

*Thermal Stability of Al₂O₃ Coatings
Deposited on
Si and High Performance Materials*

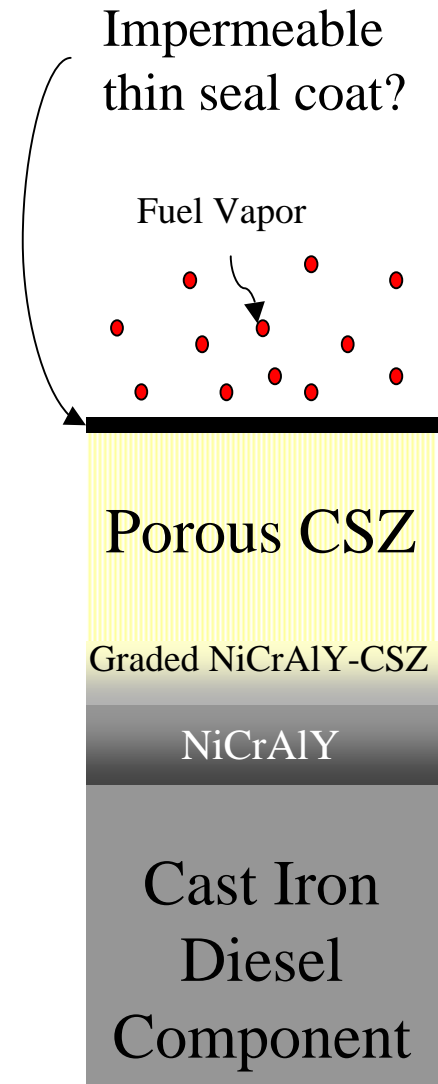
J. D. Meyer

Department of Chemical, Biochemical, and Materials Engineering
Stevens Institute of Technology

February 9, 2000

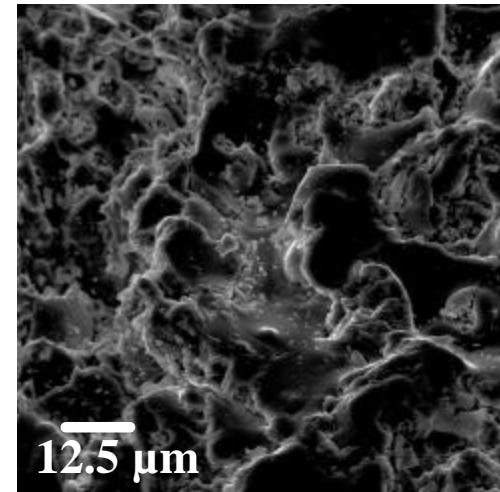
Initial Seal Coating Work Reveals Volume Shrinkage Due to Crystallization: A Serious Obstacle

- Thermal Barrier Coatings (TBCs) are being considered to improve diesel engine efficiency
 - CeO_2 -stabilized ZrO_2 (CSZ) prepared by air plasma spray (APS) is made porous for strain tolerance and enhanced thermal insulation
- Unexpectedly, testing at Caterpillar revealed a decrease in engine efficiency when components were coated with a TBC
 - One possible reason may be the porosity of the TBC, which is suspected to “entrain” fuel from the combustion chamber prior to ignition [B. Beardsley, 1990]
- Thick MOCVD Al_2O_3 coatings deposited on APS-CSZ adhered, but cracked significantly



This Project Explores the Feasibility of Sealing the Surface of the TBC by Applying a Seal Coat

- Materials Criteria
 - Non-porous and impermeable
 - Good adhesion to CSZ
 - High thermal stability
 - No debit to CSZ strain tolerance
 - Resistance to erosion and wear
- Processing Criteria
 - Processing temperatures below 500°C to avoid tempering of iron components
 - Conformal coating on complex, porous TBC surface



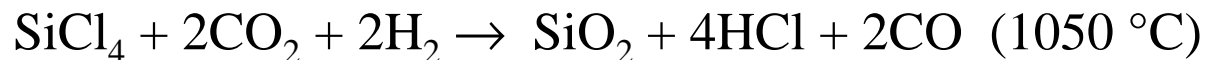
Surface morphology
of APS-CSZ
(as received)

Candidate Seal Coating Materials Were Screened Without Cast Iron Substrate

- “Free-standing” APS-CSZ coupons (1x1cm) were coated with:

MATERIAL	CTE (x10 ⁻⁶ /K)	MODULUS (GPa)
α-Al ₂ O ₃	8	380
3Al ₂ O ₃ ·2SiO ₂	6	145
SiO ₂ (fused)	0.5	70
CSZ	~10	~200
Si	3	163

- High-temperature chloride-based CVD processes were used:



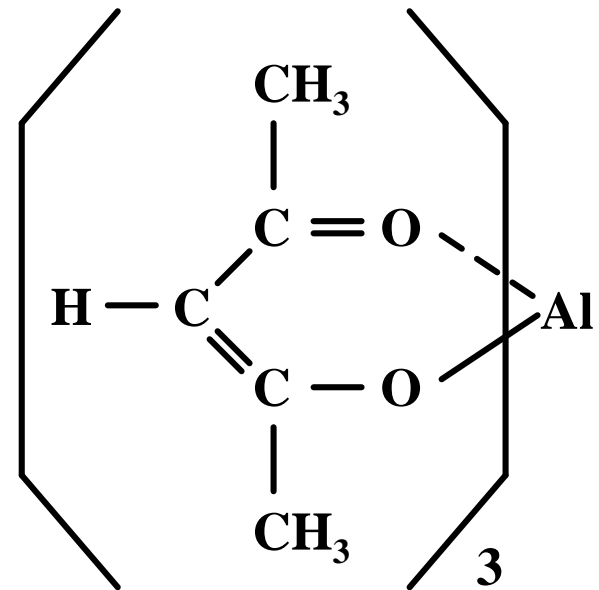
- Thermally cycled to 1150°C in air to assess seal coating/CSZ stability

