# Nanoscale Metal Oxide Coatings for Corrosion Protection of Component Materials used in Supercritical $CO_2$ Environments

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## Statement of Purpose

**Problem Statement:** Generation IV power reactors use supercritical $CO_2$ ($sCO_2$) as the heat transfer fluid. New materials that can handle the harsh environment of $sCO_2$ are required to enable power generation and prevent issues with corrosion and erosion or efficiency degradation.

**Project Overview:** Funding provided by the DOE's STTR program is supporting the development of nanoscale ceramic barrier coatings to protect metal components from harsh $sCO_2$ environments.

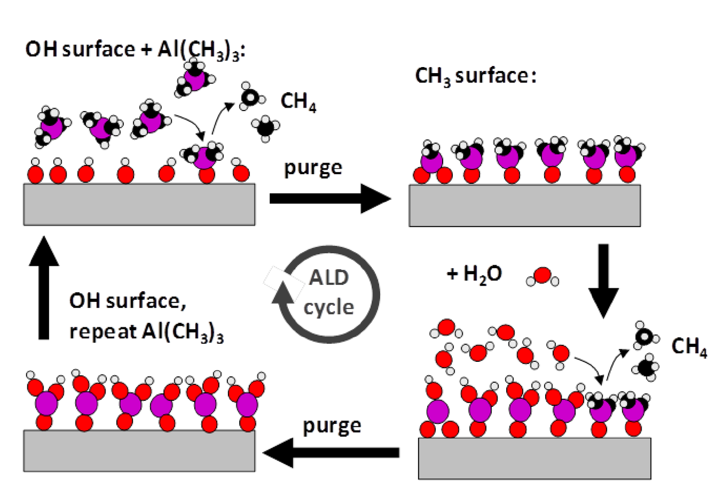
**Technical Objective:** Our project team is developing a vapor phase deposition technology called Atomic Layer Deposition (ALD) to address material issues for metals and metal alloys in supercritical $CO_2$ power generators. Specifically our team is investigating if ALD coatings will allow use of lower cost materials (SS316).

**Tasks:**
1. Identify potential coatings
2. Deposit and characterize ALD coatings on SS316
3. Test in supercritical $CO_2$ environment
4. Investigate impact of thermal cycling
5. Investigate ALD application requirements

