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Surface Modification Methods of Zirconium Alloy Fuel Cladding Tube for Mitigation of Corrosion Product Deposit in Simulated PWR Primary Coolant

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PWR components & materials

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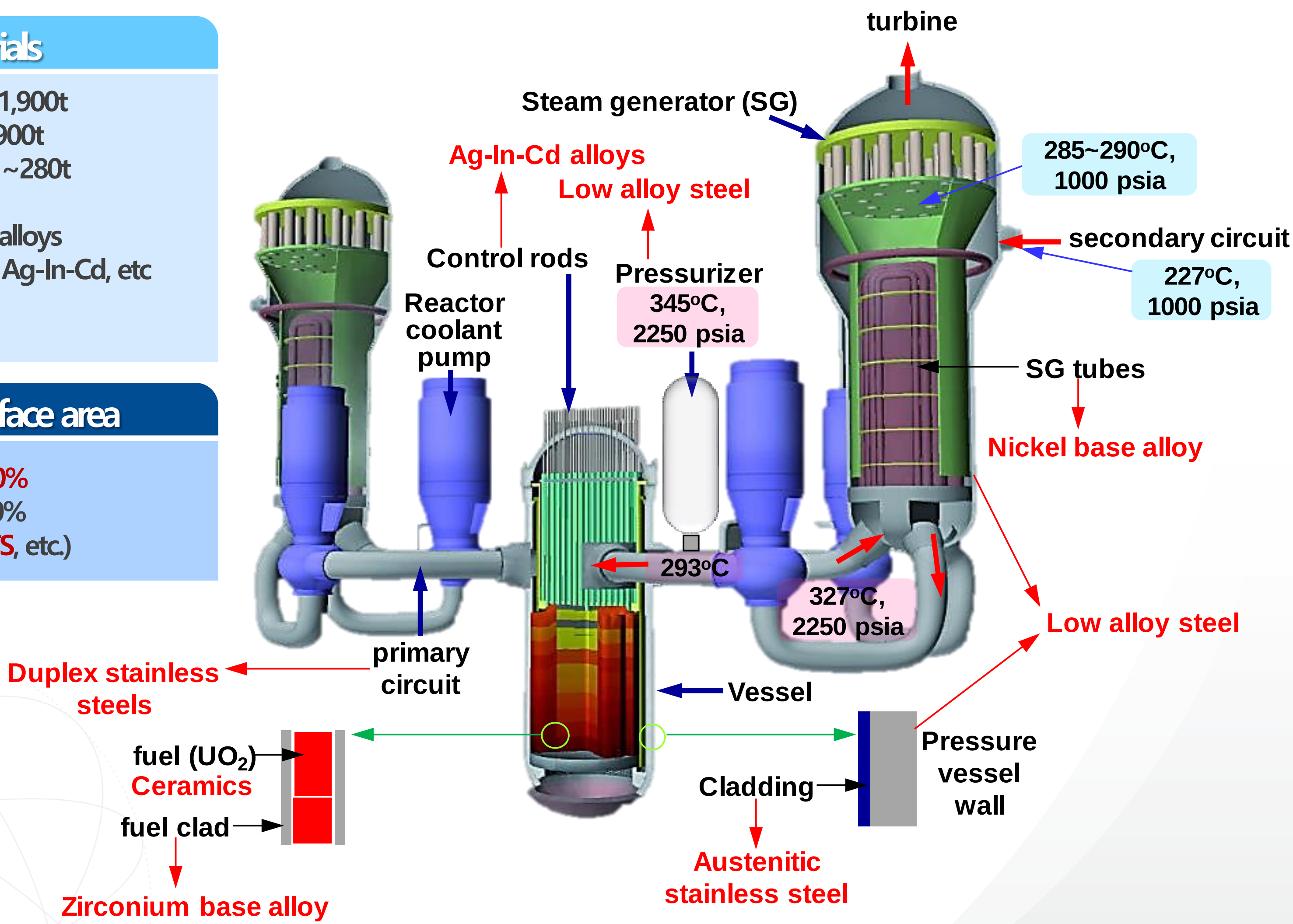
Materials

- ◯ Low alloy steels : ~1,900t
- ◯ Stainless steels : ~ 900t
- ◯ Nickel base alloys : ~280t
- ◯ Others:
  - Zirconium base alloys
  - Nuclear alloys : Ag-In-Cd, etc
  - Ceramics
  - Cu, Ti, etc.

Primary surface area

- ◯ Ni base alloys : ~70%
- ◯ Zr base alloys : ~20%
- ◯ Others : ~ 10% (STS, etc.)



Corrosion products & problems

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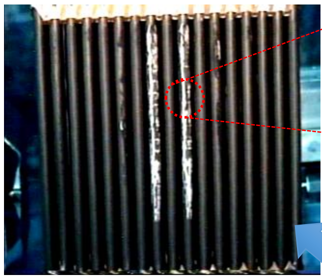
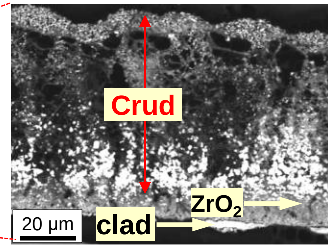
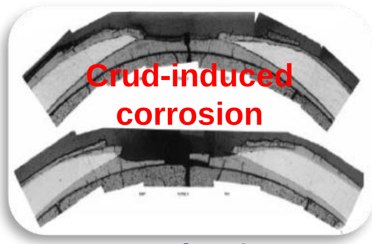
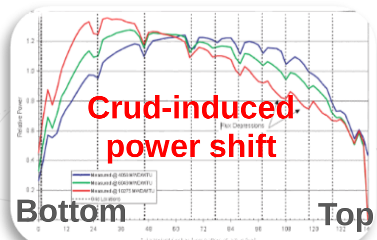
Role	Species	Concentration
Burnable poison	H_3BO_3	0 – 2300 ppm
pH adjust	LiOH	0.1-3.5 ppm (6.8 – 7.4)
Minimize radiolytic oxygen	H_2	25 – 50 STP cc/kg
Corrosion control	O_2	0.1 ppm (< 10ppb)
Corrosion product	Fe, Ni, Co, Cr	No spec.
Impurity	Cl, SiO_2, F	Each<0.15ppb
Pressure		2250 psi
Temperature		286 – 323 °C

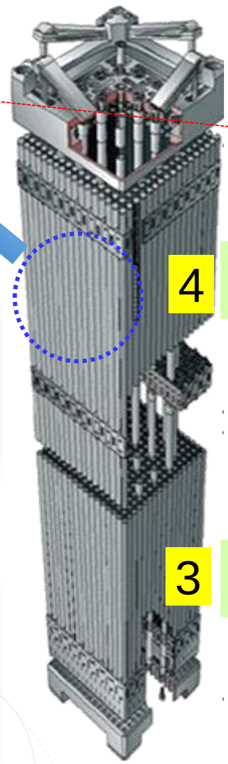






Fuel safety





Core

1 Corrosion & release

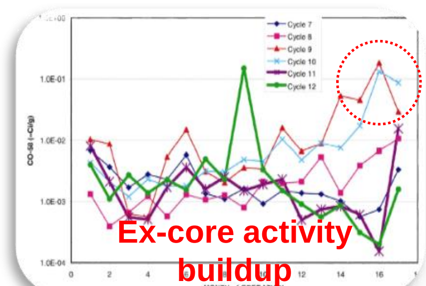
2 Transport (ions, oxides)

3 Deposition & activation

4 Rerelease & transport

5 Redeposition & incorporation ex-core

Ex-core



Worker dose exposure (Human safety)

Crud deposition gradually increase because of power uprate, lifetime extension, higher burnup !!