Major Precursor Types

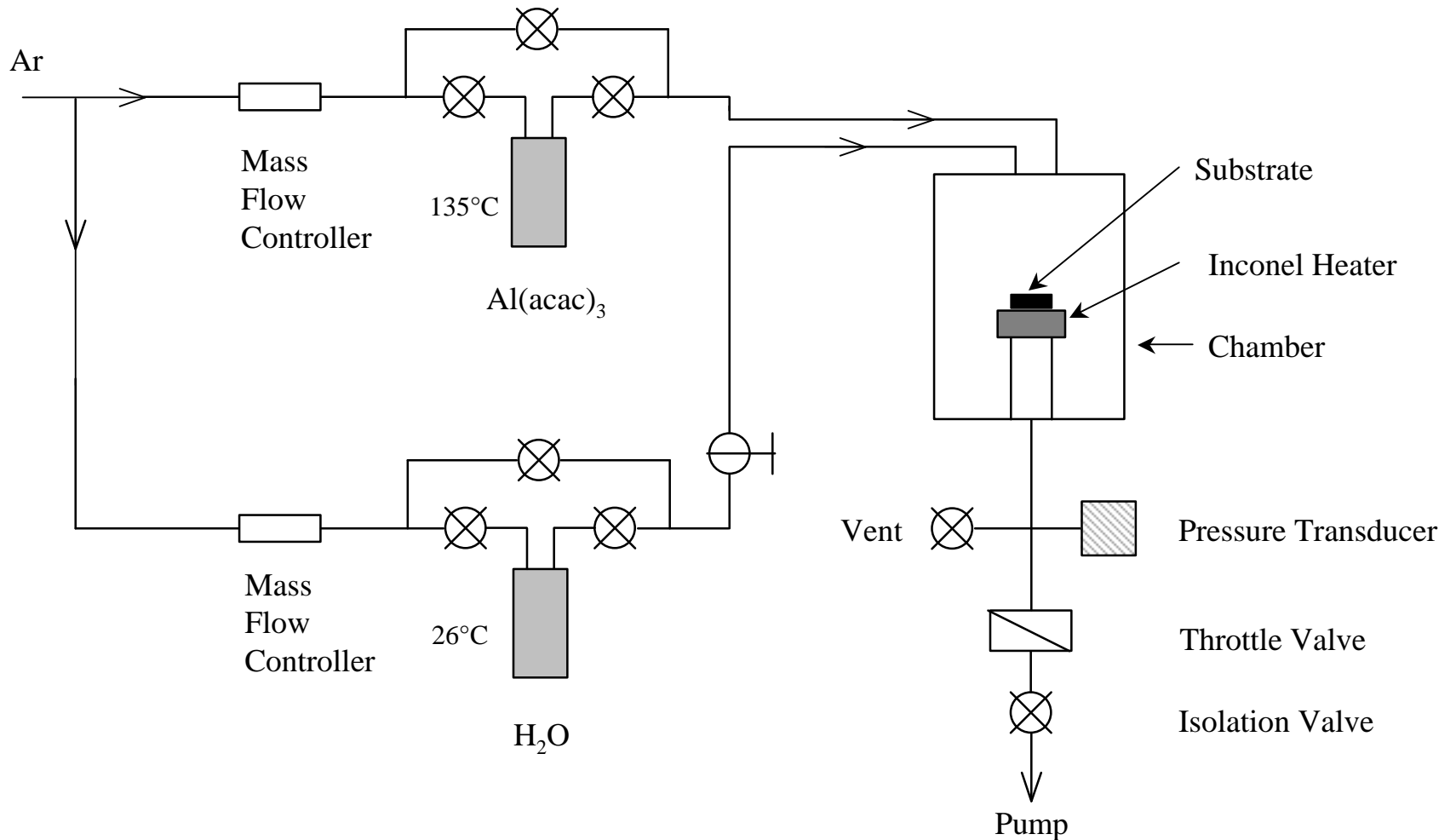
- Halides (AlCl_3)
 - Operational range mostly $> 700^\circ\text{C}$
 - Stable, good for α (generally not formed below 950°C)
 - Process can be problematic: high leak/oxygen sensitivity, homogeneous nucleation
- Metalorganics
 - Operational range b/w 250 and 1000°C
 - Volatile, but subject to C contamination
 - Aluminum Alkoxides - $\text{Al}(\text{OR})_3$: High porosity, impurities, hydrophobic
 - Aluminum Acetylacetonate
 - Aluminum Alkyl Compounds - AlR_3
 - unknown, homogeneous nucleation, poor adhesion, sensitive to humidity
 - Others: Esoteric or not well known

Al(acac)₃ and H₂O Were Selected to Prepare Low-temperature Al₂O₃ Seal Coating

- Major reasons:
 - Decomposes readily (well below 500°C)
 - Low toxicity and cost
 - Relatively moisture-insensitive
 - Stable compound at room temperature
 - Some carbon contamination observed
- Inclusion of water vapor appears to help eliminate carbon contamination [J.S. Kim, *et al.*, 1993]

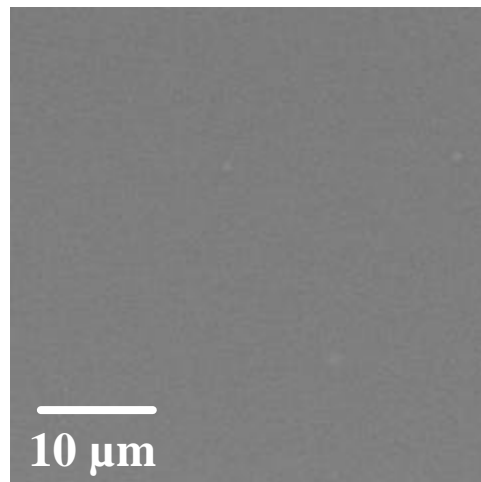


Cold-wall Al_2O_3 MOCVD System Constructed

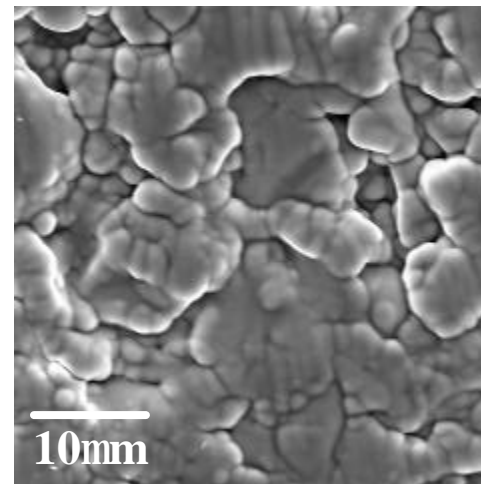


MOCVD Al₂O₃ Seal Coating Process Parameters Were Optimized

Substrate temperature	505 ±5°C
Total pressure	1.33 kPa
Argon supply rate (Al(acac) ₃ / H ₂ O)	120 / 20 cm ³ /min
Effective flow rate (Al(acac) ₃ / H ₂ O)	0.43 / 0.67 cm ³ /min
Al(acac) ₃ vaporization temperature	130-135°C



Al₂O₃ on Si



Al₂O₃ on CSZ

Experimental Approach to Testing MOCVD Al₂O₃ Seal Coating

- Potential problems with MOCVD Al₂O₃ coating:
 - Amorphous Al₂O₃ with possible C and H impurities
 - Significant volume shrinkage expected upon crystallization (~ -9%)
- Substrate issues:
 - CSZ-coated iron flexure bar
 - Free-standing CSZ: CSZ without iron substrate
 - Silicon: ease of characterization, but large thermal mismatch
- Thermal exposure from 700°C to 1200°C in air for 20 hrs.

