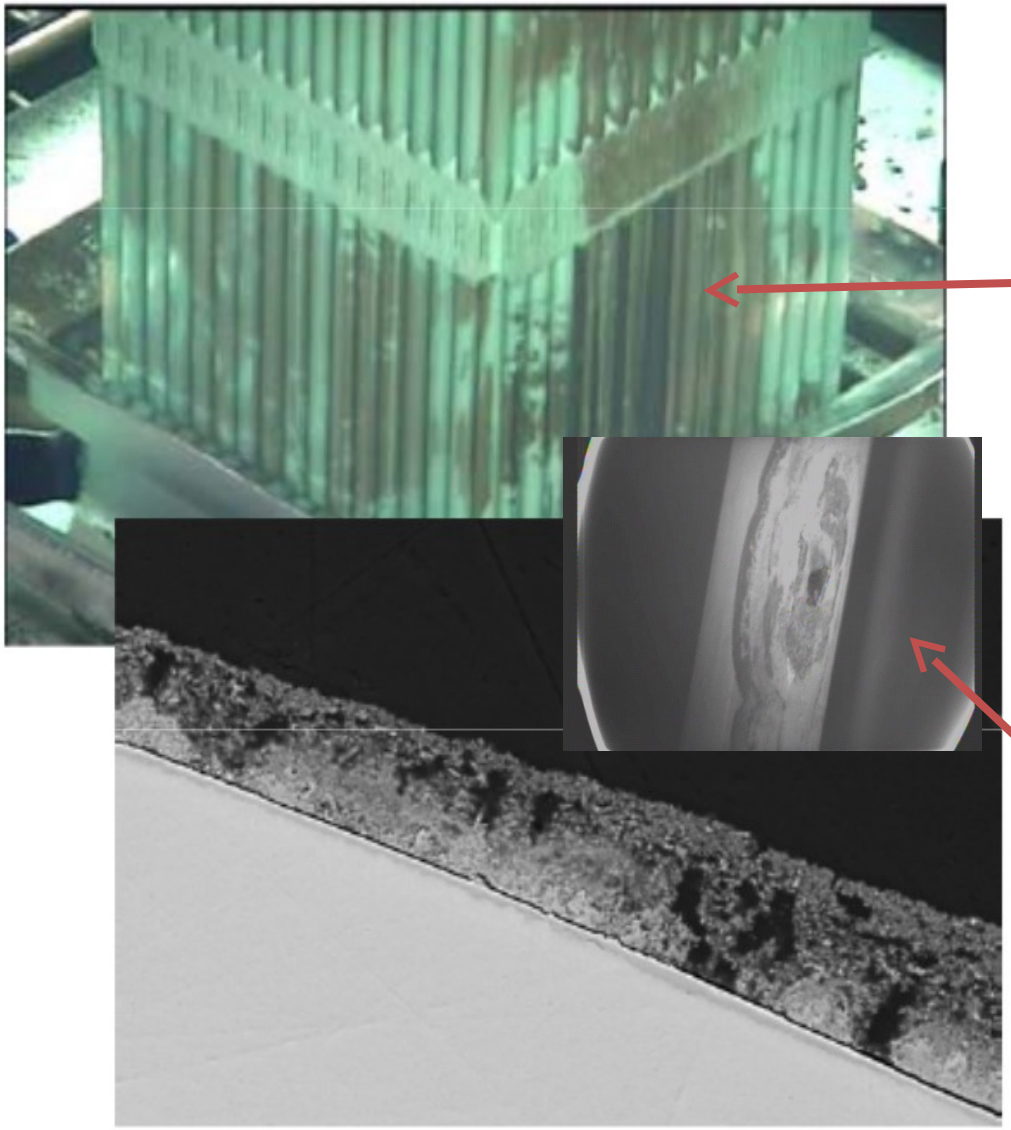
CASL-U-2015-0109-000

Outline

- Introduction to CRUD[1]
- Simulating CRUD's Effects on Fuel Performance
- Validation & Coupling Activities
- Experimental Thrusts
  - CRUD Resistant Materials
  - PWR CRUD loop Construction

[1]Chalk River Unidentified Deposits

CRUD: Porous Corrosion Product Deposition



Problem Definition

- Reactor internals corrode, releasing products into coolant
- Sub-cooled boiling creates porous deposits
- Boric acid in coolant hides out in CRUD pores

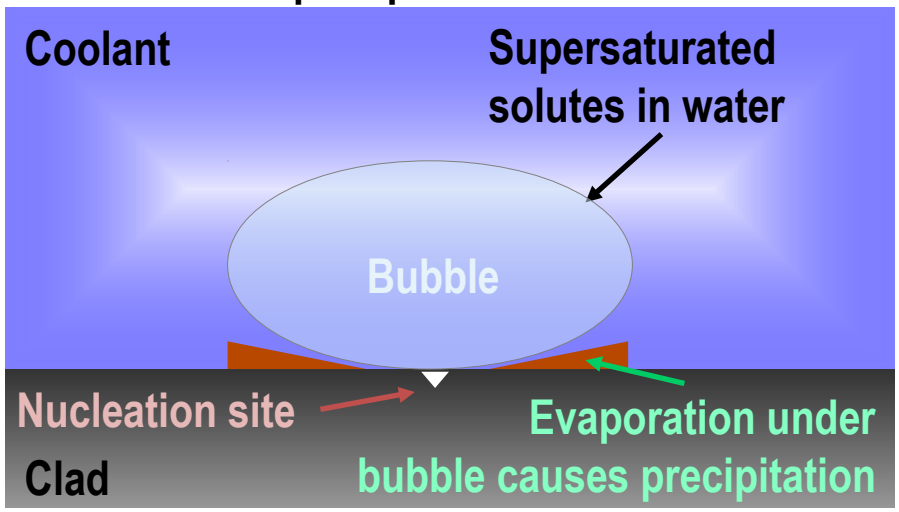
Effects on Plant

- CRUD-Induced Power Shift (CIPS) due to boron
- CRUD-Induced Localized Corrosion (CILC) due to degraded heat transfer
- Increased worker dose due to CRUD activation

Images: D. Wells. "EPRI Chemistry and Radiation Management PWR Primary Water Chemistry Guidelines Revision Project Updates – Optimized Fuel Crud and SRMP Revision." EPRI P-TAC Summer Meeting, Atlanta, GA, 8/29/2012.

The Anatomy of CRUD

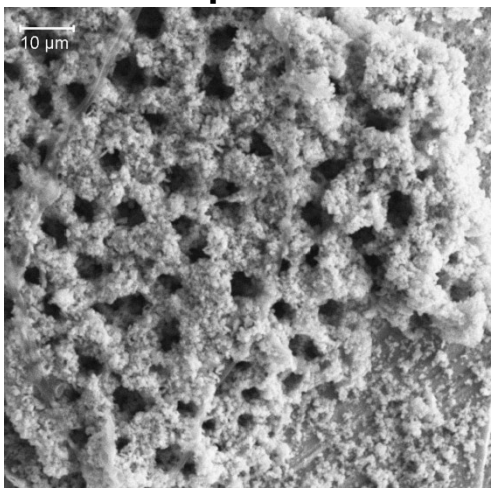
Porous CRUD precipitates underneath bubble



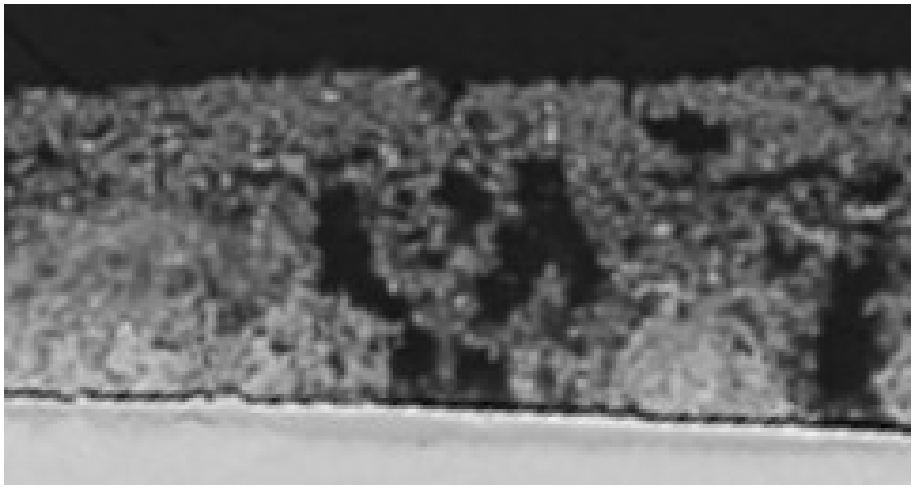
Major Features

- Porous deposits on upper spans of fuel rods
- Skeleton of (Ni, Fe, Cr, Zn, Zr) oxides from steam generator, reactor internals
- Boiling chimneys from bubbles
- 1-100 μm thick
- Solubles ($LiBO_2$, $Li_2B_4O_7$, B_2O_3…) precipitate in the pores

Top View

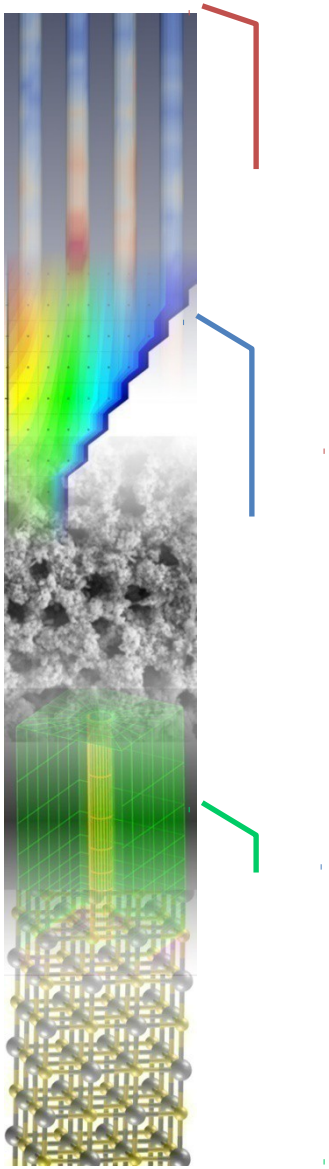


Side View



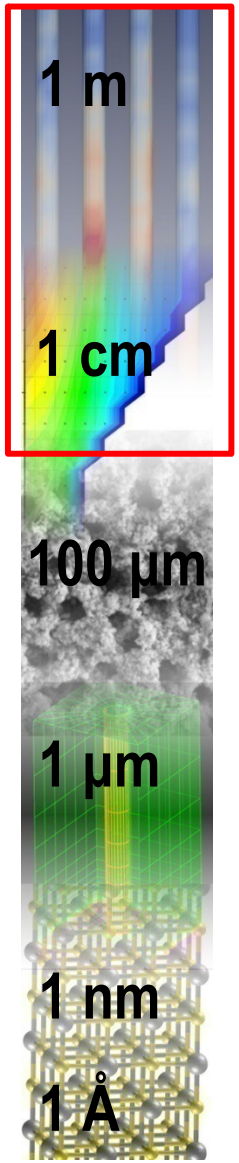
Images: J. Deshon. "PWR Axial Offset Anomaly (AOA) Guidelines, Rev. 1." EPRI Technical Report #1008102, p. 51 (2004).

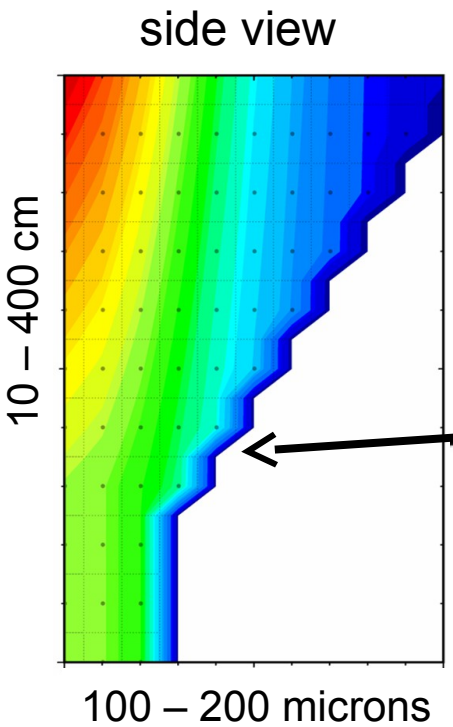
The CASL Approach to Multiscale Materials Modeling: CRUD as an Illustrative Example

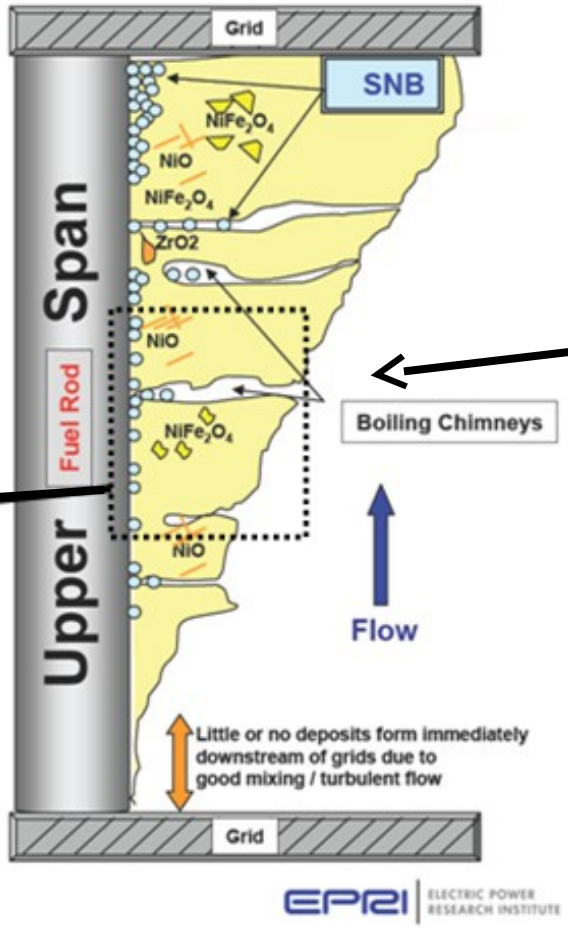


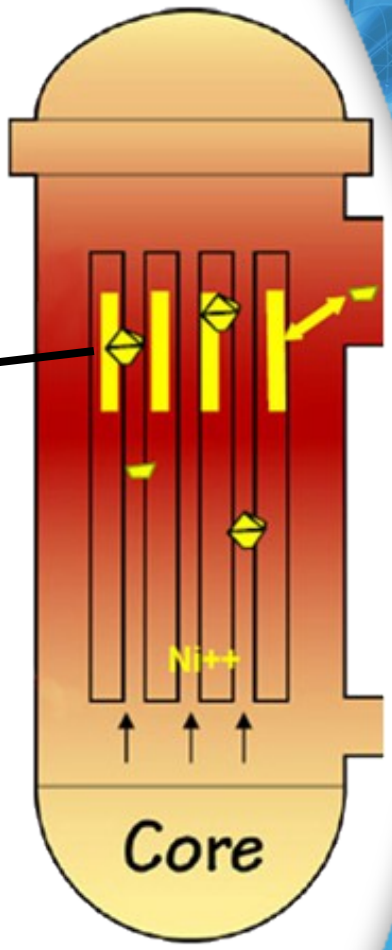
- Top-Down Approach
- Ultimate Goal: 3D Engineering Framework (MAMBA)
  - Predict :
  - CRUD thickness
  - Peak cad temperature
  - Boron loading
  - Couple to fuel performance codes
- High-Fidelity Info from the Mesoscale (MAMBA-BDM)
  - Finer level of granularity
  - Couples CRUD to cladding corrosion
  - Same parameters at MAMBA
  - Higher computational cost
- Filling in the Details: Atomistics & Thermodynamics
  - Identify & compute missing fundamental data
  - Pass info up to MAMBA-BDM, such as:
  - NiO cluster formation
  - Species-dependent boron compound precipitation
  - Thermodynamic phase stability

Engineering Scale: MAMBA Framework



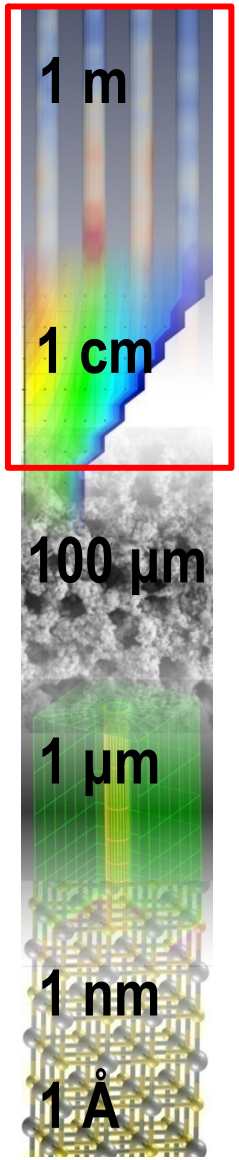


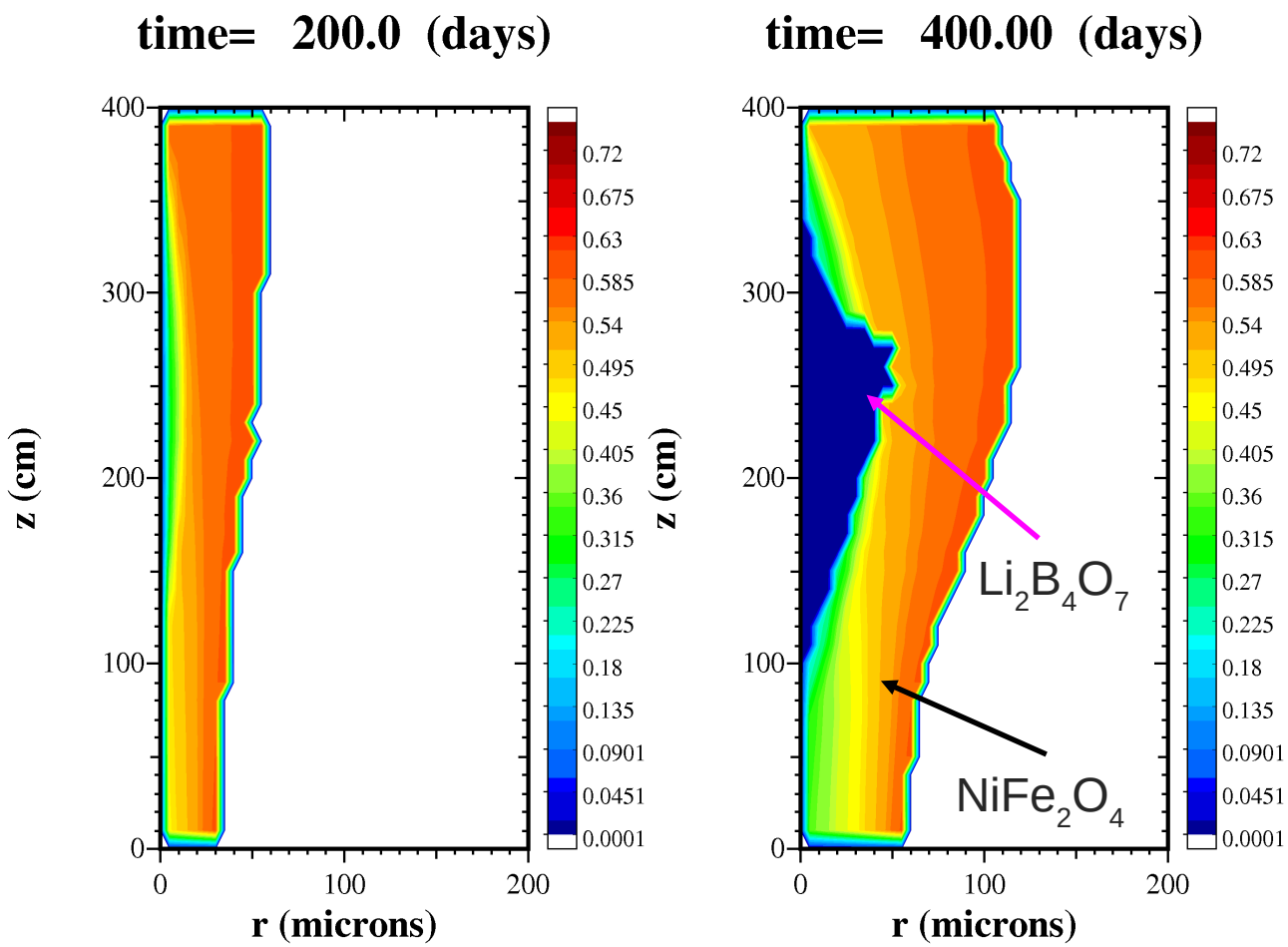




- MPO Advanced Materials/Boron Analyzer
- Examines CRUD buildup on upper spans of core
- Node size: ~1cm x ~10µm (pancake shaped)

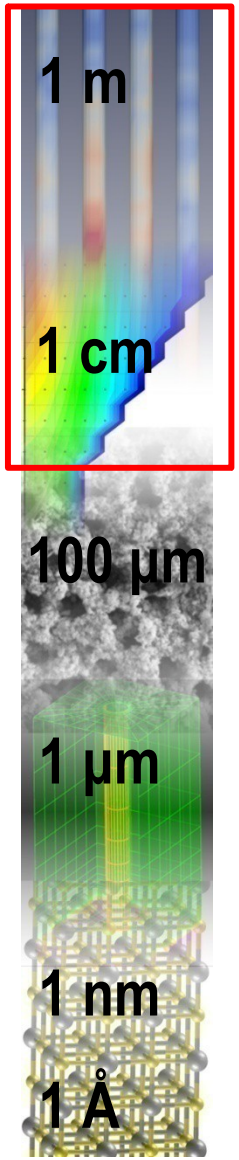
Engineering Scale: MAMBA Framework

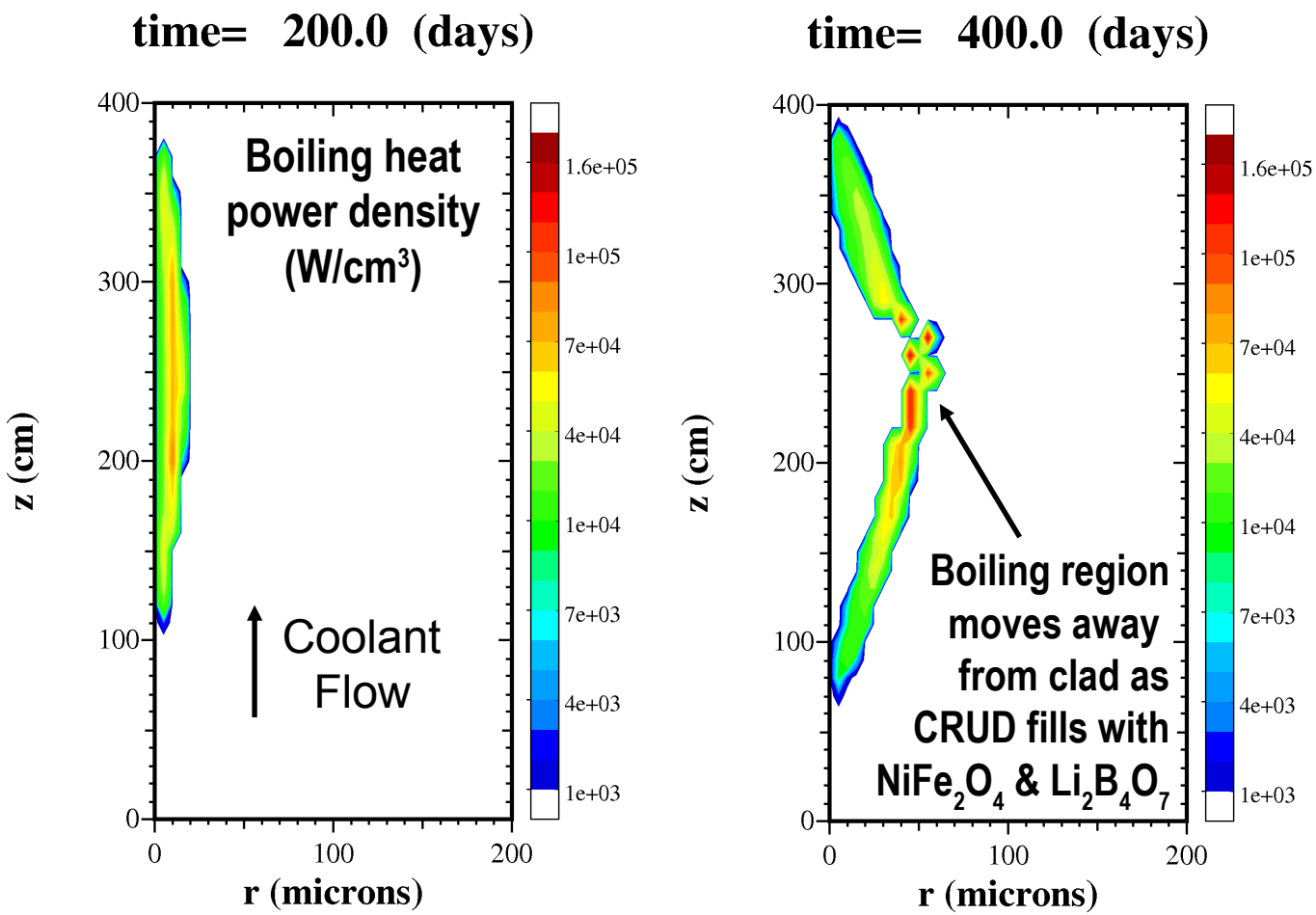




- Empirical or physics-based relations for key phenomena
  - Boiling rate, CRUD skeleton growth, soluble precipitation
- Soluble precipitation is binary in nature (fills pores)