How to reduce the crud deposition on fuel clad?

Crud-induced power shift (CIPS or AOA)

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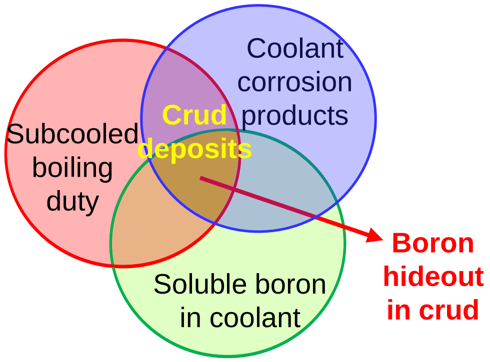
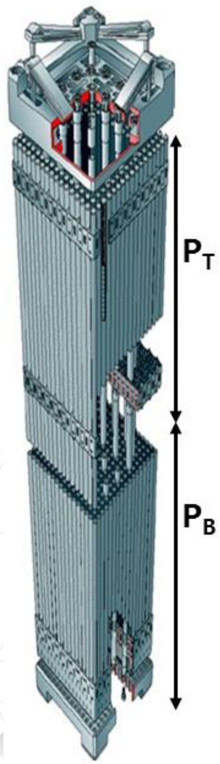
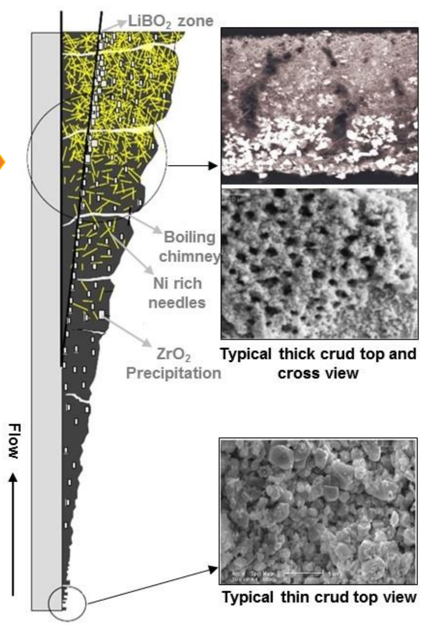
- Axial offset anomaly (AOA) or CIPS : Abnormal core power shift
- Axial Offset (Westinghouse) = $(P_{top} - P_{bot})/(P_{top} + P_{bot})$ x100
- Axial Shape Index (OPR1000, CE) = $(P_{bot} - P_{top})/(P_{bot} + P_{top})$ x 100
- Axial Offset Anomaly (AOA): |Measured A.O. – Predicted A.O.| > 3%

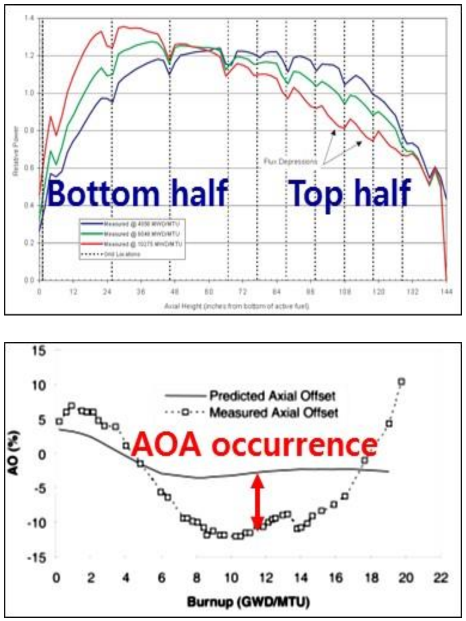
[Root-cause of CIPS]





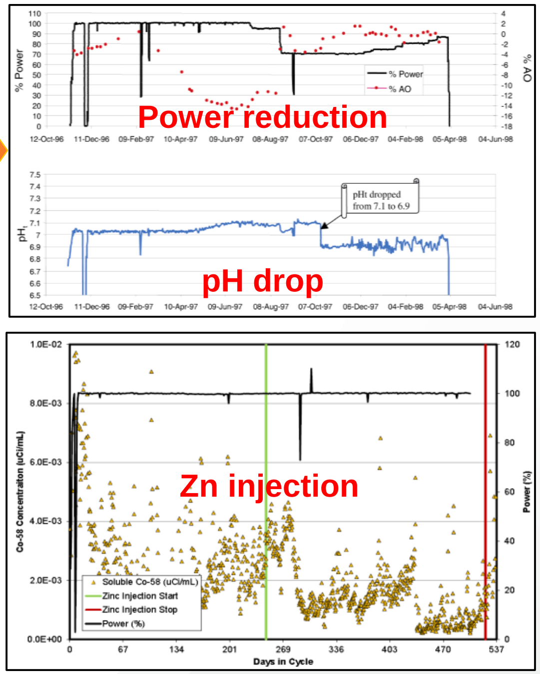


Heavy crud deposition



AOA (or CIPS)

Problem

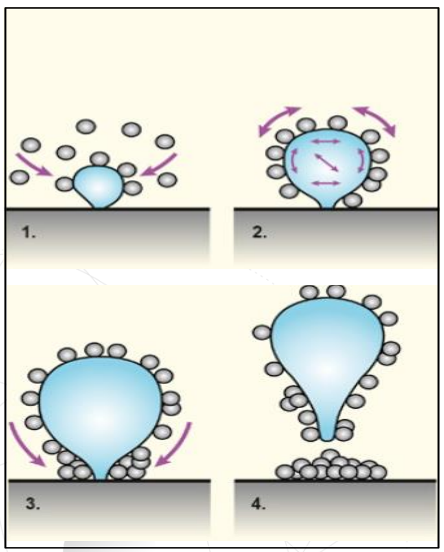


Ultrasonic cleaning, fuel redesign ···

Response

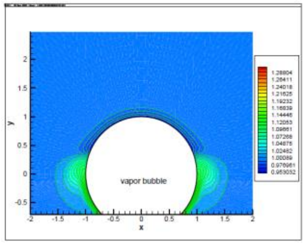
Reduction of corrosion product deposition

- **Source term reduction: reducing corrosion and release from Ni-base alloys or stainless steels**
  - Chemistry control: DH concentration increase, pH increase, zinc injection ···
  - Surface control: reduction of roughness or residual stress, removal of surface states, pre-passivation, etc ···
- **Removal of crud source: advanced resin, optimized primary-side cleanup ···**
- **Crud deposition reduction: reducing adsorption energy of cladding surface**
  - Chemistry control: pH increase, zinc injection ···
  - Surface control: reduction of roughness (for boiling site or nucleation site), chemical etching, coating (interaction with the corrosion product particles in coolant)



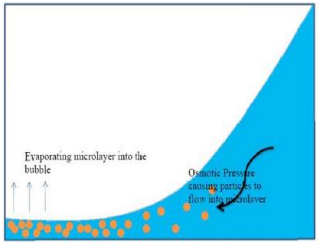
[Iwahori et al., 1979]

