

Conformal Coatings On Additive Manufactured Robust Alloys for Mitigation of Oxidation, Erosion, and Corrosion

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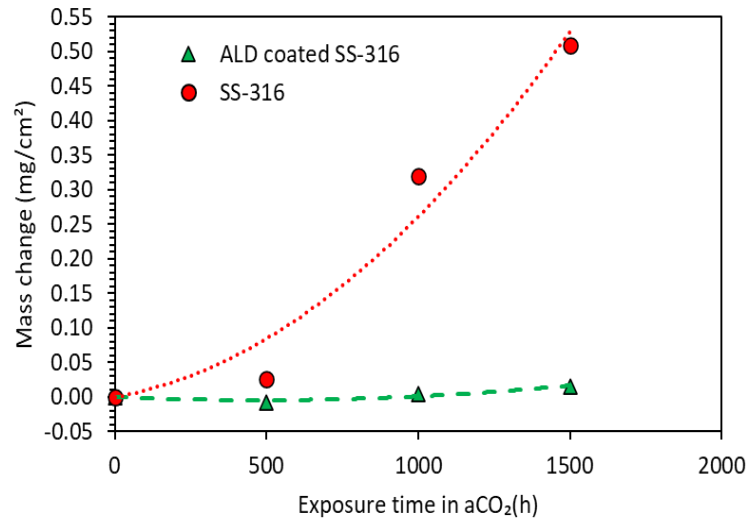
HIGHLIGHTS:

Additive Manufacturing & Atomic Layer Deposition (ALD) ALD Coating of Additive Manufactured Prototypes

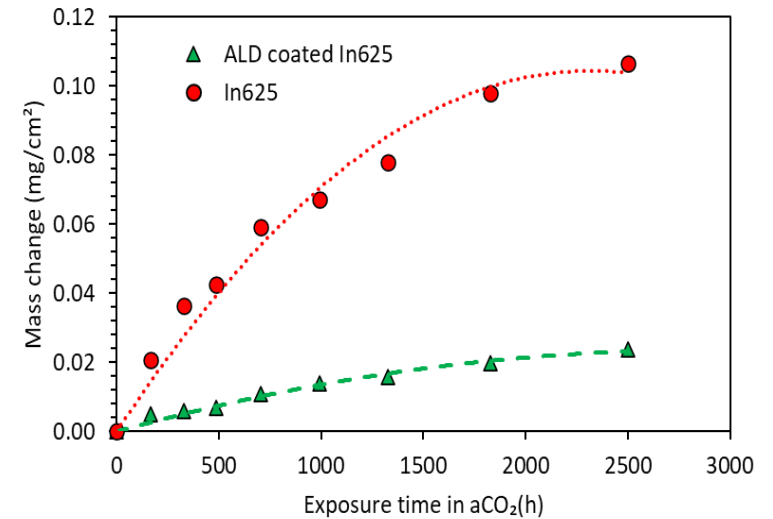


As-printed

ALD coated



ALD coated and baseline Stainless Steel 316 under CO₂ at 650°C for 1500 h.



ALD coated and baseline Ni-based alloy IN-625 under CO₂ at 750° C for 2500 h.

Conformal ALD coating applied to both external and internal surfaces
ALD Coating Additive Manufactured Prototypes Mitigating Oxidation in CO₂ environments

OVERVIEW

➤ Project Background & Challenges

- ❖ Materials enabling supercritical CO₂ power cycles technology
- ❖ Coatings to mitigate oxidation, corrosion, erosion at high-temperatures

➤ Project Scope

- ❖ Project objective
- ❖ Technical approach

➤ Current Results

- ❖ Holistic integration of atomic layer deposition (ALD) into design & advanced manufacturing of novel alloys
- ❖ ALD coating of 3D printed prototypes
- ❖ Conformal coating to mitigate oxidation, corrosion at high-temperatures
- ❖ ALD refurbishing of serviced components
- ❖ ALD coating scale up

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High-Temperature Materials Supply Chain Challenges

sCO₂ Brayton cycle technology has attracted attention due to its small footprint, simple layout, and high efficiency in excess of 50%. Today, direct sCO₂ cycle plants are designed for (1). turbine inlet temperatures of 1150°C (2). primary heat exchanger inlet temperatures of 750°C, due primarily to the materials limitations.

Challenges are faced by (1). Combustion and Turbomachinery (2). Heat exchangers (3). Materials (4). Pollution Control. This high performance sCO₂ Brayton cycle technology is contingent upon the performance of alloys employed in the heat exchangers.

“Hot side of the high-temperature recuperator (HTR) at a temperature from 700-760°C, which is the limit for nickel-based alloys used in exhaust piping at the expected operating pressures. Problems could arise from material degradation.”

For extended operation at extreme conditions such as temperatures and pressures of up to 800°C and 30 MPa, with CO₂ as fluid, the heat-exchangers alloys need to possess

(1). High mechanical strength integrity; (2). High robustness towards oxidation taking place on the external surface; (3). High resistance of carburization that is simultaneously taking place on the internal surface of heat-exchangers with complex geometry.

Research Needs of High-Performance Materials

(1). New metallic alloys for heat exchangers, turbines, and combustors. For instance, Oxide dispersion strengthened alloys. (2). More effective thermal barrier coatings. (3). Multifunctional surface coating layer for increasing the alloys resistance towards oxidation and carburization simultaneously.

Dogan, Omer N., Weiland, Nathan T., Strakey, Peter A., Lawson, Seth A., Black, James B., Jesionowski, Gary A., and Gioia, Chris J.. [Direct Supercritical CO₂ Power Cycle Technology Research and Development: Technology Gaps and Research Needs](#). United States: N. p., 2018. Web. doi:10.2172/1603329.

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Project Objective & Technical Approaches

Objective:

Develop novel high-temperature alloys with (1). High mechanical strength integrity; (2). High robustness towards oxidation; (3). High resistance of carburization. The designed alloys are expected to be applied to heat-exchanger for its operation in sCO₂ at high temperatures (over 750 °C, such as 800 °C) and high pressure (30 MPa).

Technical approaches:

- Integrate **Additive Manufacturing (AM)** fabrication into well-developed alloys (such as stainless steels, Ni-based alloys), AM will be used to manufacture the complex heat flow channels and eliminate the construction failure that could be introduced during the conventional welding process.
- To increase the strength and oxidation resistance, **nano-particles**, including dense nano-oxide precipitation will be introduced into the novel alloys during the printing process.
- A conformal protective **oxide coating layer** will be simultaneously applied on both the **internal and external surface** of the additive manufactured components (with complex geometry) using the **atomic layer deposition (ALD)**.
 - The ALD layer will be conformal, uniform, pin-hole free, dense, and ultra-thin with negligible weight gain to increase both the oxidation and corrosion resistance at elevated temperatures.
 - ALD is further utilized to refurbish the components after service & oxidation exposure.

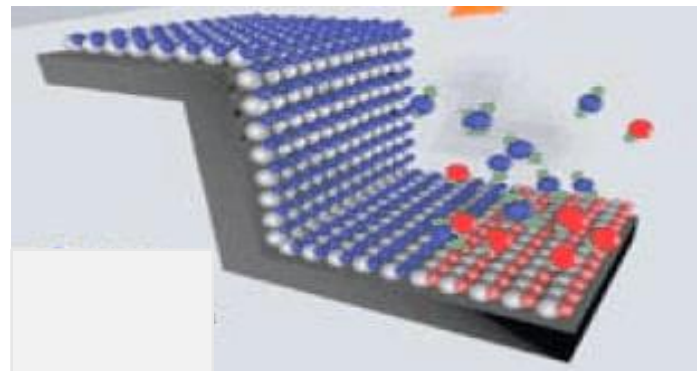
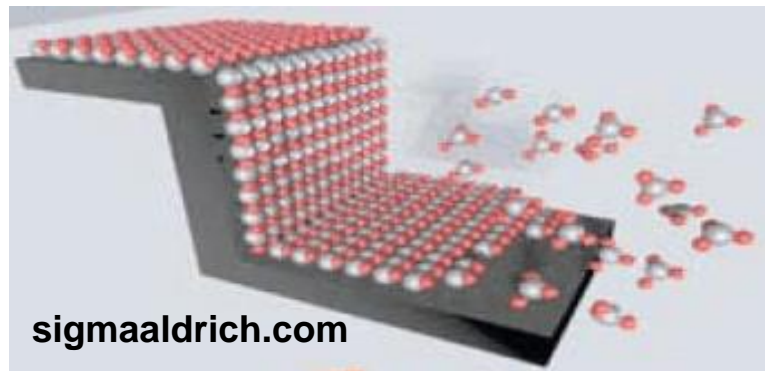
Justification of ALD coating of additive manufactured components

Choice of ceramic coating layer:

- The diffusion coefficient of different gas species, including Carbon, and Oxygen in covalently bonded substances of oxide ceramics is several times lower than that in metals.
- **Barrier coatings**, such as oxidation and corrosion-resistant Al_2O_3 are one of the key enablers for mitigation of both the oxidation and carburization of the heat-exchangers.