Dependence of Phase Appearance

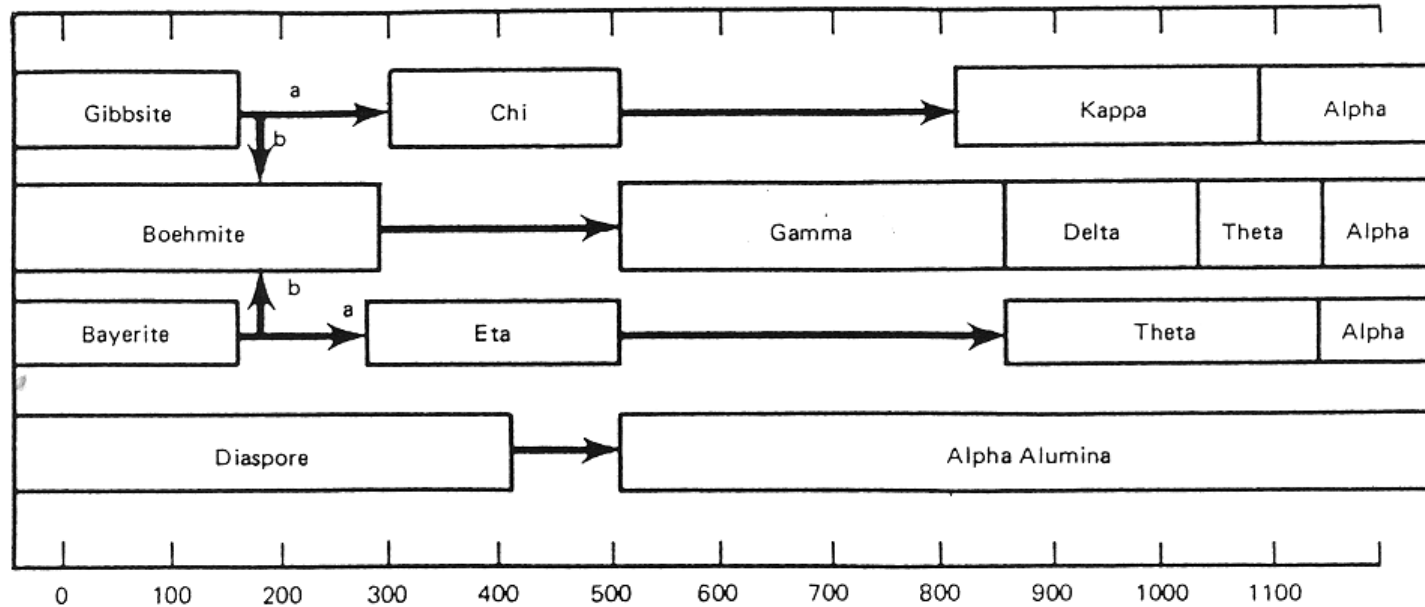


Figure 1. Transformation series of different aluminium hydroxides and aluminium oxide hydroxides in air (Temperature in °C). Open area indicates range of transition. Path b is favoured by moisture, alkalinity and coarse particle size (100 μm), path a by fine crystal size (below 10 μm). Reprinted from Reference [1] (p. 17) with the permission of The American Ceramic Society.

- Primary:
 - Starting Material (precursor)
 - Temperature
- Secondary:
 - Annealing parameters
 - Impurities
 - Crystallinity
 - Atmosphere

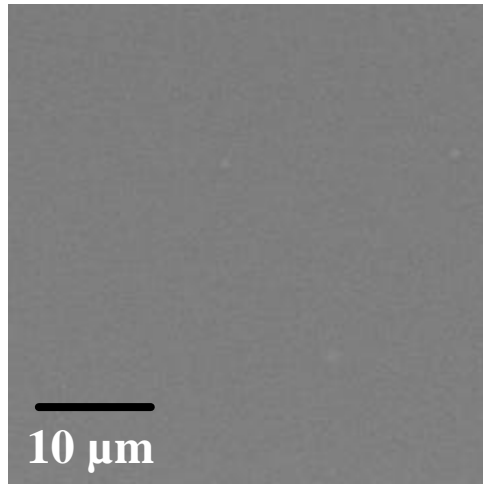
Initial Coating Nucleation & Growth

- Highly correlated to the supersaturation of precursors
- Reduction in temperature results in an increase in nucleus density
- Substrate variations will adversely affect nuclei density-affecting adhesion
 - non-uniform phase distribution (cemented carbides (*I.e.*, tool tips) results in varied nucleus density and hence, grain size
- No consensus reached in literature

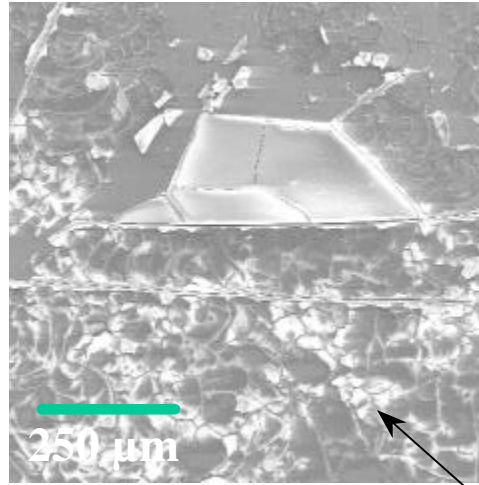
Sustaining Coating Growth

- Increased temperature, to a major extent, only changes phase deposition/transformation kinetics
- System pressure
 - Generally, lower pressure is favored for species creation during precursor decomposition
 - Under ~6.7kPa (50 Torr), reports have been made of roughly linear increase of growth rate with P_{total}
- Precursor partial pressures control deposition by depriving the reaction system of a sufficient amount of a vital constituent- “choking” the deposition process and effecting control on the morphology

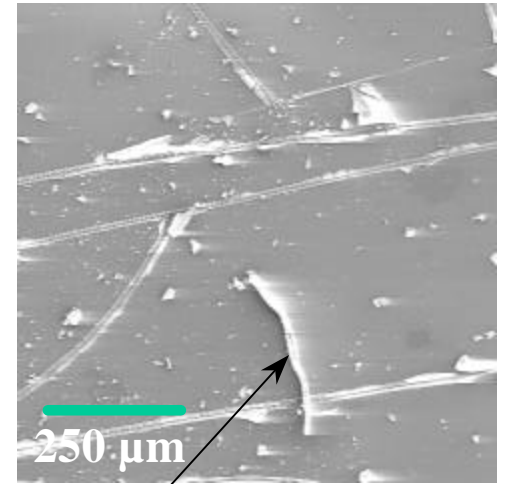
Thick (2.25 μm) Al_2O_3 on Si Spalled upon Annealing



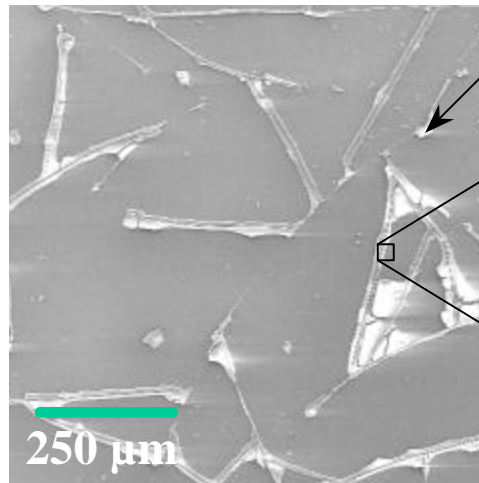
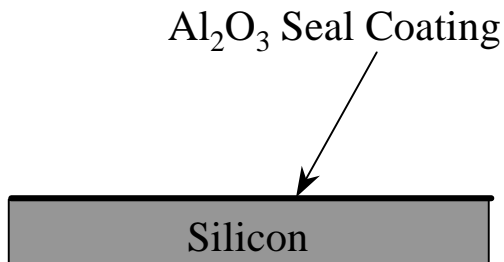
As coated