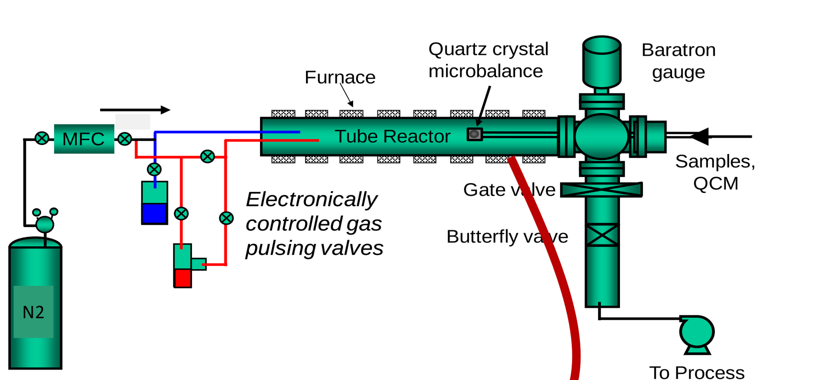
## Technical Background

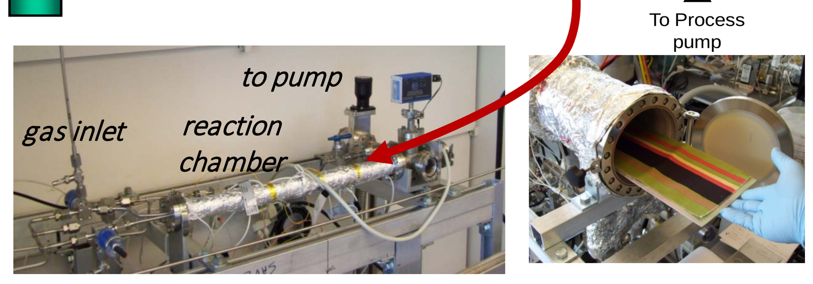
### Introduction to ALD

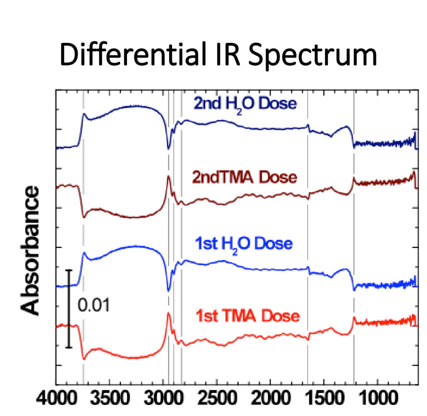
- Sequential CVD process
- Temporal or spatial separation of reactants
- Half-reactions are self-limiting
- Controllable thickness at sub-nm scale
- Vapor phase reactive species
- Thickness determined by number of ALD cycles