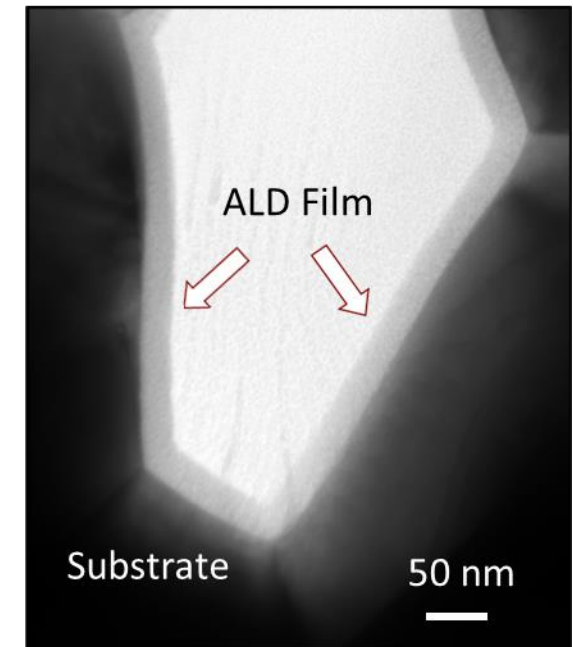
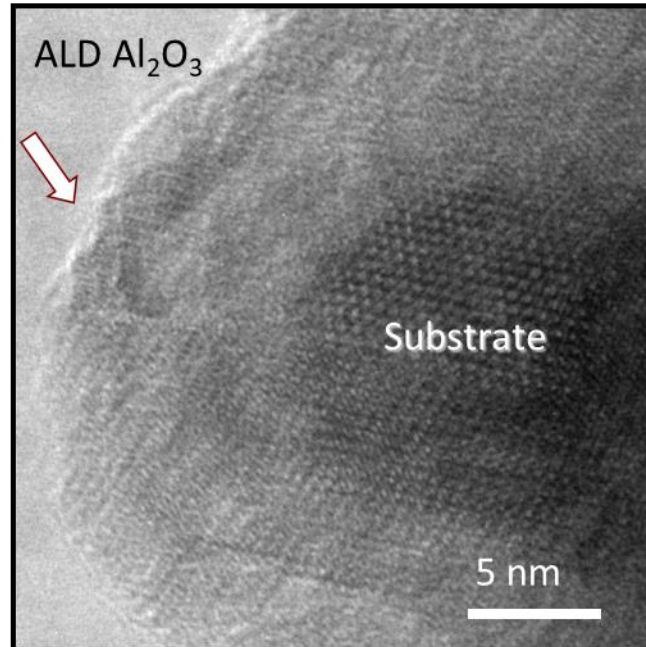
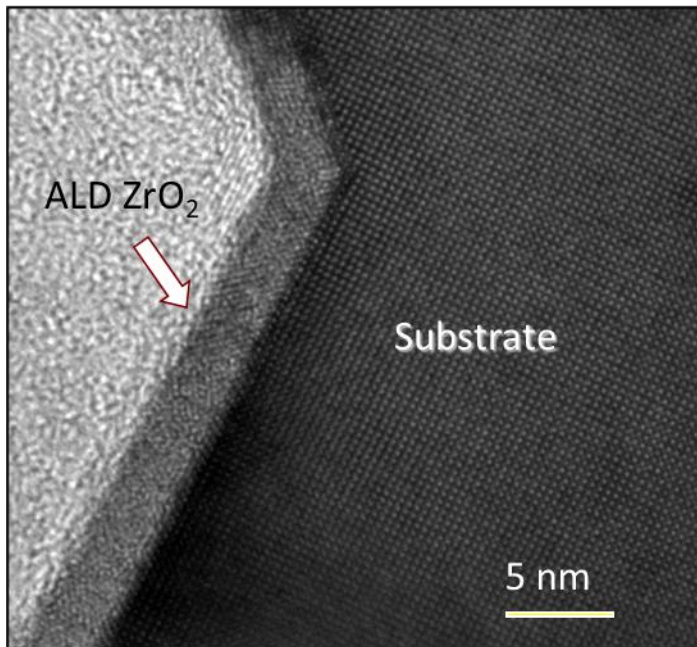
Choice of coating methods:

- Many **coating** methods, including chemical vapor deposition, physical vapor deposition, and plasma sprays, have been applied to **increase the oxidation and corrosion resistance**.
- **Chemical vapor based atomic layer deposition (ALD)** is uniquely suitable for depositing **uniform and conformal films covering both the exterior and encapsulating the interior** of manufactured components possessing complex three-dimensional topographies with a high aspect ratio.

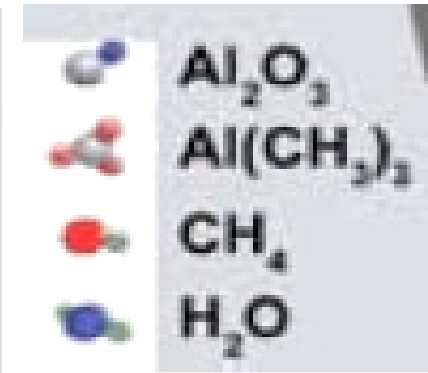
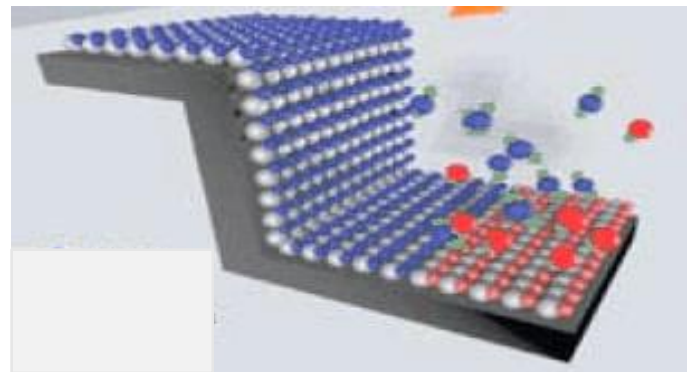
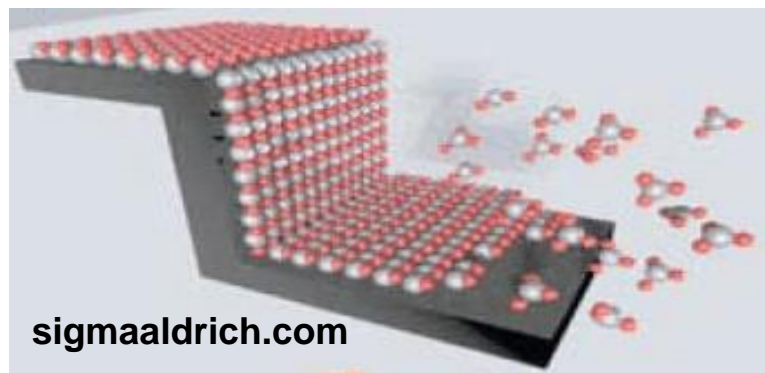


- ALD is applicable to **substrate** with large surface area, porosity, complex shape, ultra high aspect ratio.
- **ALD coating layer** could be thin, controllable thicknesses to atomic level. Uniform over entire substrate. Conformal in deep trenches. High quality, reproducible, easy scale-up.

Atomic Layer Deposition (ALD): Vapor Based, Sequential Chemical Vapor, **As-Deposited-States**.

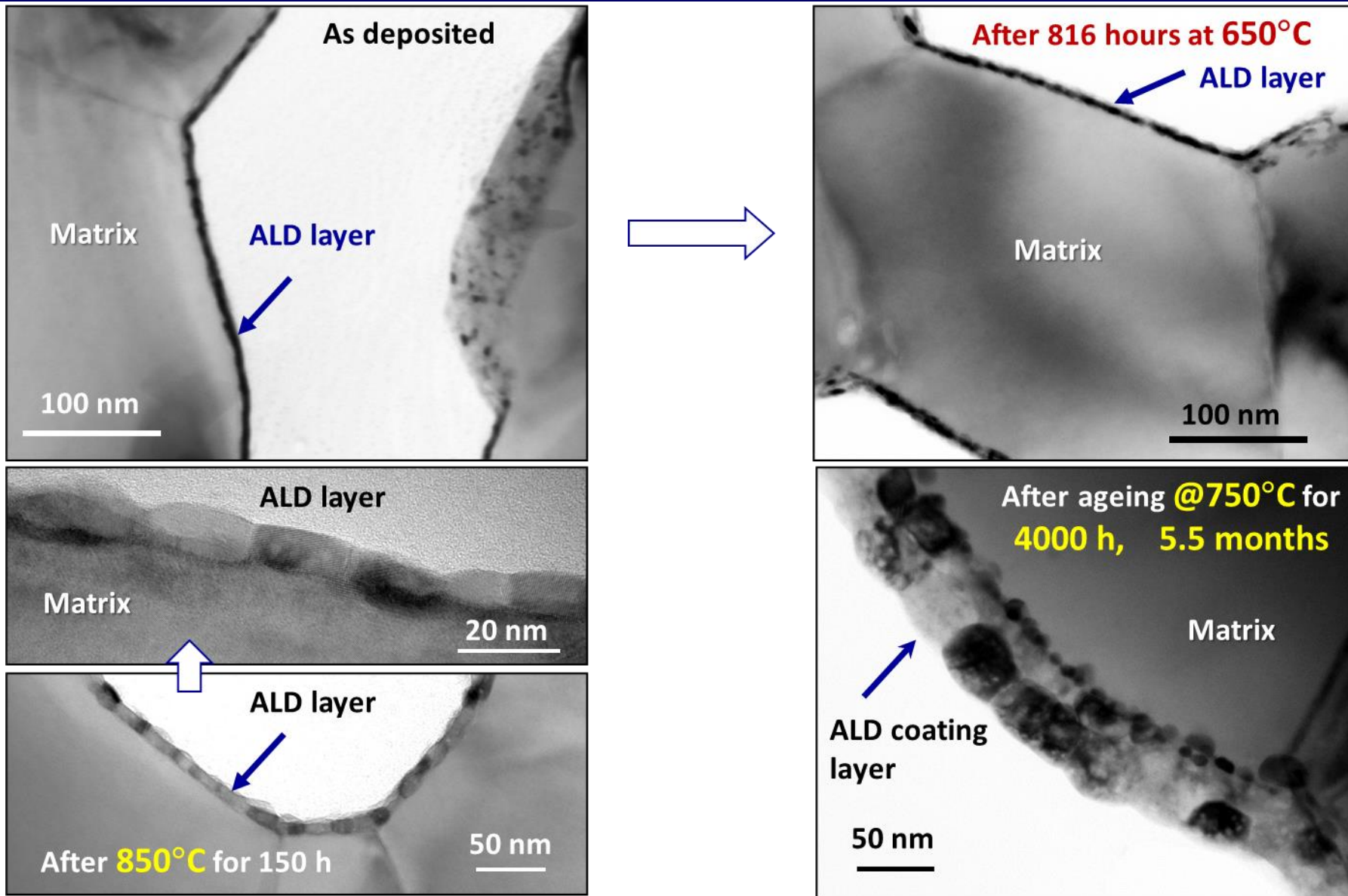


ALD is unique in coating as-made heat-exchanges with complex shapes.



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ALD Application at High Temperatures: **Thermally Stable ALD Layer** Developed by Our Group



Nano oxide ALD layer can be stabilized at 650-850°C, for application in heat-exchangers for sCO₂.

Nano-scale oxide ALD layer can be designed in terms of chemistry, and layer structure.