800°C



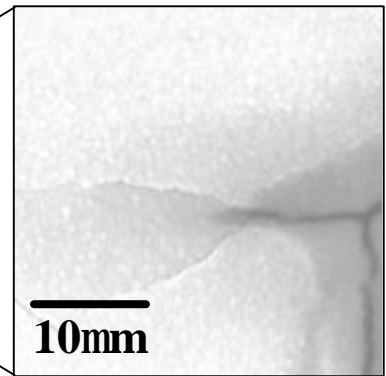
900°C



1200°C

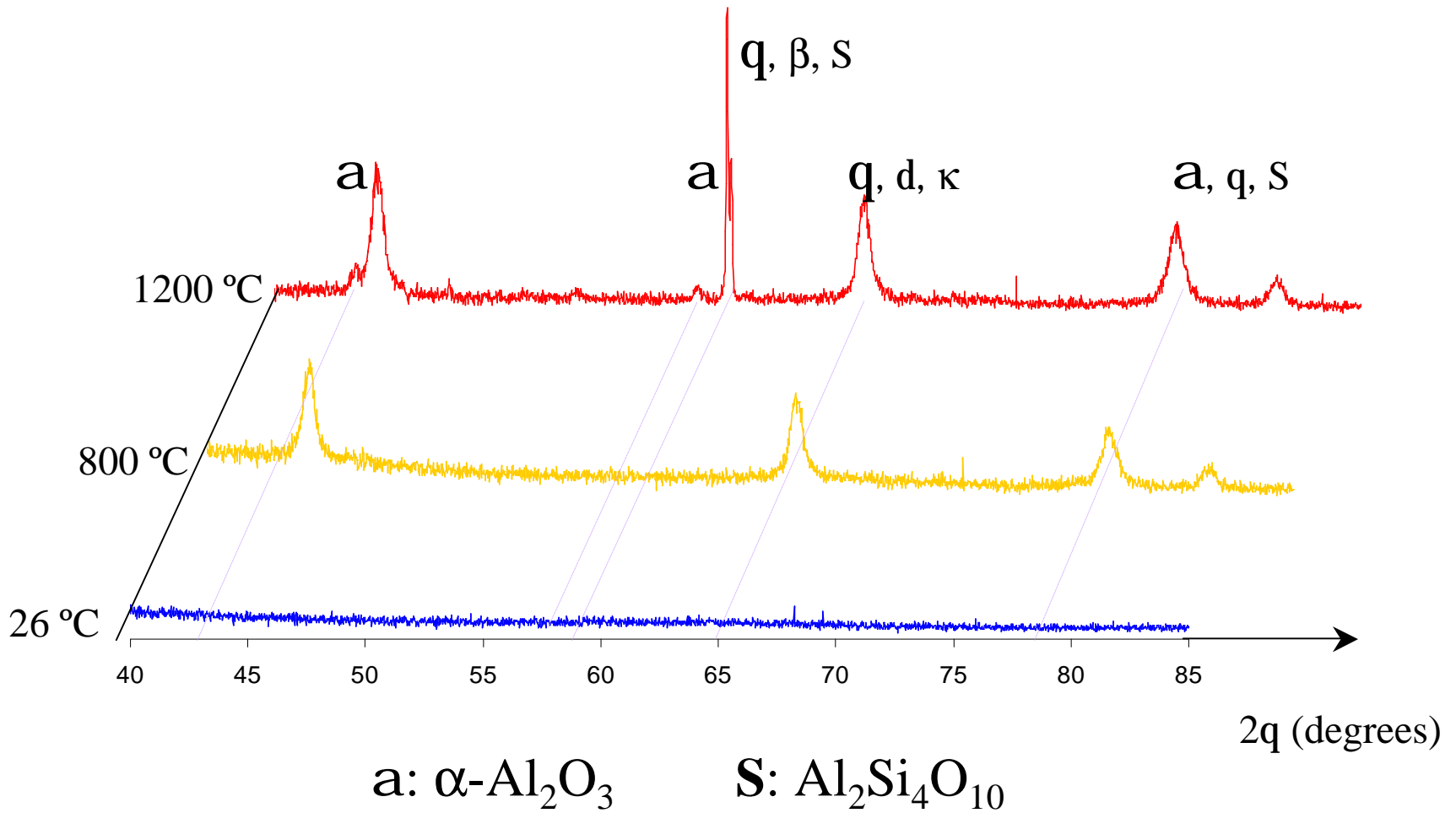
Non-spalled Al₂O₃

200x



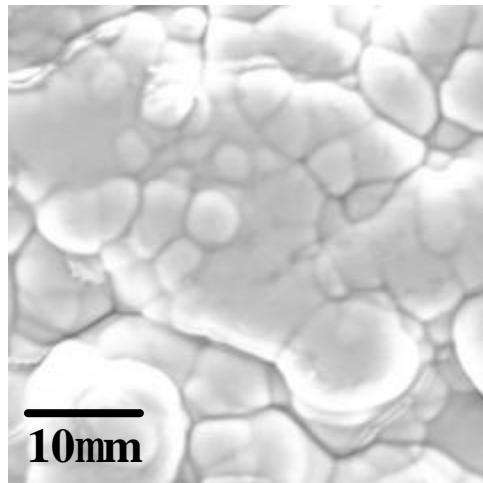
10 μm

Crystallization of MOCVD Al_2O_3 Occurs Relatively Rapidly (20 Hours) at 700°C to 1200°C

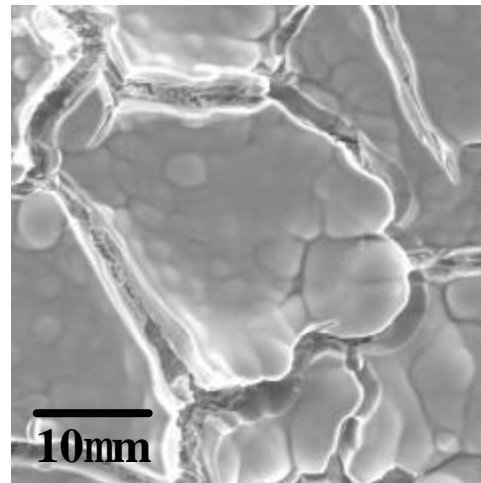


Not much Al_2O_3 remained on the substrate for XRD analysis

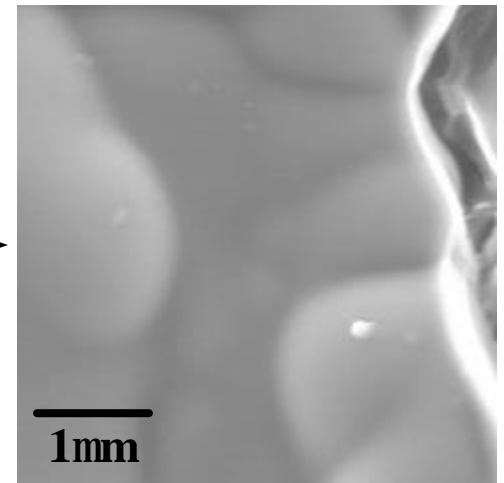
MOCVD Al₂O₃ on Un/Constrained CSZ/Iron Cracked Upon Annealing