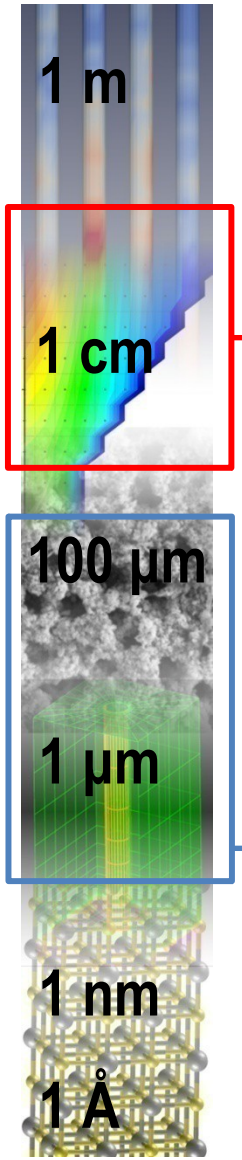
Engineering Scale: MAMBA Framework

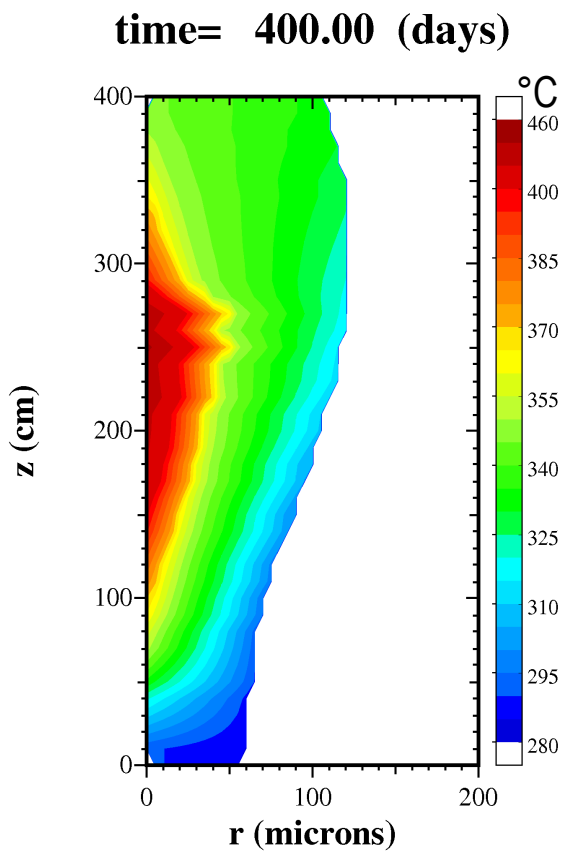




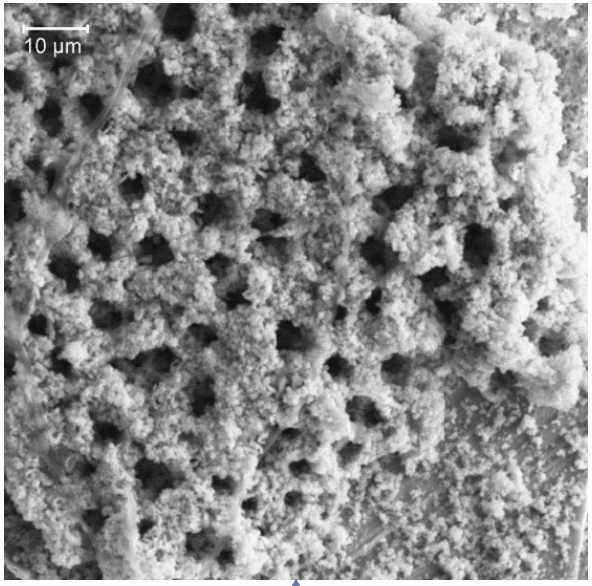
- Boiling region moves as CRUD pores fill w/ precipitates
- Cladding heats up as boiling heat removal departs
- This can lead to CIPS & CILC

Engineering Scale: Limitations



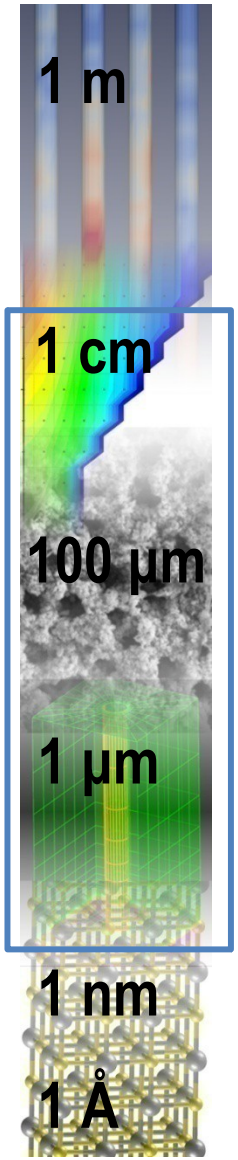


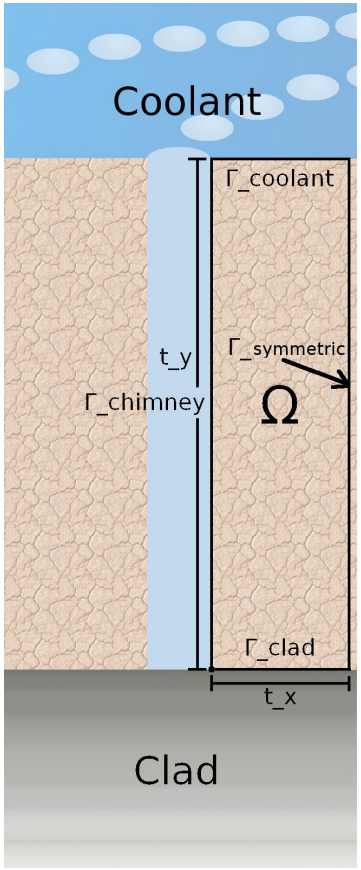
GAP!

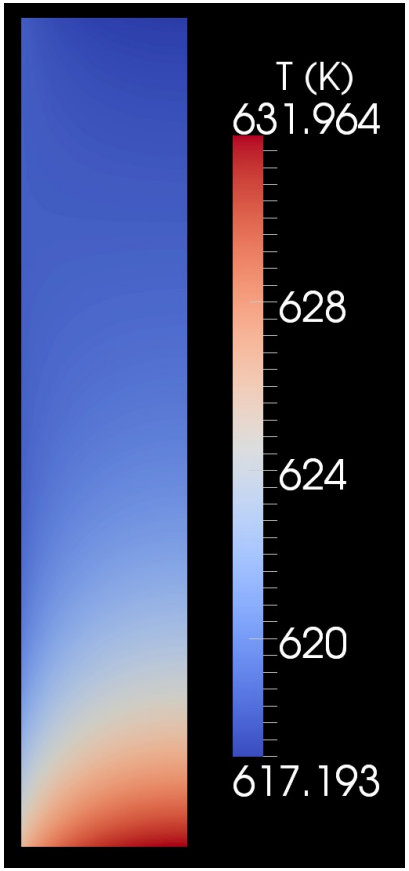


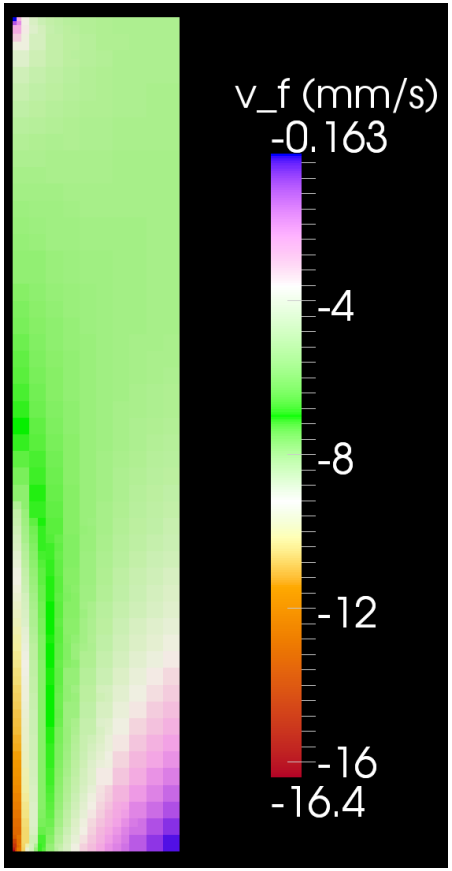
- Can't address CRUD microstructure
  - Too computationally intense for full core simulation
- Lower fidelity for key parameters (peak clad temp.)
  - Higher accuracy required to address corrosion risk

Micro/Mesoscale Framework: MAMBA-BDM



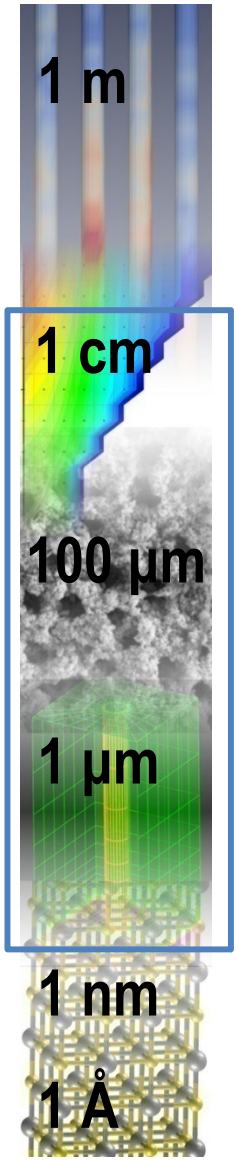


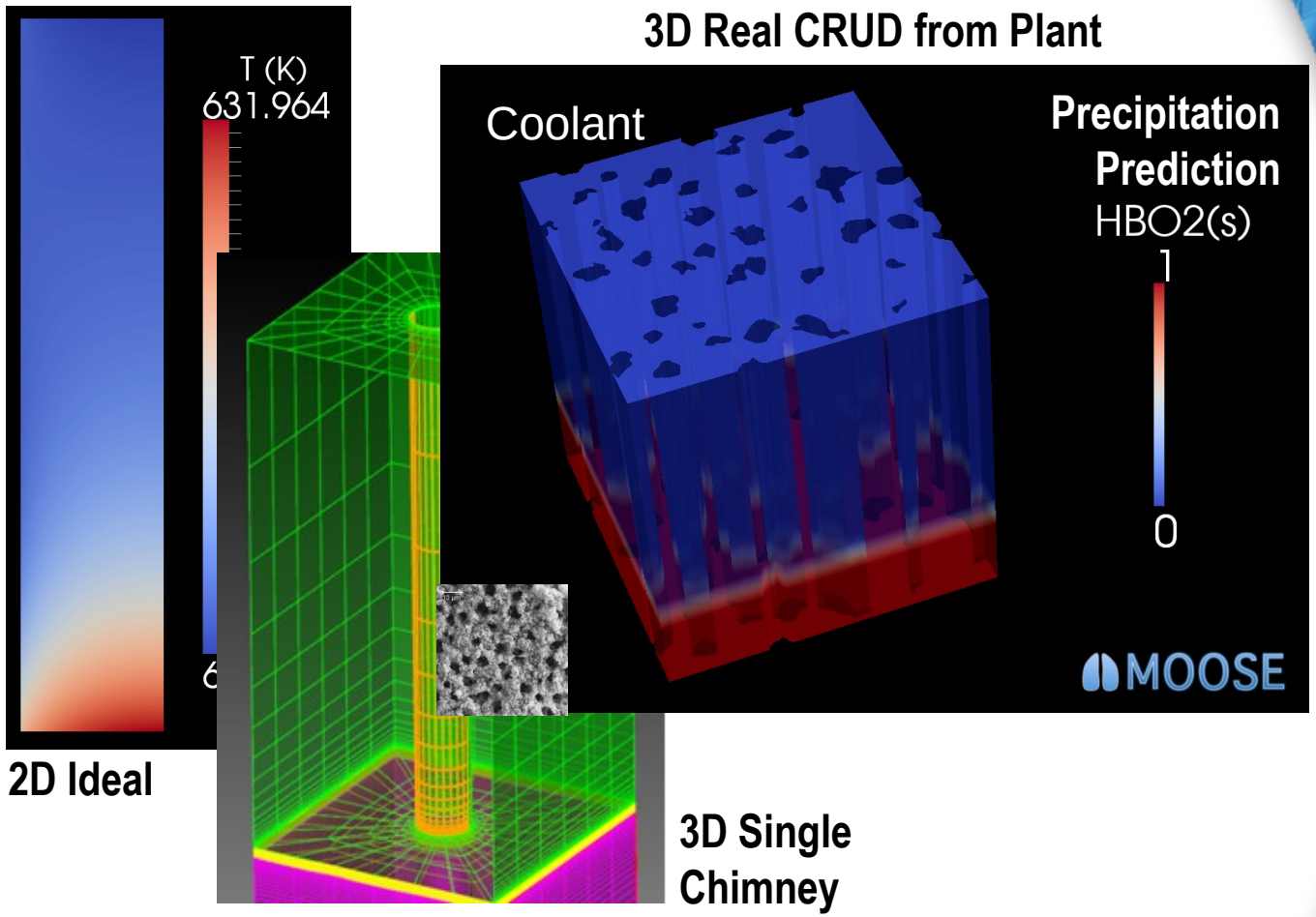




- **Addresses fine details of CRUD microstructure**
  - Pore size distribution, boiling chimneys, multiple chemical species
- **Fully coupled distributions & material properties**
  - More computationally intense, but it's worth it!!!

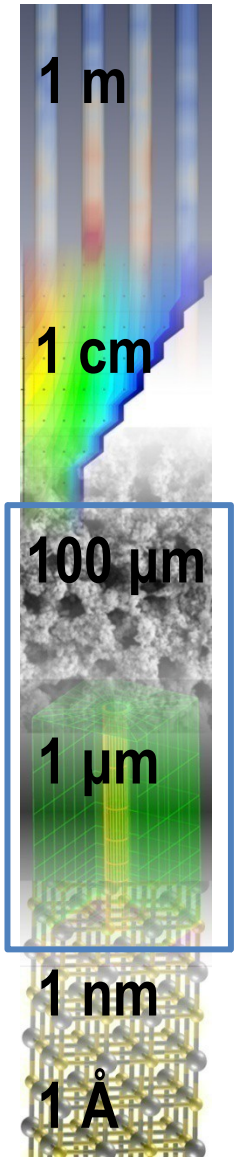
Micro/Meso: MAMBA-BDM Implementation

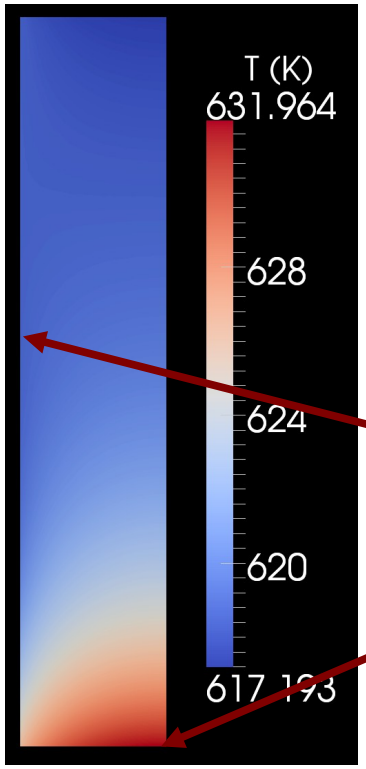




- Written in INL's MOOSE framework, ***geometry/dimension agnostic***, highly parallelizable
- Allows rapid treatment of *many* types of problems
- Single chimneys, regular arrays, real CRUD microstructure…

Micro/Meso: 2D Results



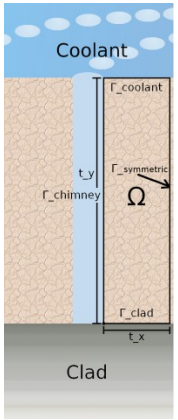


Simulation Parameters:

- Clad heat flux = 1 MW/m^2
- $T_{coolant}$ = 600 K
- $P_{coolant}$ = 15.5 MPa
- Skeletal porosity = 50%
- $[H_3BO_3]_{coolant}$ = 1200 ppm
- $h_{conv,CRUD\text{-}coolant}$ = 12,000 W/m^{2}K

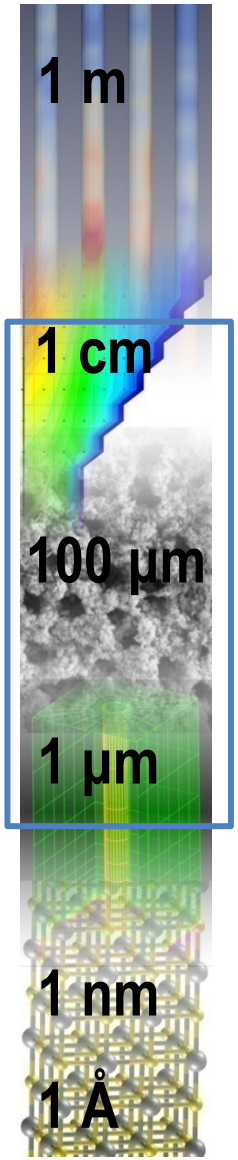
Boiling chimney maintains T_{sat}

Hot spot on cladding, away from chimney

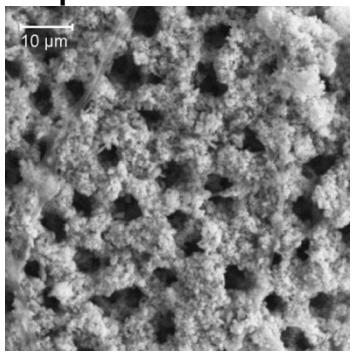


- Peak clad temperature at cladding, away from boiling
- Heat transferred by both conduction & convection
- Wick boiling assumed at CRUD/chimney interface

Micro/Meso: Modeling Real 3D CRUD

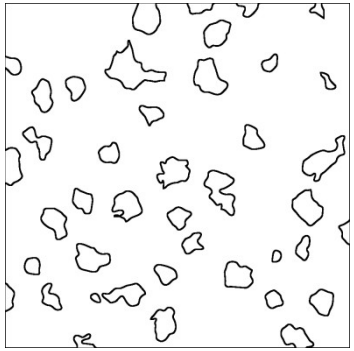


Acquire Microstructure

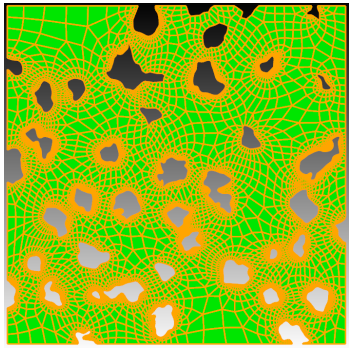


J. Deshon. "PWR Axial Offset Anomaly (AOA) Guidelines, Rev. 1." EPRI Tech. Report #1008102, p. 51 (2004).

Extract Boundaries



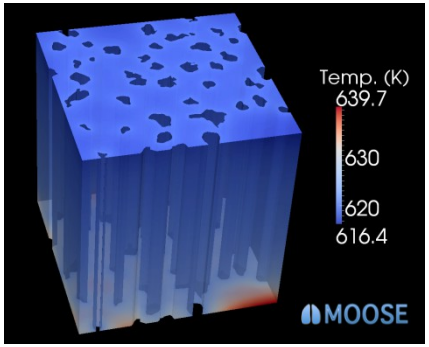
Create CRUD Mesh



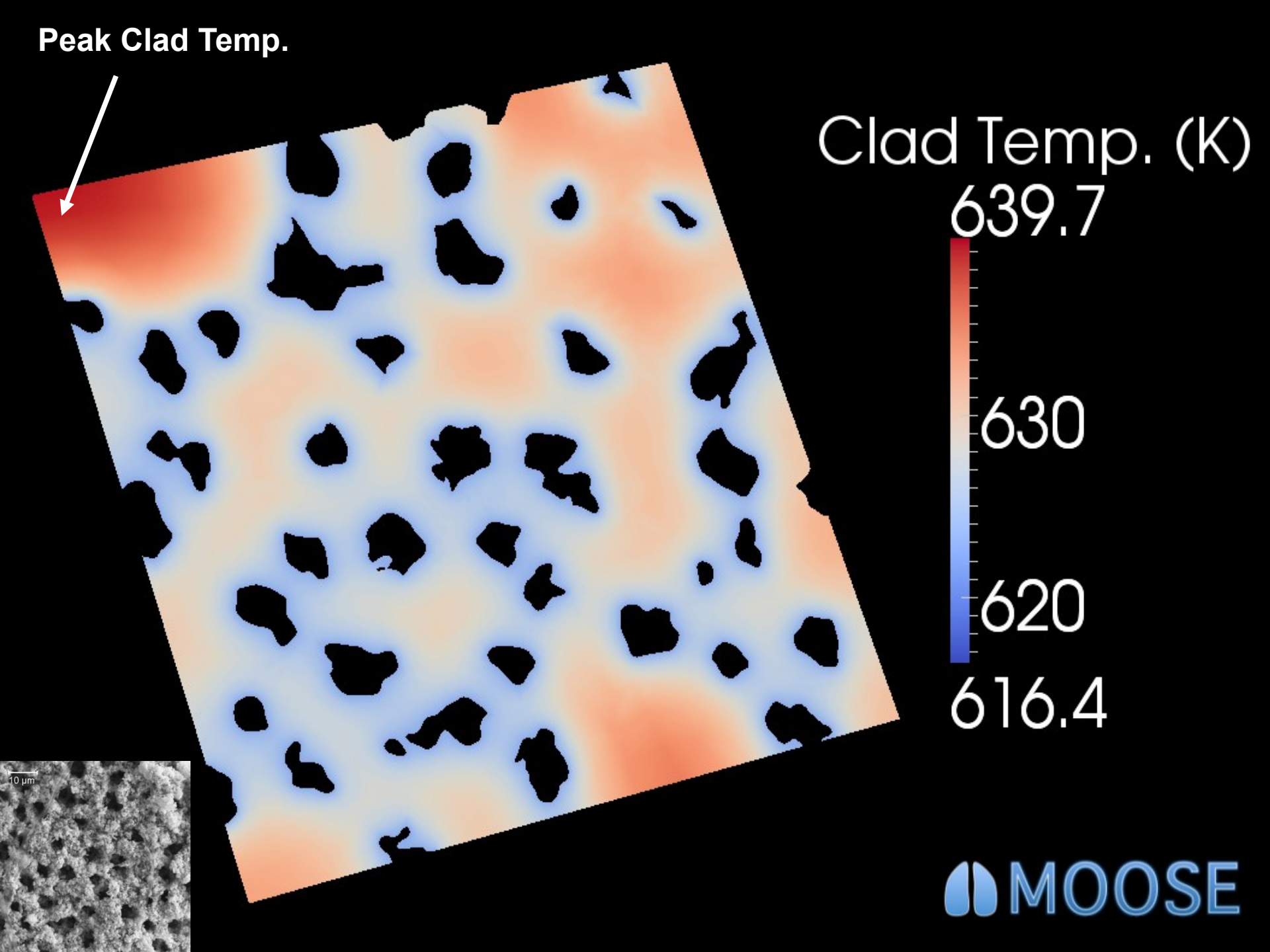
Develop Separate Physical Model

Image: http://www.reptilienzoonockalm.at/Tierbestand.htm

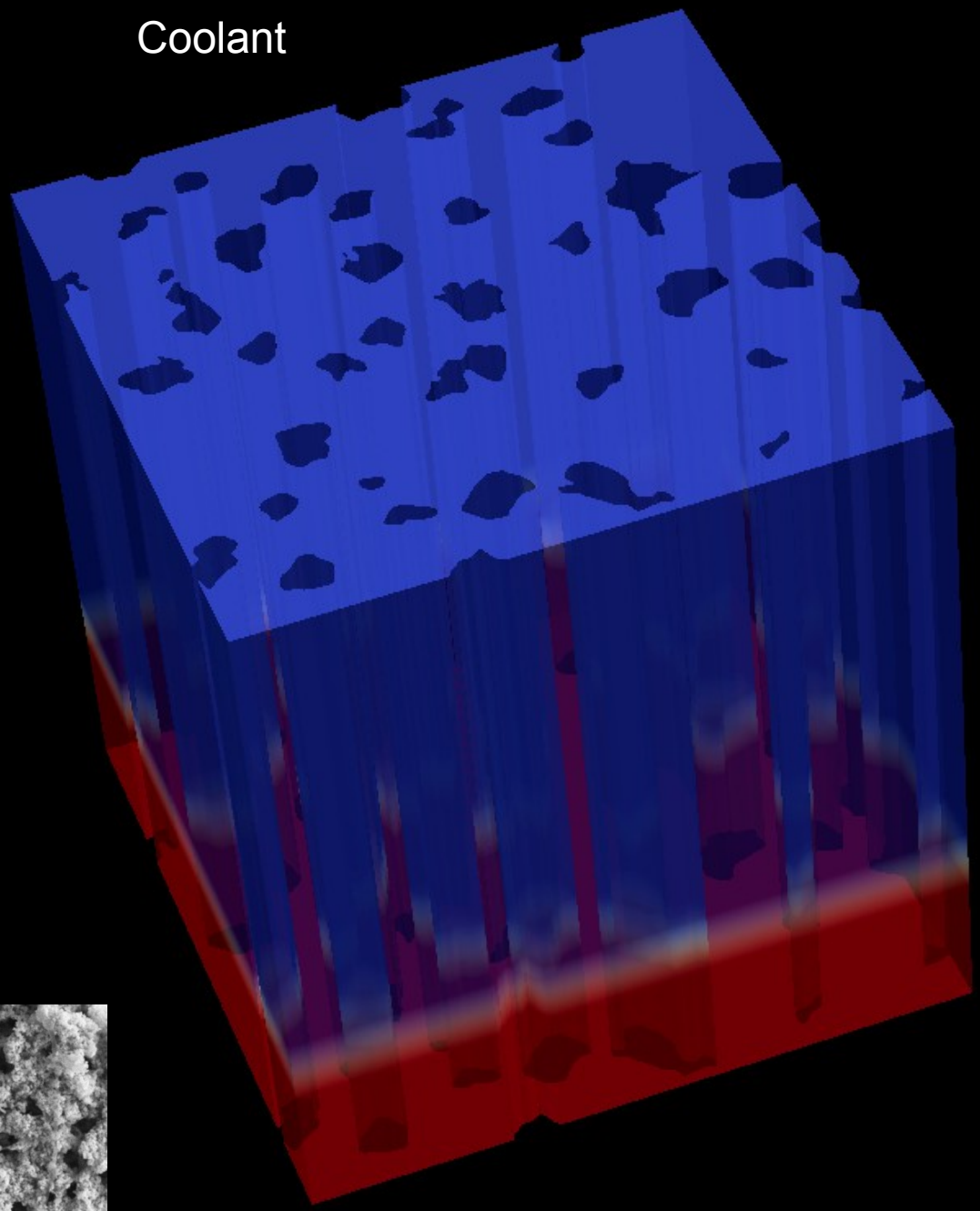
Simulate Real Microstructure

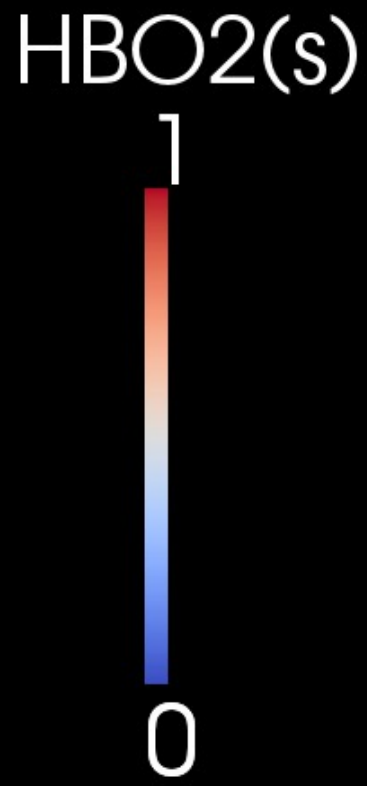


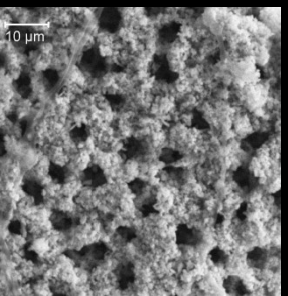
- Use image processing techniques on plant CRUD
- Apply MAMBA-BDM models on new mesh
- Map boundary conditions appropriately, run!