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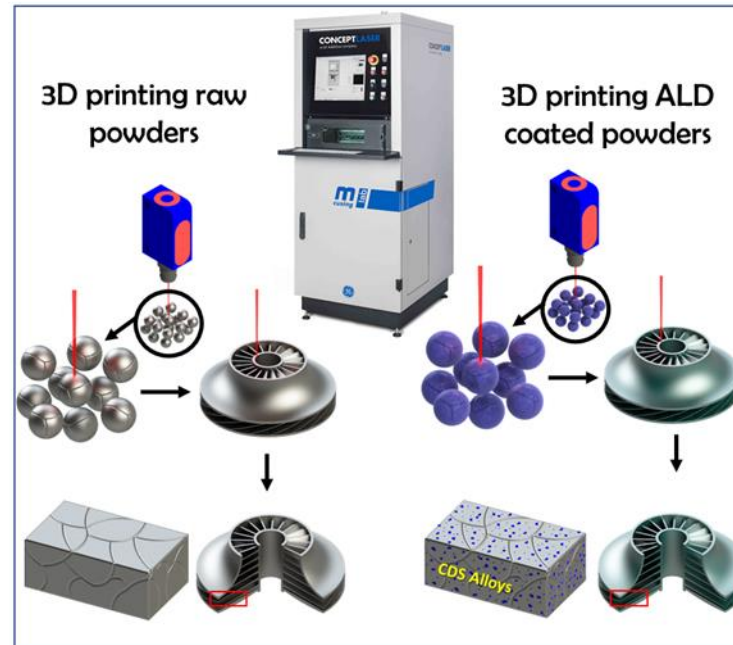
- ❖ **Holistic integration of atomic layer deposition (ALD) into design & advanced manufacturing of novel alloys**
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Additive Manufacturing of Metallic Components

Step-1: ALD coating of 3D powders



Step-2: Printing of Powders into components



Step-3: ALD coating Components



Holistic integration of ALD into design and advanced manufacturing, and final surface (internal & external) finishing of novel alloys and device components to achieve:

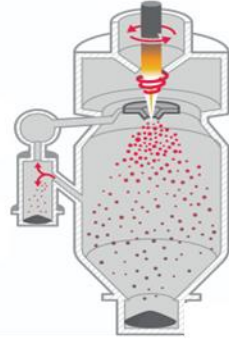
- High mechanical strength integrity;
- High robustness towards oxidation;
- High resistance of carburization.

ALD coating of Metallic Powders for 3D printing

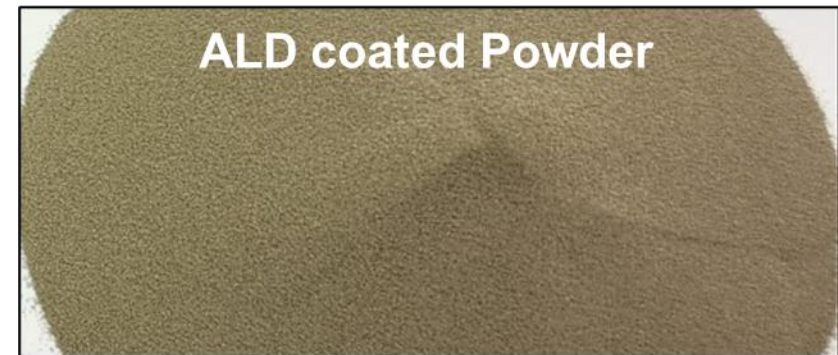
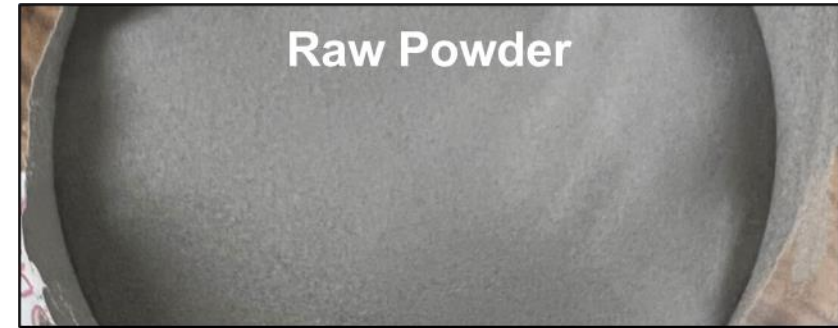
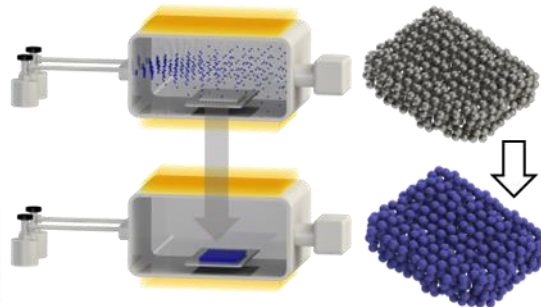
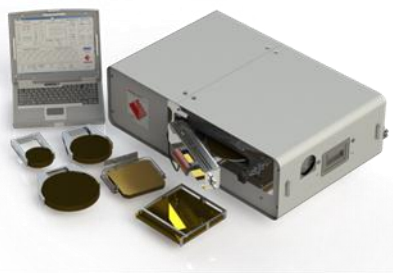
Step-1: ALD coating of 3D powders



Atomized Alloy Powders
(Commercially available)

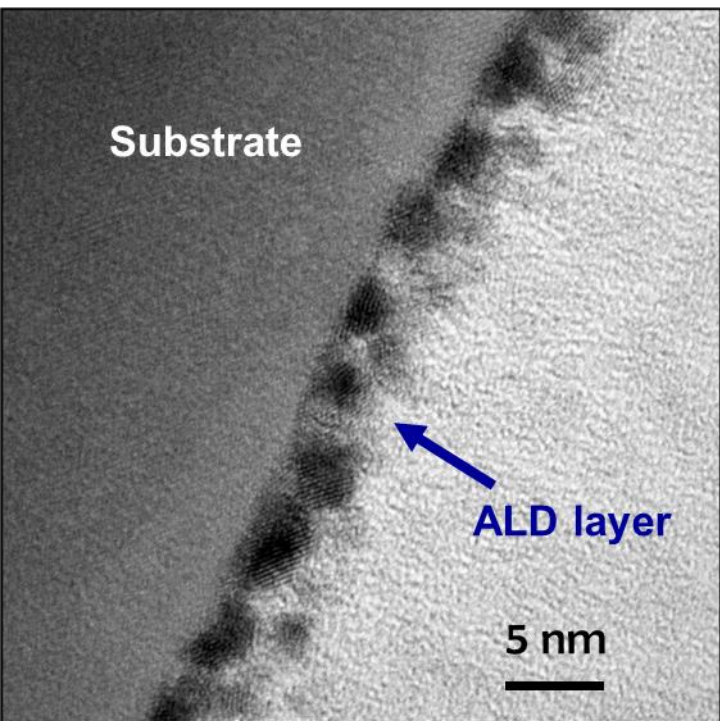
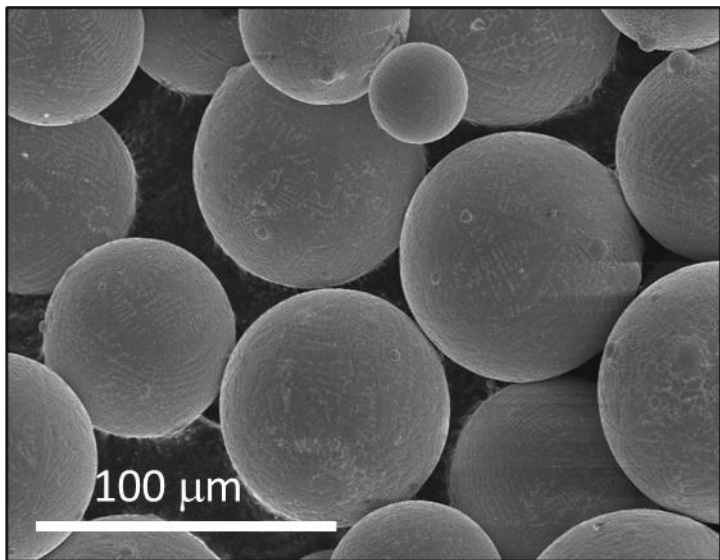


ALD Coating of Powders

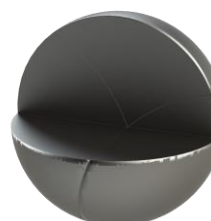
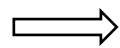
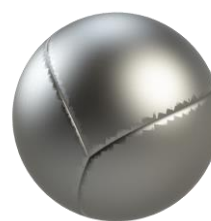
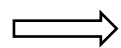
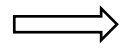


The gaps among the spherical powders allows the ALD gas vapor penetration for ALD coating.

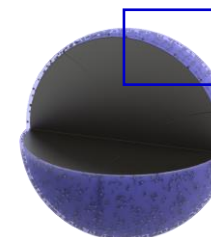
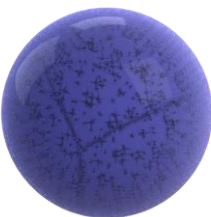
ALD coating of Metallic Powders for 3D printing



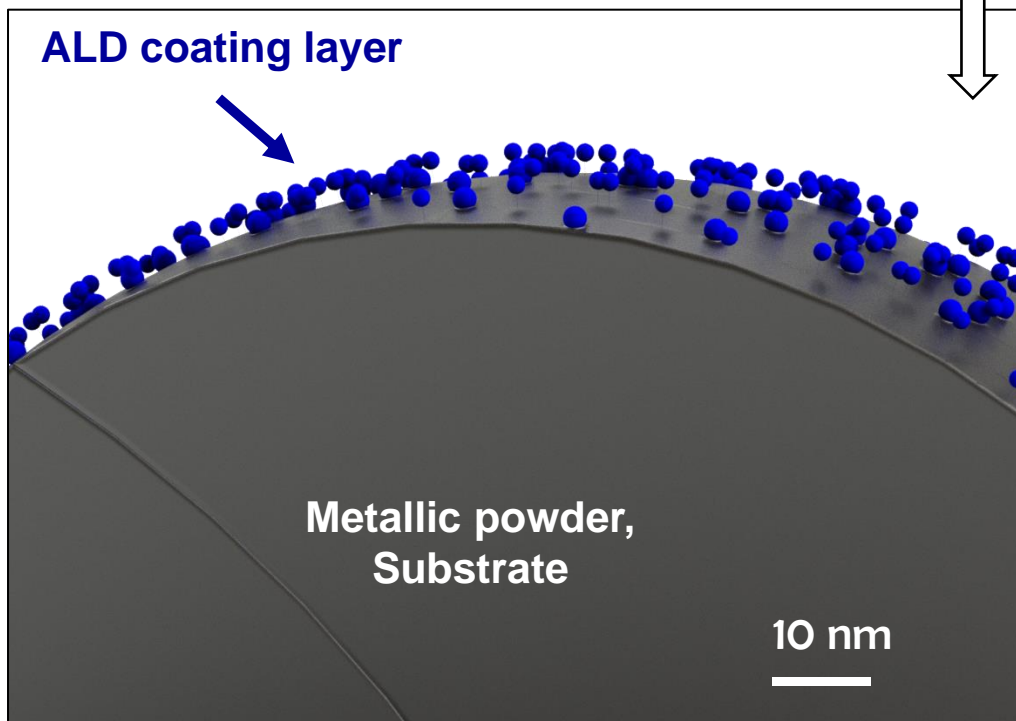
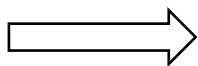
Raw Powder