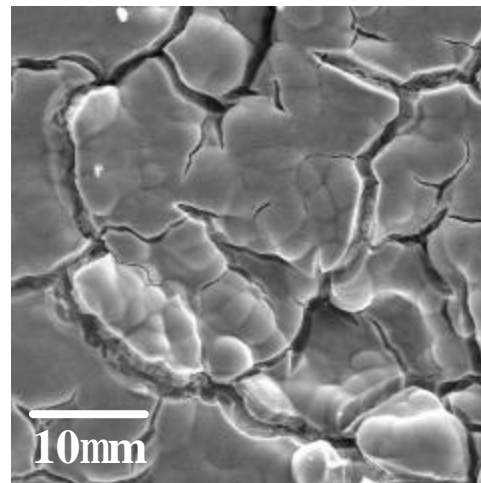
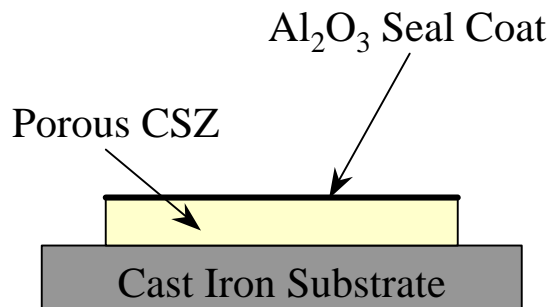
As coated.



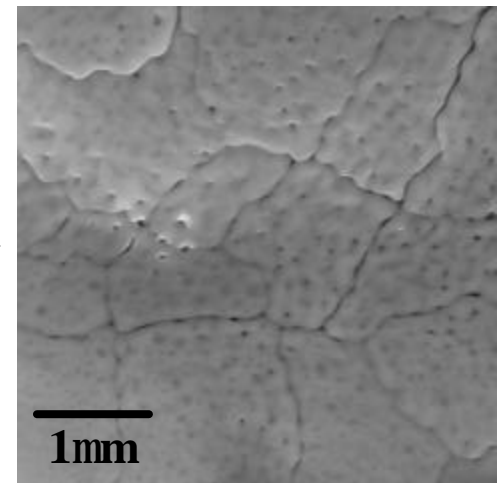
10x →



900°C



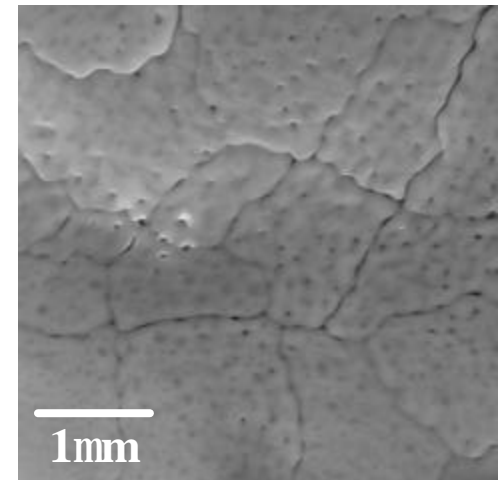
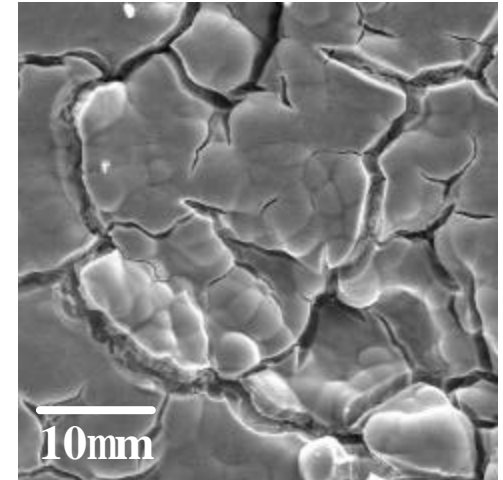
10x →



1100°C

“Thick” Al₂O₃ Coating Cracked During Annealing

- Annealing of thick (2.25 μm) MOCVD Al₂O₃ coatings leads to inadequate adhesion and sealing
 - CTE mismatch
 - Volume shrinkage due to crystallization (~9%) (θ - \rightarrow α - Al₂O₃)
- Work by F.F. Lange stipulates that thin coatings (~100nm) are better able to contain tensile stress systems
 - crack propagation occurs only when free energy of any film would be reduced; strain energy depends on film thickness
 - There is a critical film thickness associated with a maximum internal energy



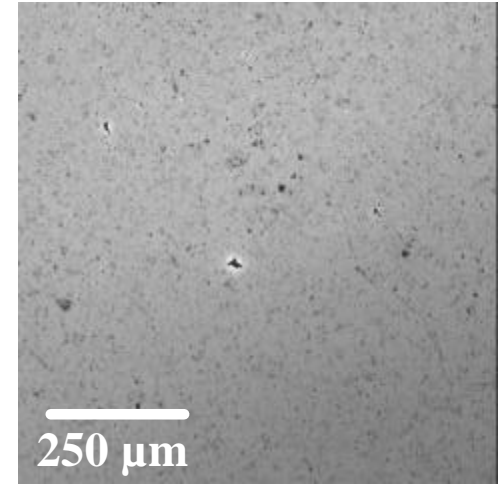
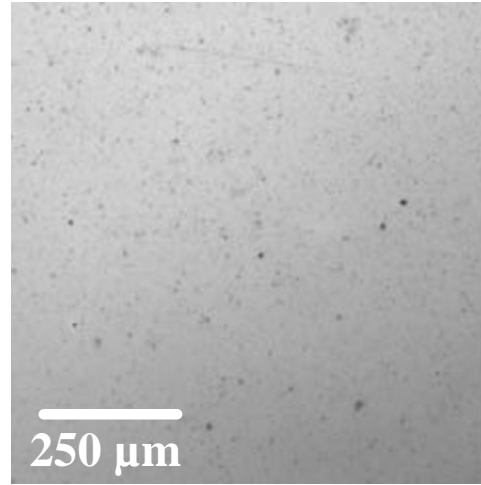
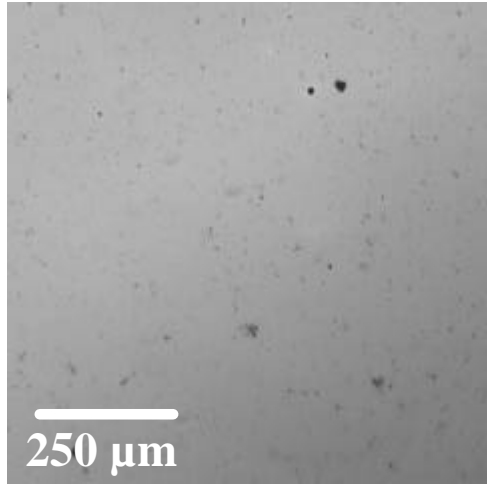
Sub-micron Coatings Exhibited Slight Cracking