Peak Clad Temp.
Clad Temp. (K)
639.7
630
620
616.4
10 µm
MOOSE

Precipitation Prediction

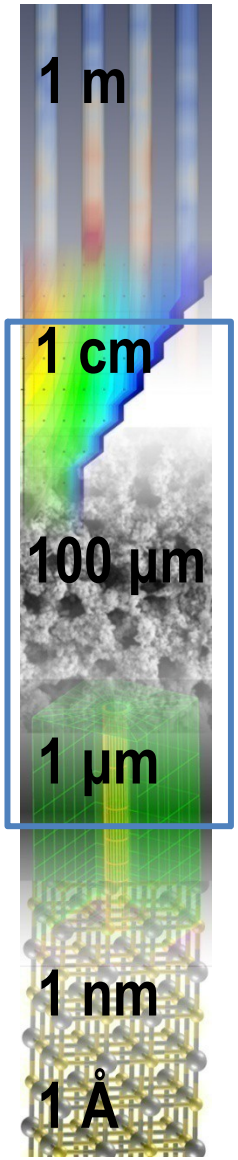


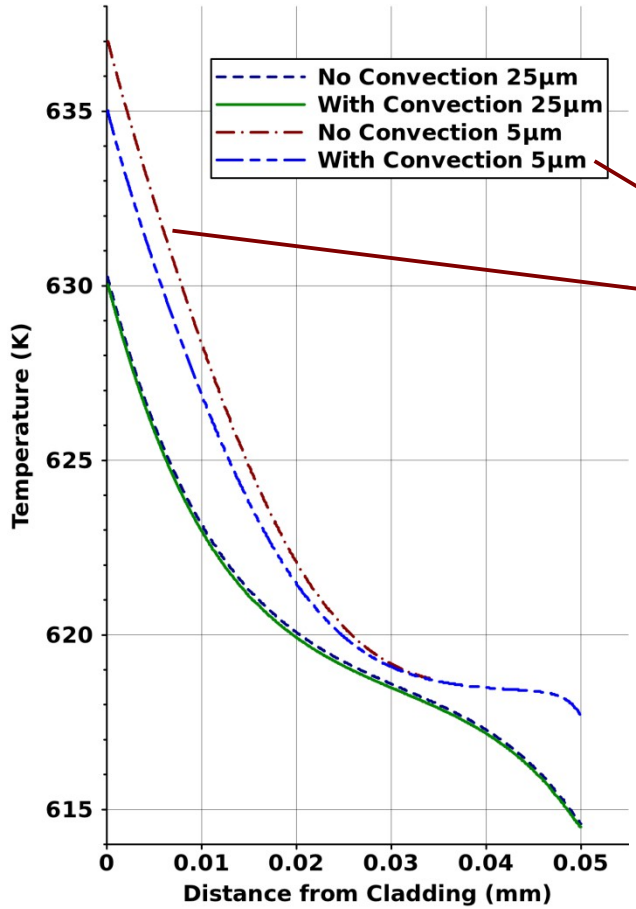




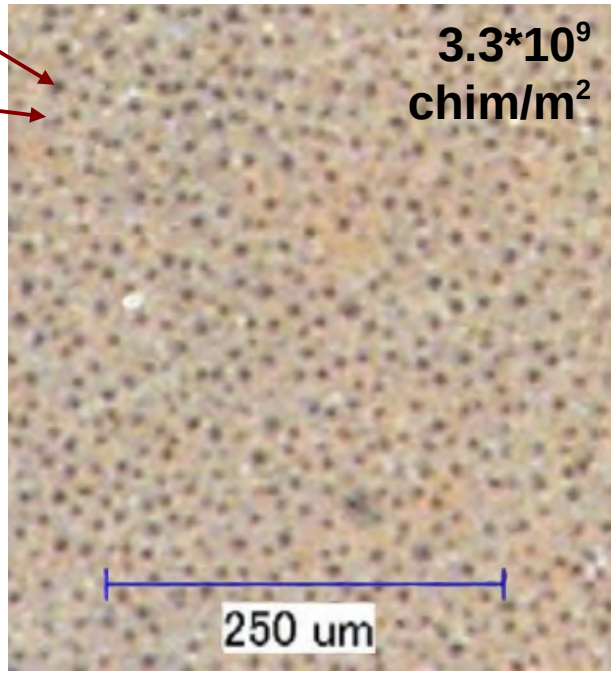
MOOSE

Micro/Meso: Effect of Heat Convection



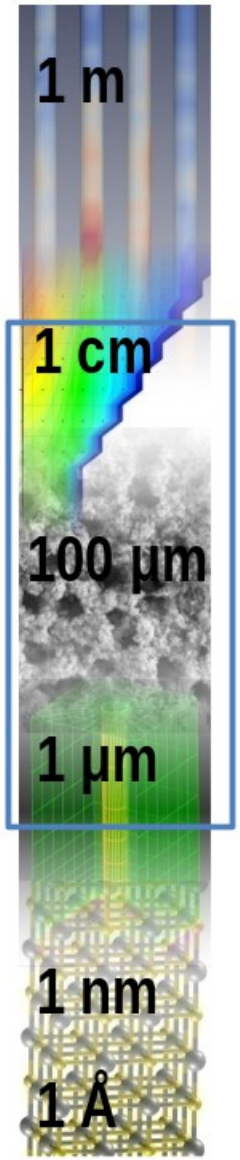


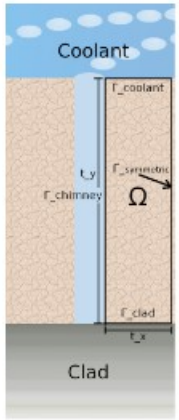
Importance increases with chimney density

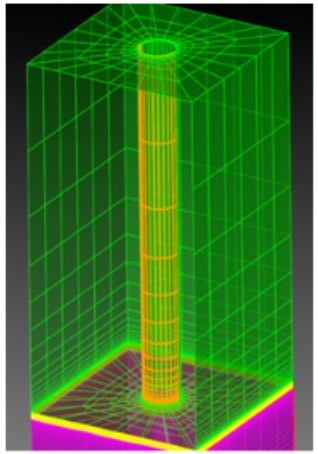


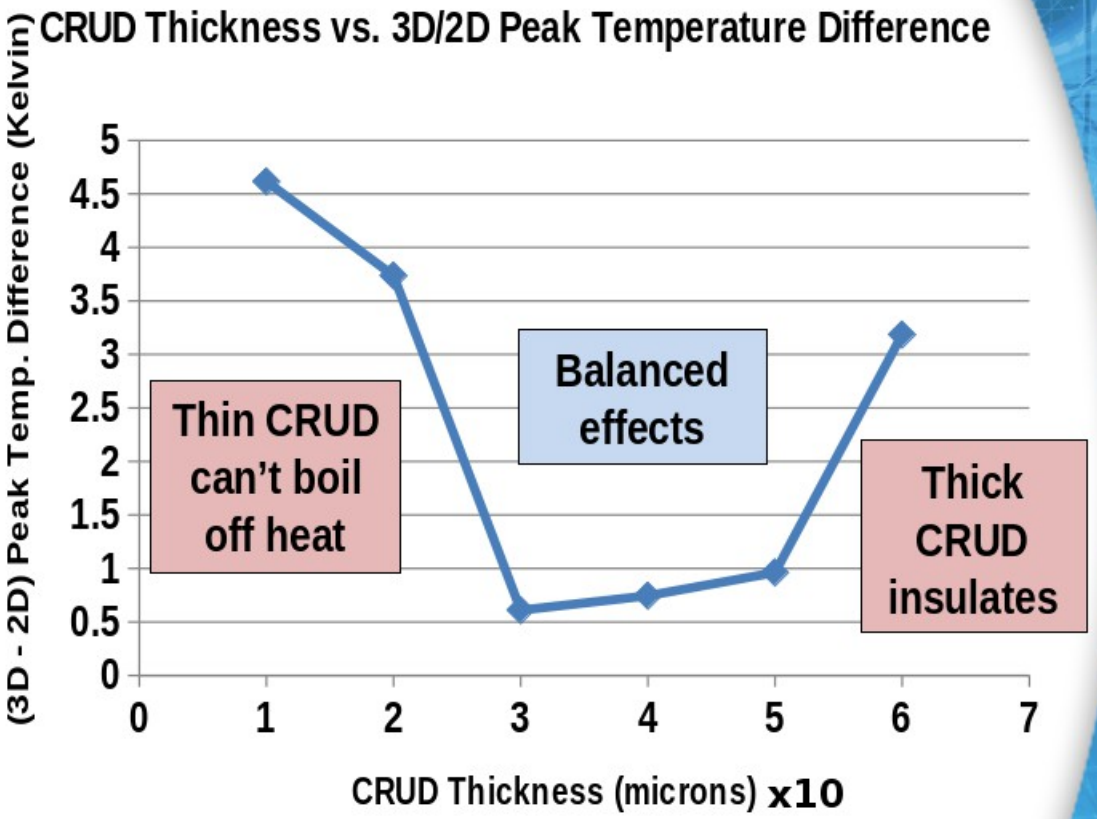
- Convection is *non-negligible* for tight spaced chimneys
  - Can change peak clad temp. by 2K, corrosion rate by 10-15%
- Realistic case for plant & synthetic CRUD

Micro/Meso: Effect of Real/Ideal Geometry



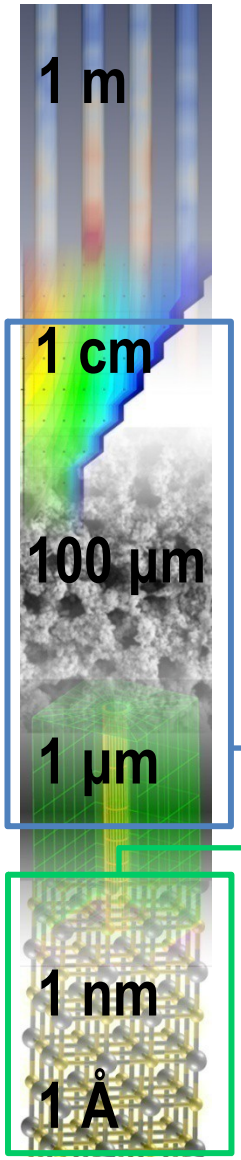


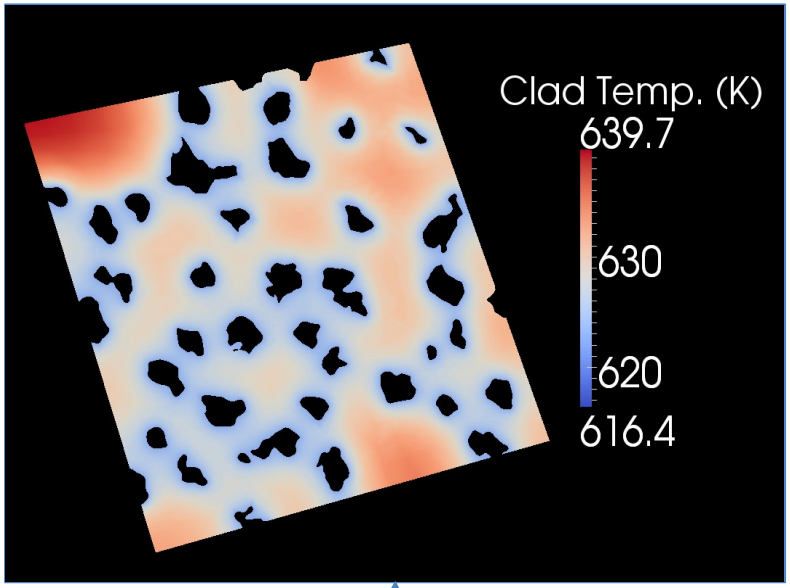




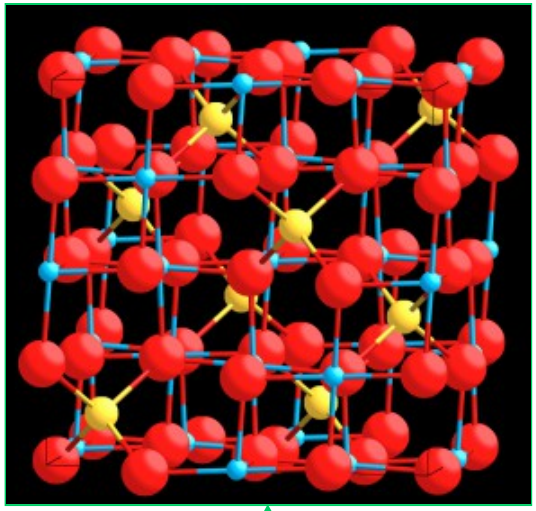
- 2D case: Idealized geometry
  - Revolved cylinder, symmetric boundary conditions
- 3D case: Real geometry
  - Slab with corners, periodic boundary conditions

Micro/Mesoscale: Limitations



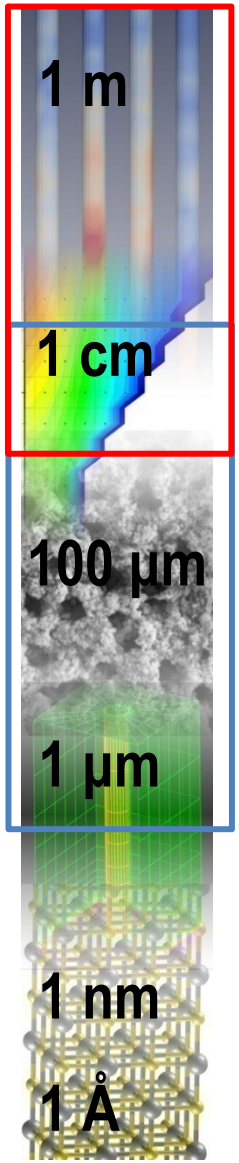


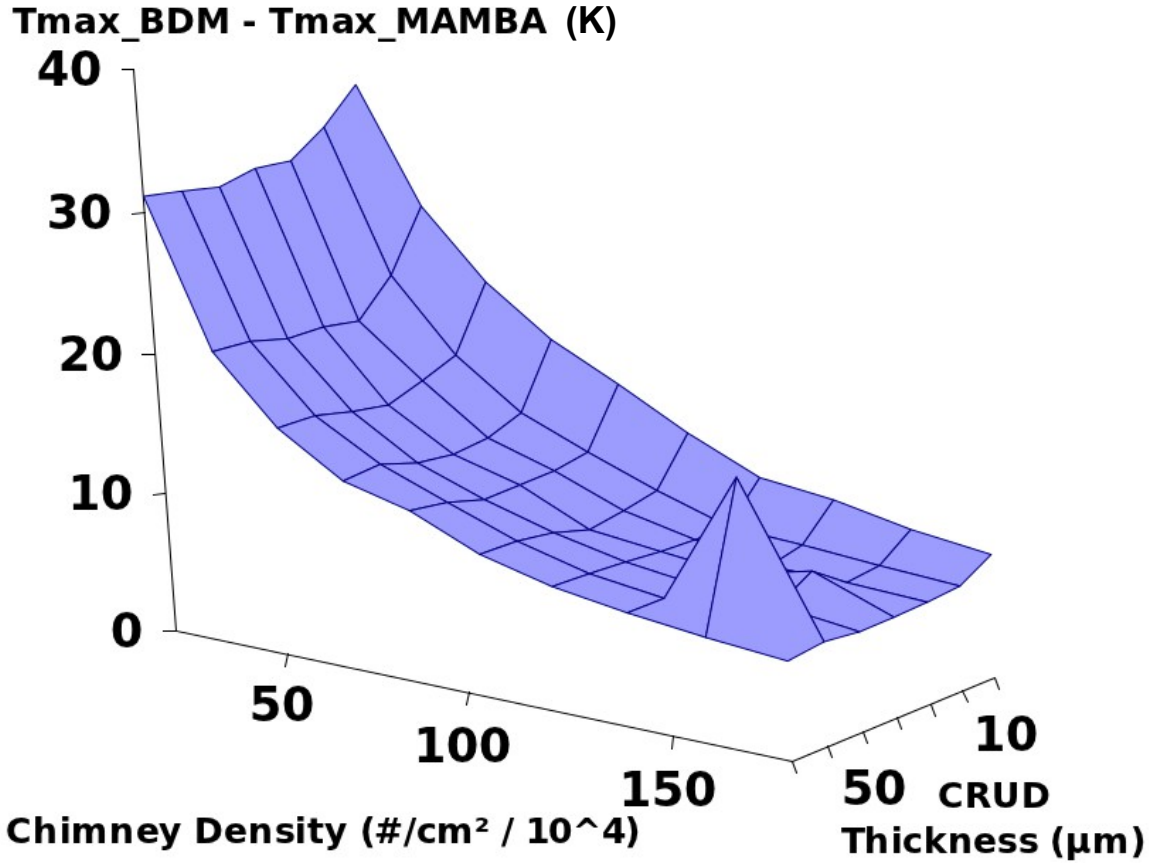
GAP!



- Fundamental data haven't been computed
- k_{cond} of $NiFe_2O_4$, solubility of $Li_2B_4O_7$, (Ni-Fe-Cr-Zn-O) phase stability
- Without this data, MAMBA-BDM can't capture the full complexity of CRUD, can't make true predictions

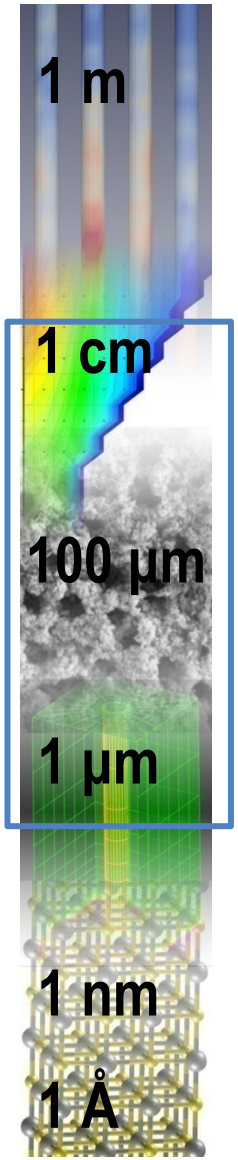
Upscaling: Microscale to Engineering Scale





- MAMBA & MAMBA-BDM run with identical parameters
  - Identifies regions of parity, and where microscale input is required
- Pre-computed lookup table most likely, with on-demand MAMBA-BDM as backup/sanity check

Validation: Microscale



- **EPRI Report #1022896**
  - **Measured effective thermal conductivity of synthetic CRUD**
- **Showed very low values compared to MAMBA-BDM**

Ref.	This Work	Models		Experiments	
		[1]	[2]	[3]*	[4]
k_{effc} $\left[\frac{W}{mK}\right]$	5.04	4.40	2.29	0.519 - 1.39	0.82 - 1.82

*Boiling cases (rods 110-117) used

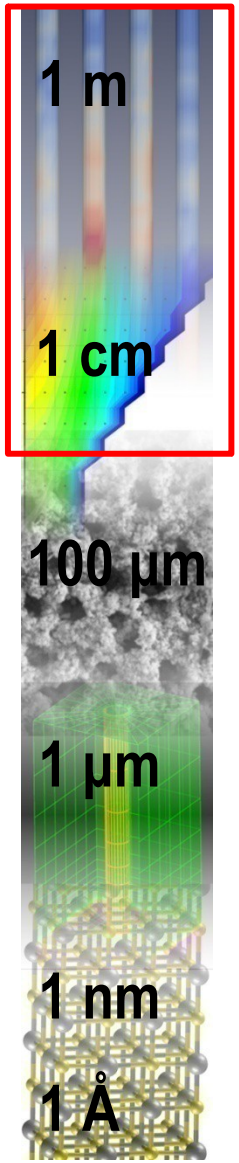
Rod	TC	Crud Thickness (microns)	Porosity (%)	Effective Thermal Conductivity (Btu/hr-ft-°F)
110	1	66	72	0.4130
110	X2	43	76	0.4150
110	X3	88	72	0.5920
111	1	42	73	0.3000
111	2	49	70	0.3450
111	3	46	69	0.3120
111	4	42	56	0.3110
112	1	61	49	NA
112	2	85	66	NA
112	3	58	63	0.3840
112	4	69	67	NA
116	1	99	57	NA
116	2	66	66	NA
116	3	78	62	0.8030
116	4	54	67	0.5870
117	1	120	66	NA
117	2	76	60	NA
117	3	67	59	0.4750
117	4	70	61	0.4790

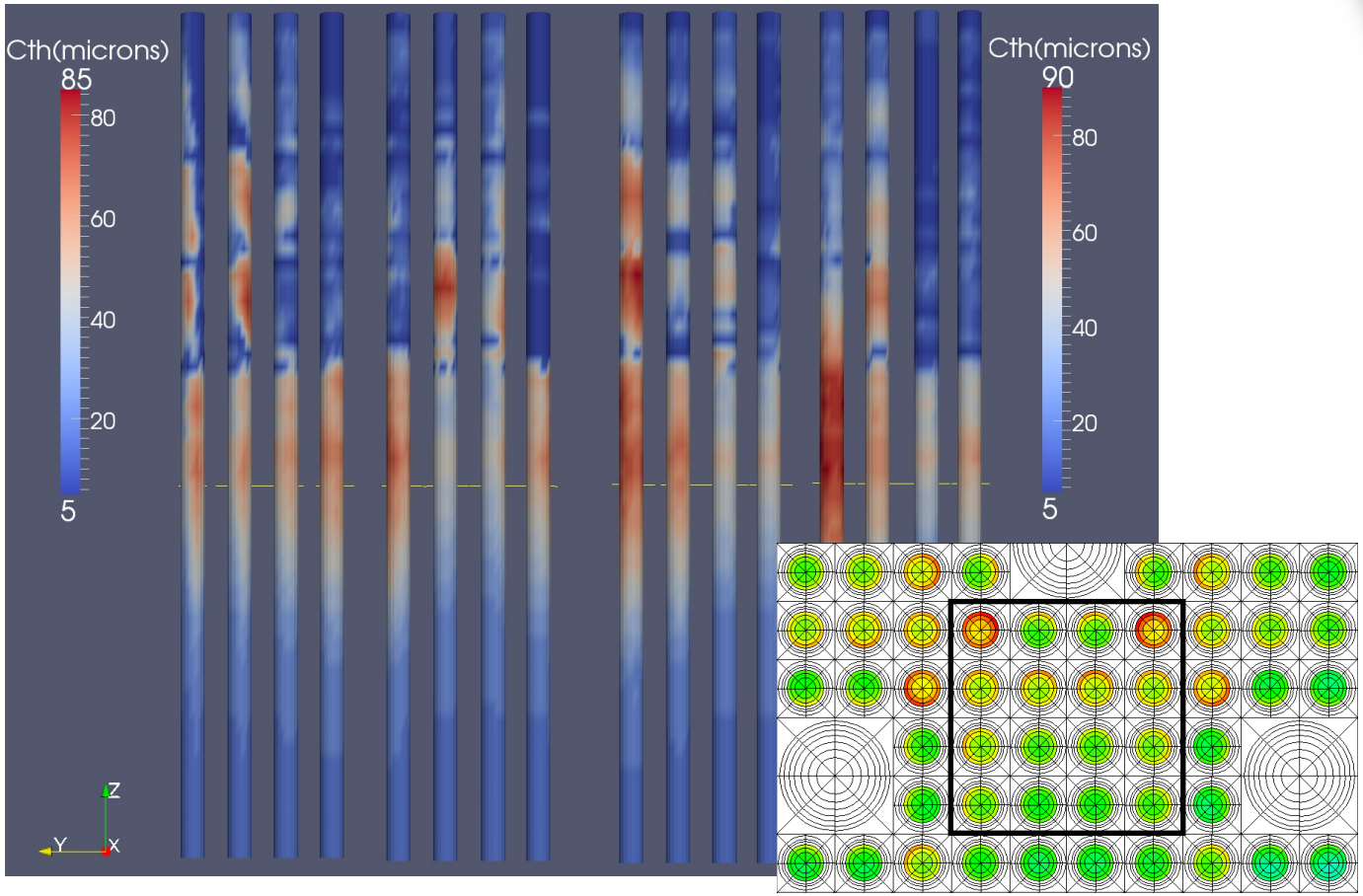
[1] C. Pan, B. G. Jones, and A. J. Machiels. *Nucl. Eng. Des.*, 99:317–327, (1987).
[2] I. Haq et al. *Nucl. Eng. Des.*, 241(1):155–162 (2011).
[4] J. L. Uhle. Boiling Heat Transfer Characteristics of Steam Generator U-Tube Fouling. Ph.D. Thesis, MIT, 1996.