ALD coated Powder



Particles of ~ 3 nm
is deal for ODS

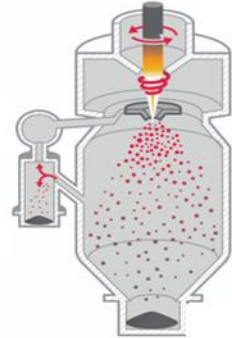


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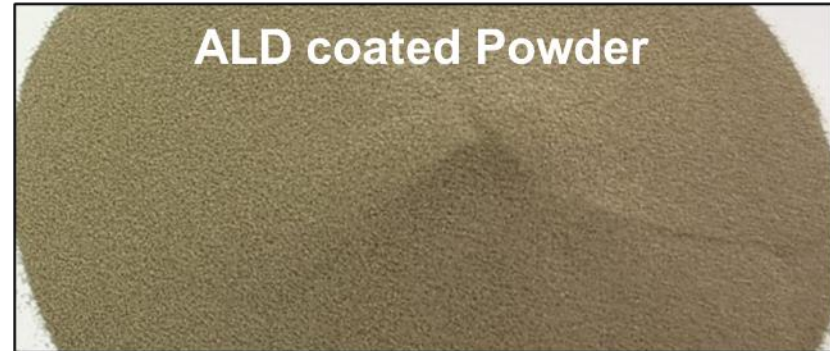
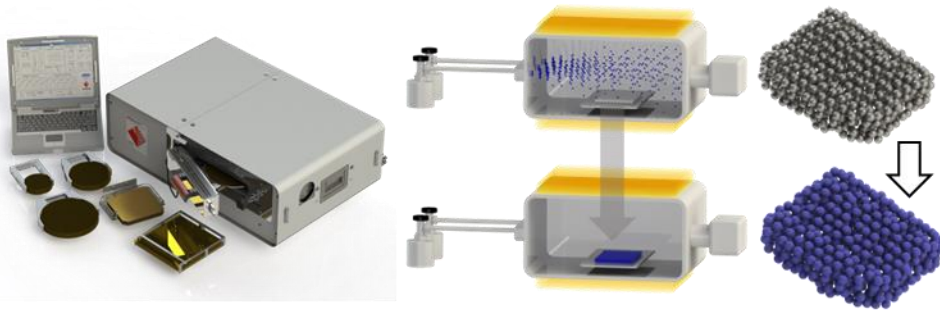
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Atomized Alloy Powders
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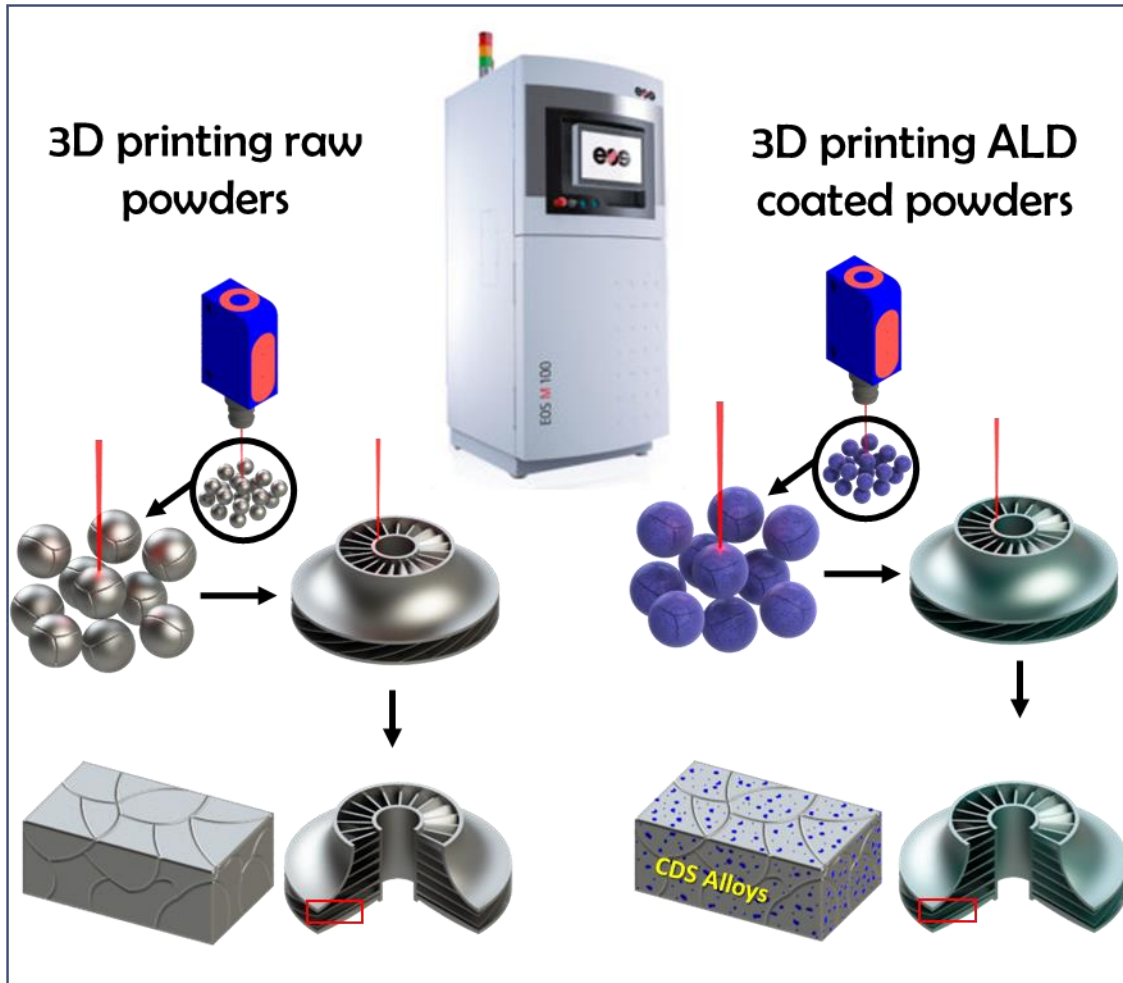
ALD Coating of Powders



- ALD could introduce nanoparticles into the metal matrix after printing,
- ALD coating enables a new category of Ceramic dispersion-Strengthened alloys (CDS) that could be designed.
- Those ceramic dispersed particles could include, not limited to, oxide, nitride.
- Dispersed nano-particles could be designed in term of chemistry, size and density.

ALD Conformal Coating Both the External and Internal Surfaces

Step-2: Printing of Powders into components



Step-3: ALD coating Components



- ALD coating of internal and external surface of 3D printed components.
- Finishing ALD coating will be conformal, uniform, dense, pinhole-free, and thin.
- Coating will be multifunctional, including increasing oxidation and carburization resistance.

Conformal Coating on the 3D printed Prototype

Uncoated



ALD Coated



ALD Coated

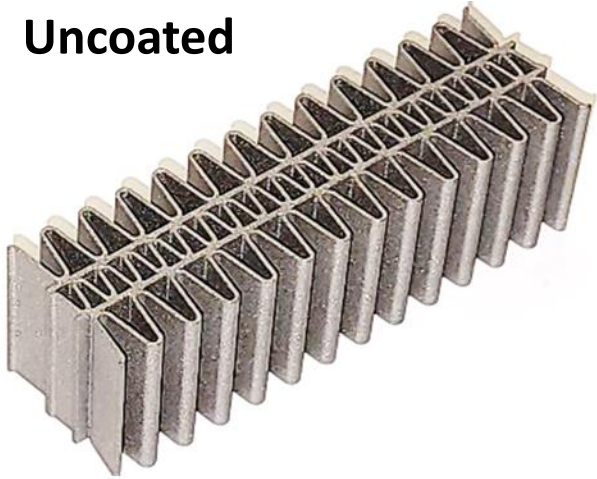


ALD coating is applicable to various metals with various geometry.

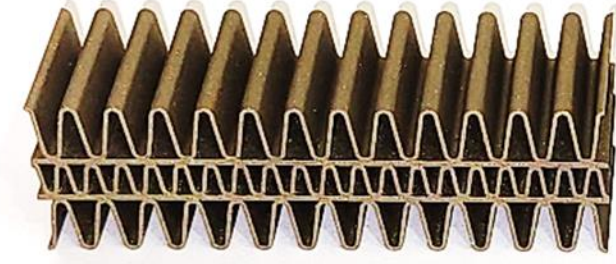
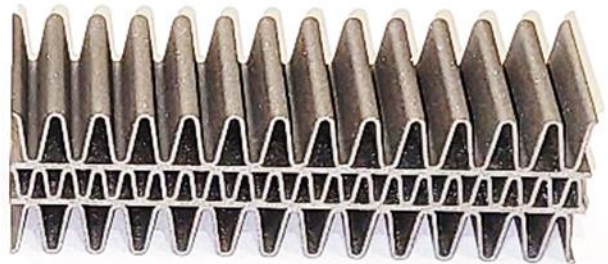
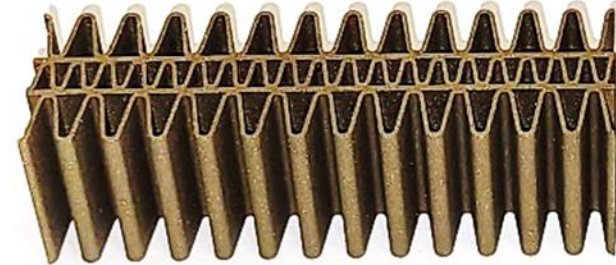
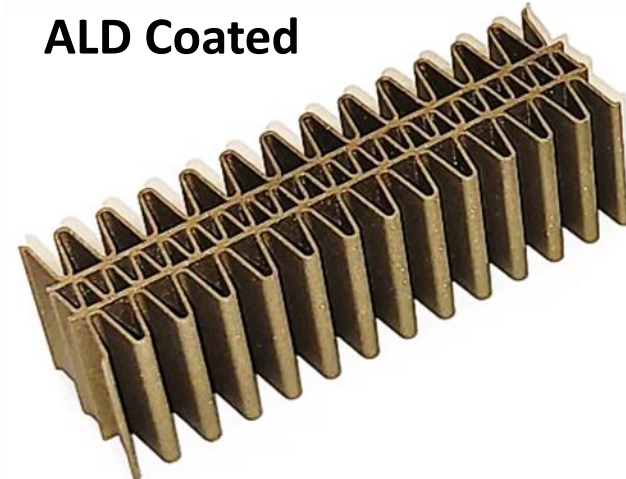
Conformal ALD coating is applied to both the external and internal surfaces