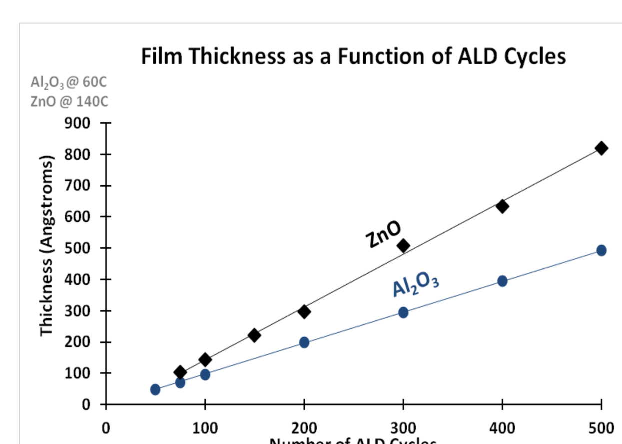



Q. Peng et al. *Nano Letters*. 2007, 7, 719



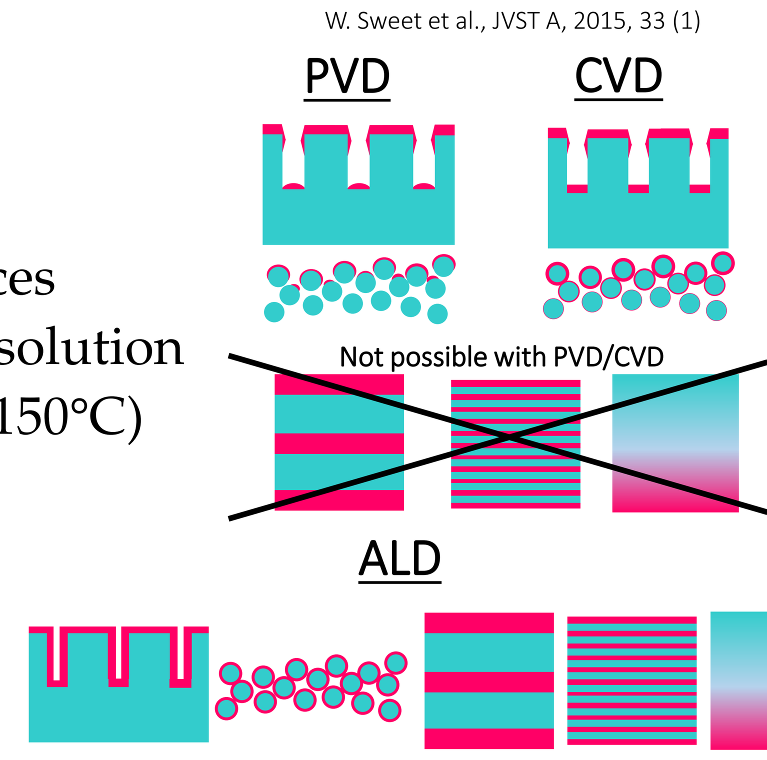




W. Sweet et al., JVST A, 2015, 33 (1)

### Advantages of ALD

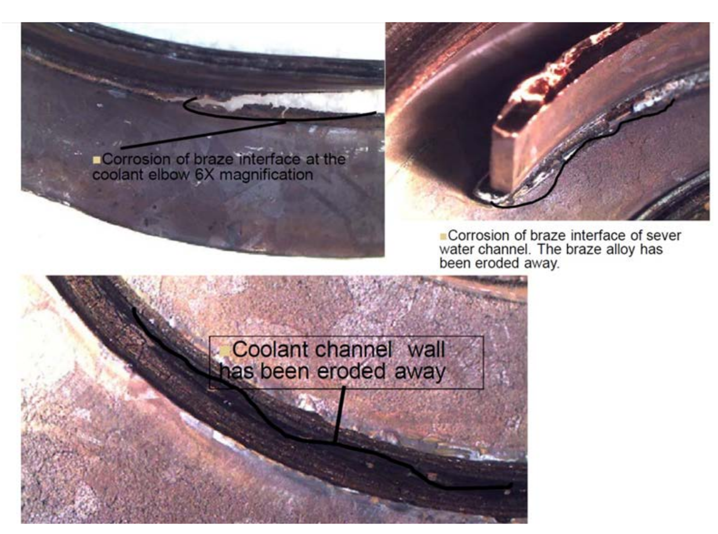
- Conformal coatings on hard to coat surfaces
- Precise growth control, sub-nanometer resolution
- Solvent free, Low process temperature (<150°C)
- Large selection of materials to deposit
- Metals, metal oxides, polymers




### ALD in Manufacturing

- Cycle time seconds to minutes
- Many active ALD and related companies
- ALD used in electronics manufacturing
- Continuous – Spatial ALD methods
- Cost <$1.00 to coat 1m$^2$

## Example: Corrosion Protection of RF Sources and Components

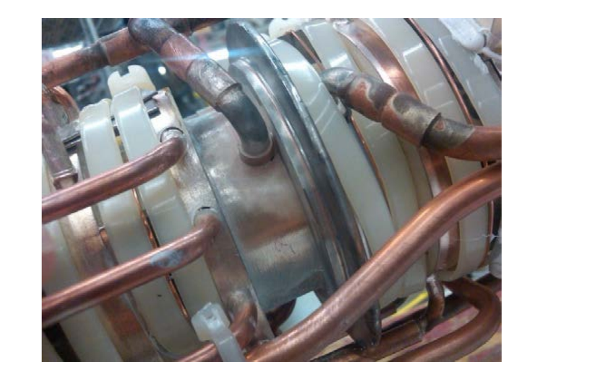



**Need:** Isolate metals from coolant fluid (water, ethylene glycol)

**Solution:** Apply a thin (10-50 nm) ceramic coating over coolant surfaces
-Note: thin coating does not impact thermal cooling performance

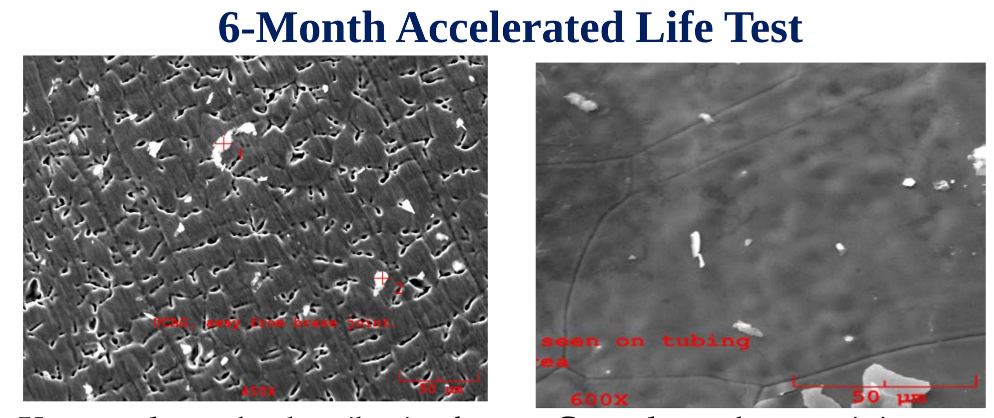
**Key challenge:** Protective coatings must be applied **after** final assembly – eliminates plating and sputtered coatings