[3] J. Deshon. Simulated fuel crud thermal conductivity measurements under pressurized water reactor conditions. Technical Report 1022896, EPRI, October 2011.

- **Comparison of effective thermal conductivity**
- **MAMBA-BDM overestimates compared to data**
- **Two-phase fluid would correct this, more realistic**

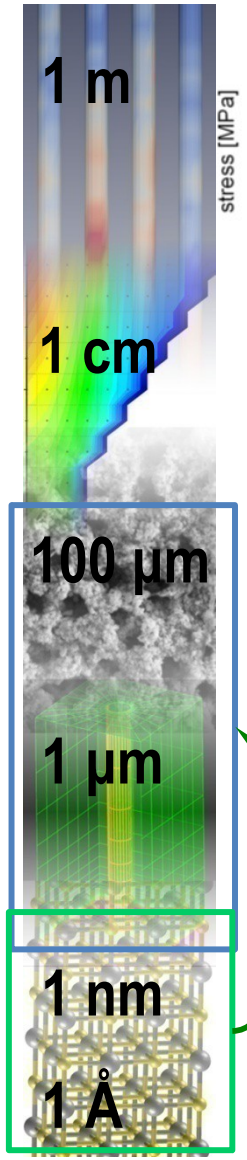
Linking to CFD & Fuel Performance Codes

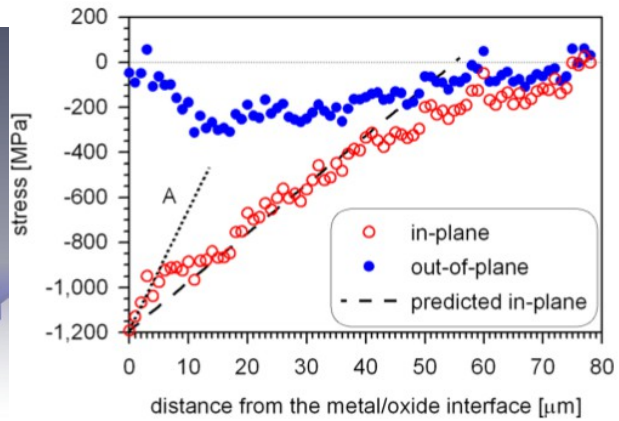


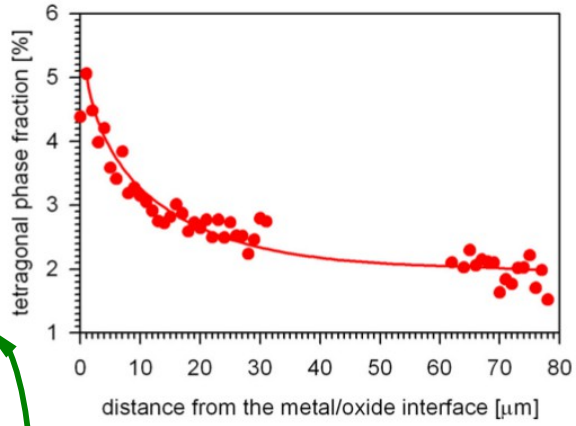


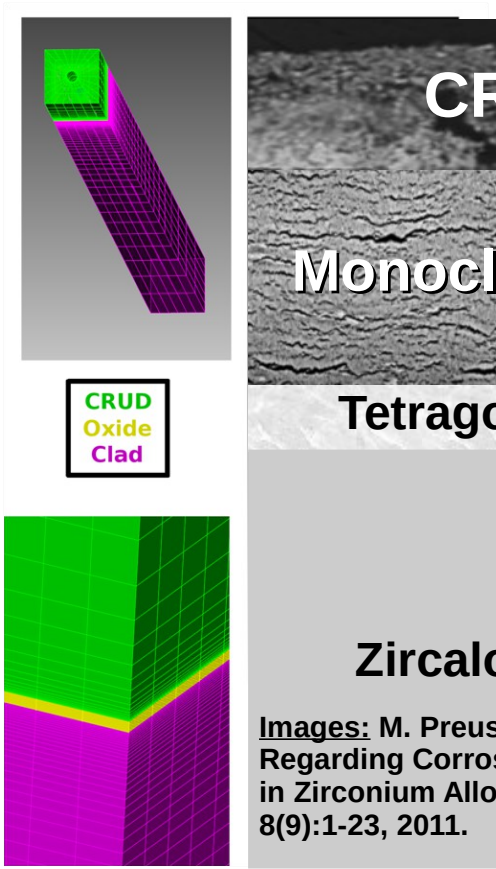
- MAMBA coupled to DeCART (neutronics) & StarCCM+ (CFD)
- Turbulent kinetic energy enhanced CRUD erosion
- Positive feedback between CRUD temperature & deposition
- Negative feedback between boron buildup & power level

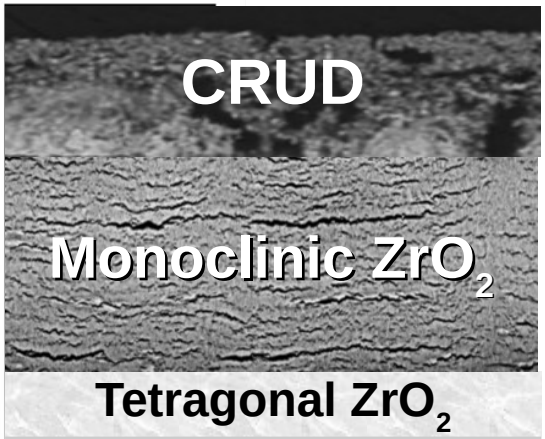
Linking CRUD and Corrosion









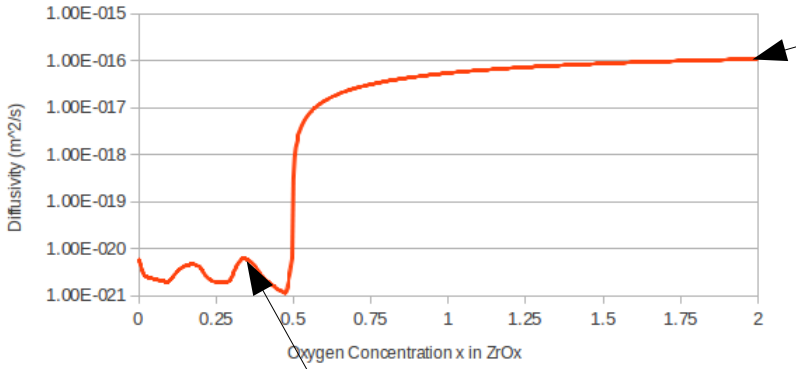


Zircaloy metal

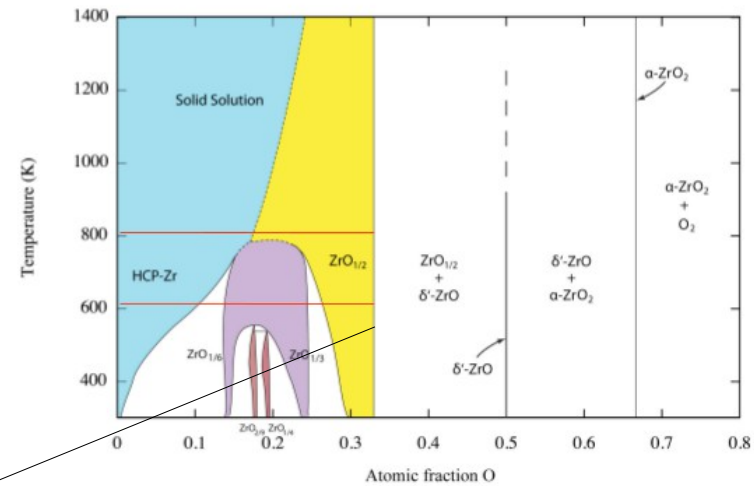
Images: M. Preuss et al. "Studies Regarding Corrosion Mechanisms in Zirconium Alloys." J. ASTM Int. 8(9):1-23, 2011.

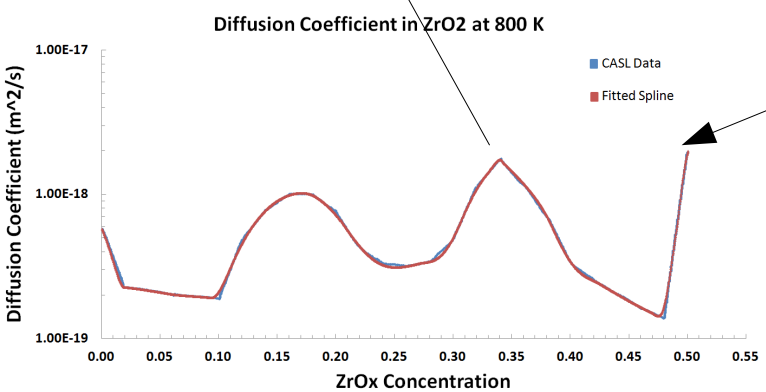
- Start from Zr-O phase diagram (from CASL)
- Back out O diffusion coefficients in Zr, ZrO, ZrO_2
- Develop pseudo phase field model to track oxidation
- Incorporate stress in monoclinic/tetragonal phase change

Hognose Uses CASL Atomistic Data!



M. Youssef, B. Yildiz. Modeling of Oxygen Transport in Zirconium Oxide. CASL Atomistic Data.





B, Puchala, J. Thomas, A. Van der Ven. "First-principles prediction of corrosion processes in extreme Environments." CASL Telecon, 2012-12-06

Self-Diffusion of Oxygen in ZrO_2

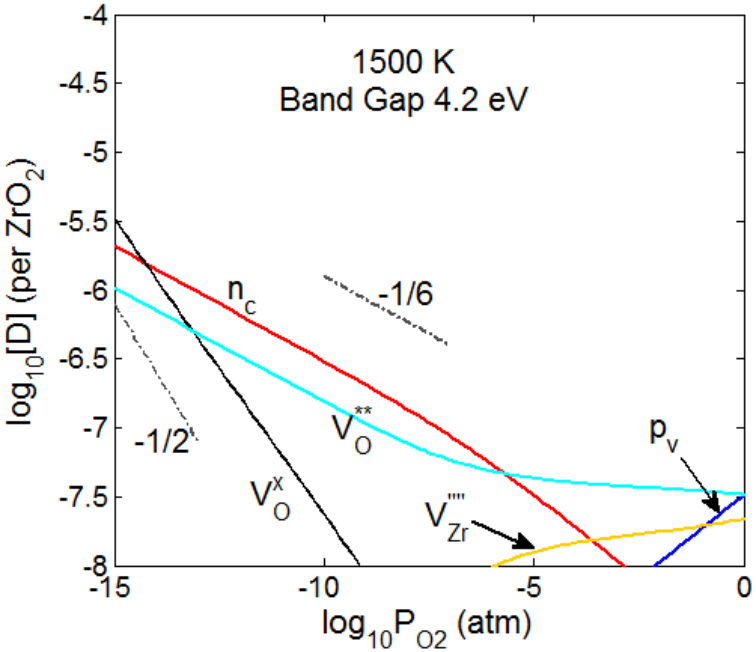
$$D_{self} = \sum_{defects} concentration \times migration$$

- Defect formation *free energy* computed using Density Functional Theory.
- Concentration was determined by imposing the charge neutrality condition.

- Migration barriers computed using the Climbing Image Nudged Elastic Band Method

Self-Diffusion of Oxygen in ZrO_2

Concentrations / Sample Migration Barriers in eV



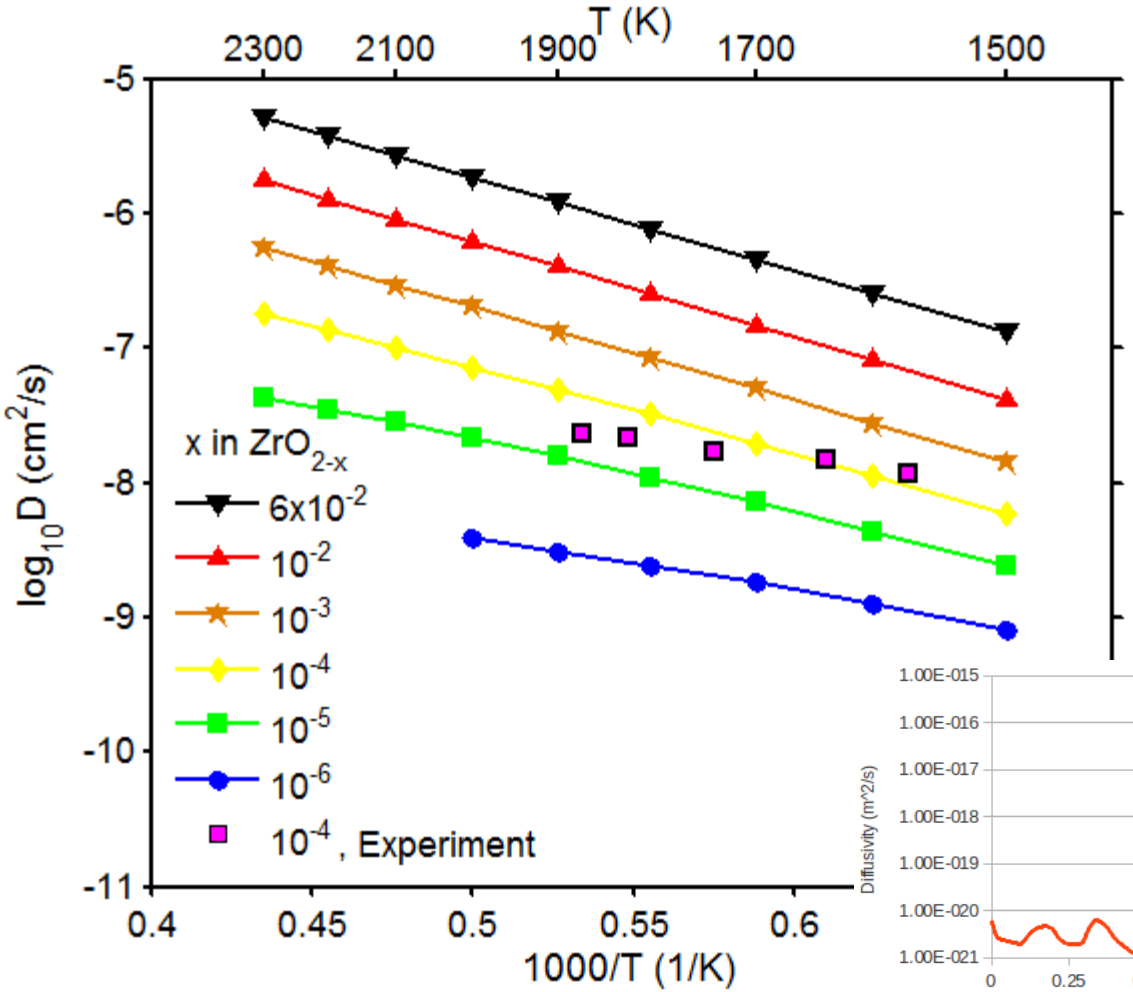
M. Youssef, B. Yildiz, Phys. Rev. B 86, 144109 (2012)

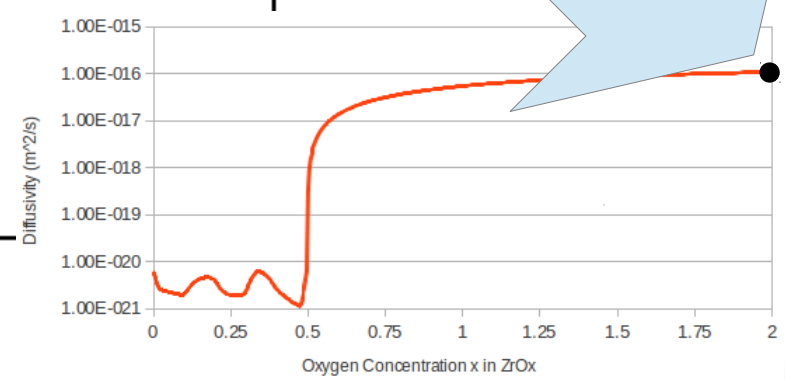
	<001>	<100>
V_O^x	1.24	1.48
$V_O^{\bullet\bullet}$	0.58	0.38

$V_O^{\bullet\bullet}$	*2+ oxygen vacancy*
V_O^x	*neutral oxygen vacancy*
$V_{Zr}^{////}$	*4- zirconium vacancy*
n_c	*Conduction band electrons*
p_v	*Valence band holes*

Self-Diffusion of Oxygen in ZrO_2

Oxygen Self-Diffusivity

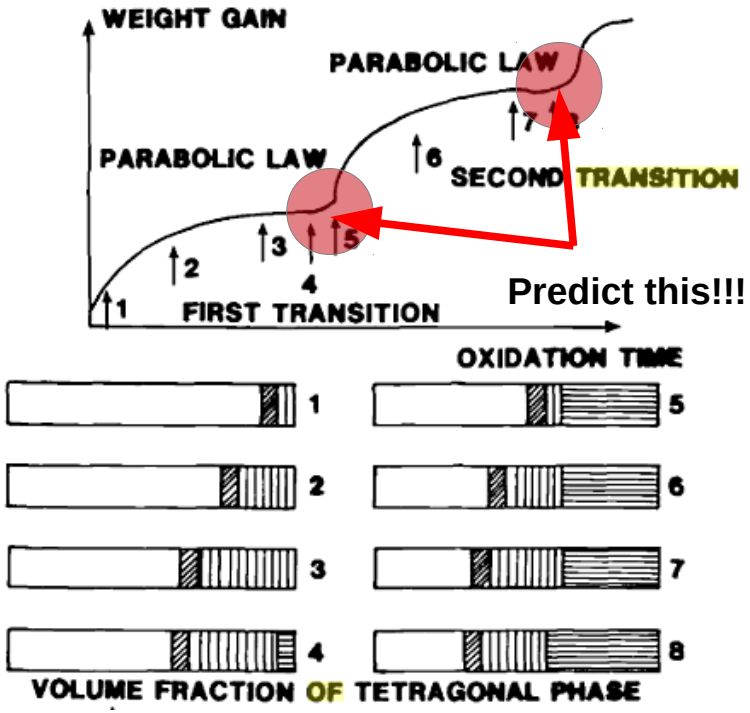




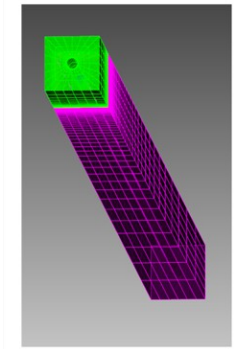
M. Youssef, B. Yildiz, (in preparation for publication)

Experimental data from: K. Park, D. Olander, J. Electrochem. Soc. 138, 1155 (1991)

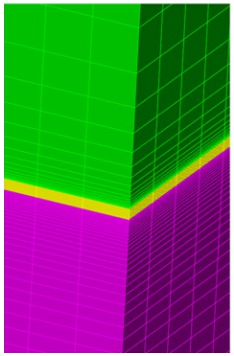
Hognose Next Steps

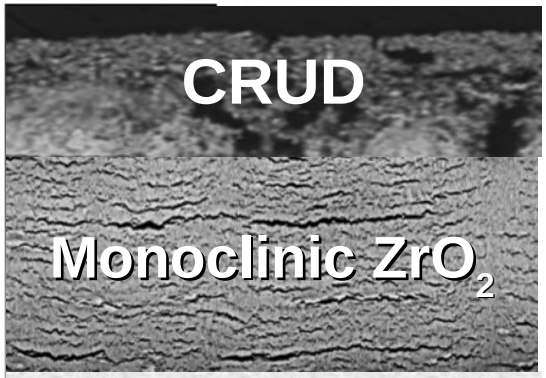


J. Godlewski, J. P. Gros, M. Lambertin, J. F. Wadier, and H. Weidinger. Raman spectroscopy study of the tetragonal-to-monoclinic transition in zirconium oxide scales and determination of overall oxygen diffusion by nuclear microanalysis of o-18. In Zirconium in the Nuclear Industry: Ninth International Symposium, 1991.



CRUD
Oxide
Clad





Tetragonal ZrO_2

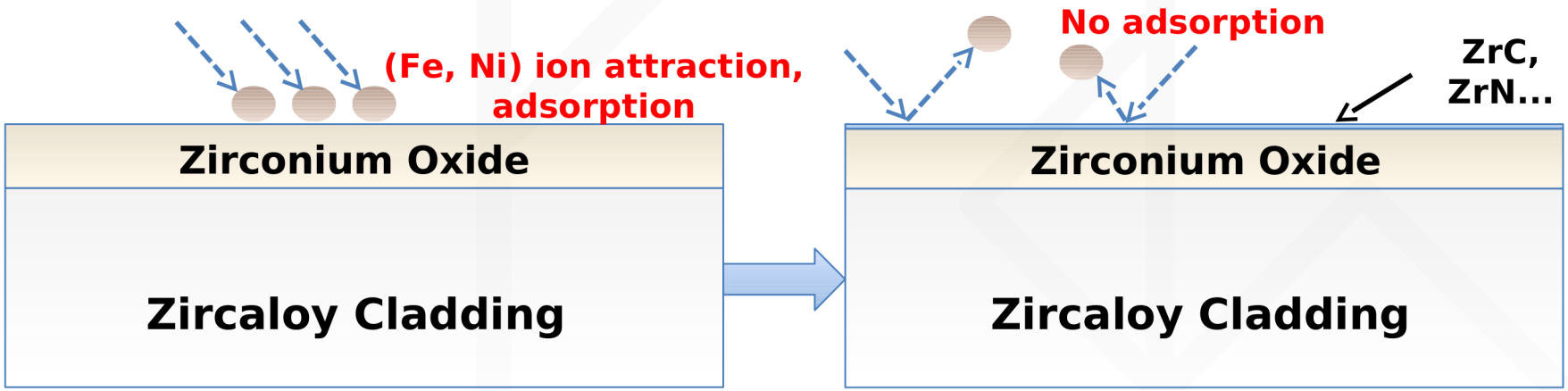
Zircaloy metal

Images: M. Preuss et al. "Studies Regarding Corrosion Mechanisms in Zirconium Alloys." J. ASTM Int. 8(9):1-23, 2011.