Conformal Coating on the 3D printed Prototype

Uncoated

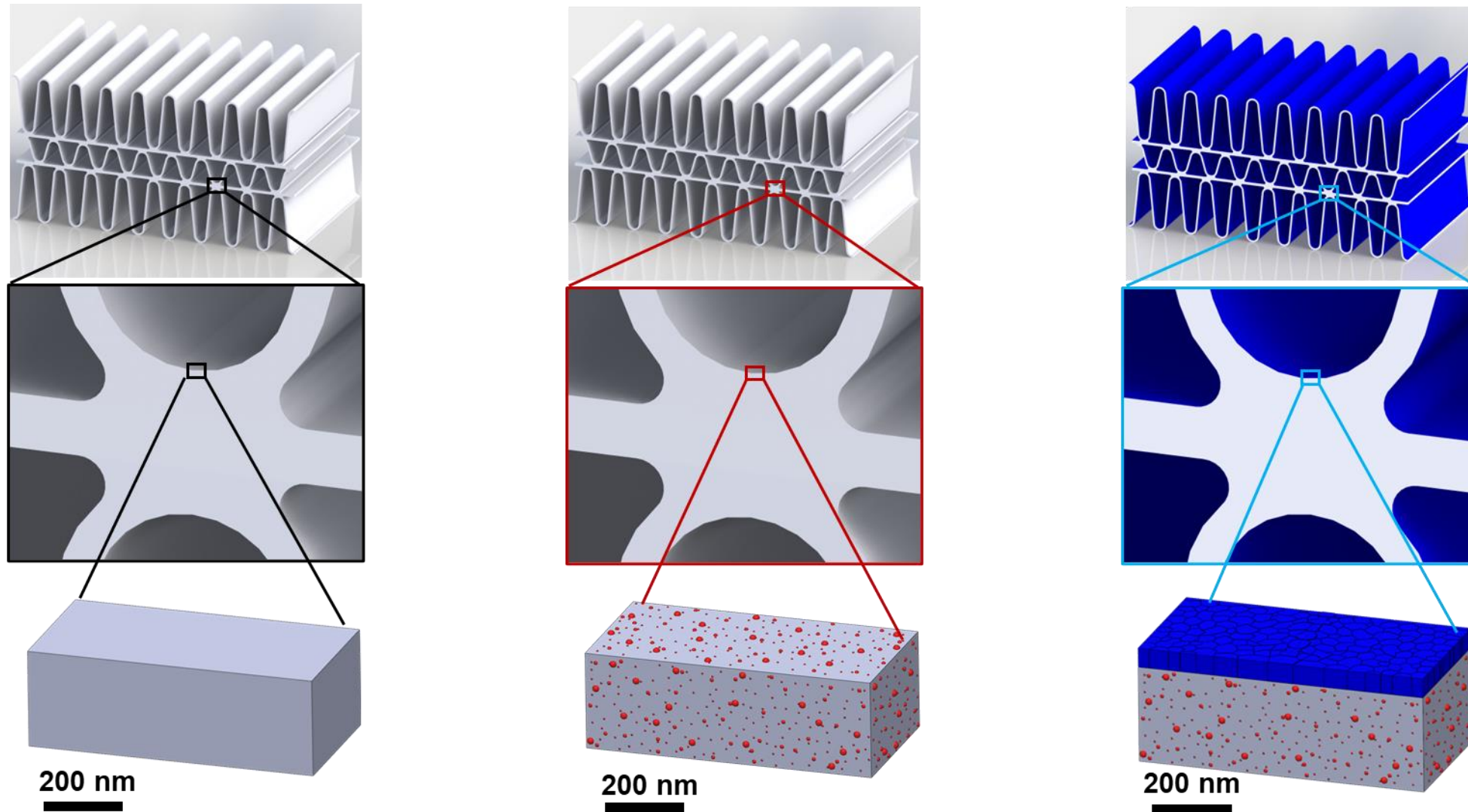


ALD Coated



Conformal ALD coating is applied to both the external and internal surfaces

Heat Exchangers: Integrated ALD Coating Powders & Components



Through such a comprehensive design, the developed high-temperature materials are expected to possess superior strength, high resistance towards external surface oxidation, internal surface carburization, and corrosion and can be applied to heat-exchanger for its operation in $s\text{CO}_2$ at high temperatures (over $750\text{ }^\circ\text{C}$, such as $800\text{ }^\circ\text{C}$) and high pressure (30 MPa).

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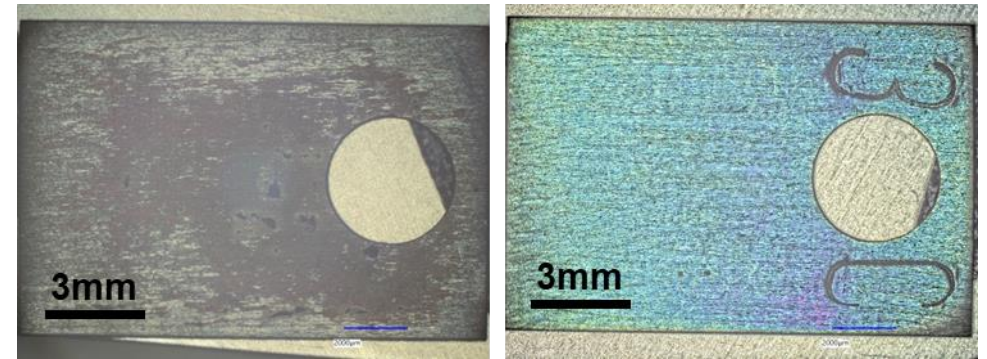
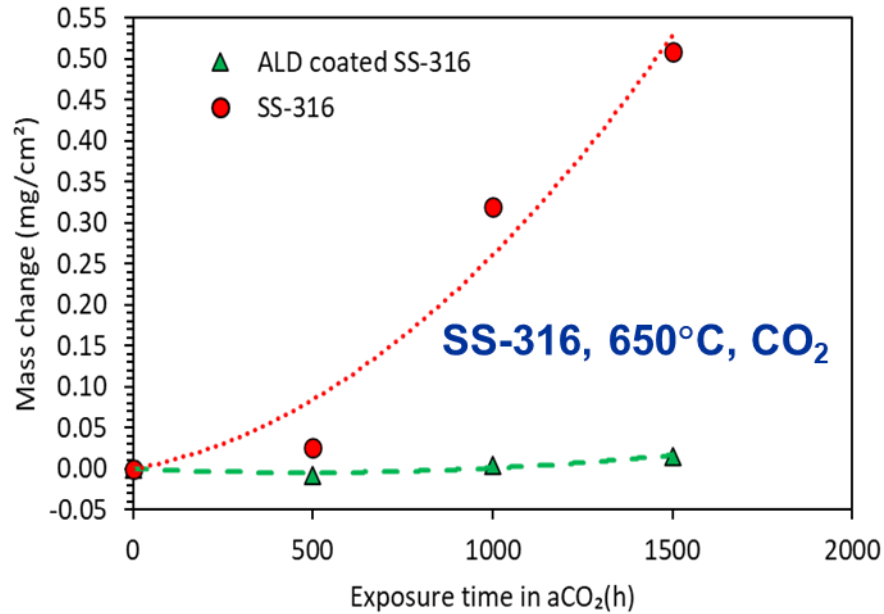
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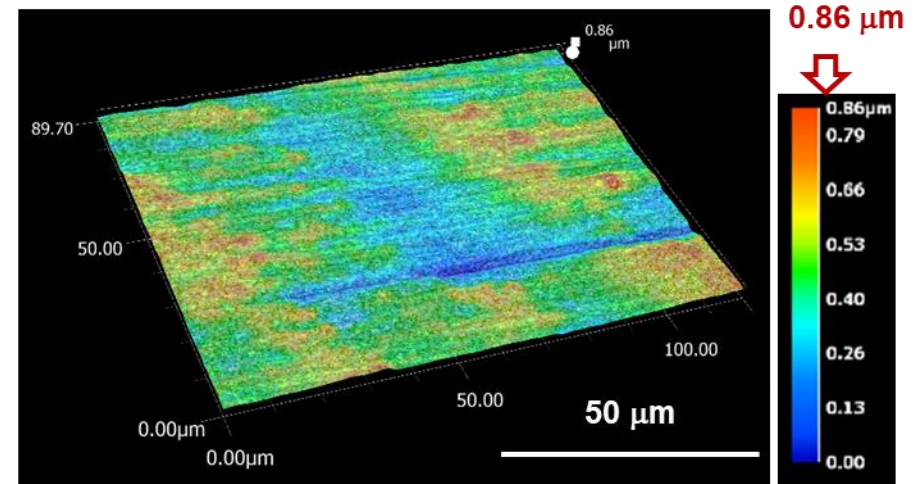
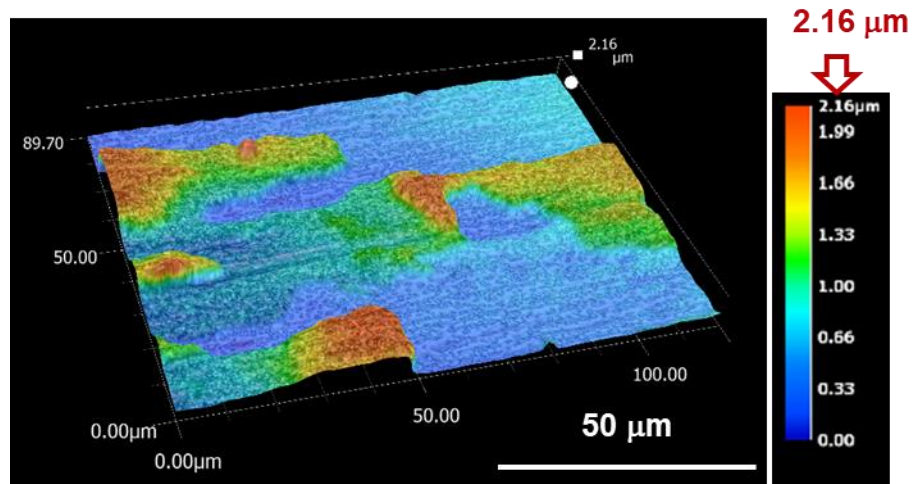
ALD Coating Increase Oxidation & Carburization Resistance at 650°C