**Approach:** Use ALD to coat interior surfaces following RF component assembly



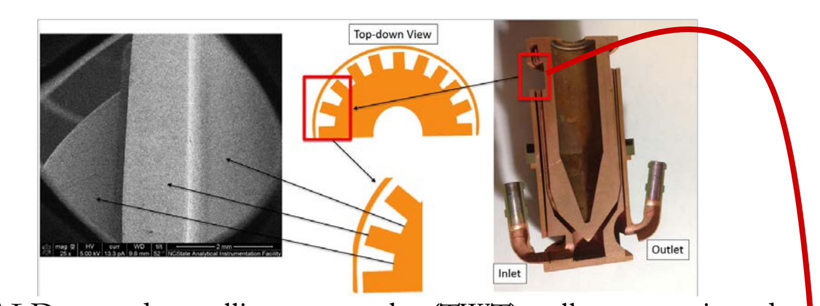

8" long brazed copper tubing samples supplied by CPI for ALD coating and accelerated life testing.

**Proof of Concept Demonstration: 6-Month Accelerated Life Test**

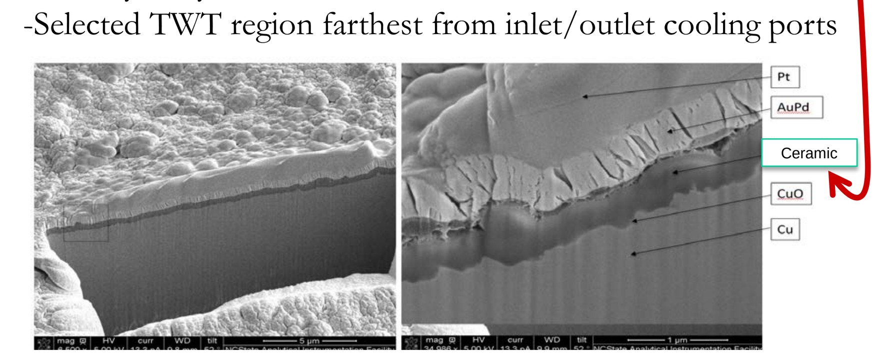


Uncoated sample - heavily pitted    Coated sample – no pitting

*Test funded by DOE SBIR Phase II Grant No. DE-SC0006338*




-ALD coated travelling wave tube (TWT) collector sectioned for analysis by FIB-SEM
-Selected TWT region farthest from inlet/outlet cooling ports



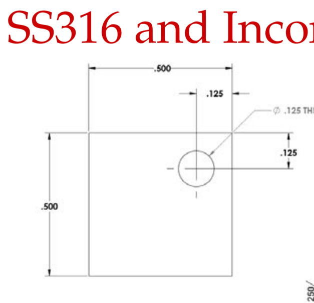

## Nanoscale Ceramic Barriers for Protection in $sCO_2$ Environments

**Part 1:** Deposit ALD coatings on SS316 and Inconel 625

*Reactor Configuration*
- Hot-walled, viscous flow tube
- Up to 300°C heating
- 0.5-5 Torr operation
- Inert carrier gas (Nitrogen or Argon)

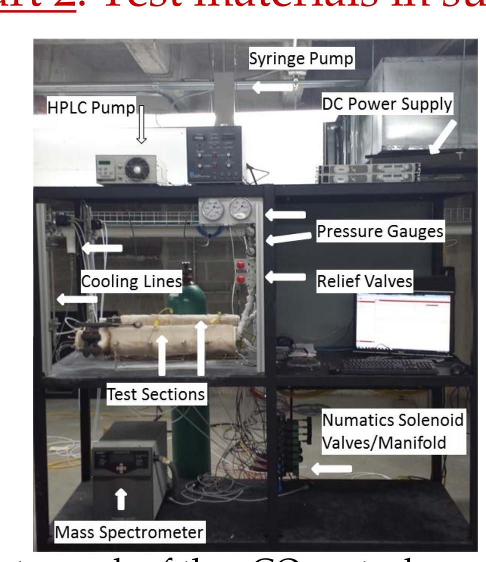
*Safety*
- Mechanical and electronic safety interlocks
- Gas detectors, charcoal and alkaline gas scrubbers
- N2 purged fluorocarbon pump