CANES
MIT Center for
Advanced Nuclear Energy Systems

Experimental Goals

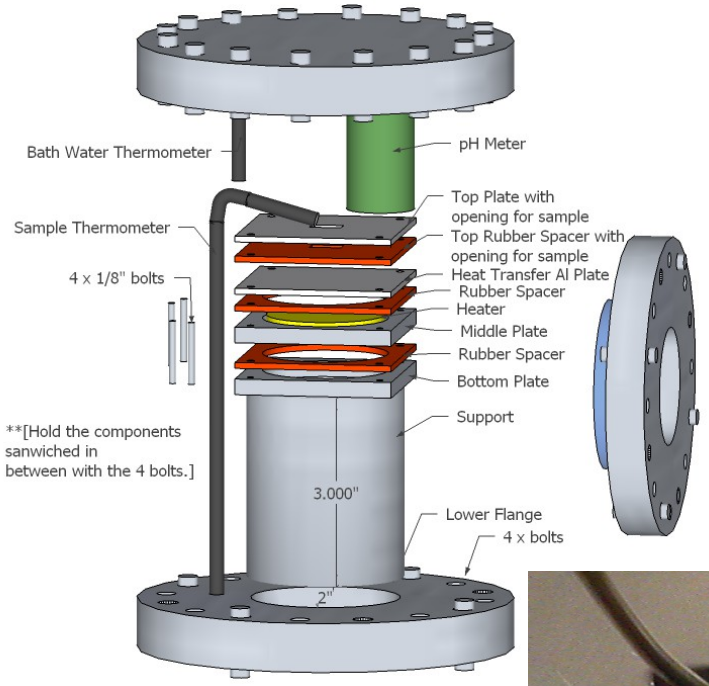
- Pre-screen materials at P_{atm} for possible CRUD resistance
- Test candidate materials at PWR conditions with simulated CRUD precursors (NiO, Fe_3O_4, $NiFe_2O_4$)
- **<u>Slow or stop the growth of CRUD in LWRs</u>**

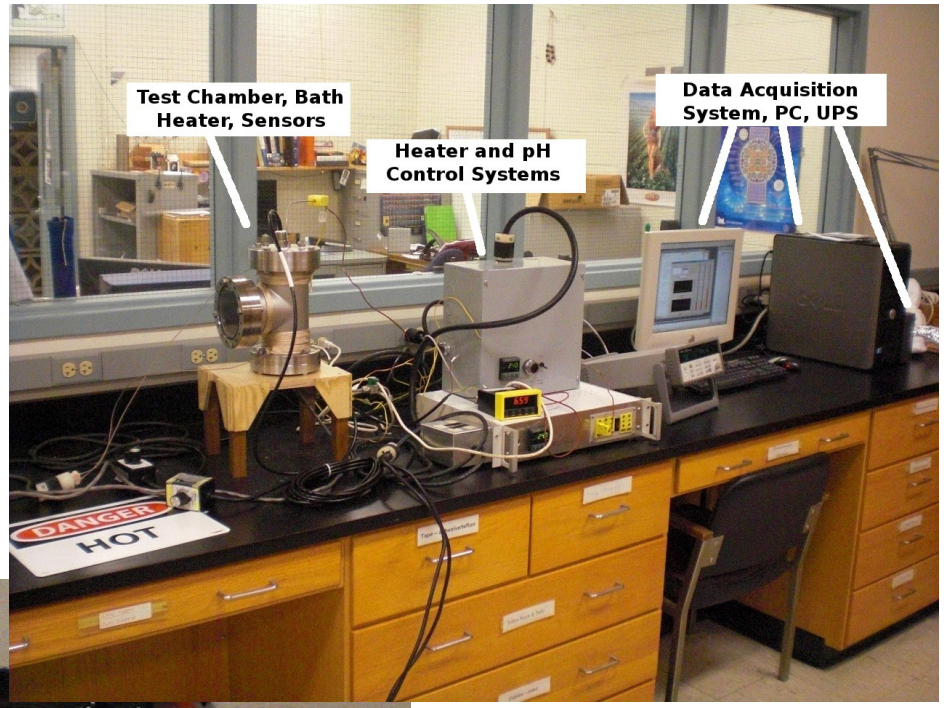


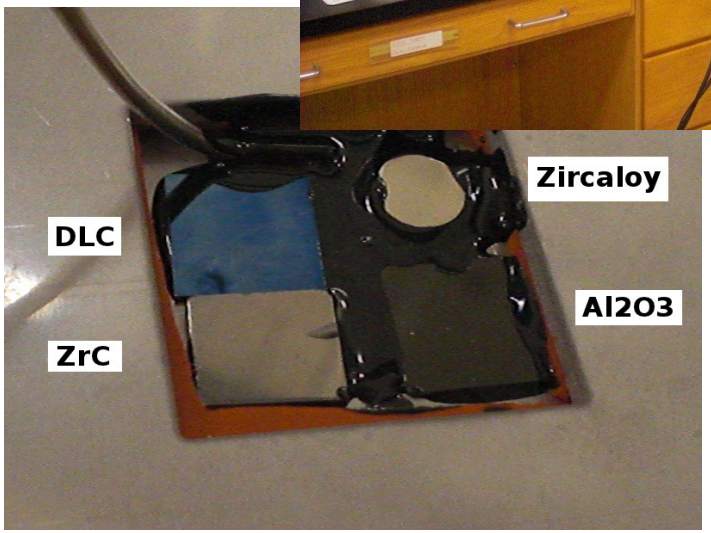
Experiments: Different Substrate Materials

- **Sub-cooled boiling for 1hr, 10ppm NiO, Fe_3O_4 nanoparticles, 1500ppm H_3BO_3, 5ppm LiOH**
- **All materials tested grew tenacious CRUD... except ZrC!**
  - **Al_2O_3, Zircaloy-4, diamond like carbon (DLC), TiO_2, SiO_2 showed strong CRUD-surface bond**
  - **ZrC only had CRUD particles on surface**
- **CRUD-clad bond examined by dual-beam SEM/FIB (focused ion beam)**

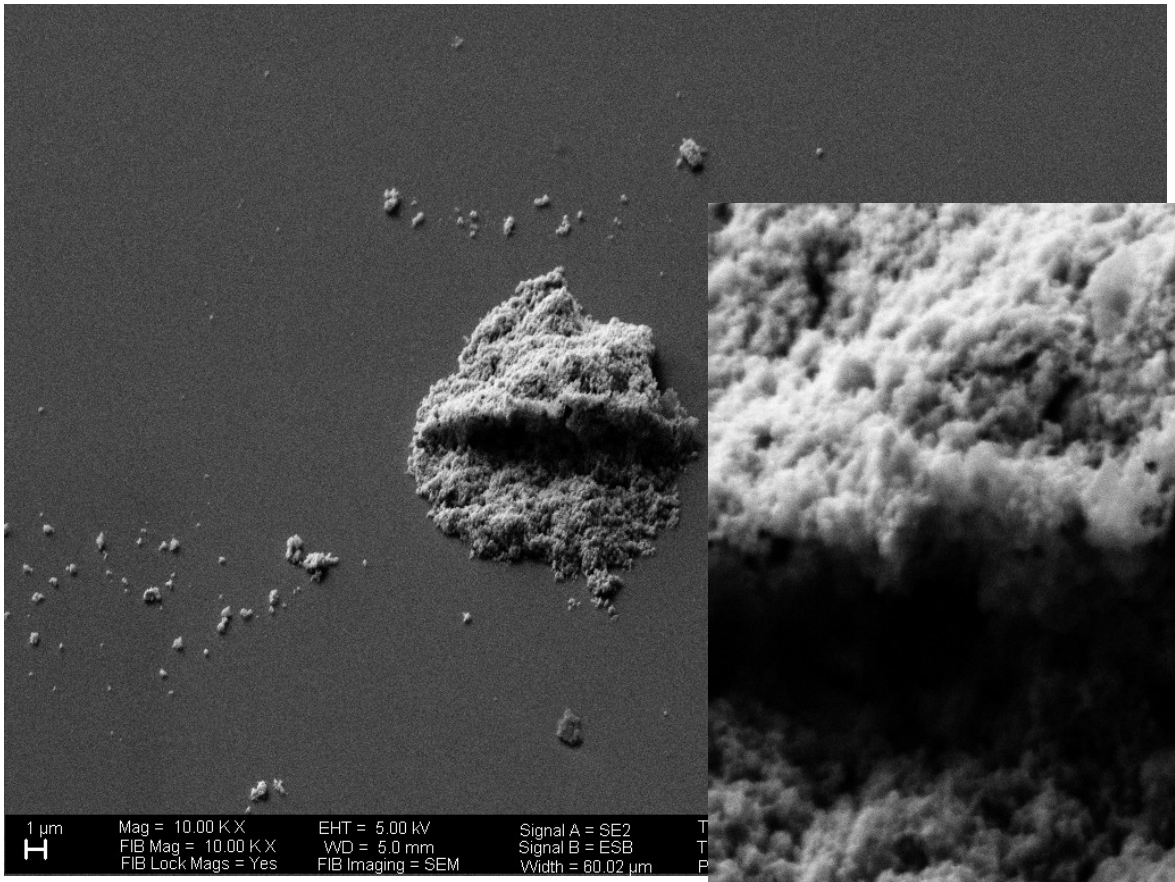
Experiments: Pool Boiling

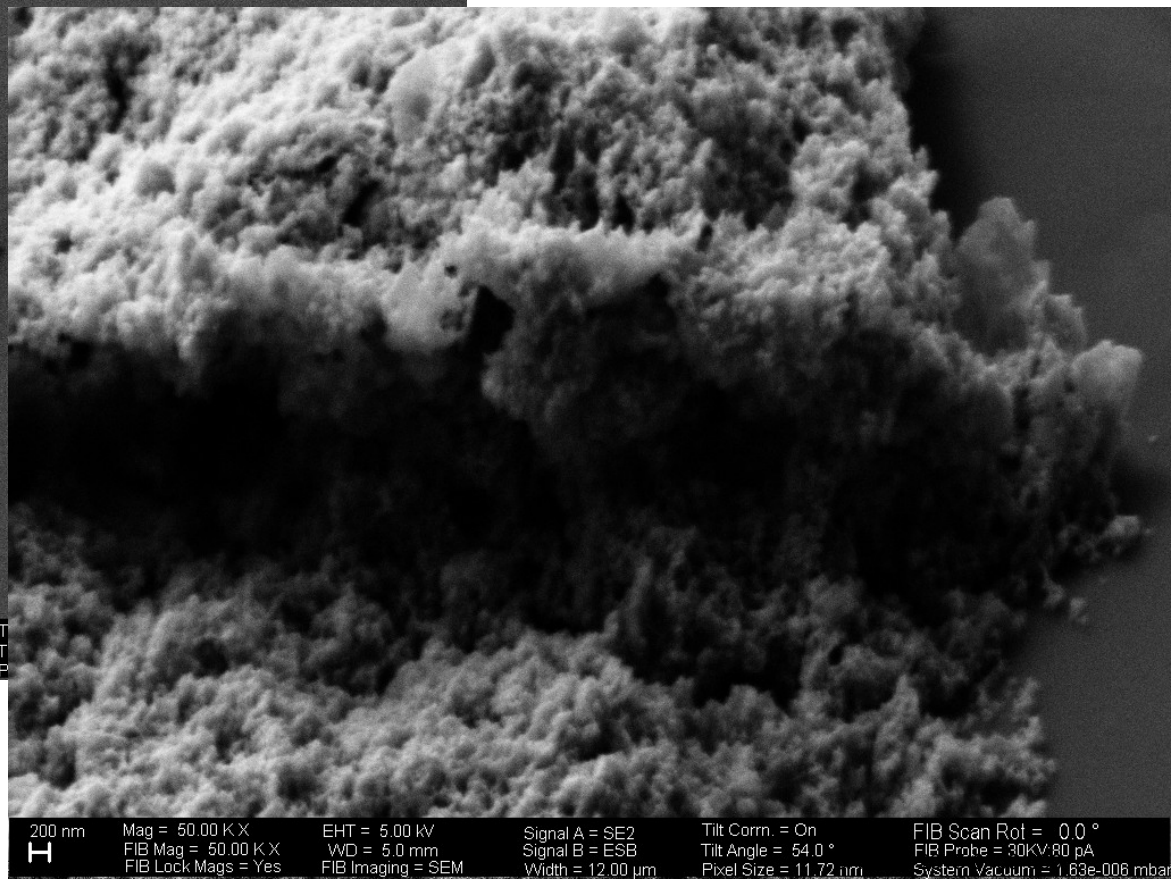




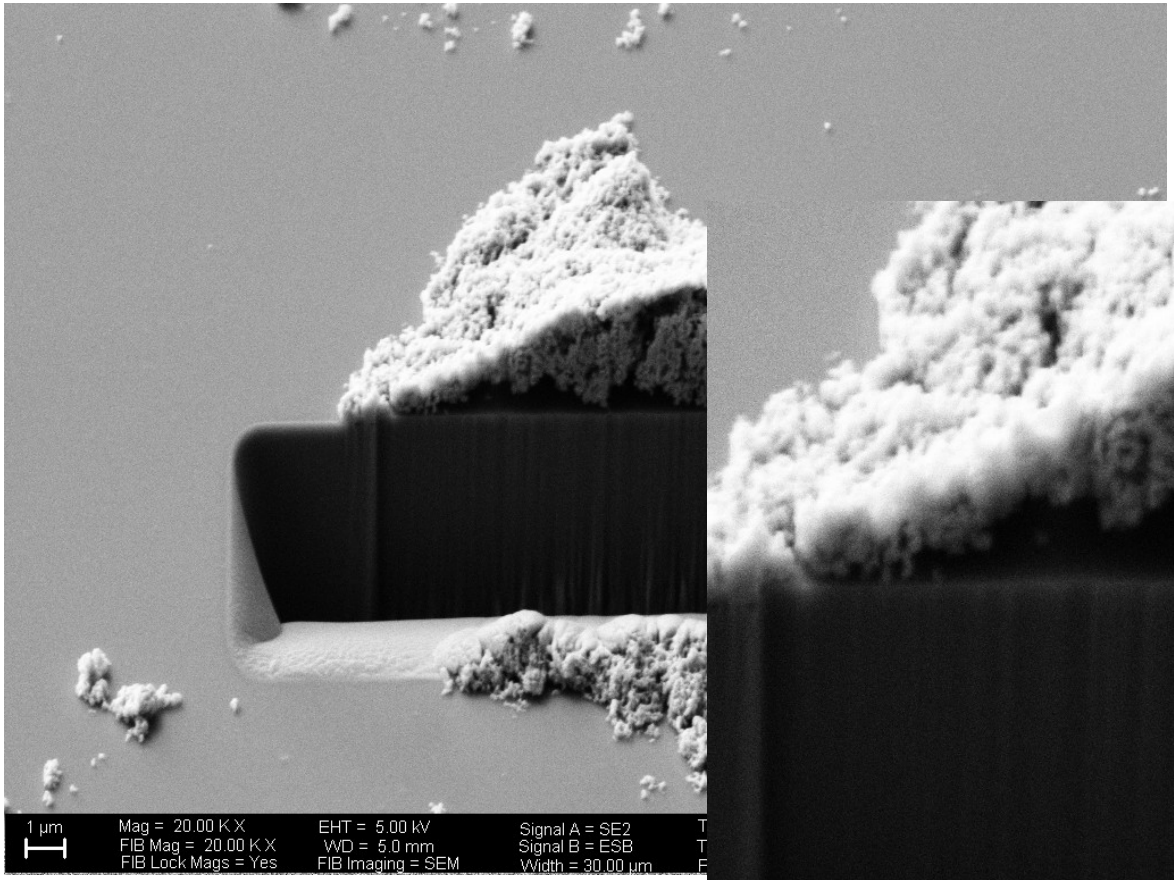


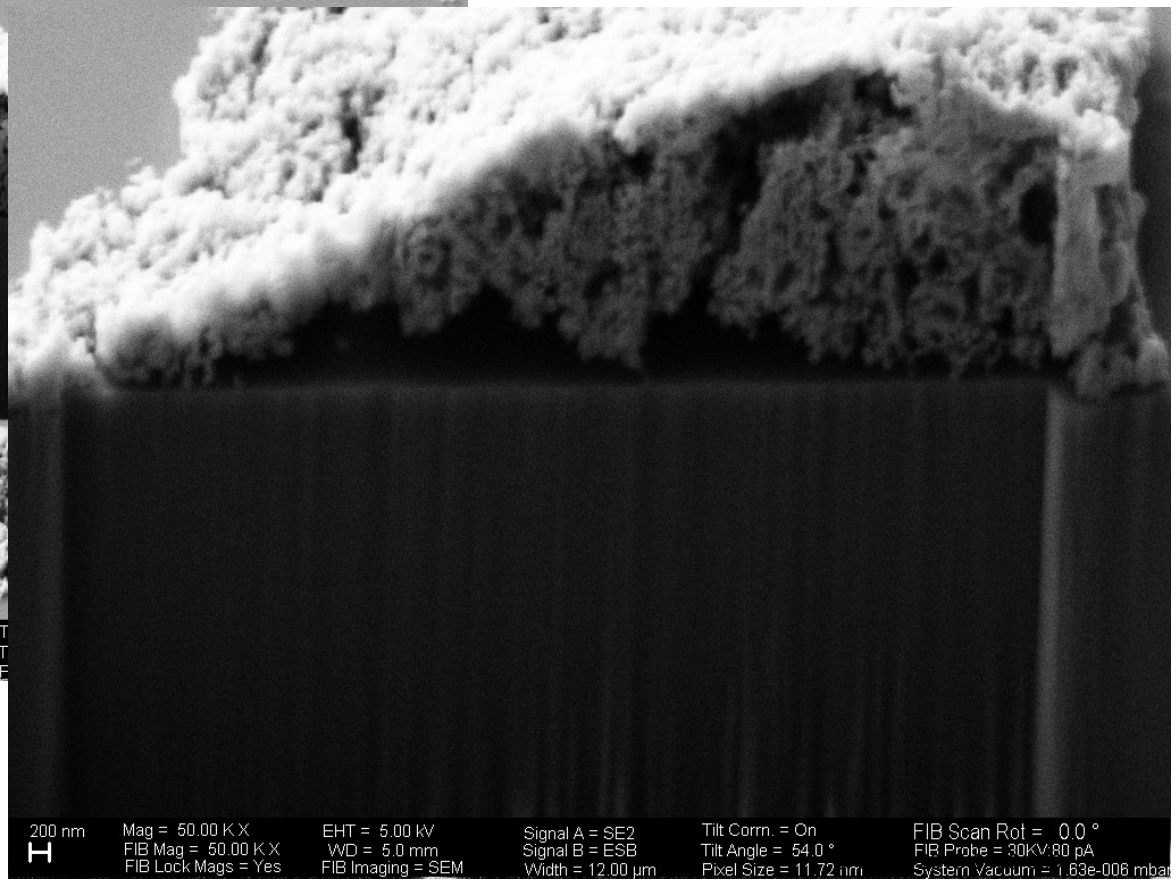
Experiments: CRUD on SiO_2, No Boiling (Control)



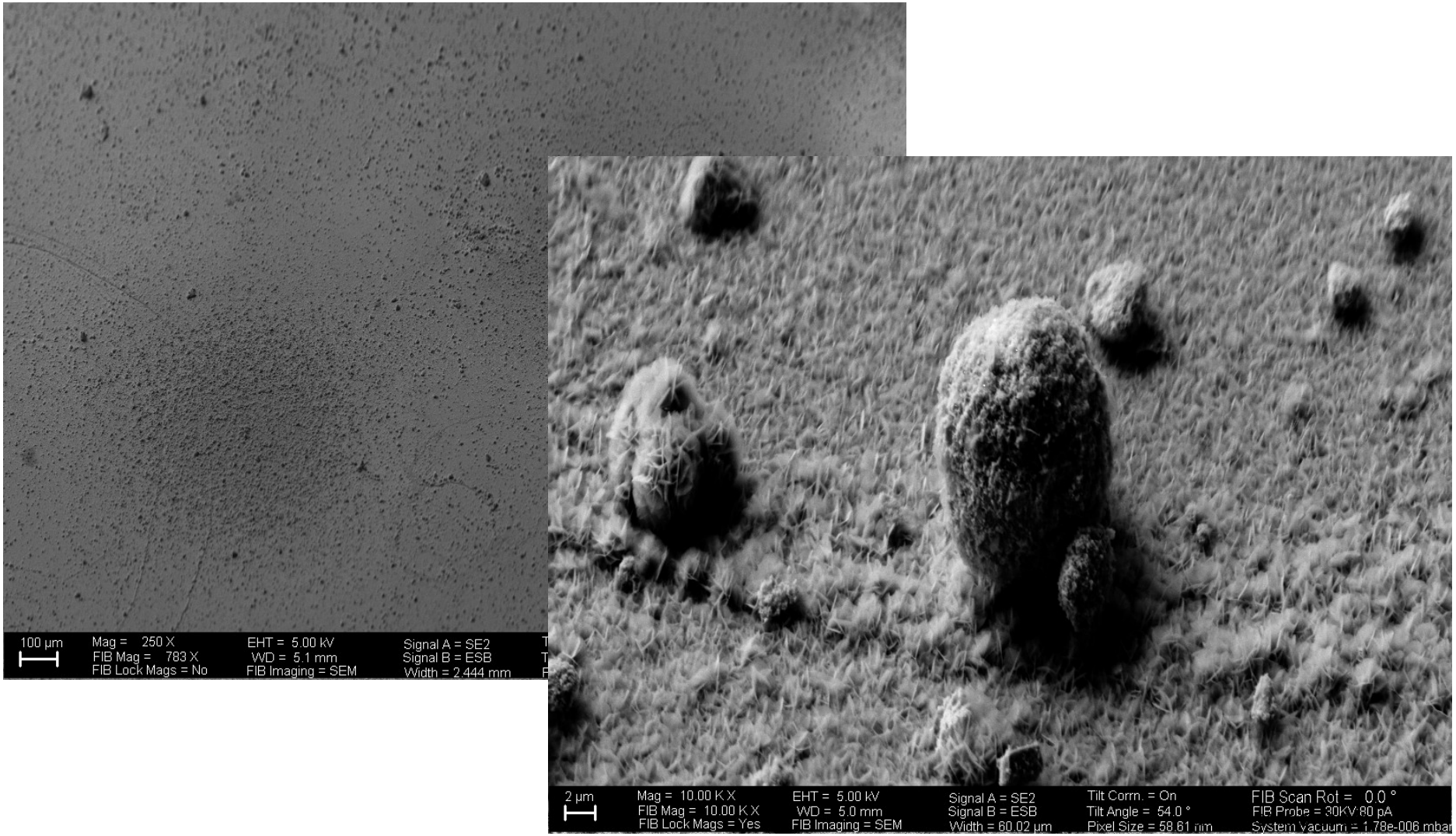


Experiments: CRUD on SiO_2, No Boiling (Control)