SS 316

ALD coated SS 316

In aCO₂ and @650°C, after 500 hours



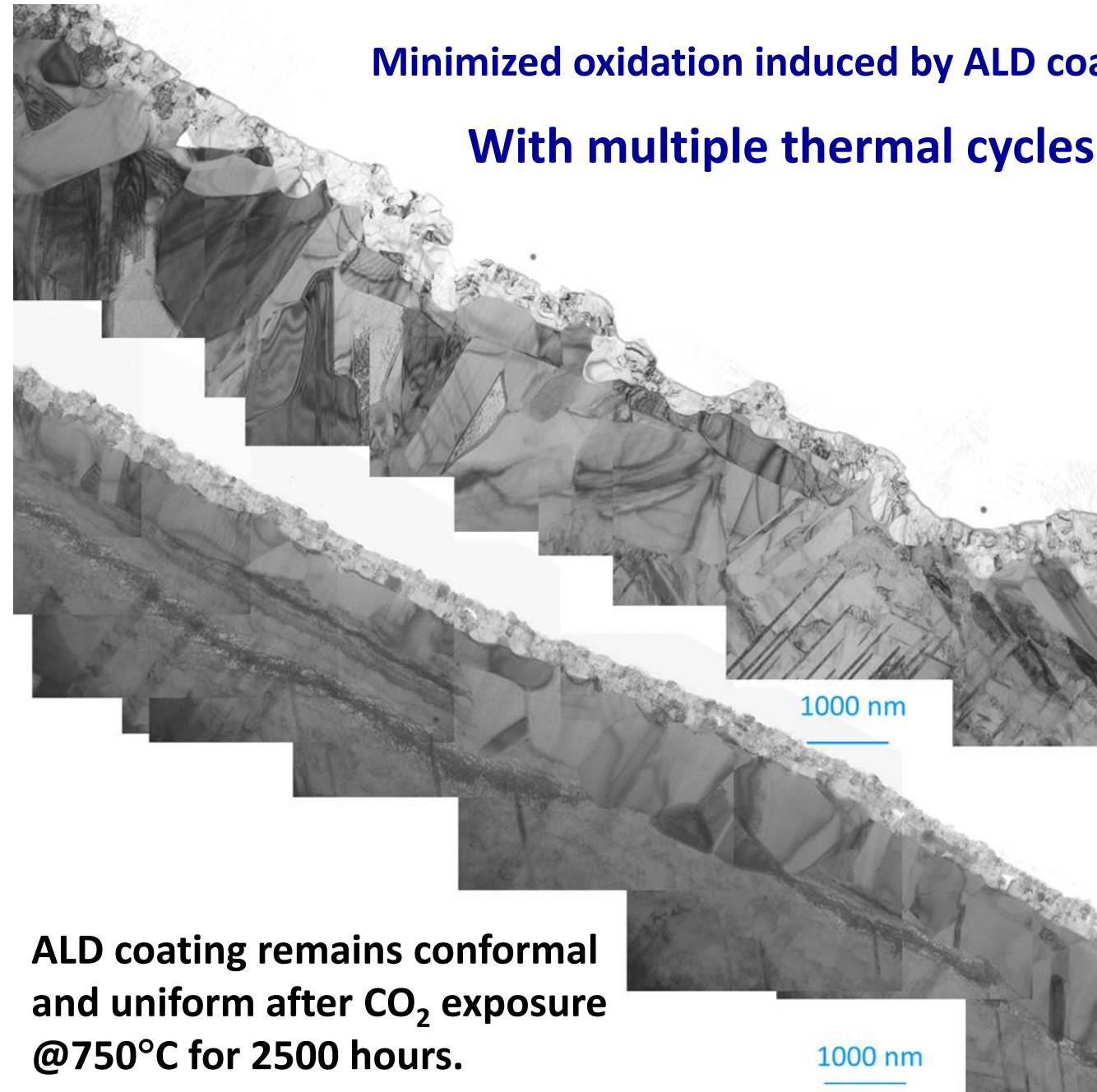
Minimized oxidation induced by ALD coating. No spallation in the ALD coated SS-316.

Collaboration with Dr. Casey Carney, Dr. Richard Oleksak, Dr. Omer Dogan from NETL.

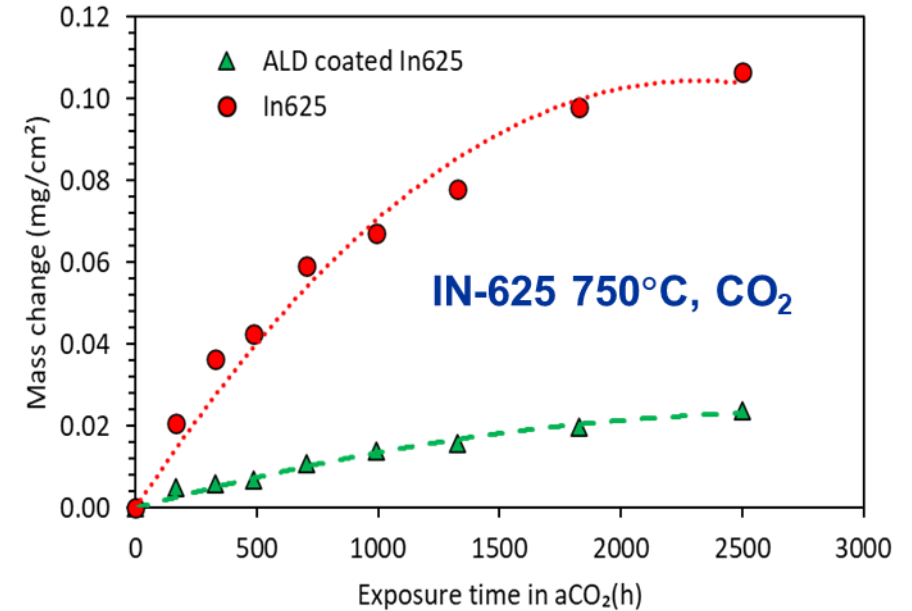
ALD coating blocked Cr outward diffusion: CO₂ at 750°C for 2500 h.

Minimized oxidation induced by ALD coating.

With multiple thermal cycles



ALD coating remains conformal and uniform after CO₂ exposure @750°C for 2500 hours.