290 nm

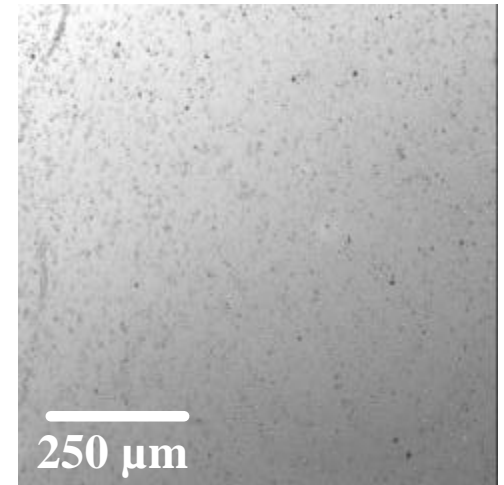
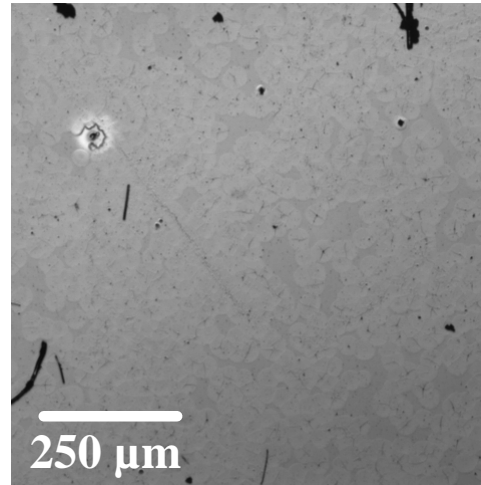
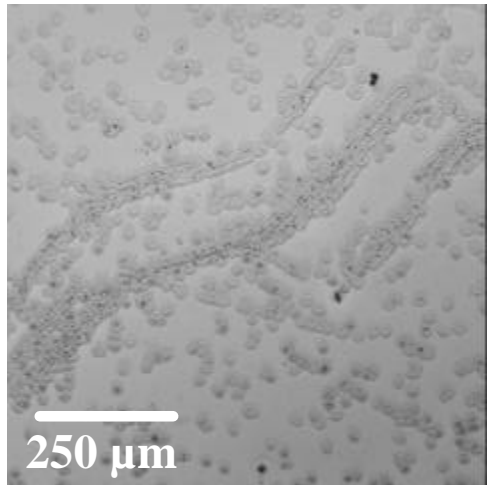
260 nm

160 nm

700°C

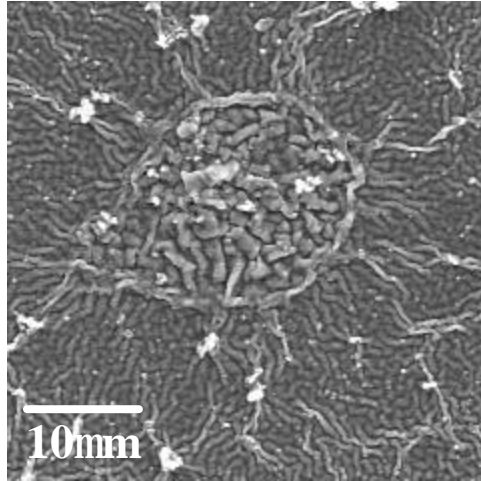


1100°C

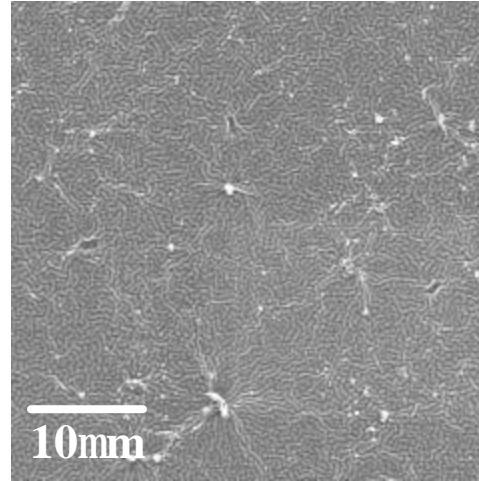


Annealing of Very Thin Coatings on Silicon Resulted in Roughening of Surface

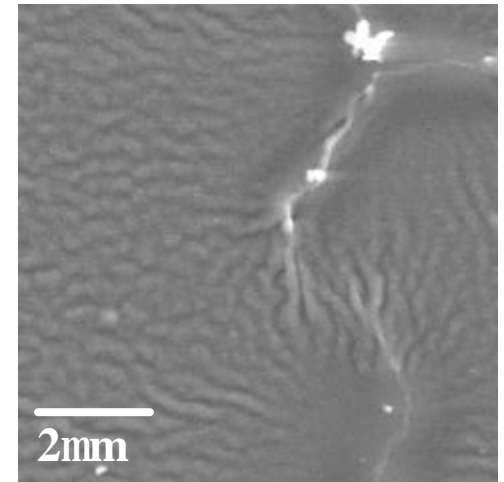
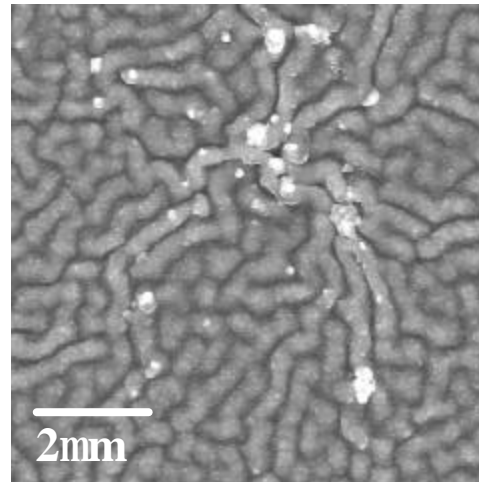
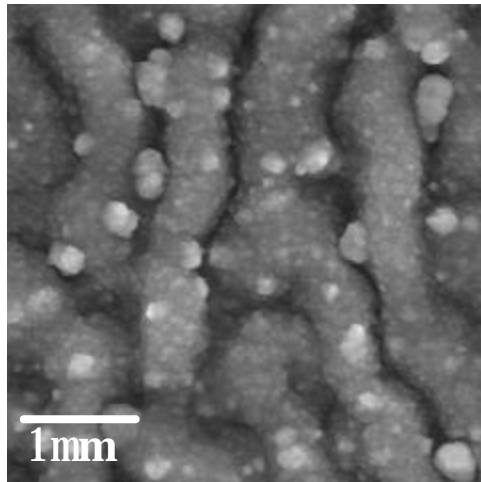
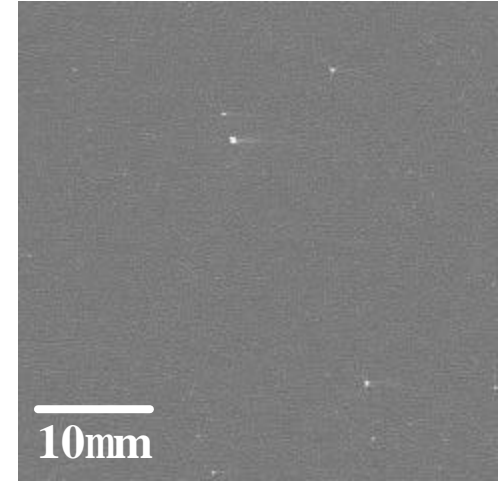
110 nm