Solute concentration distribution near vapor bubble

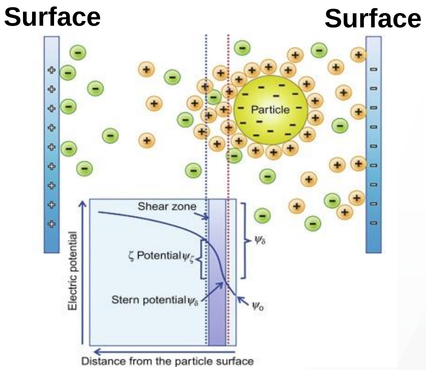


[Qinyang and Barclay., 2002]

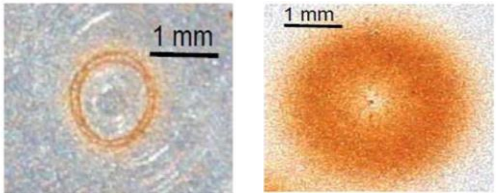
Solute transport into evaporating micro-layer



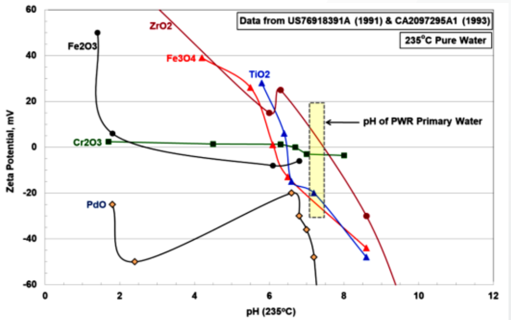
[Bindra., 2009]



Ring shaped deposits under boiling conditions



[Bindra., 2009]



Fuel crud deposition test

Basic properties of fuel cladding materials

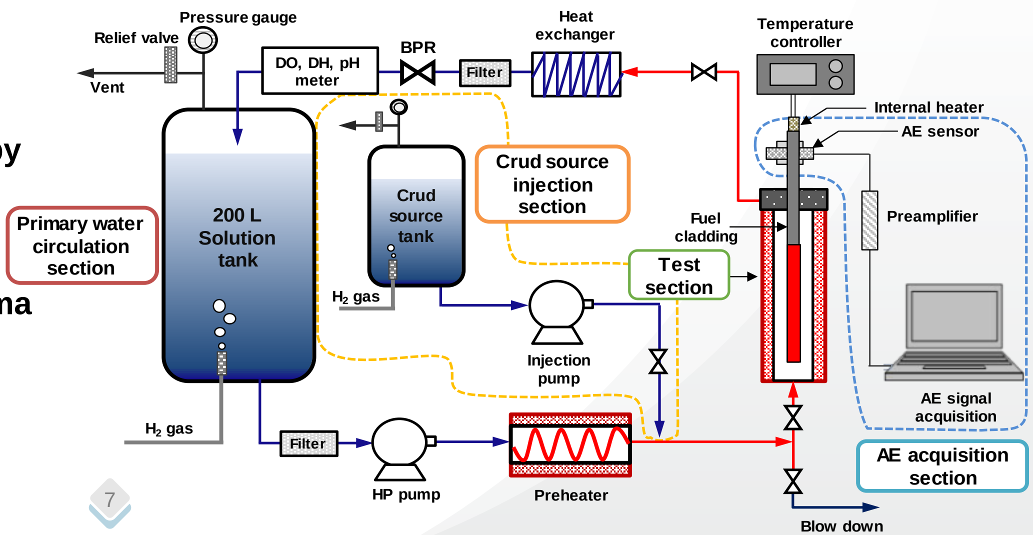
Composition (wt.%)					Mechanical properties (at RT)		
Sn	Fe	O	Nb	Zr	YS(MPa)	UTS(MPa)	Elong.(%)
1.0	0.1	0.1	1.0	Bal.	612.5	819.2	15.8

Fuel cladding surface treatment and crud deposition test

Test ID	Treatment	Cladding feautre	Heat flux (W/cm^2)	Water temp.(°C)/ Pressure (MPa)	DO/DH conc.	Test time (hours)	Solution in test section
T1	As-received Chemical etching (Roughness effect)	R_a=0.15 μm R_a=0.05 μm	20	328/ 13.0	DO < 5ppb DH=35 cc/kg·H_2O	120h	1500ppm B 3.5ppm Li 3.93ppm Fe 0.16ppm Ni
T2	Pre-oxidation (Crud deposition driving force)	No oxidized 0.71 μm-oxidized 4.55 μm-oxidized					
T3	Al_2O_3-coating (Deposition driving force)	As-received Al_2O_3-coated				168h	

Deposited crud analysis

- **Morphology : Scanning electron microscopy (SEM)**
- **Chemical composition : Scanning TEM (STEM) equipped with EDS**
- **Deposit amount : Inductively coupled plasma -atomic emission spectroscopy (ICP-AES), etc**
- **Boiling event : Acoustic emission analysis**



Effect of surface roughness

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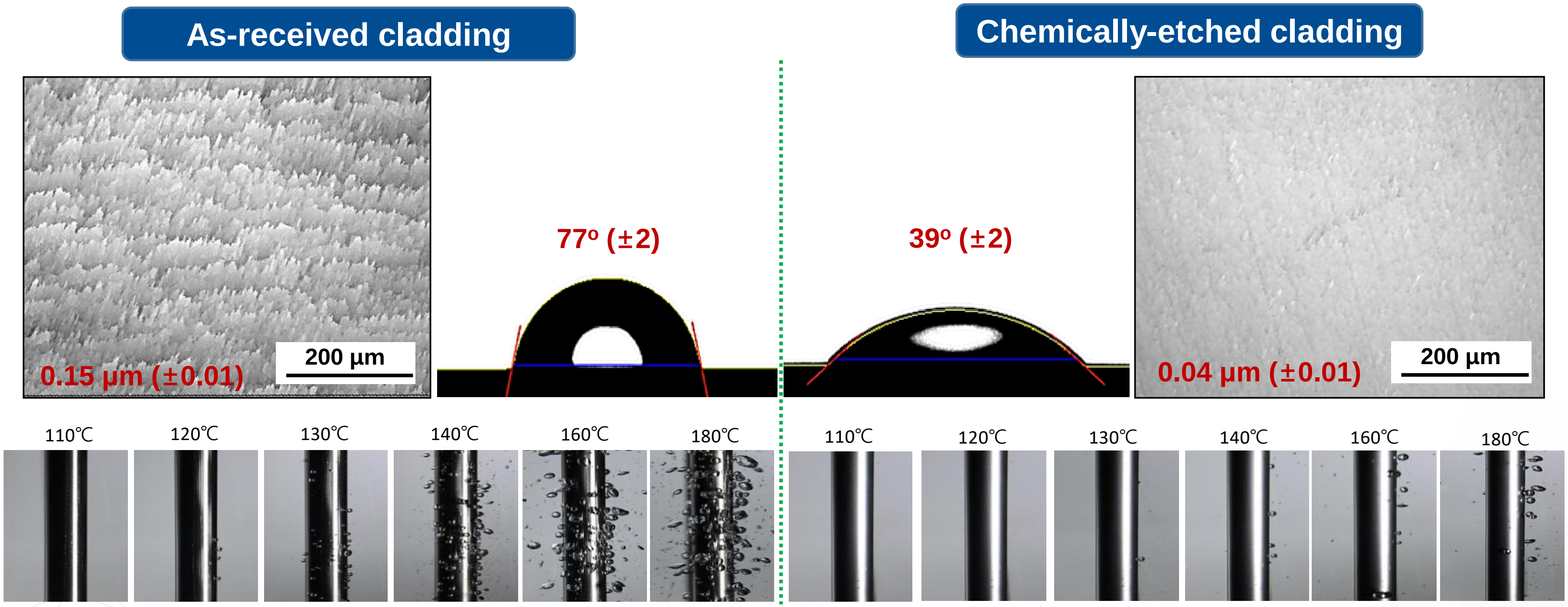
(T1) Analysis of surface properties