*ALD Growth Conditions*
- Deposition temperature: 150-300°C
- Target coating thickness for $sCO_2$ testing ~ 50nm



ALD laboratory at NC State University. ALD reactors are indicated by red arrows.

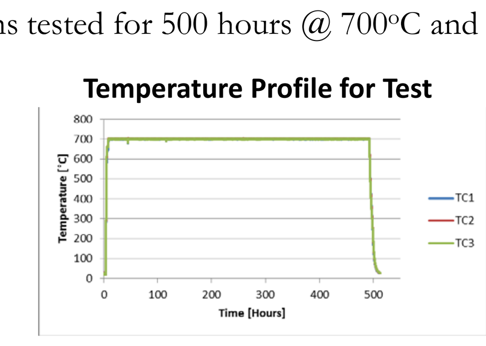
**Part 2:** Test materials in supercritical $CO_2$ environments

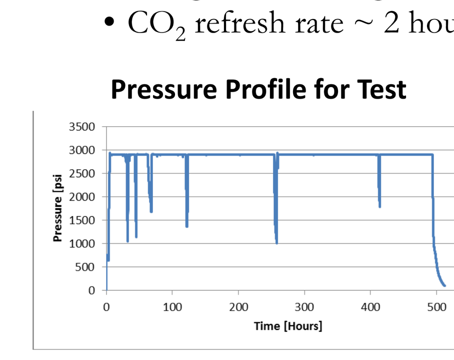



Photograph of the $sCO_2$ autoclave exposure facility at the University of Wisconsin

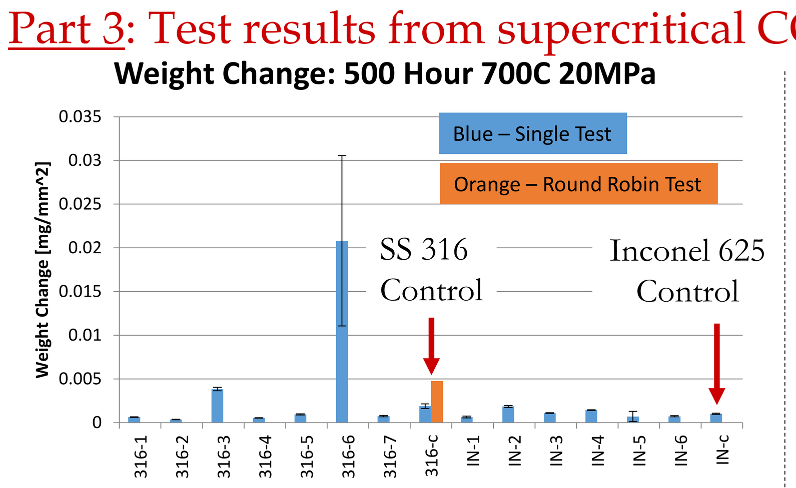
- Testing completed using SC-CO2 autoclave at University of Wisconsin- Madison (Dr. Mark Anderson)
- Expose coupons to high pressure and high temperature CO2 environments (research grade CO2 with a purity of 99.9998%)
- Coupons tested for 500 hours @ 700°C and 20MPa

Key Features of $sCO_2$ Test Setup:
- Temperature control allows system to operate within ±1°C
- Pressure control within ± 5psi
- System operates at an average flow rate range of ~0.10 kg/hr
  - $CO_2$ refresh rate ~ 2 hours