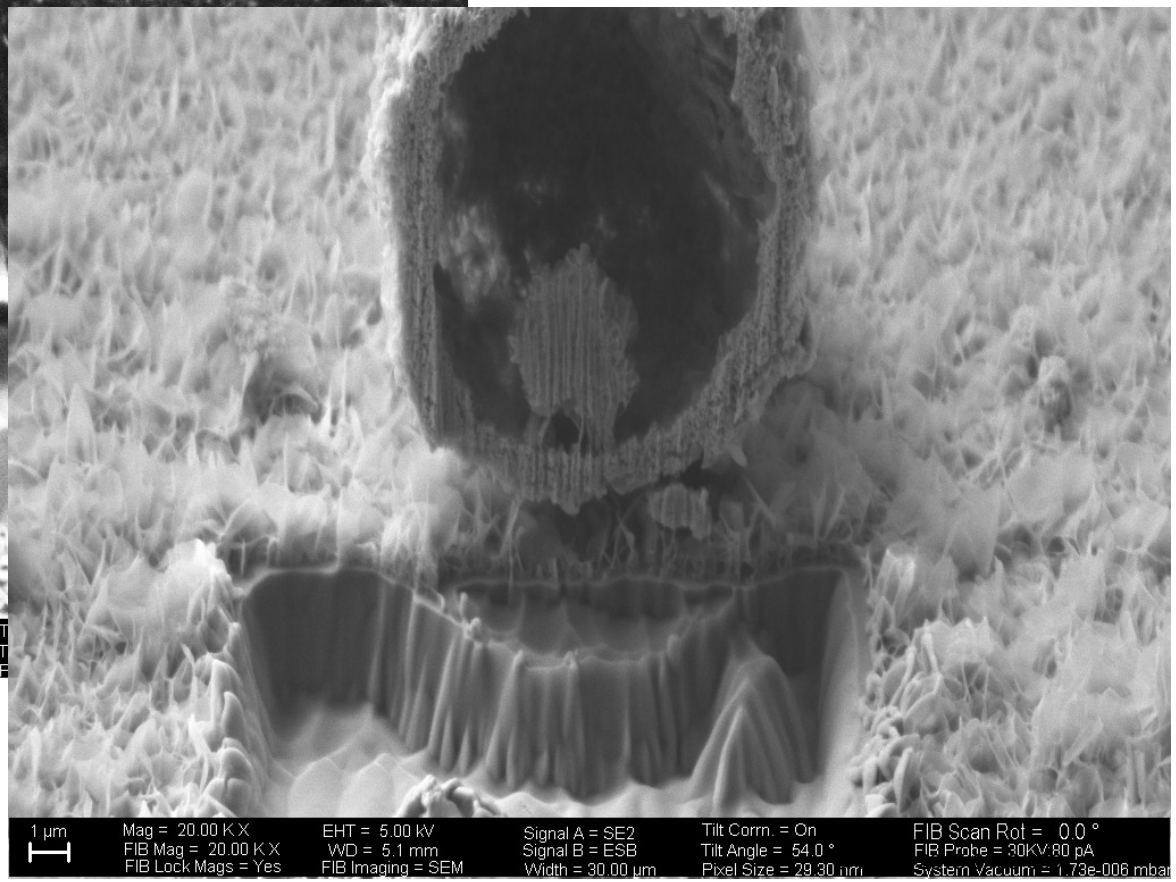




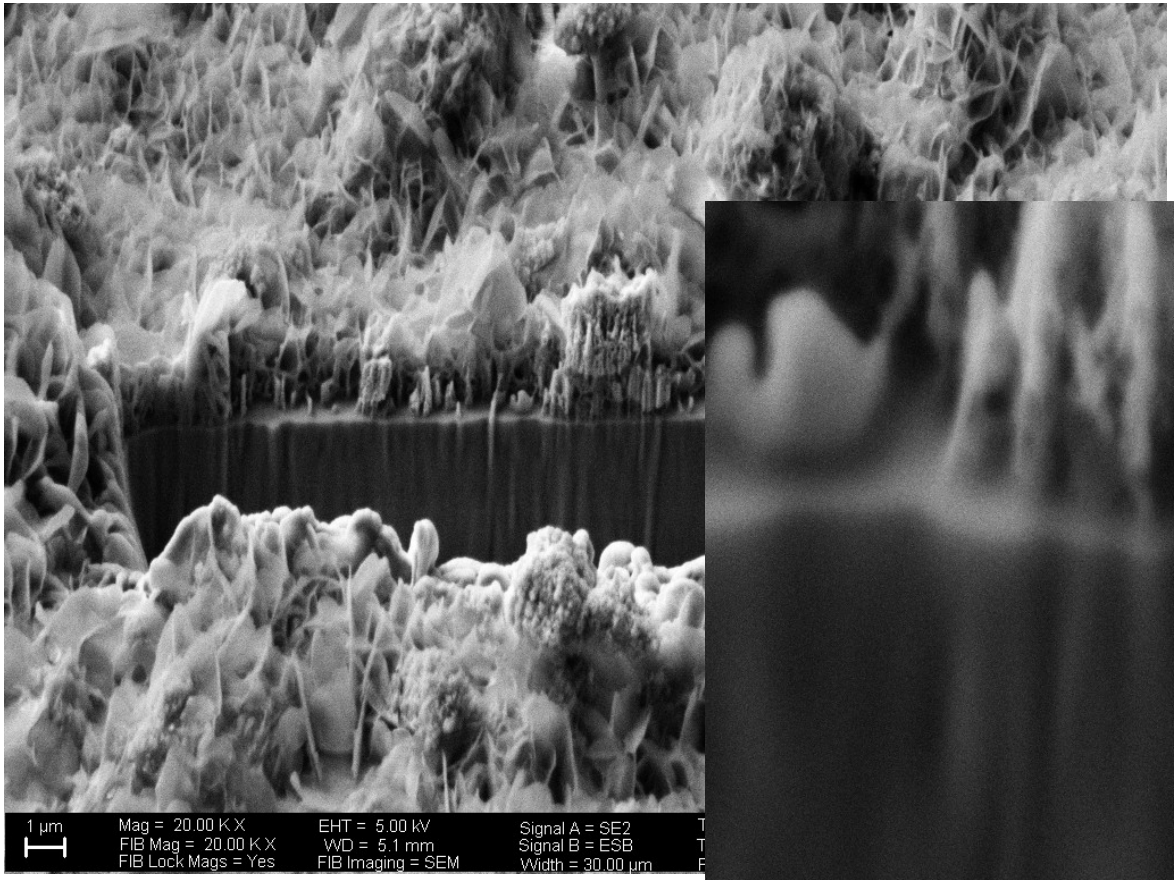
Experiments: CRUD on TiO_2

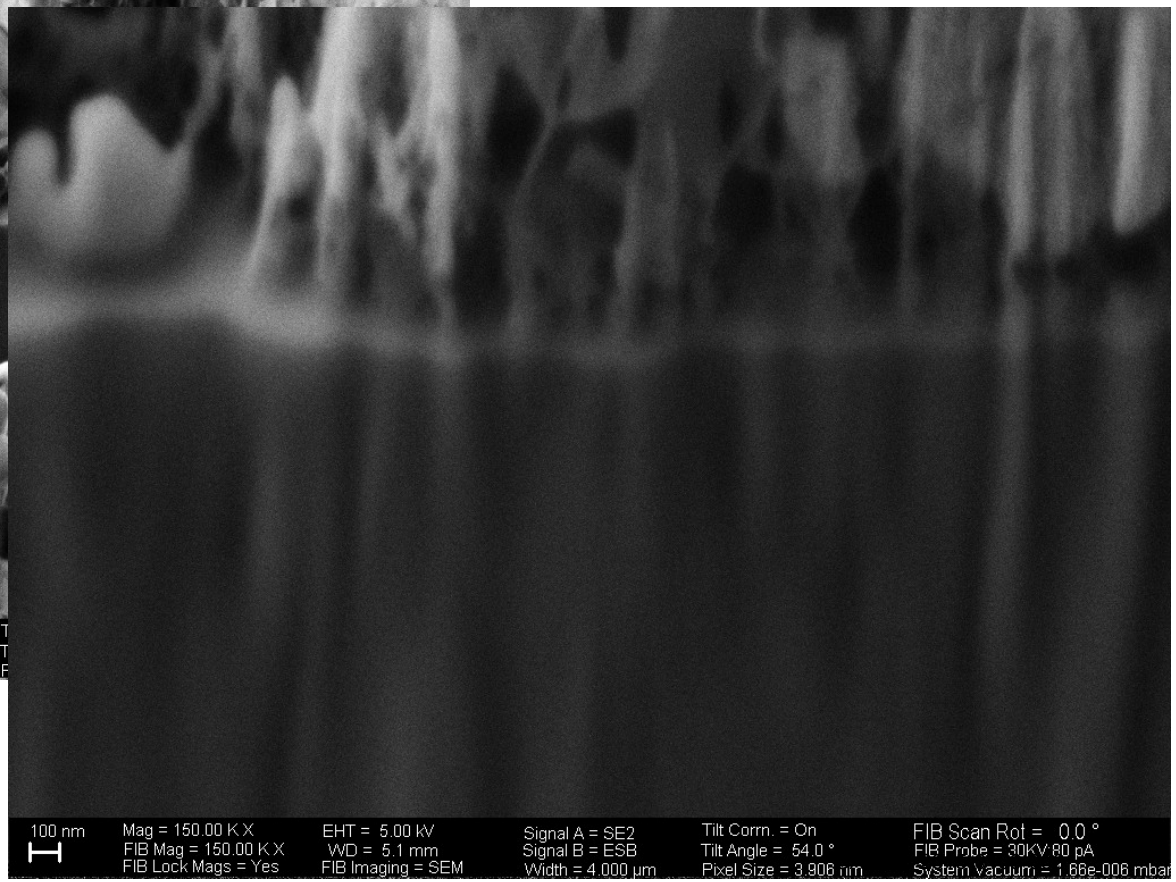


Experiments: CRUD on TiO_2

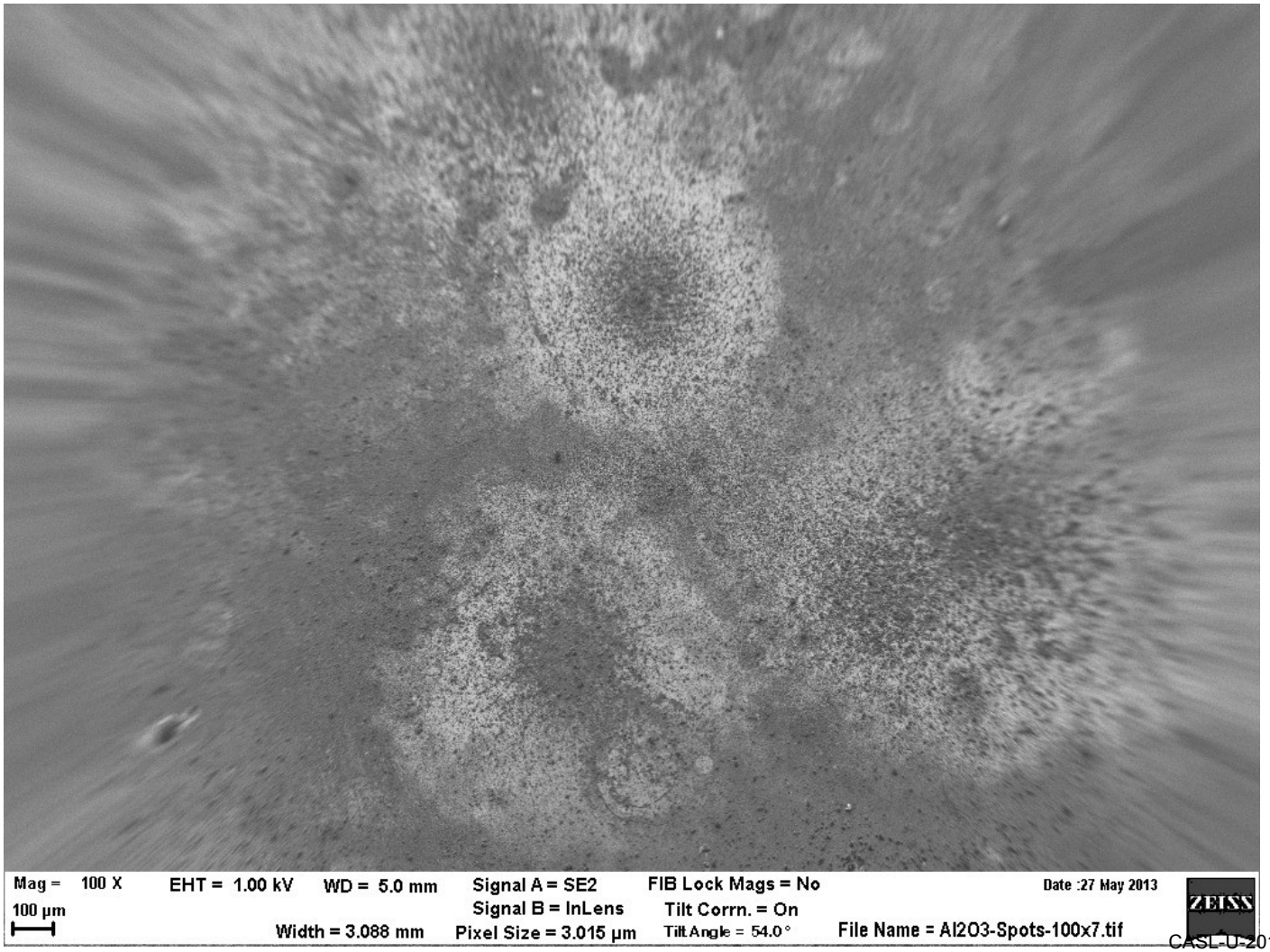


Experiments: CRUD on TiO_2

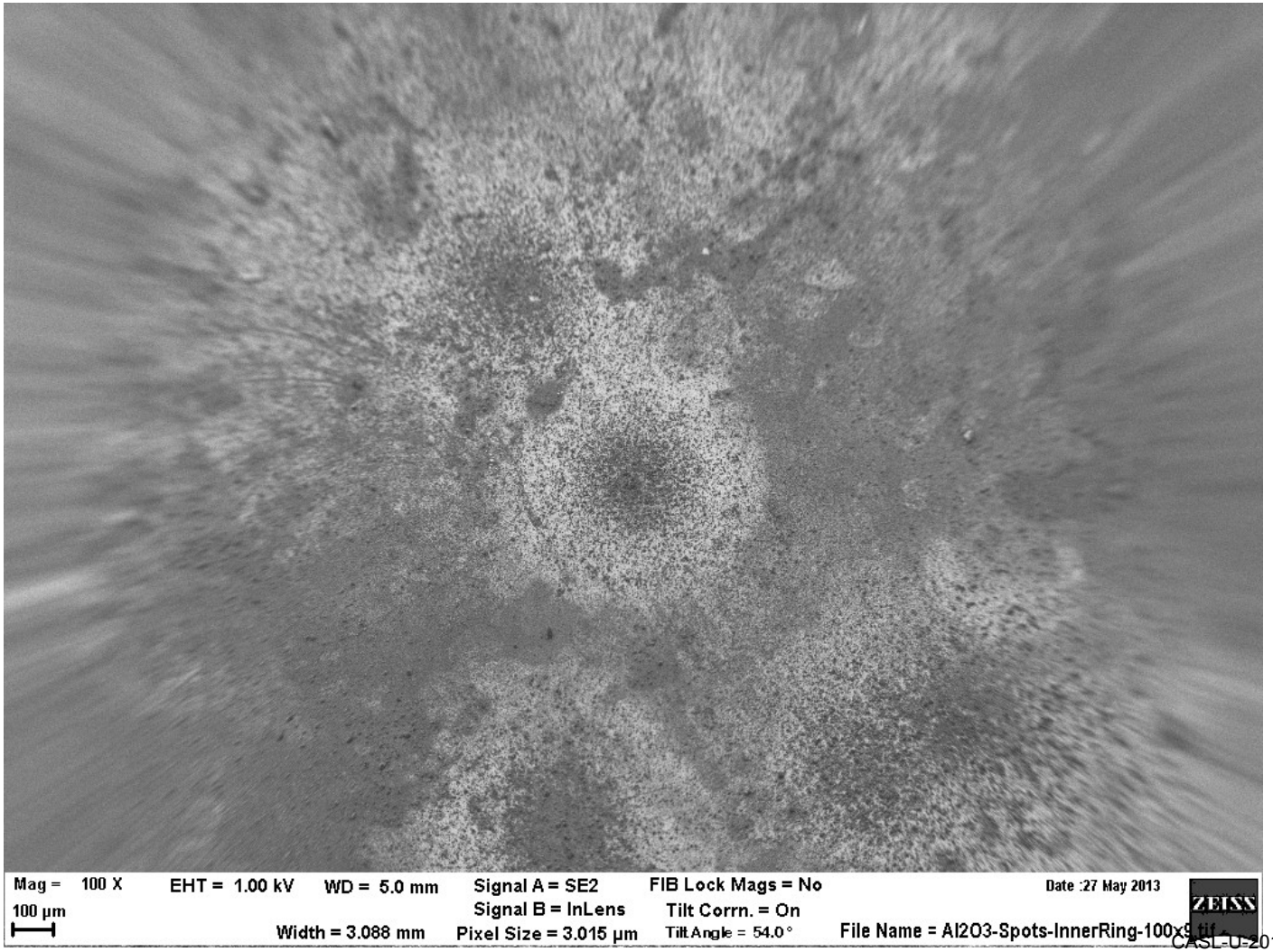




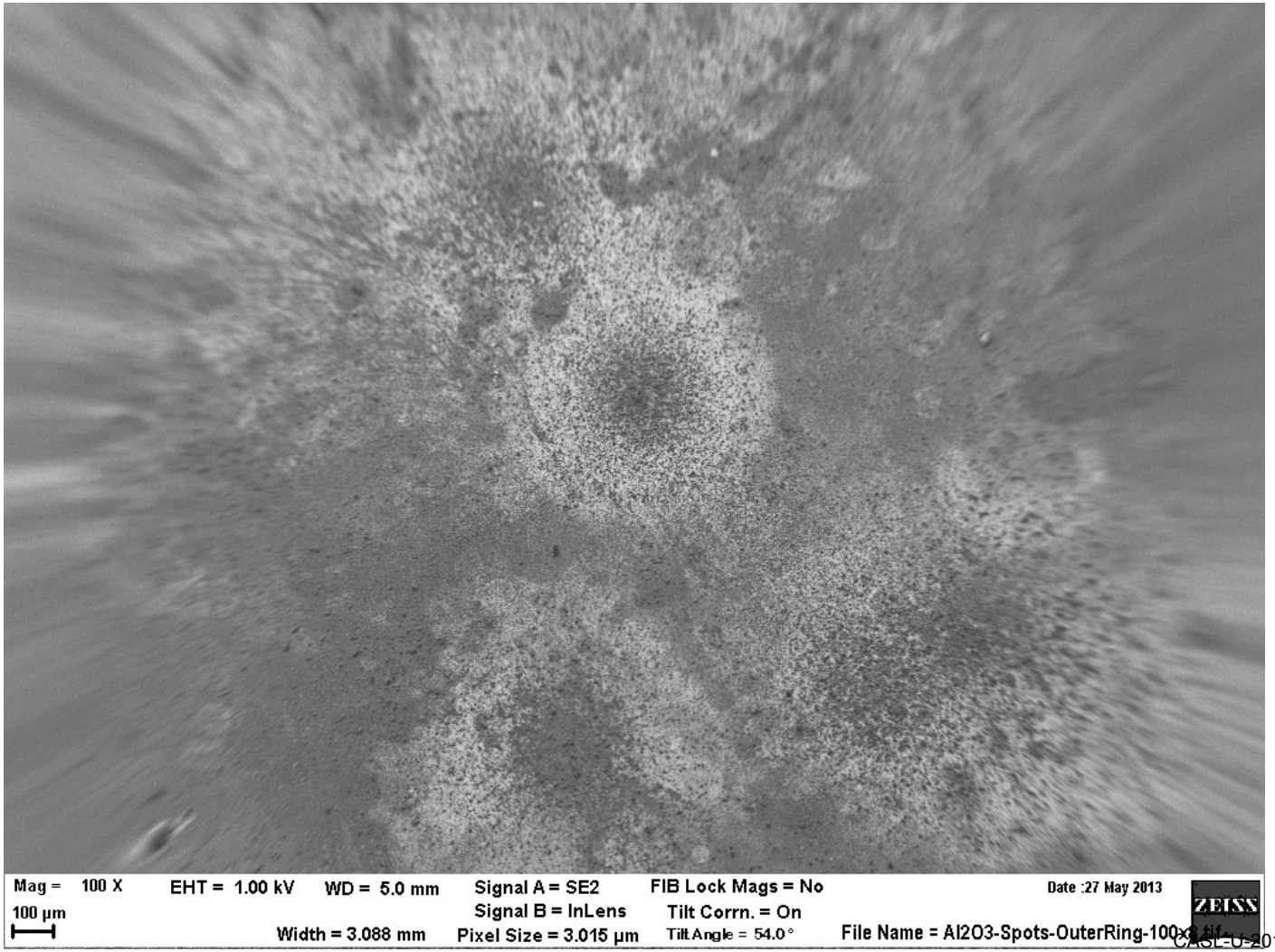
Experiments: Non-Boiling Areas (Background CRUD)



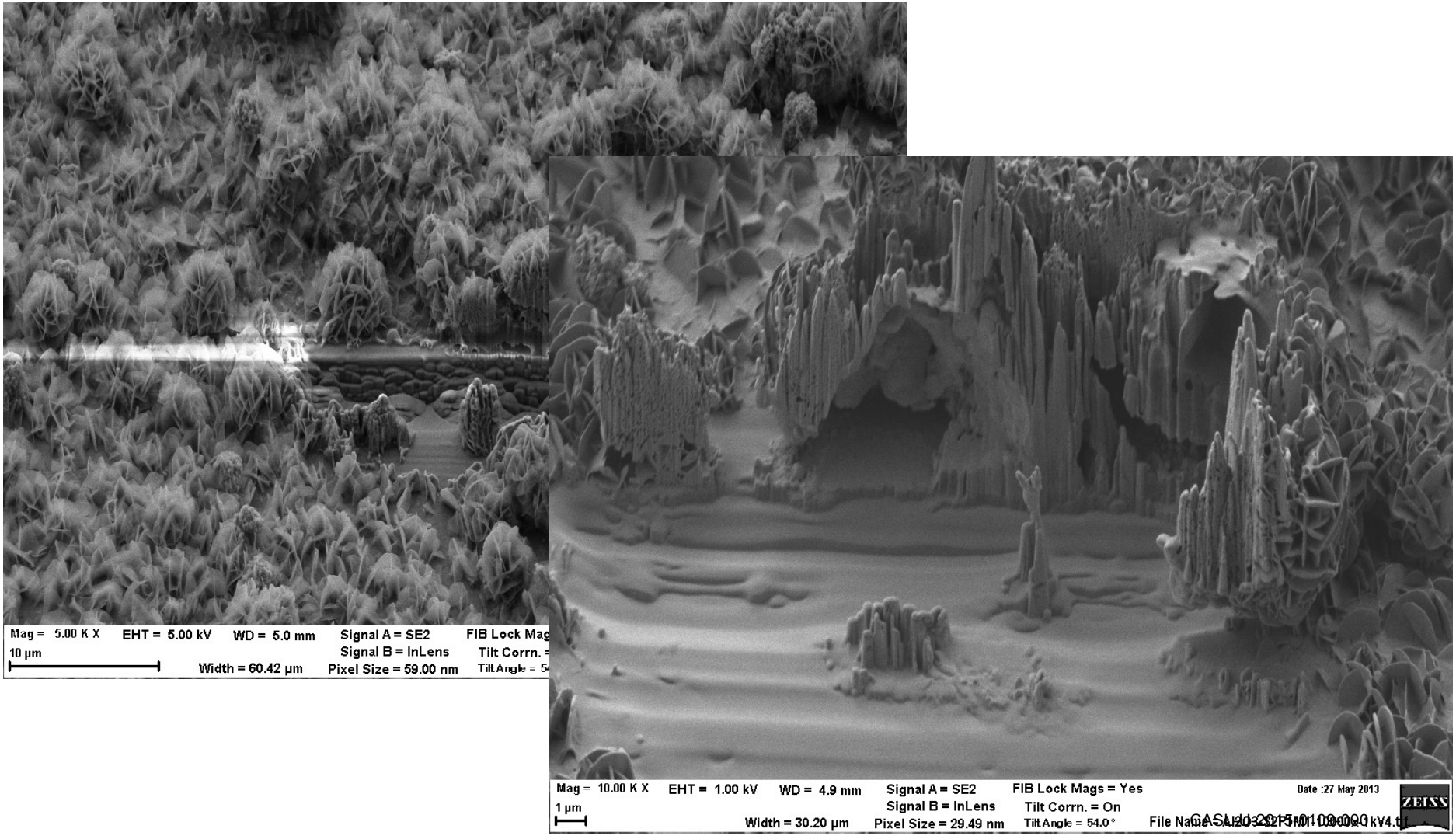
Experiments: Boiling Areas, Center Region CRUD



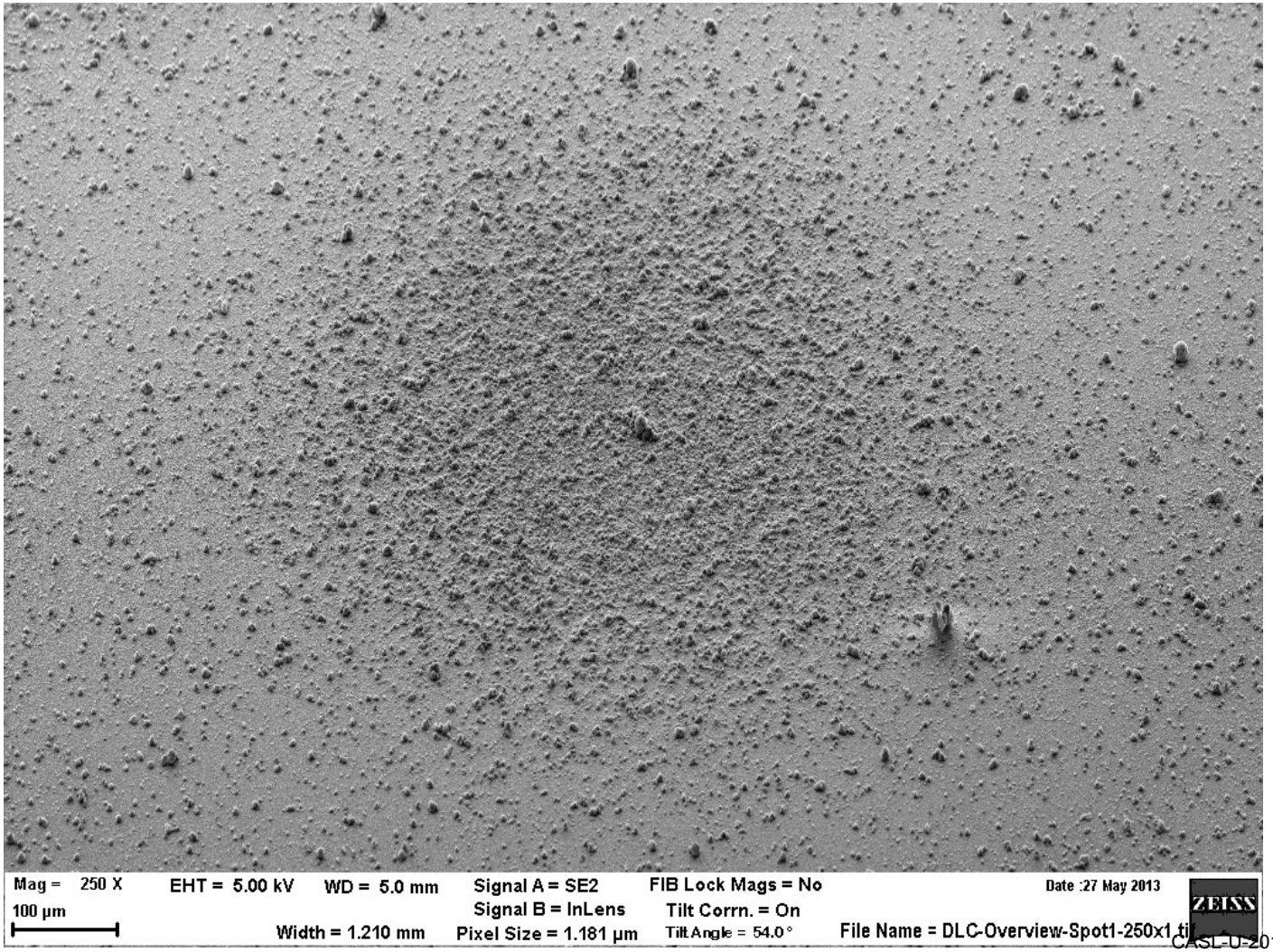
Experiments: Boiling Areas, Outer Region CRUD