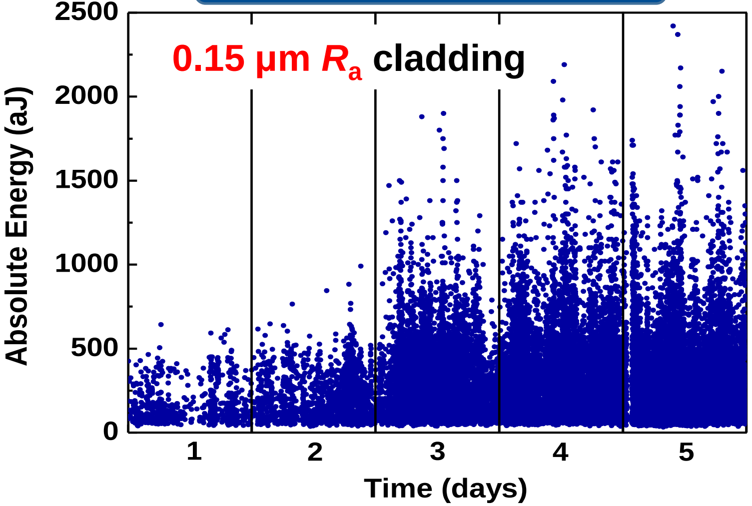


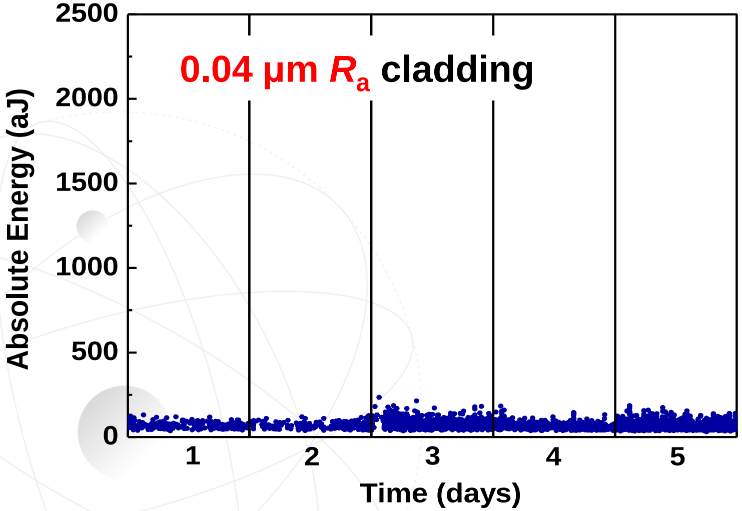
- **The roughness and water contact angle decreased by chemical etching, from 0.15 µm to 0.04 µm in roughness, from 77º to 39º in contact angle, respectively.**
- **This results the increase in onset temperature of bubble (120ºC to 130ºC) for chemically-etched specimen due to the reduction of surface roughness.**

Effect of surface roughness

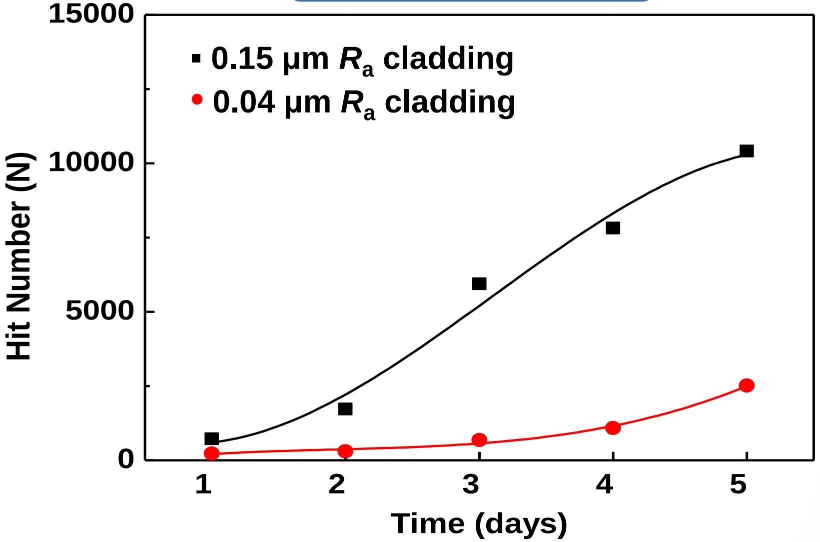
(T1) Acoustic emission signals for boiling events

AE signal energy





AE hit number



- **AE energy (bubble size)** and **AE hit number (events)** of boiling signals: 0.15 μm R_a cladding > 0.04 μm R_a cladding (**5~7 times**)
- This indicates that boiling events as an root-cause for crud deposition can be reduced by **reduction of roughness on fuel cladding tube**.