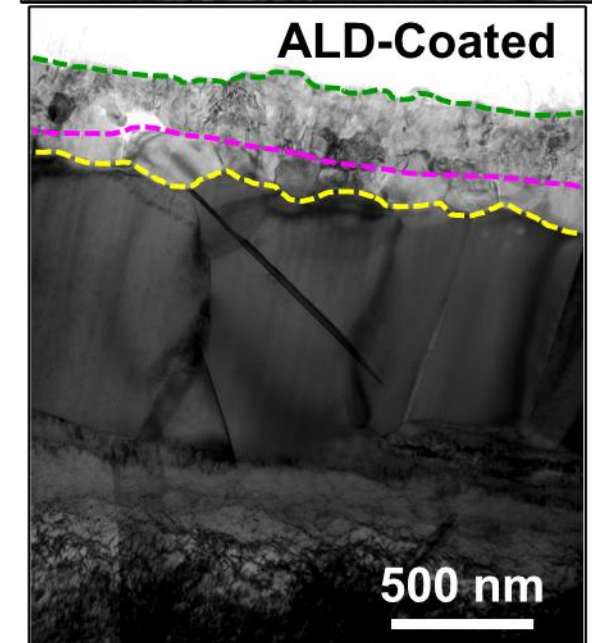
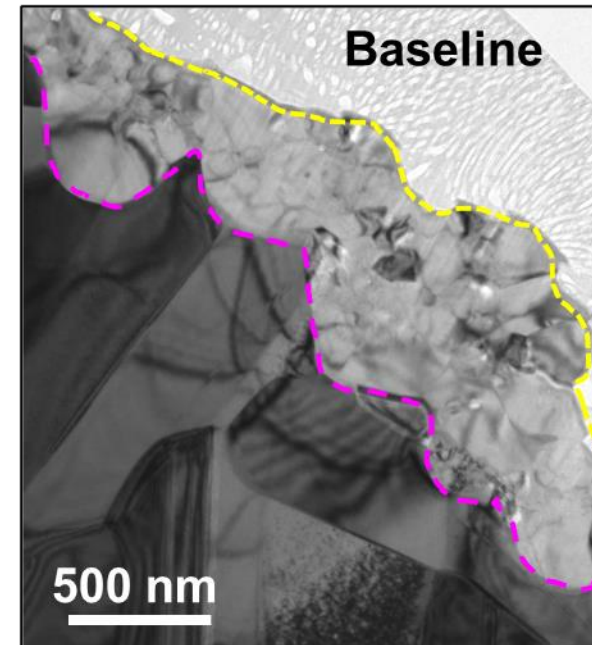
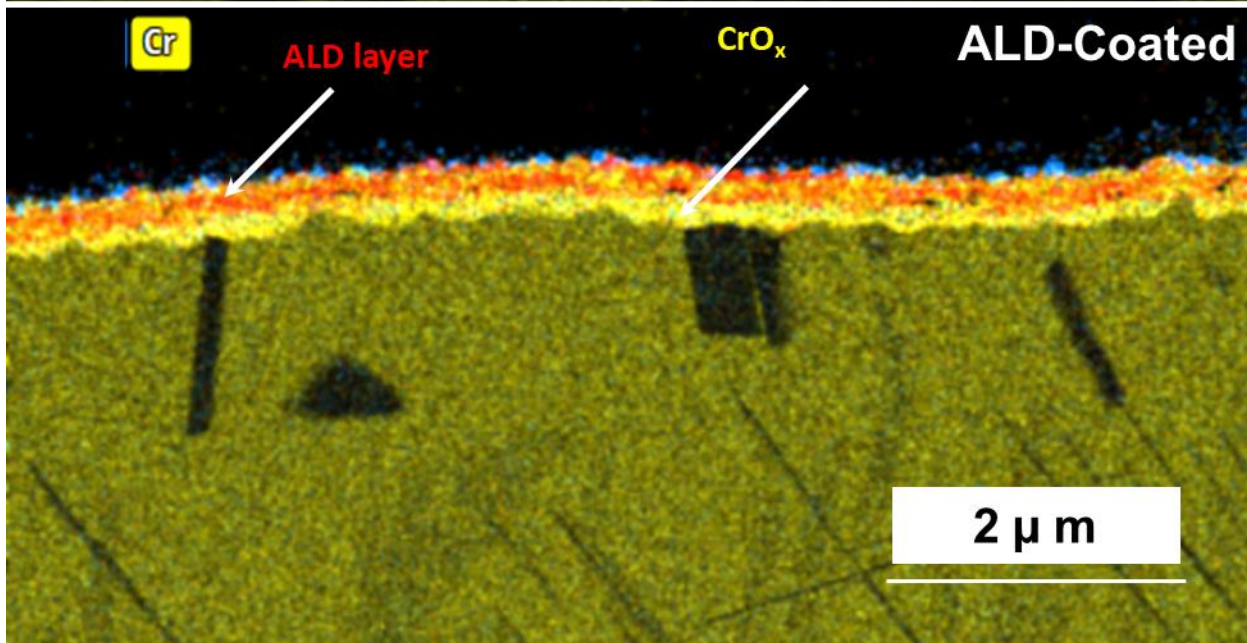
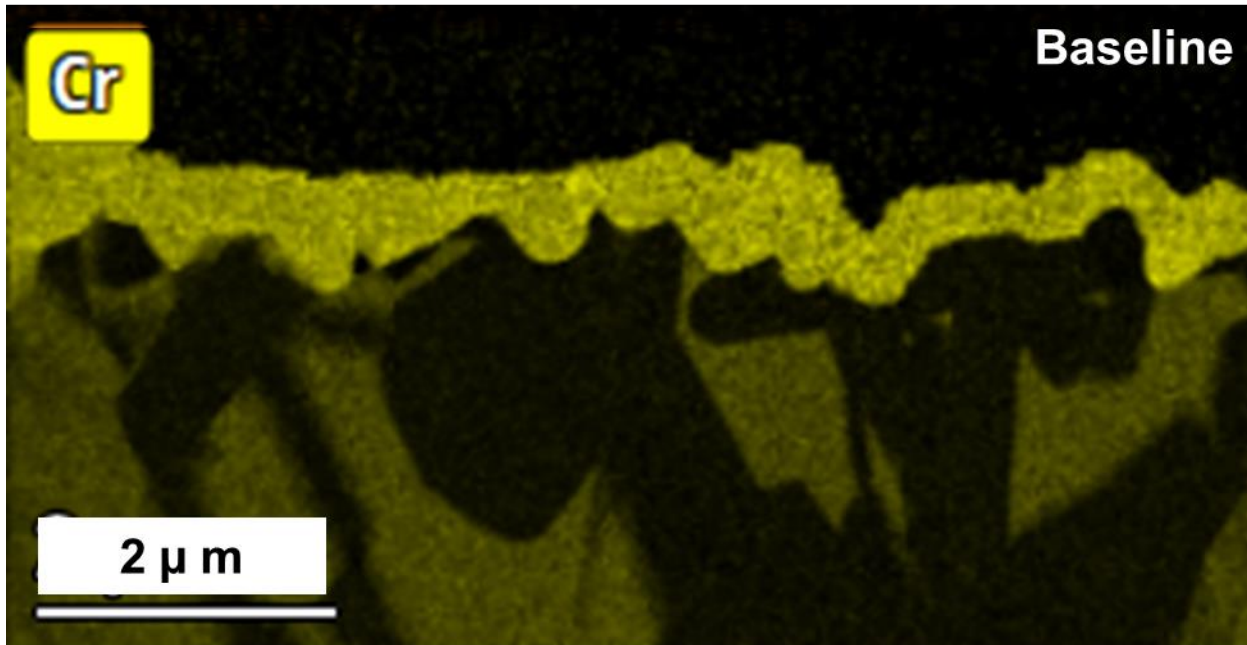
← **Baseline IN-625**

After CO₂ exposure @750° C for 2500 hours

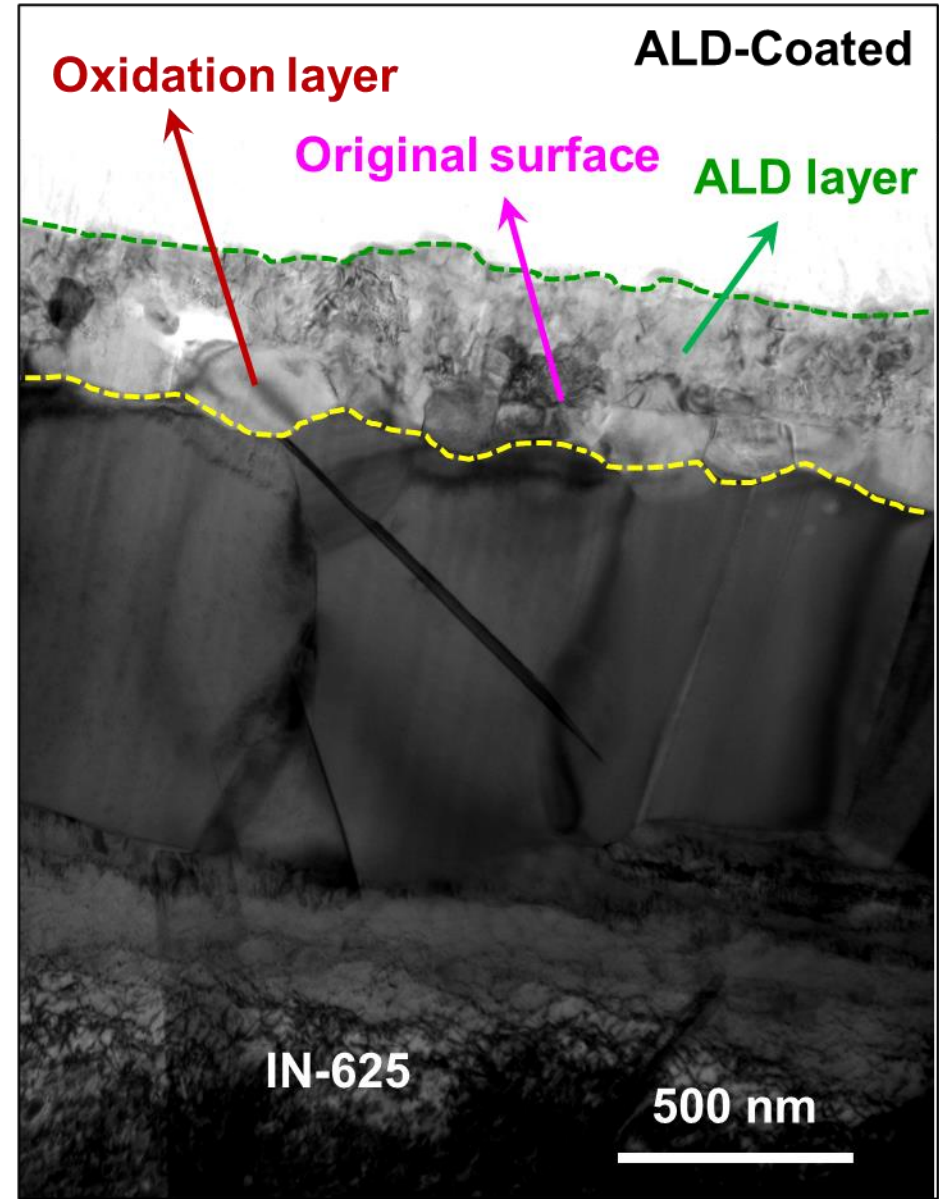
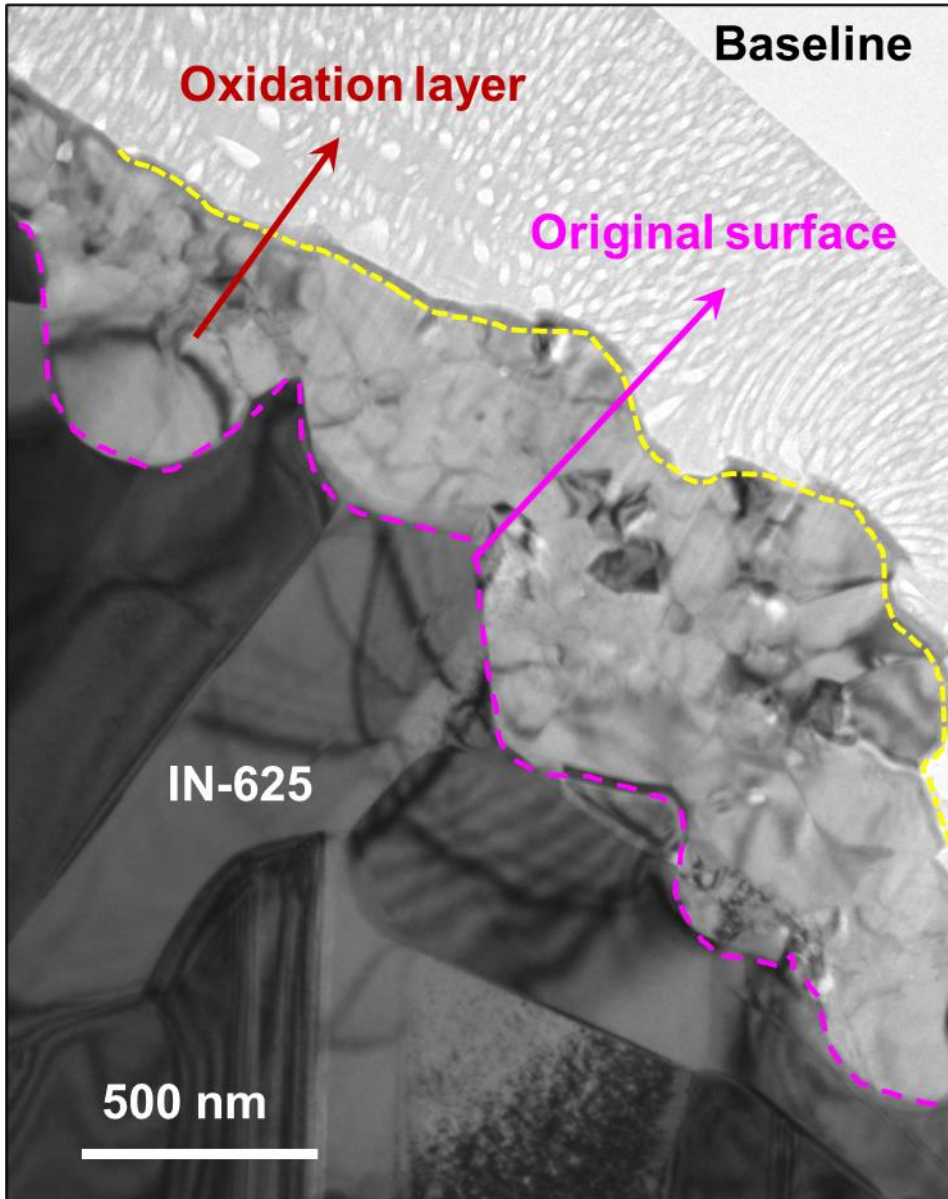
← **ALD coated IN-625**

After CO₂ exposure @750° C for 2500 hours

ALD coating blocked Cr outward diffusion: CO₂ at 750°C for 2500 h.