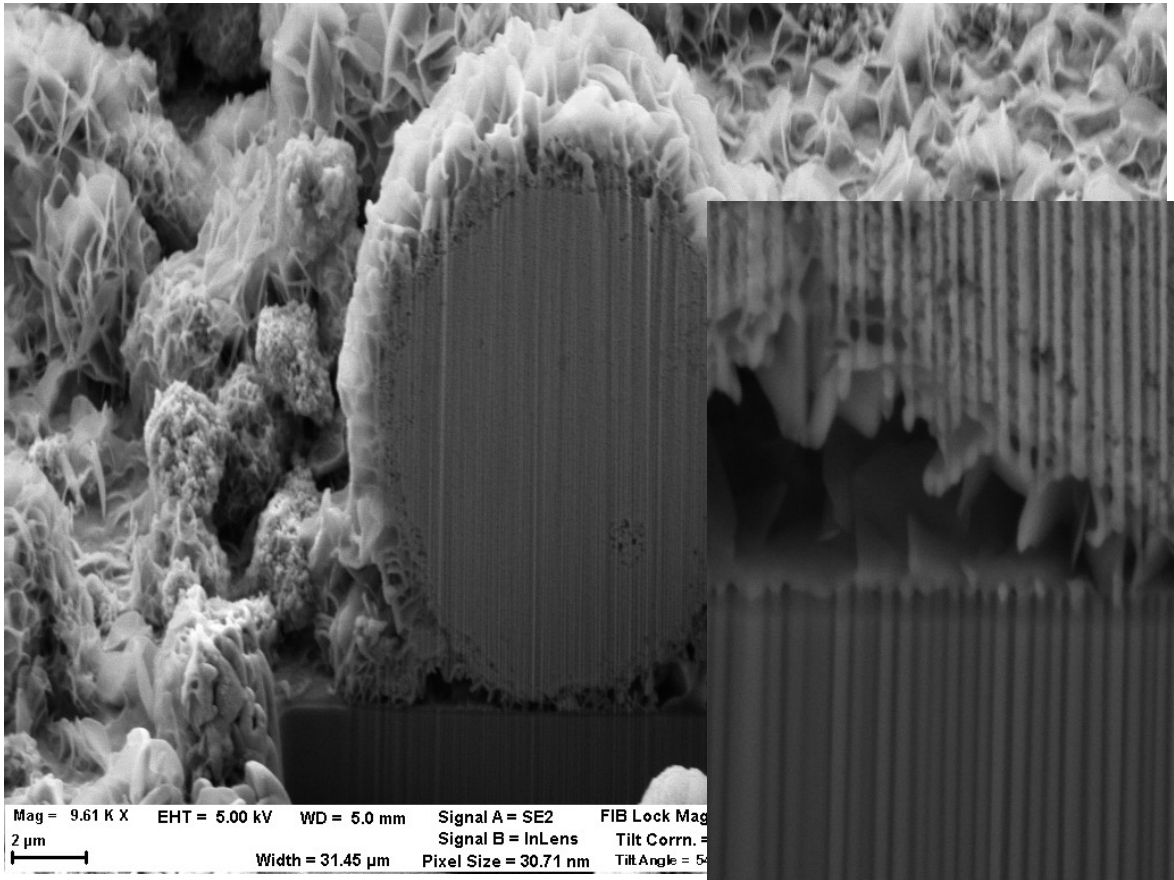
Experiments: CRUD on Al_2O_3

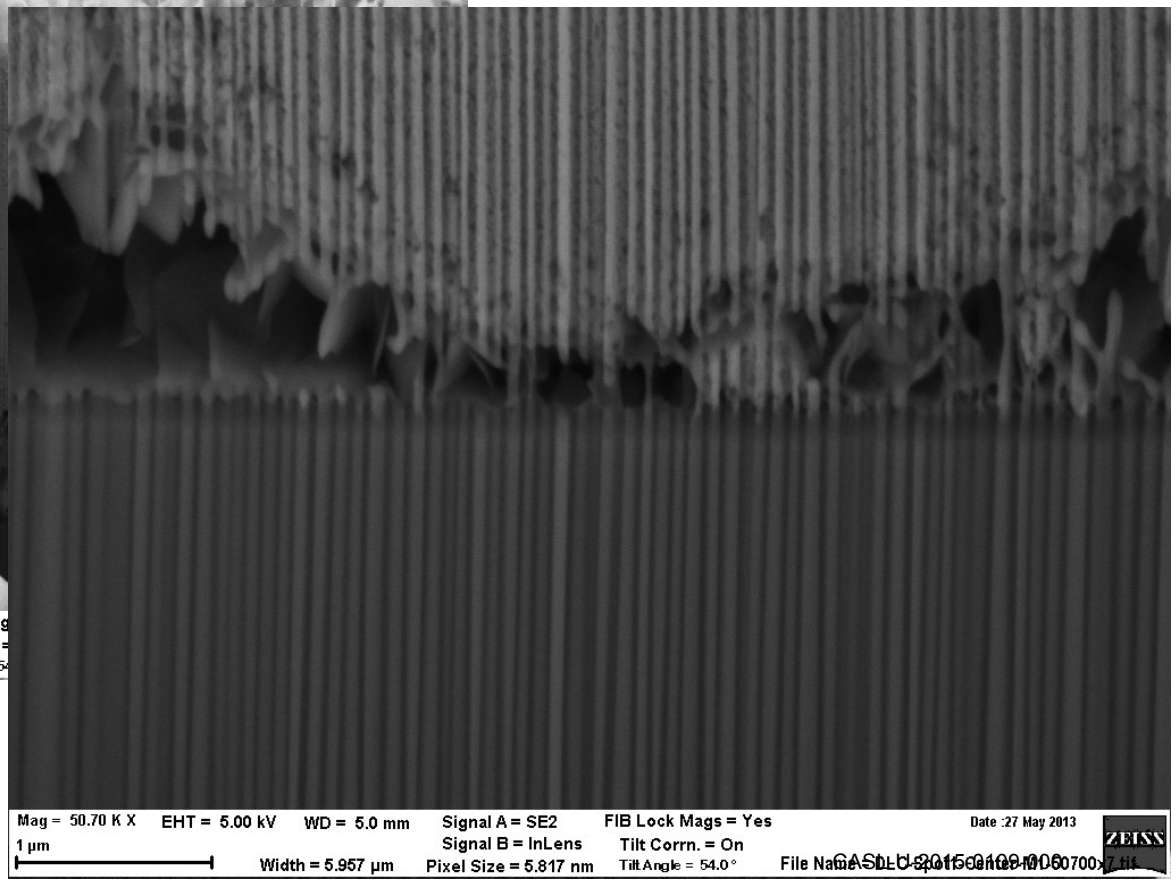


Experiments: CRUD on DLC

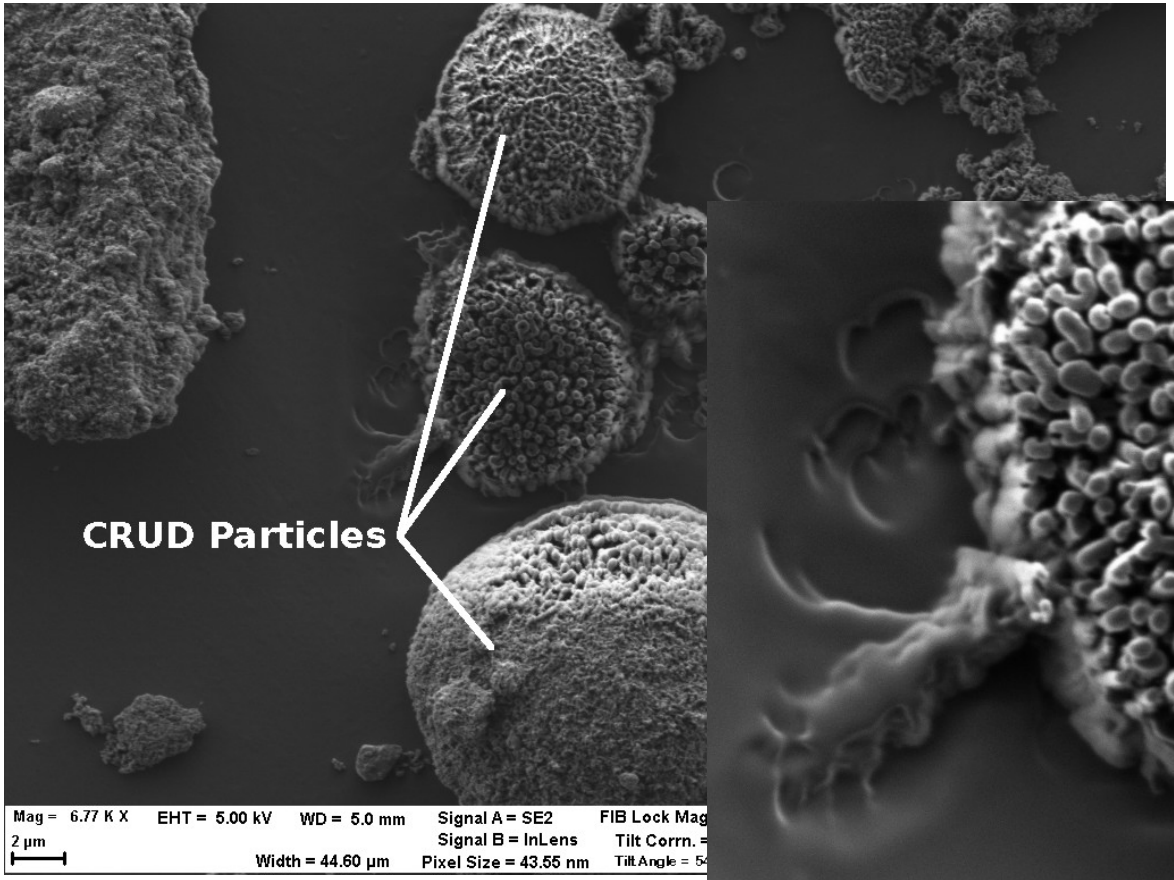


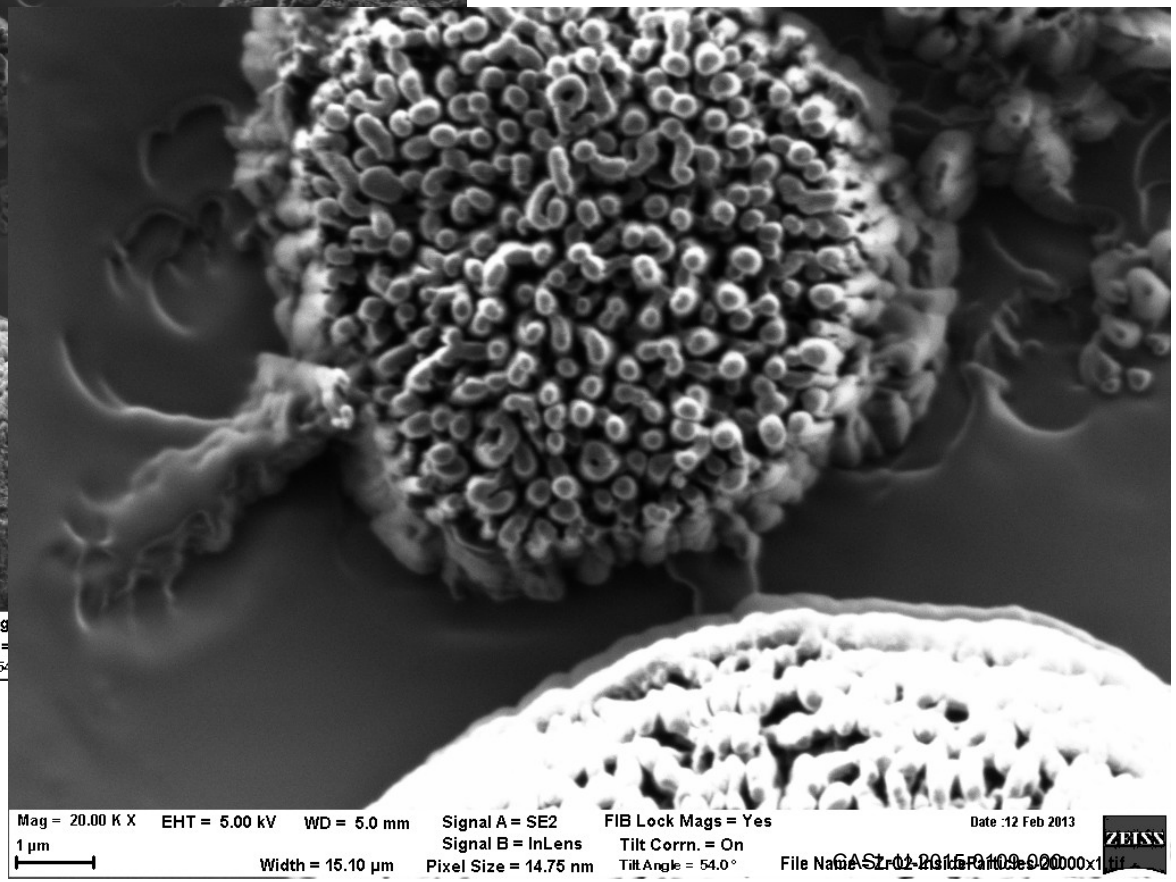
Experiments: CRUD on DLC



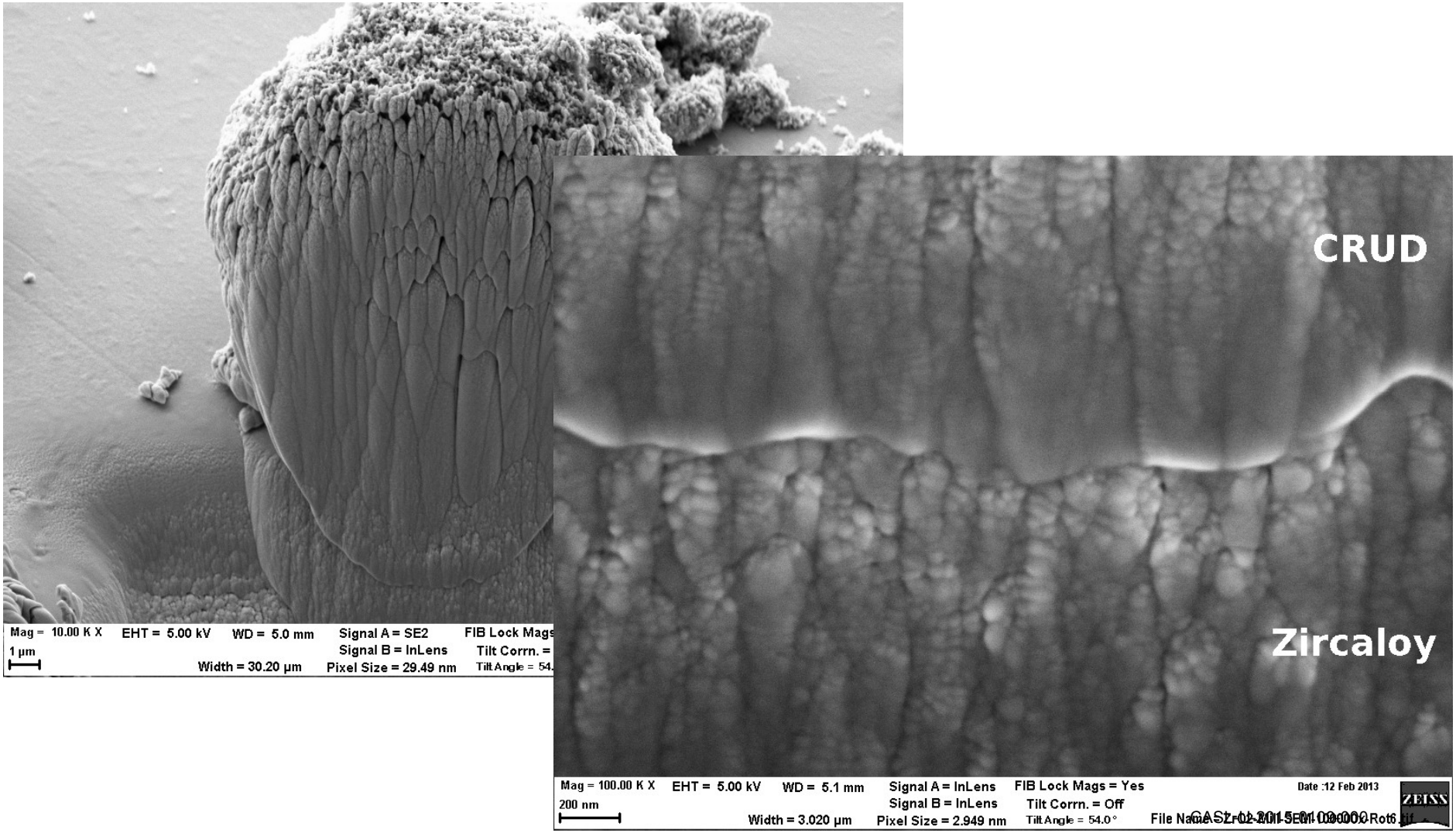


Experiments: CRUD on Zrly-4





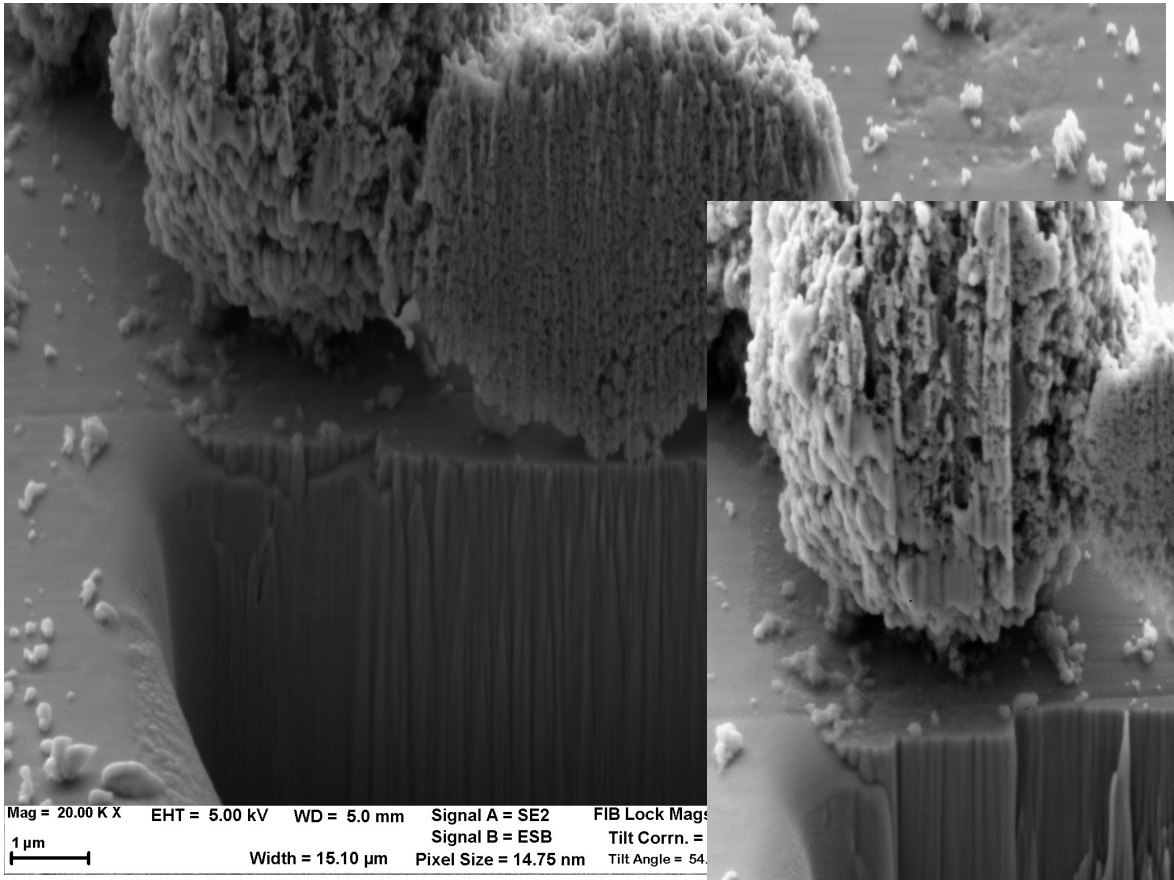
Experiments: CRUD on Zrly-4

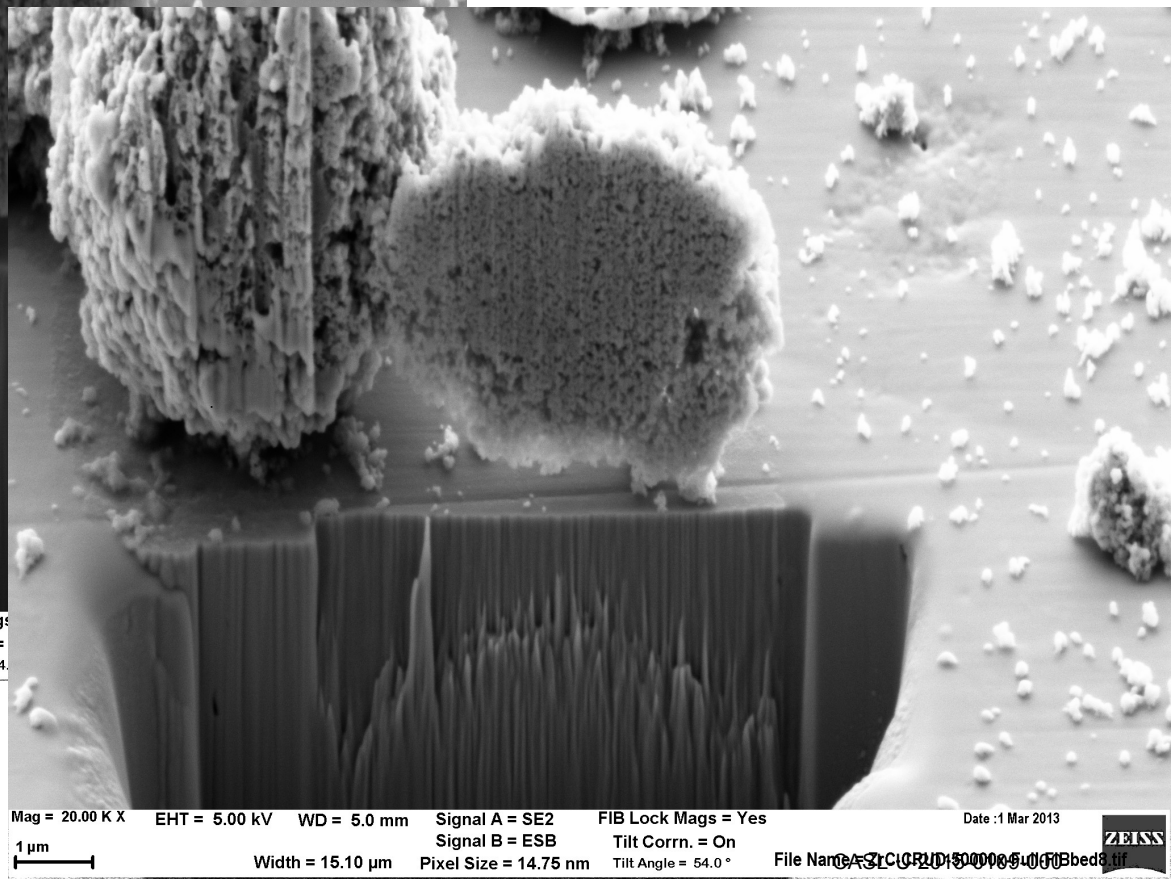


Experiments: CRUD on ZrC

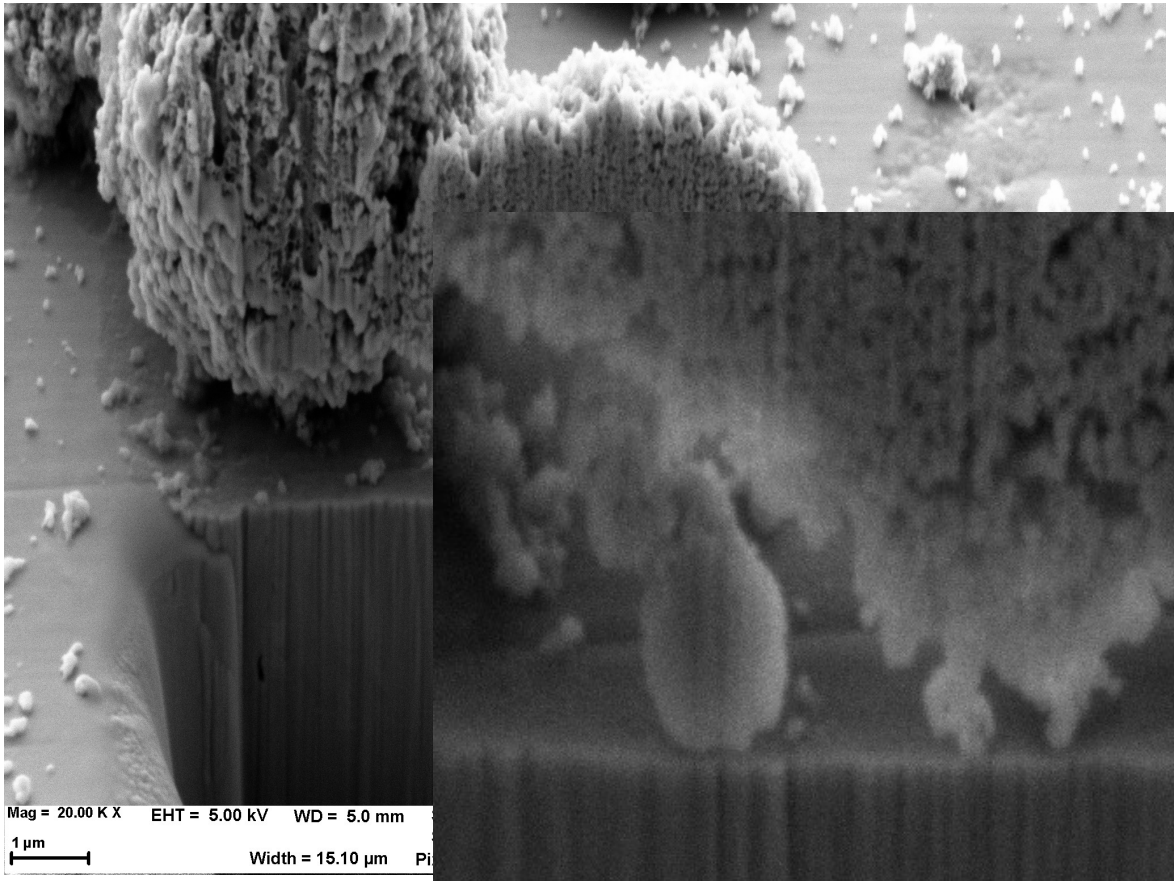
And Finally...