Effect of surface roughness

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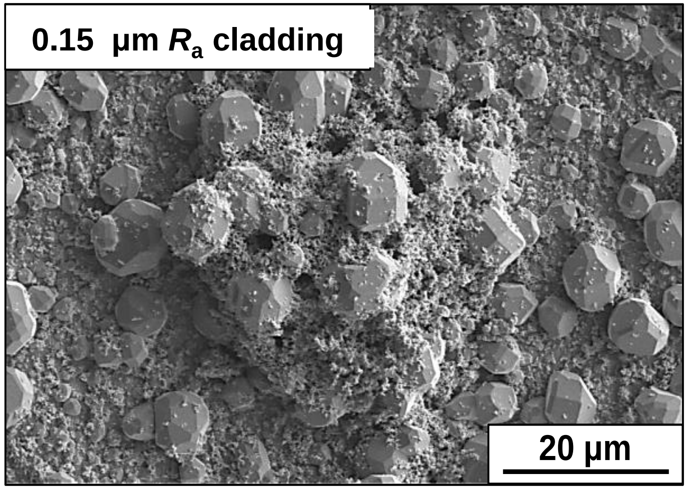
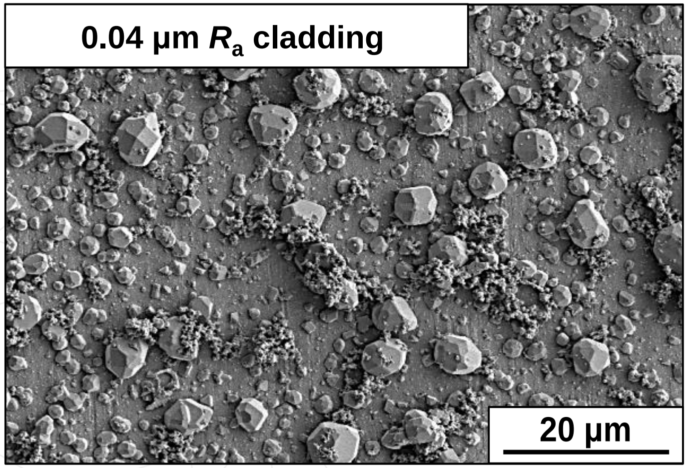
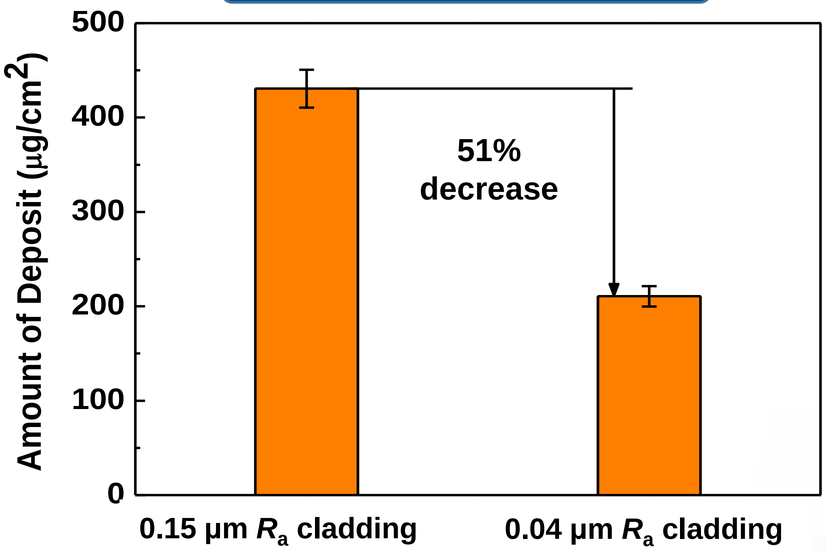
(T1) Quantity of crud deposits

SEM Image of crud





Amount of crud deposits



- Crud on both cladding tubes consists of large and small polyhedral particles having chemical composition of Fe_3O_4.
- The amount of crud decreased by 51% (2.1 times) on the smooth surface (0.04 μm R_a), compared to that on rough surface (0.15 μm R_a).

Effect of surface roughness

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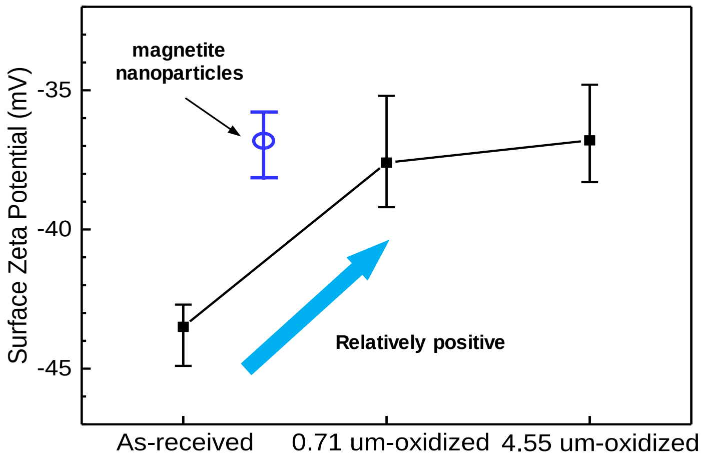
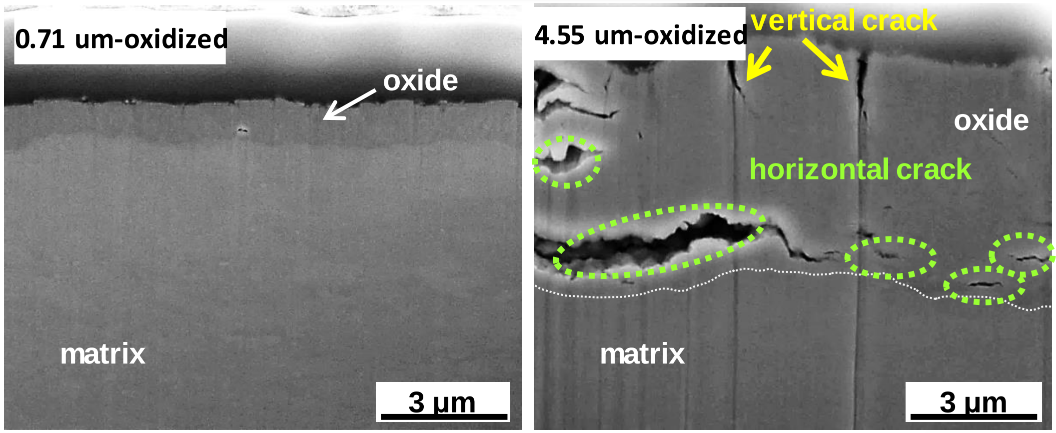
(T2) Analysis of surface properties

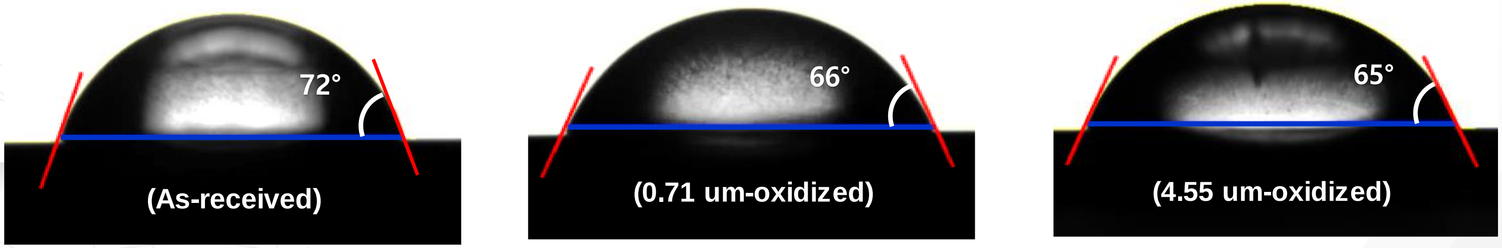
Surface zeta potential



FIB cross-sectional images



Water contact angle



- The **zeta potential difference** (within the same sign) between on magnetite particle and cladding surface **gradually decreases with increase in oxidation time**. However, many cracks were observed with increase in the oxidation time.
- **The water contact angles shows similar value** on three specimens having different surface oxidation status.