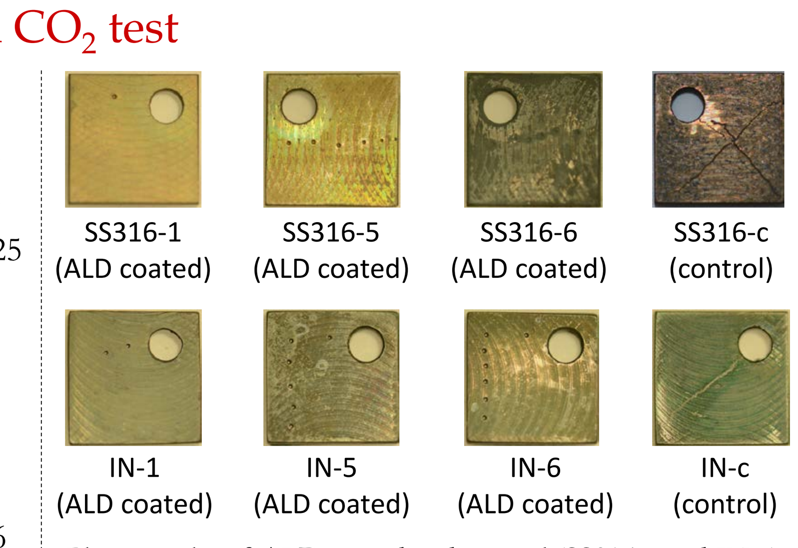



**Part 3:** Test results from supercritical $CO_2$ test



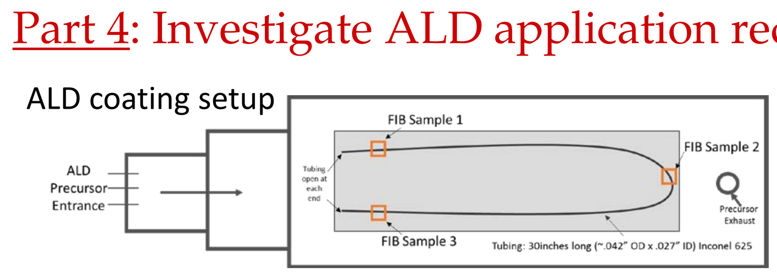

Ceramic coatings were deposited by ALD onto SS316 and Inconel 625 coupons, the weight change was measured after a 500 hour $sCO_2$ exposure



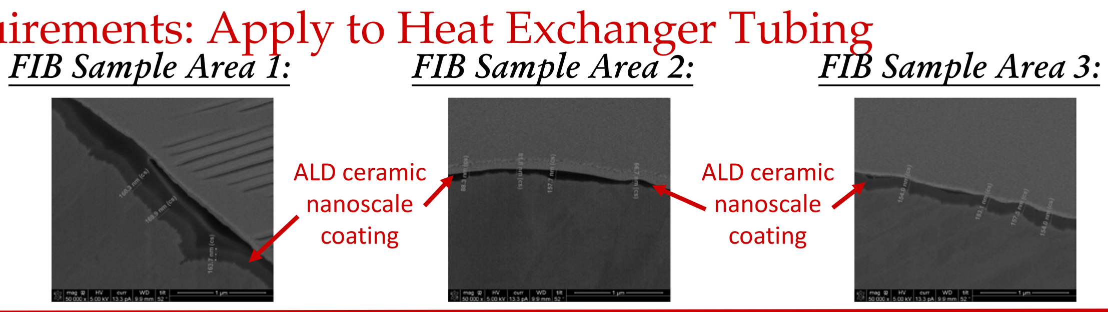

Photographs of ALD coated and control (SS316-c and IN-c) samples after 500 hour exposure in $sCO_2$ test apparatus

*Conclusions:*
- ALD coatings improve corrosion protection of SS316 over control coupons (uncoated sample)
- No real change after exposure between coated and uncoated Inconel 625 coupons. Longer exposure time and higher temperatures planned for next test phase of program.

**Part 4:** Investigate ALD application requirements: Apply to Heat Exchanger Tubing




*FIB Sample Area 1:*    *FIB Sample Area 2:*    *FIB Sample Area 3:*

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