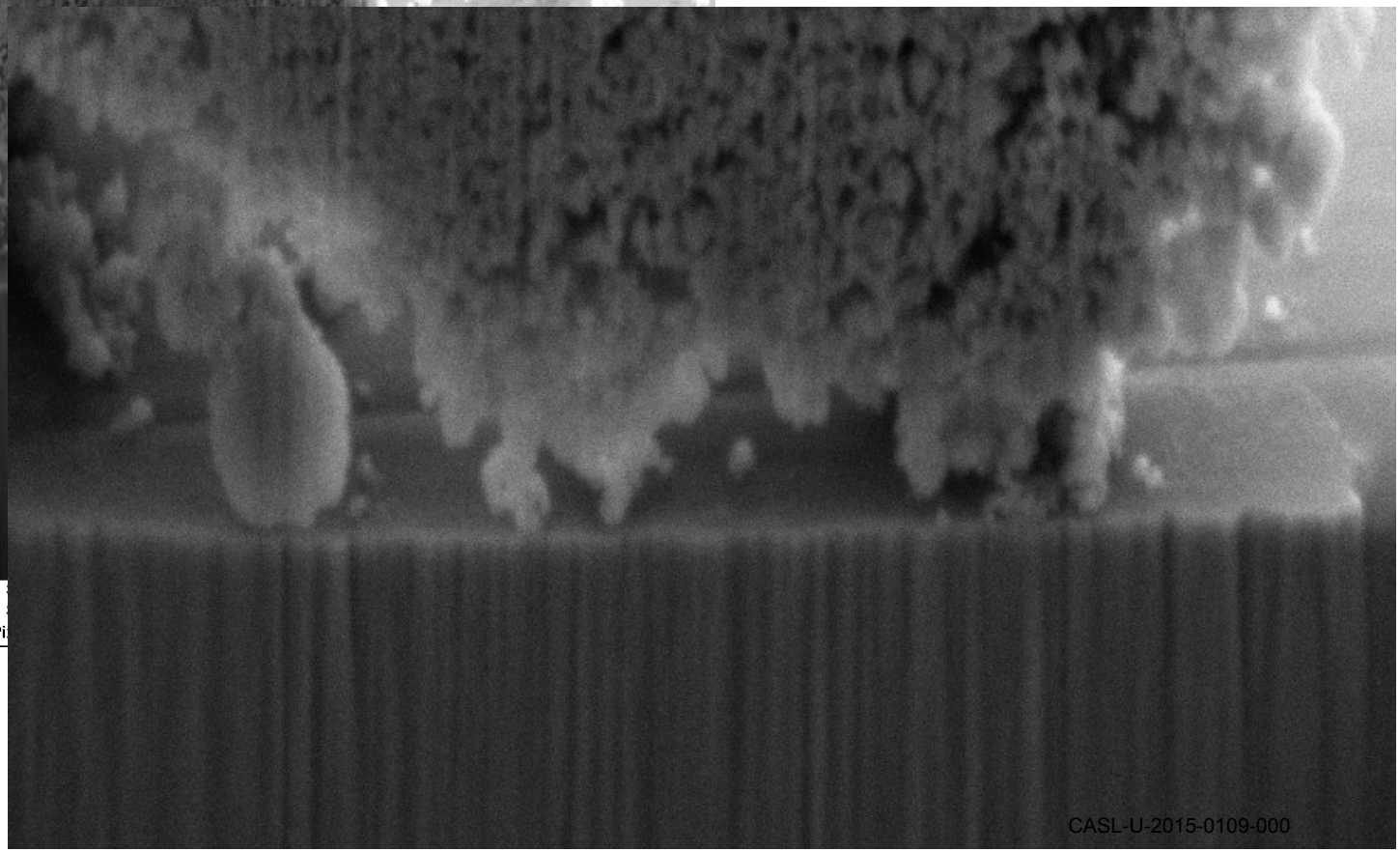
Experiments: CRUD on ZrC



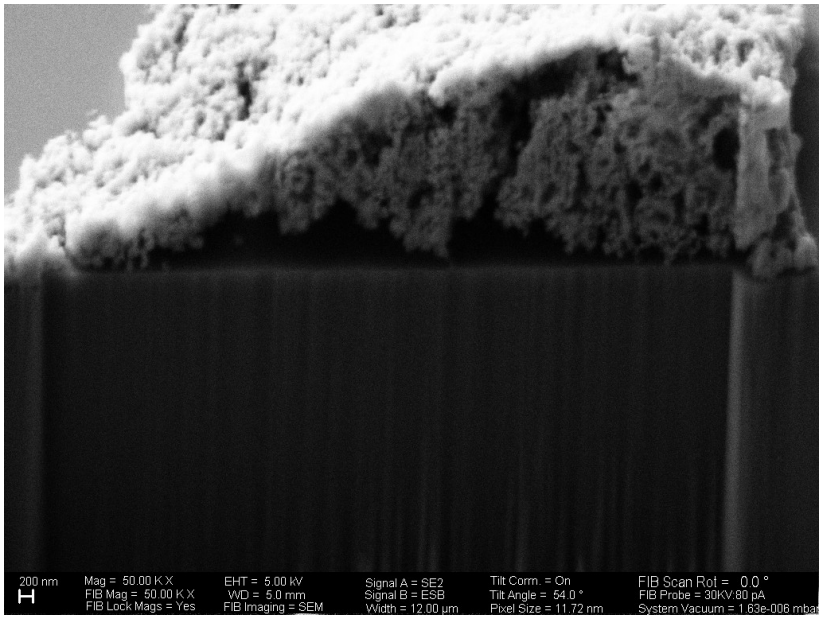


Experiments: CRUD on ZrC

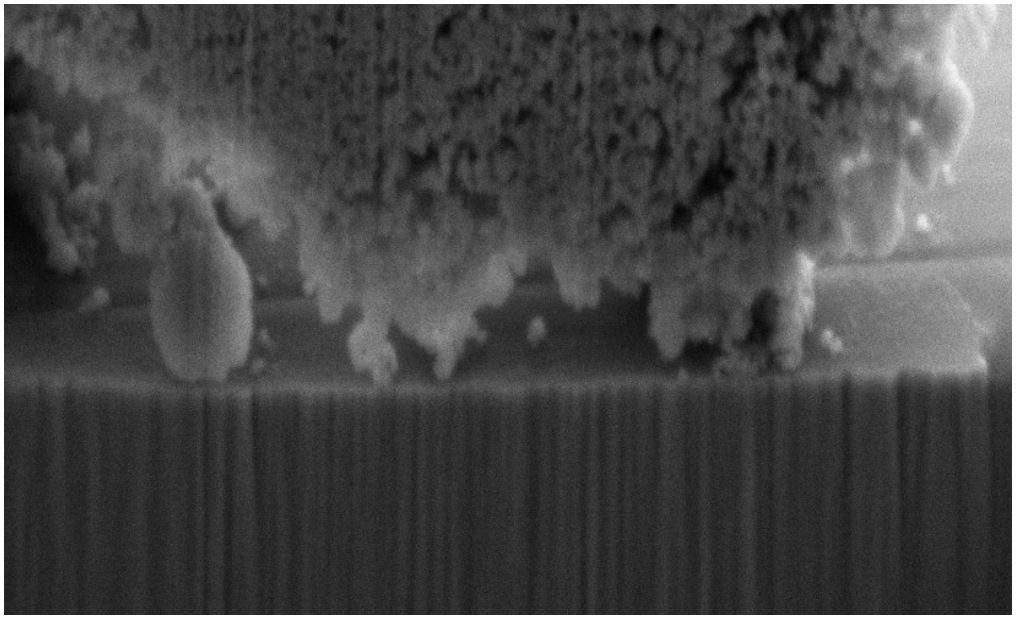




Does This Look Familiar?



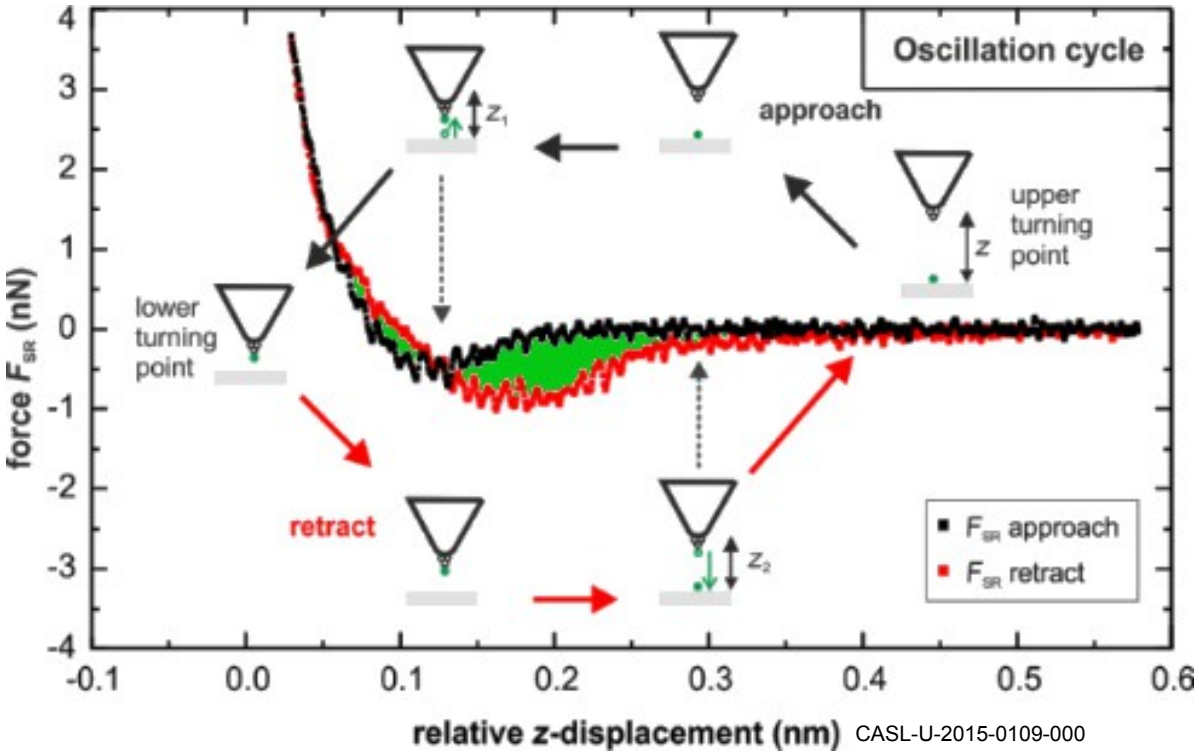
CRUD on SiO_2, no boiling



CRUD on ZrC, after 1hr sub-cooled boiling

Next: Quantify the CRUD-Clad Bond Strength

- **AFM Force Spectroscopy (AFM-FS)**
- **Directly measures adhesion energy**
  - **Functionalize AFM tip with CRUD particle**
  - **Touch surface, retract**
  - **Measure force vs. displacement**



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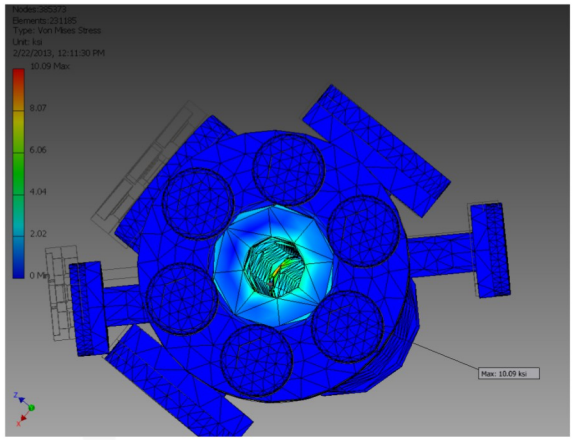
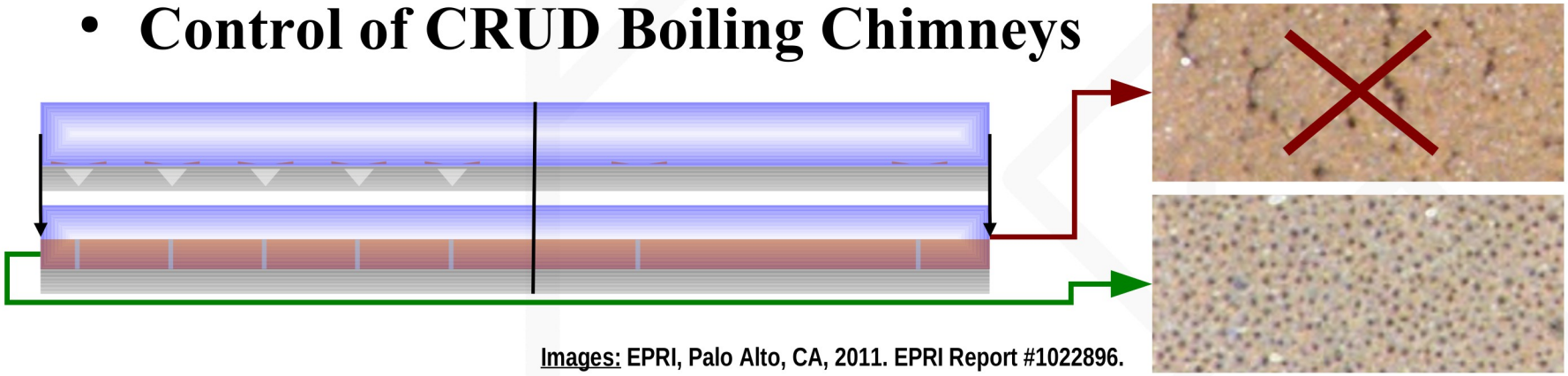
Coming Soon...

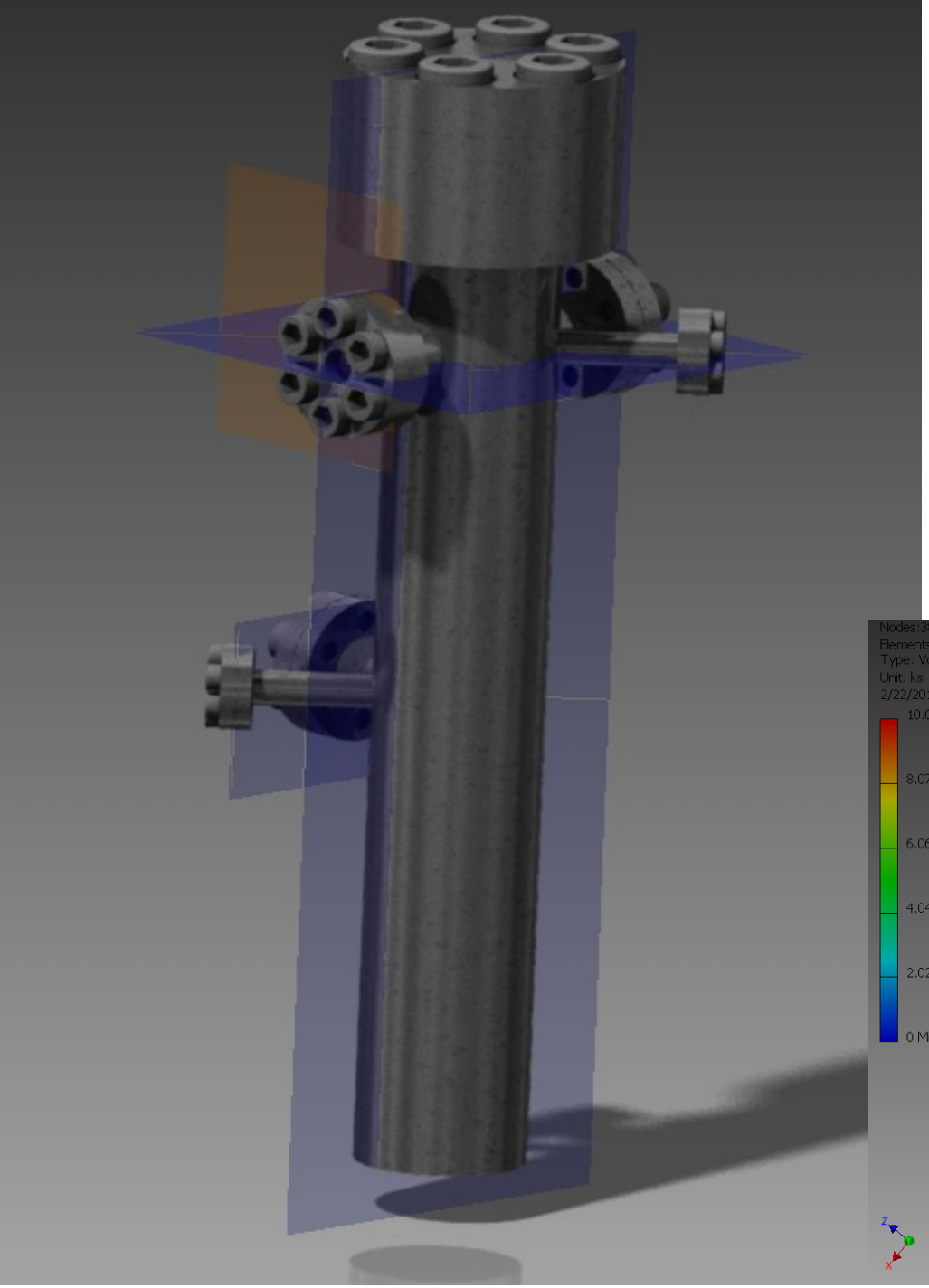
- **The MIT PWR CRUD Loop**



- **Control of CRUD Boiling Chimneys**

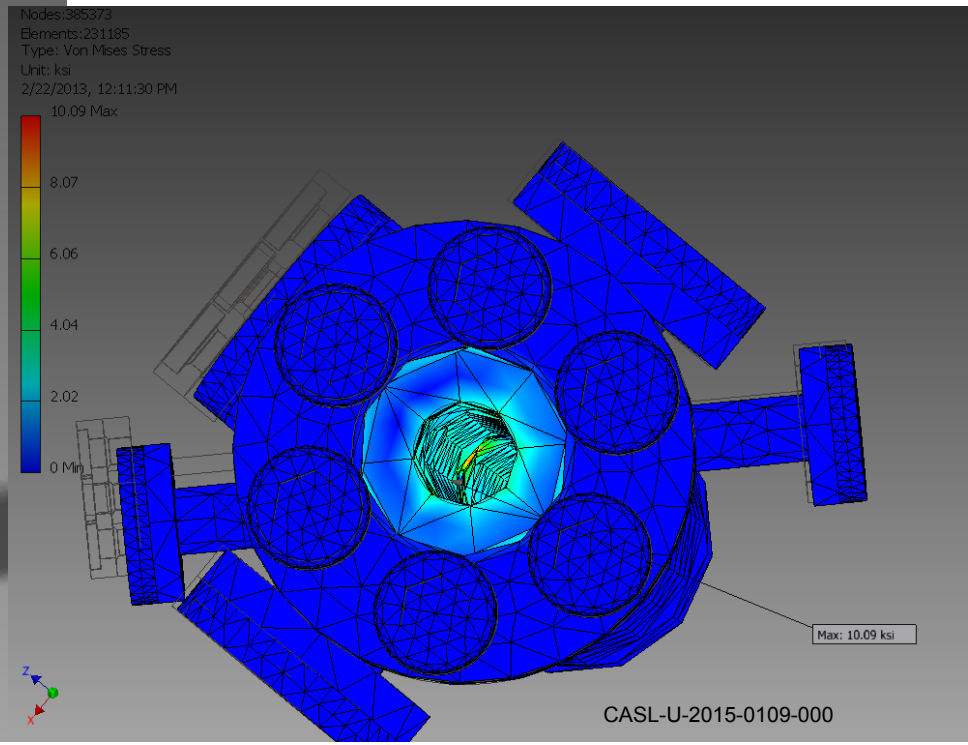


Images: EPRI, Palo Alto, CA, 2011. EPRI Report #1022896.



Autoclave Design & Stress Analysis

Sapphire windows reveal in-situ CRUD growth



PWR CRUD Loop: Autoclave Fluid Flow Analysis by CFD

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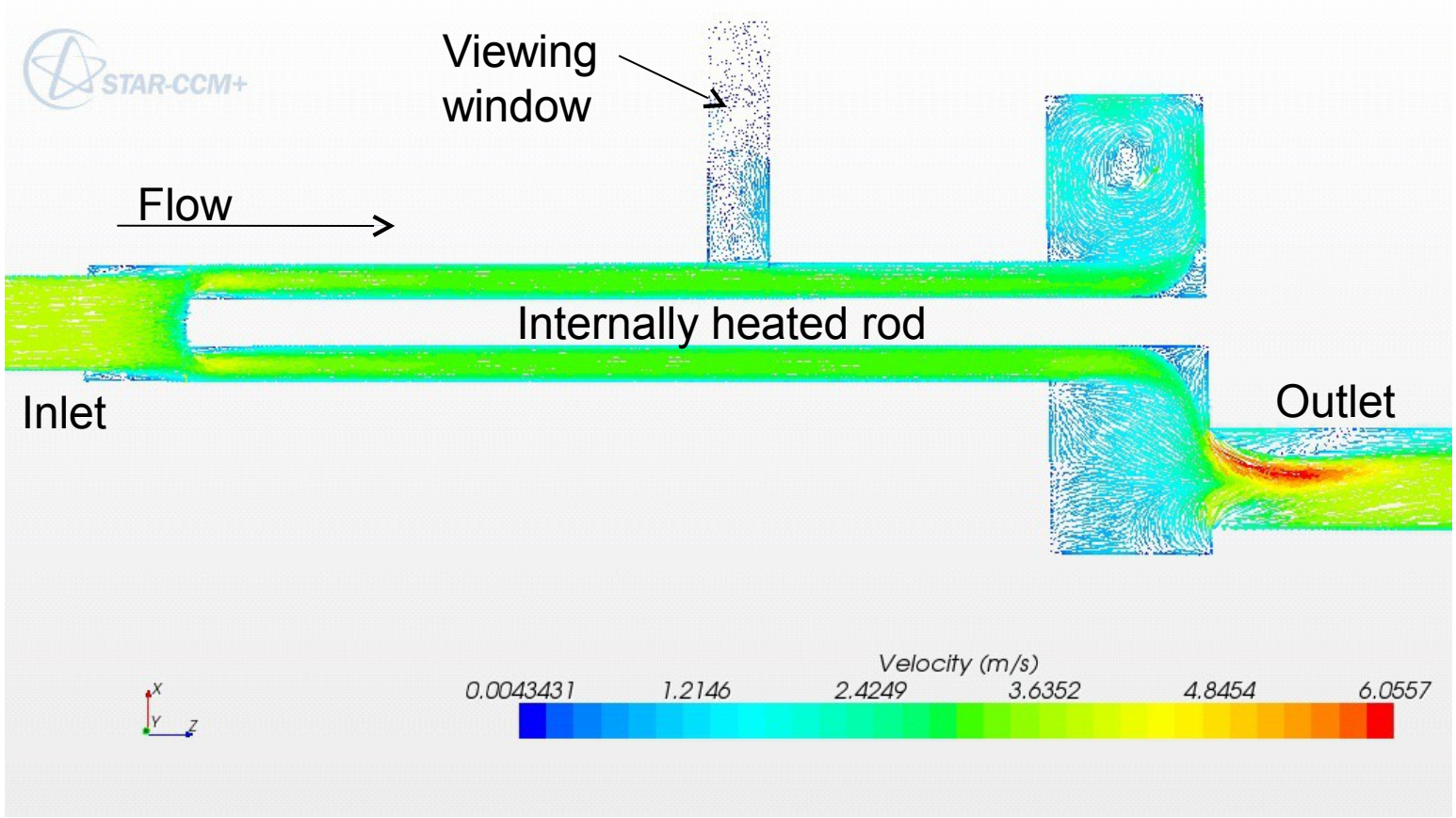
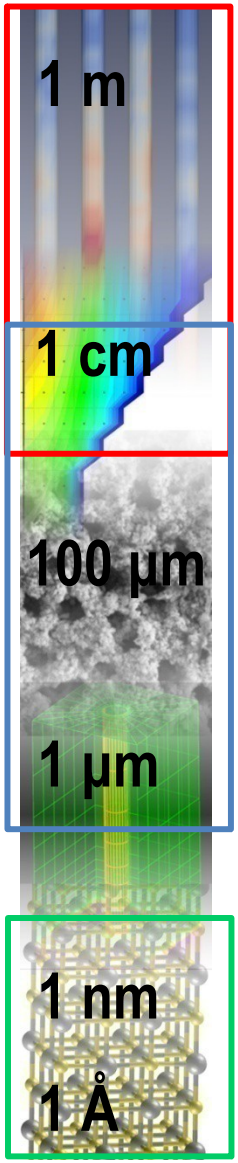
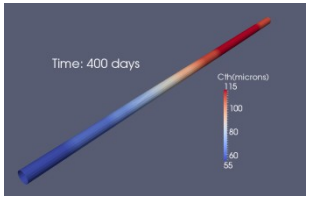


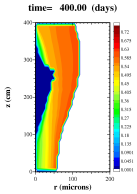
- **Flow pattern cross section**
  - **Viewing window does not affect flow at rod surface**

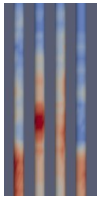
Conclusions



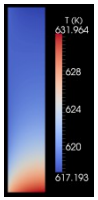
- **CASL building multiscale CRUD models**
  - **Engineering scale *MAMBA***

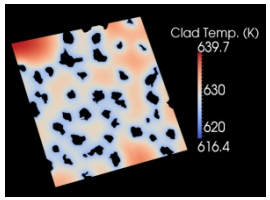


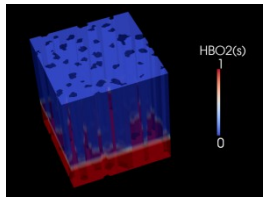


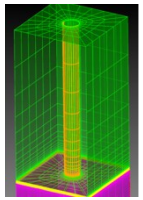


  - **Micro/mesoscale *MAMBA-BDM***









- **Validation at multiple length scales**
- **Linking to CFD & fuel performance codes**
- **Reaching towards our goal of a virtual reactor!**
- **Experiments underway:**
  - **CRUD resistant materials**
  - **PWR CRUD loop**

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CASL-U-2015-0109-000