Effect of surface oxidation

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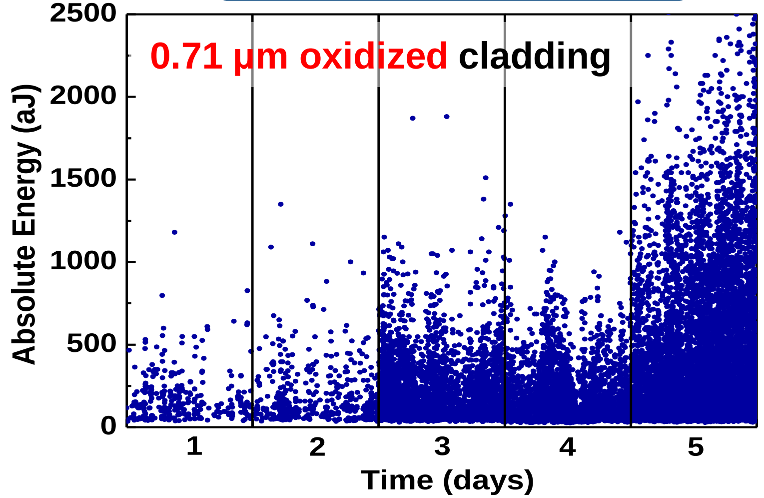
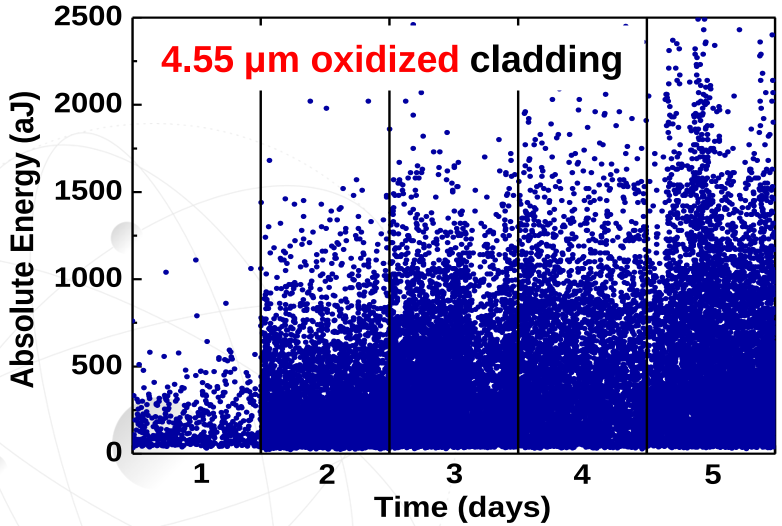
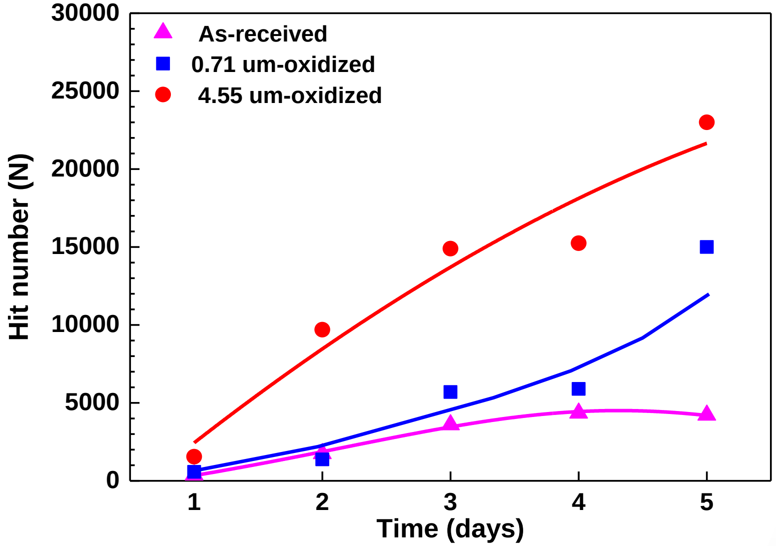
(T2) Acoustic emission signals for boiling events

AE signal energy





AE hit number



- AE energy intensity and hit number of the boiling signals increased on the cladding preoxidized with 4.55μm thickness ZrO_2, compared to that with 0.71 μm thickness ZrO_2.
- This result reveals that the boiling phenomenon can be enhanced by increase of oxide layer thickness, resulting the increase of crud deposition amount.

Effect of surface oxidation

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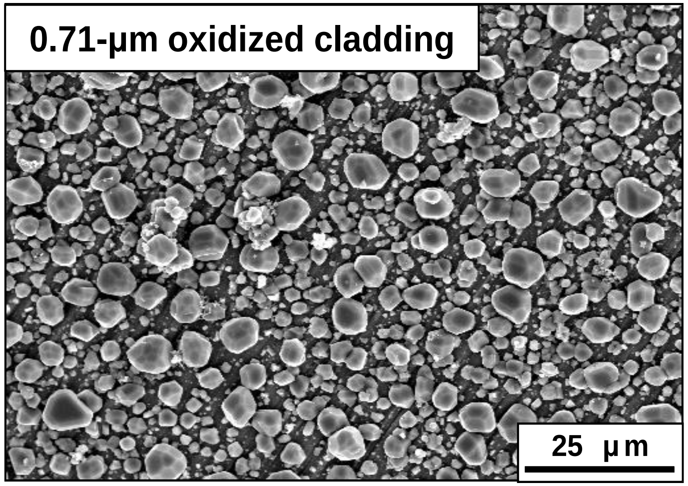
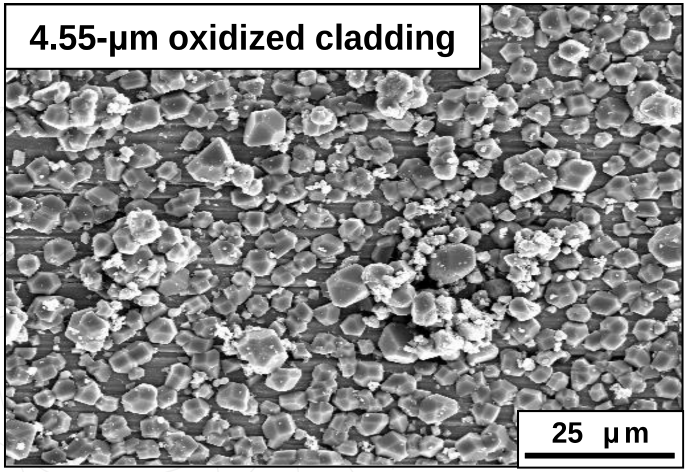
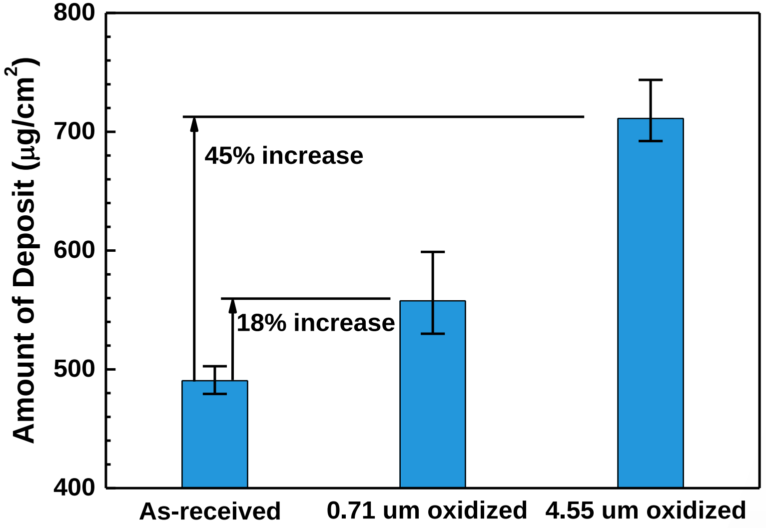
(T2) Quantity of crud deposits

SEM Image of crud





Amount of crud deposits



- Crud deposited on claddings with different oxide thickness consists of polyhedral particles having different size and chemical composition of Fe_3O_4.
- The amount of crud increased by 18% for 0.71 μm oxidation and by 45% for 4.55 μm oxidation, respectively, compared to that of as-received cladding.