70 nm



40 nm



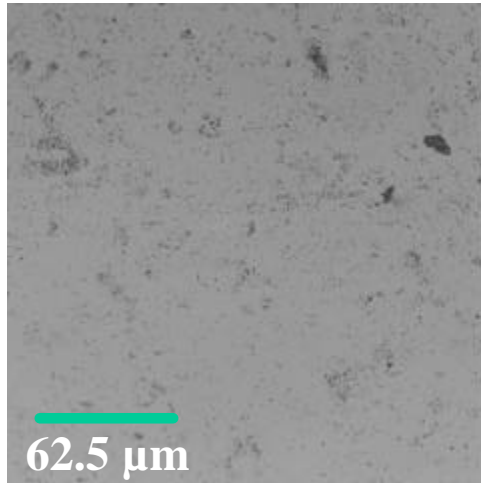
Annealing of Al₂O₃ Coatings at 1100°C for 20 Hours Showed Several Thickness-based Trends

- Thinner coatings on silicon appear to maintain a lower distribution of crack-initiating “pores”
- Despite this, transformation is not evident in XRD patterns, requiring additional effort to confirm Al₂O₃ crystallization
- Sub-100nm coatings may provide a solution to the micro-cracking problem, but are they sufficiently conformal?
- Coatings on silicon carbide appear to “coagulate” more easily as thickness drops, especially in center of samples
- Coatings on nickel alloy substrates demonstrate increased leveling as thickness decreases (by Δ of focus depth)

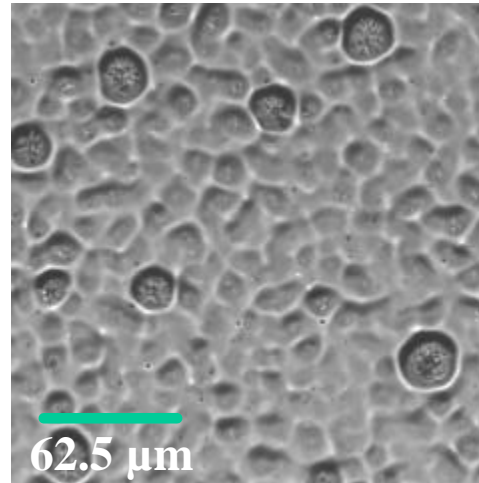
Silicon Carbide & Nickel Alloy Substrates at 1100°C

SiC

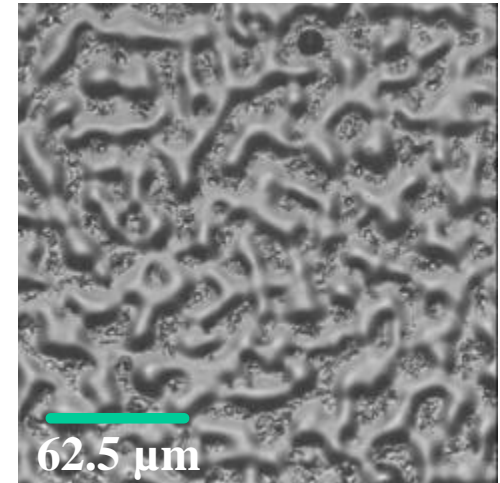
770 nm (26°C)



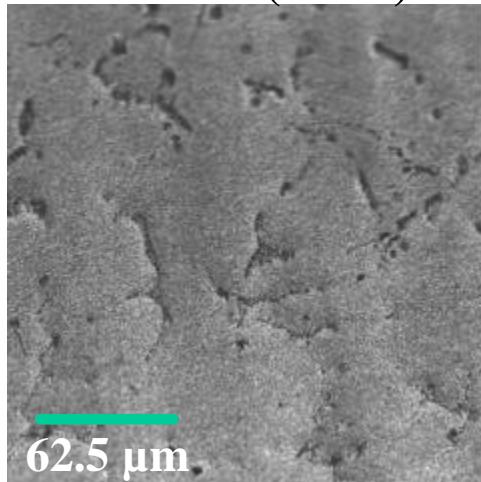
830 nm



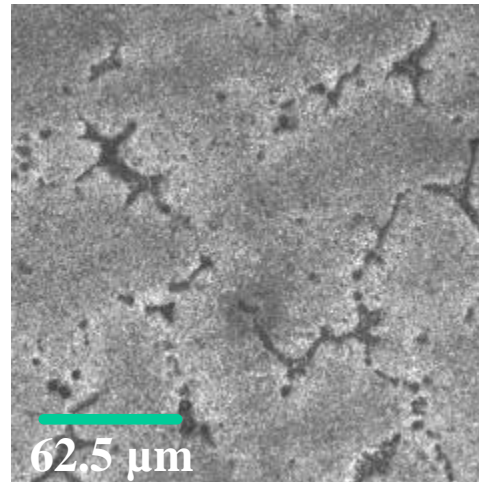
510 nm



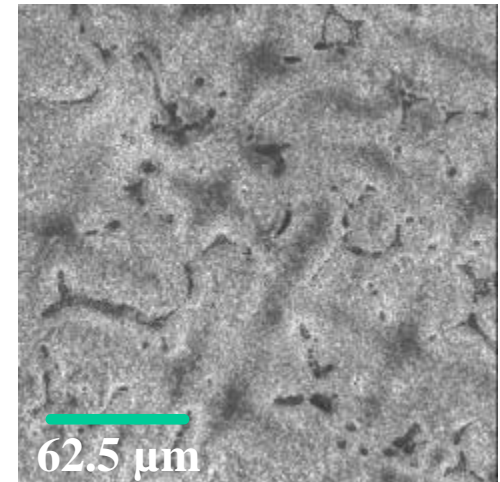
760 nm (26°C)