ALD coating blocked Cr outward diffusion: CO₂ at 750°C for 2500 h.



ALD coating layer minimized oxidation and Cr outward diffusion.

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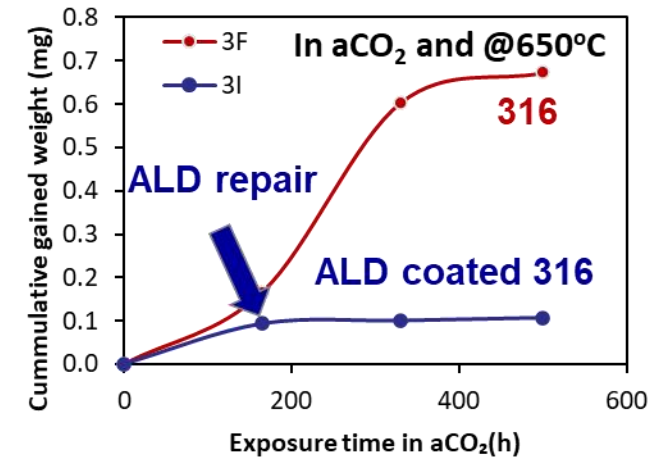
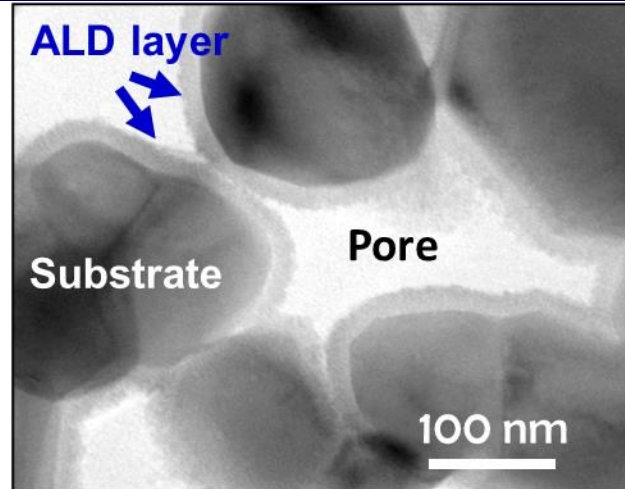
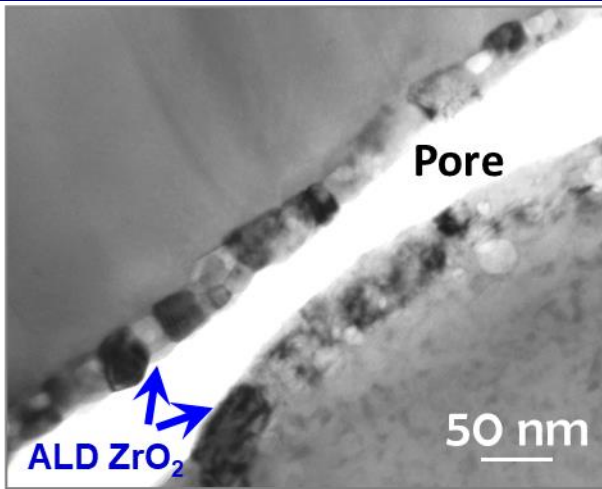
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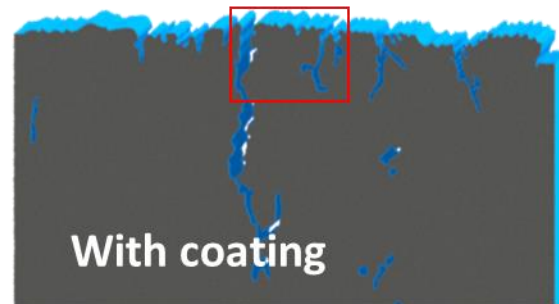
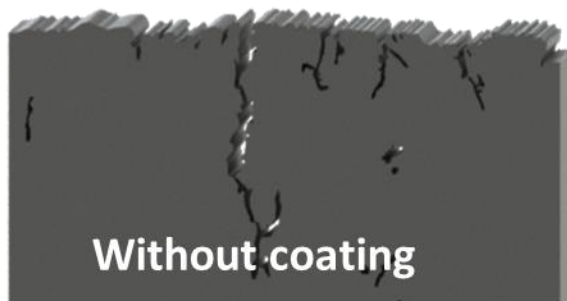
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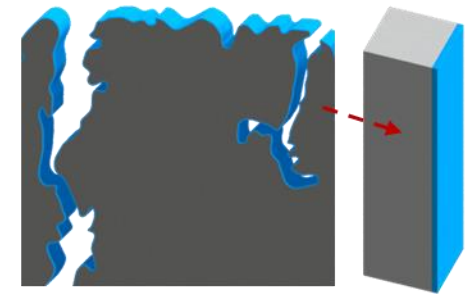
ALD: Multifunctional Environmental Barrier Coating for Refurbishing & Repurposing



ALD conformal coating on internal surface of pores.

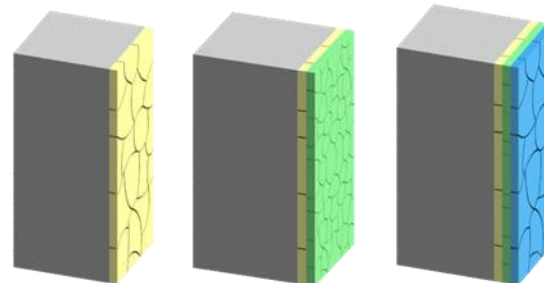


No weight gain after ALD repair

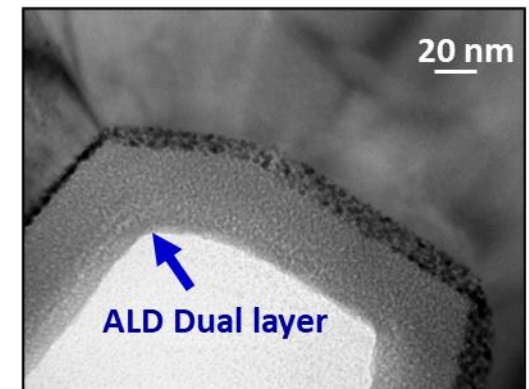


ALD refurbishing & repurposing.

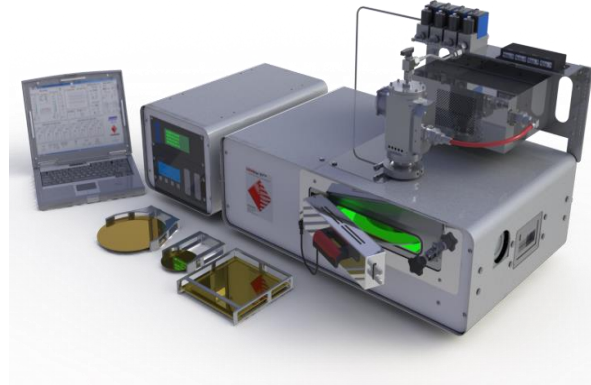
ALD coating can be designed as multifunctional with multi-layers, each layer is with different chemistry & function.



Single, dual, triple layered.



Scale-up: Commercial ALD Systems



ARRADIANCE



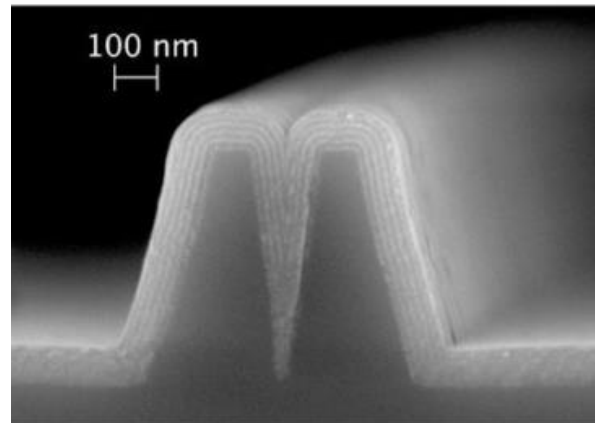
Cambridge Nanotech



Commercial ALD Large Scale Applications in Different Fields

Feature of ALD films: Conformal, adherent and homogeneous nano-scaled films which are crystalline or amorphous in an as-deposited state.

- Protective coatings
- Optics
- Magnetic recording heads
- Microelectronics
- MEMS
- Photovoltaics
- Catalyst



<https://beneq.com/en/applications/optical-coatings/>

SUMMARY

Holistic integration of atomic layer deposition (ALD) into the design and additive manufacturing of novel alloys.

- ALD coating of 3D powders to enable a new category of ceramic dispersion-strengthened alloys (CDS) that could be designed in terms of nano-particles size, density and chemistry, and with High mechanical strength integrity.
- ALD conformal coating is applied to various alloys of SS-316, IN-625:
 - ❖ ALD coating appears to be very effective to prevent the spallation and oxidation and Carburization.
 - ❖ AD coating applicable to both the internal & external surface of 3D printed components.
 - ❖ ALD are utilized to refurbish, re-coat, repurpose surface with internal cracks and oxidation.
- ALD enabled a new category of environmental barrier coatings (for various gas environment of CO₂, H₂O, O₂.....) that is effective for both the additive manufactured and serviced components for high temperature applications.

Viable & Versatile Atomic Layer Deposition For High Temperature Applications

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