Effect of surface coating

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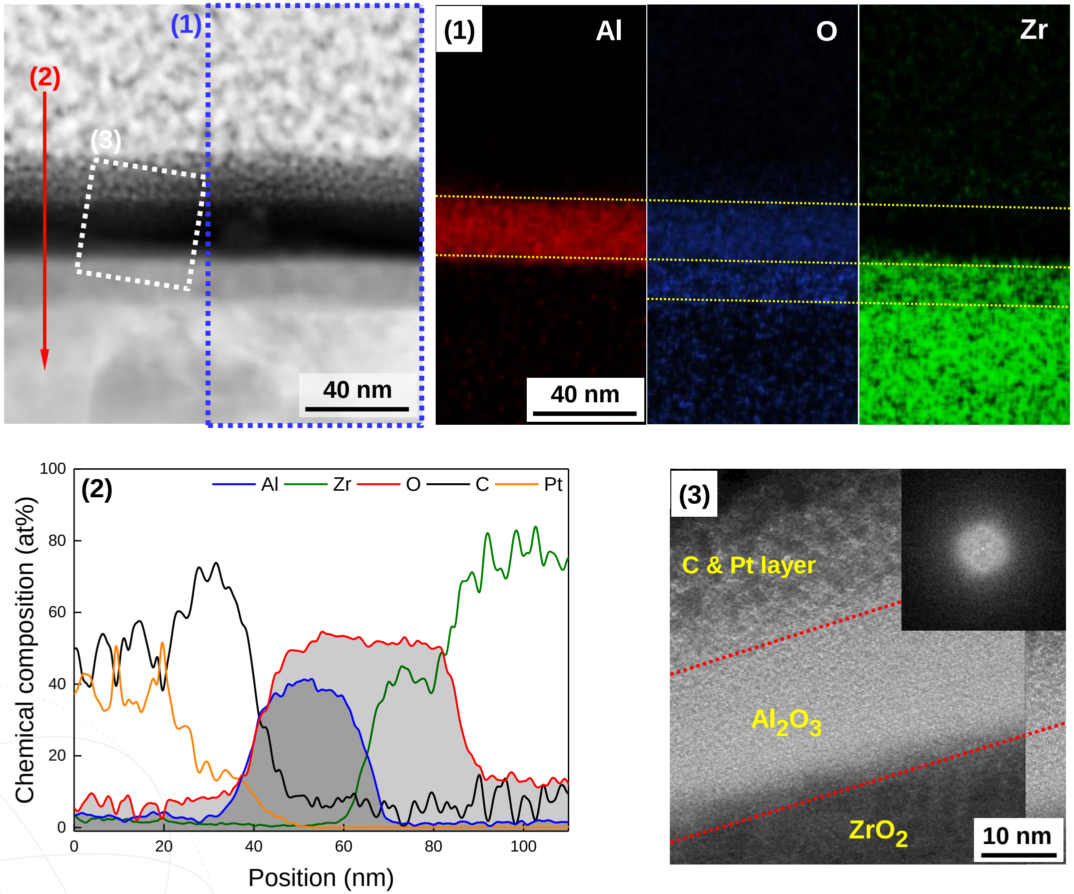
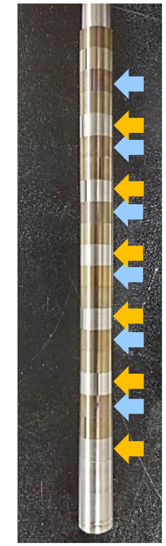
(T3) ALD coated Al_2O_3 layer





Al2O3/Zirlo

As-received Zirlo

- Al_2O_3 layer of 20 ~ 25 nm thickness was coated on as-received cladding and ZrO_2 oxide layer of 15 ~ 20 nm was formed during coating process. The Al_2O_3 layer was analyzed as an amorphous phase.

Effect of surface coating

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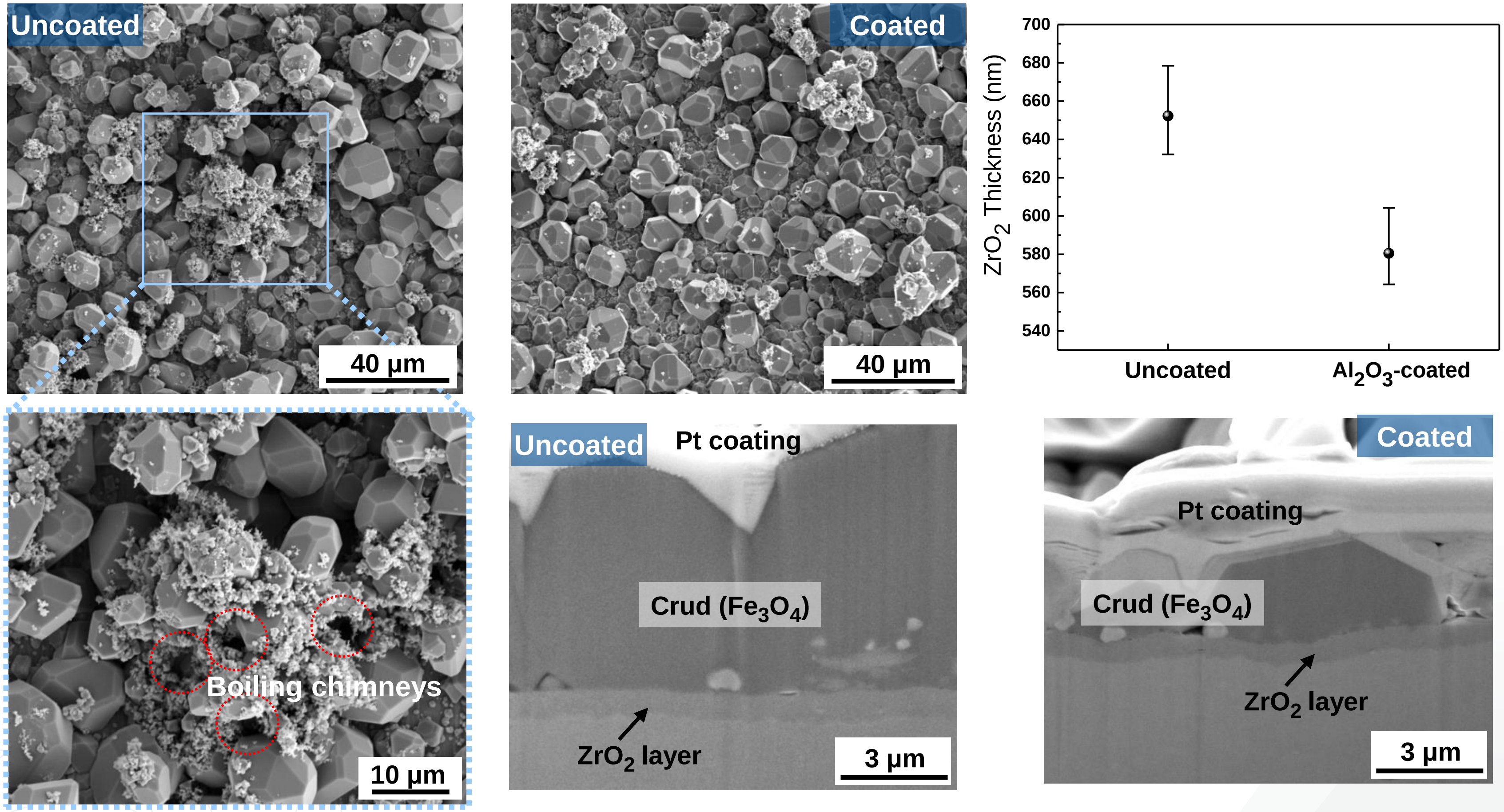
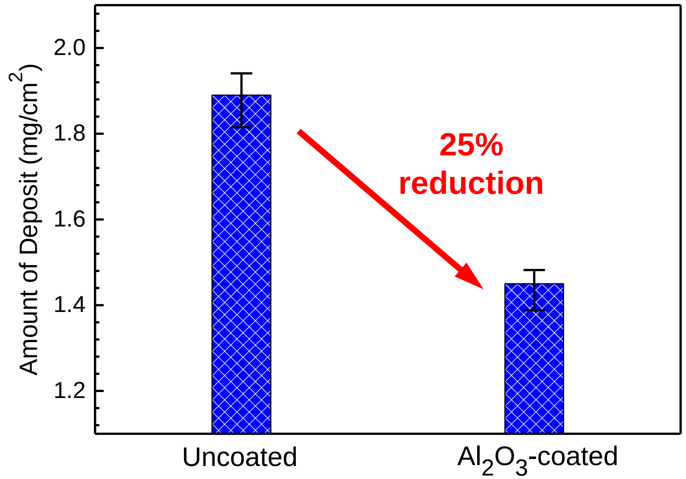
(T3) Crud morphologies

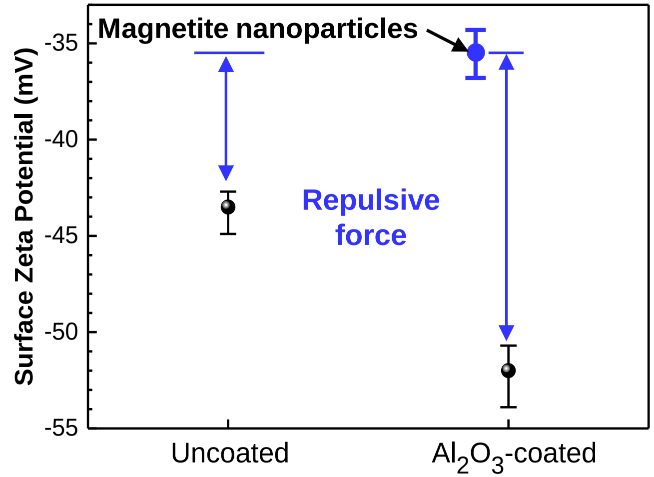


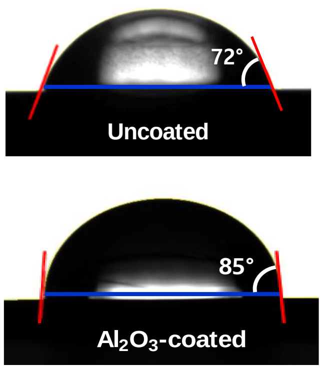
- Cruds consist of magnetite (Fe_3O_4) particles in various size on both claddings and the uncoated cladding shows thicker crud and ZrO_2 layers than the Al_2O_3-coated cladding.
- Some boiling chimneys with micrometers size were observed on crud of uncoated fuel clads.

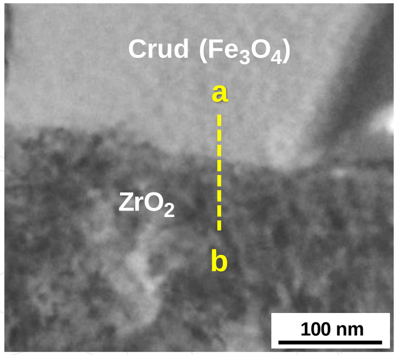
Effect of surface coating

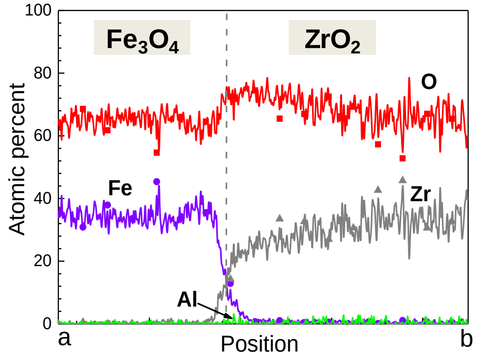
(T3) Amount of crud deposit

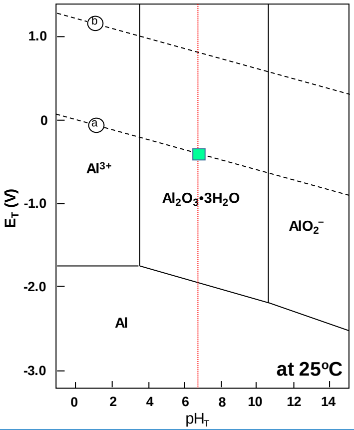


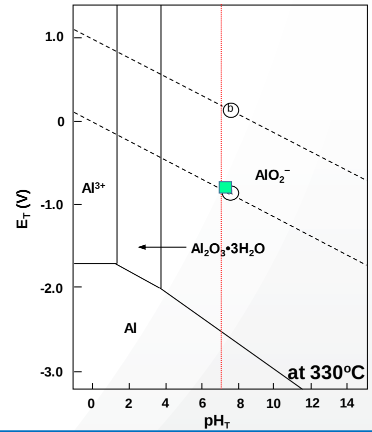












- **The deposit amount decreased by 23% for the Al_2O_3-coated specimen, comparing to the uncoated specimen.**
- **It is considered that the reduction of deposit amount is caused by increase in zeta potential difference and by increase in contact angle through Al_2O_3 coating. However, it is predicted that the Al_2O_3 layer disappear during the crud deposition due to its poor electrochemical stability in PWR primary water condition.**

Summary

✓ **The effect for crud deposition was measured and discussed in the viewpoint of the reduction of boiling behavior and the decrease in corrosion product particle – cladding surface interaction.**

1. **The amount of deposit on the chemically etched cladding decreased by about 51% compared to that on the as-received cladding due to the enhancement of heat transfer, and reduction in roughness and water contact angle.**
2. **The amount of deposit on the pre-oxidized claddings increased as the pre-oxidized layer was thickened, especially by 45% compared with that on the as-received cladding. This can be caused by decrease in zeta potential difference between cladding surface and corrosion product particles, and increase in boiling events due to formation of oxidation layer.**
3. **The crud deposition decreased by 23% through coating Al_2O_3 thin layer on fuel cladding. Furthermore, the Al_2O_3 coating leads to reduction in oxidation rate of zirconium alloy by 12%. It is seen that the decrease in crud deposition is also caused by increase in zeta potential difference and hydrophobicity. However, new coating materials will have to be searched due to the thermodynamic instability of Al_2O_3 in PWR primary water.**

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Thank you!!

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