960 nm



540 nm



Ni alloy

MOCVD Coating Process Based on Prior Work

- Chloride-based Al_2O_3 coating deposited at 1050°C contained significant amounts of $\theta\text{-Al}_2\text{O}_3$
- MOCVD Al_2O_3 coating could be prepared at 500°C , but was entirely amorphous
- Metastable Al_2O_3 coating ($\theta\text{-Al}_2\text{O}_3$ minimum?) may be required to survive annealing and crystallization
- Literature describes no MOCVD system in which a crystalline Al_2O_3 coating can be deposited below 500°C
- Alternative materials, along with a suitable coating process, still need to be explored

Conclusion: Crystallization/Thickness Dependencies

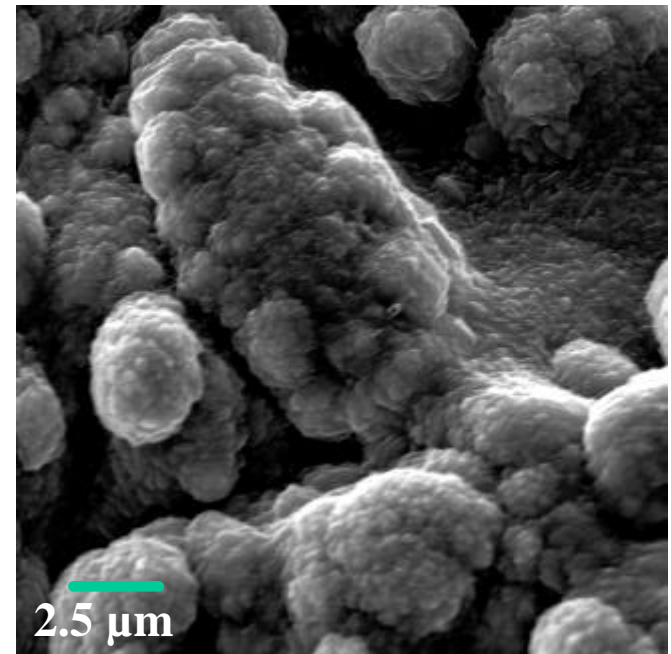
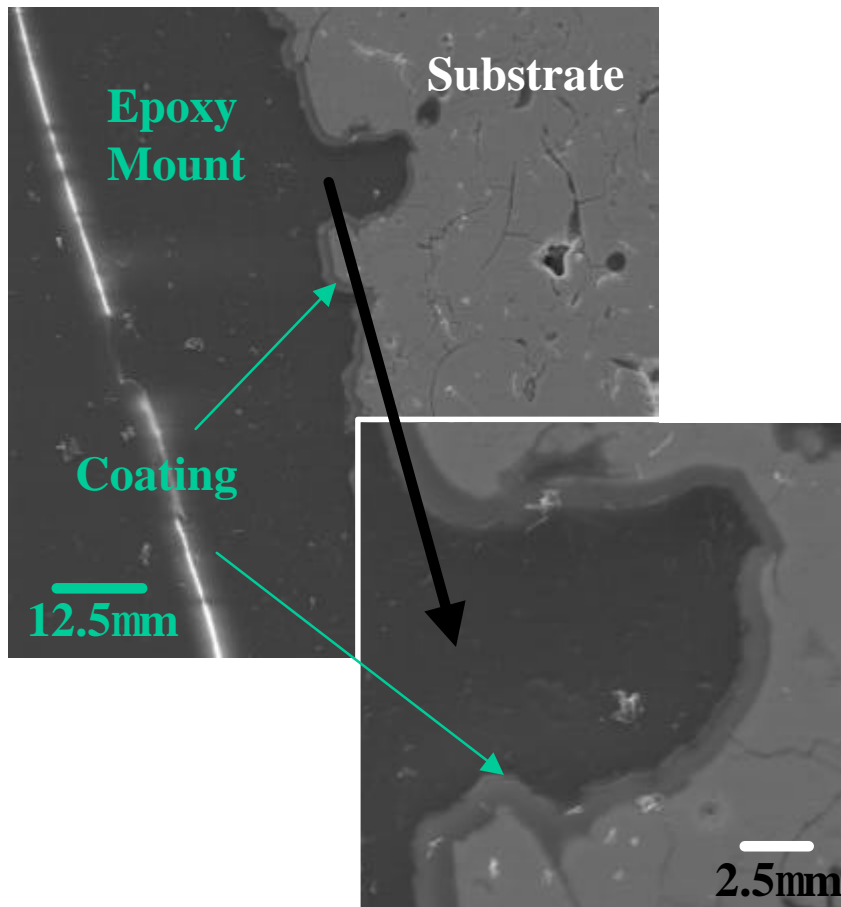
- Cracking of “thick” coatings due to +9% volume shrinkage associated with crystallization during annealing rendered initial seal coating essentially useless - leading to the investigation of sub-micron coatings
- Sub-quarter micron coatings showed decreased crack formation with reduced thickness, while sub-100 angstrom coatings maintaining integrity during crystallization despite morphological peculiarities
- Increasing deposition temperature to 1050C resulted in deposition of crystalline coatings, minor cracking evident
- Increasing system pressure reduced growth rate along with amount of powder deposited on sample, but many meta-stable Al_2O_3 phases visible just above noise

Acknowledgments

- Portions of this research sponsored by Brad Beardsley at *Caterpillar, Inc.*
- The results from the chloride-based Al_2O_3 coating work were obtained by W.Y. Lee at Oak Ridge National Laboratory under the sponsorship of Ray Johnson, *Heavy Vehicle Propulsion System Materials Program*, DOE Office of Transportation Technologies.

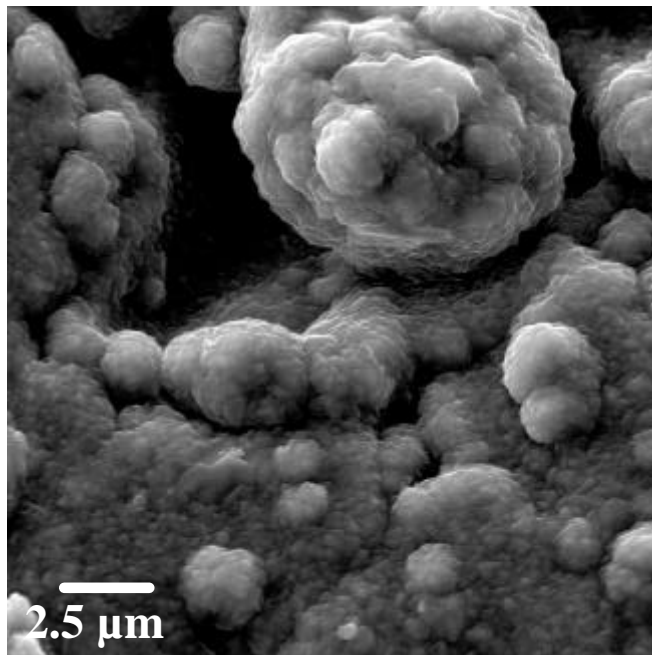
Back-up Slides

Al₂O₃ Seal Coating (from Chloride Process) Was Uniform and Conformal

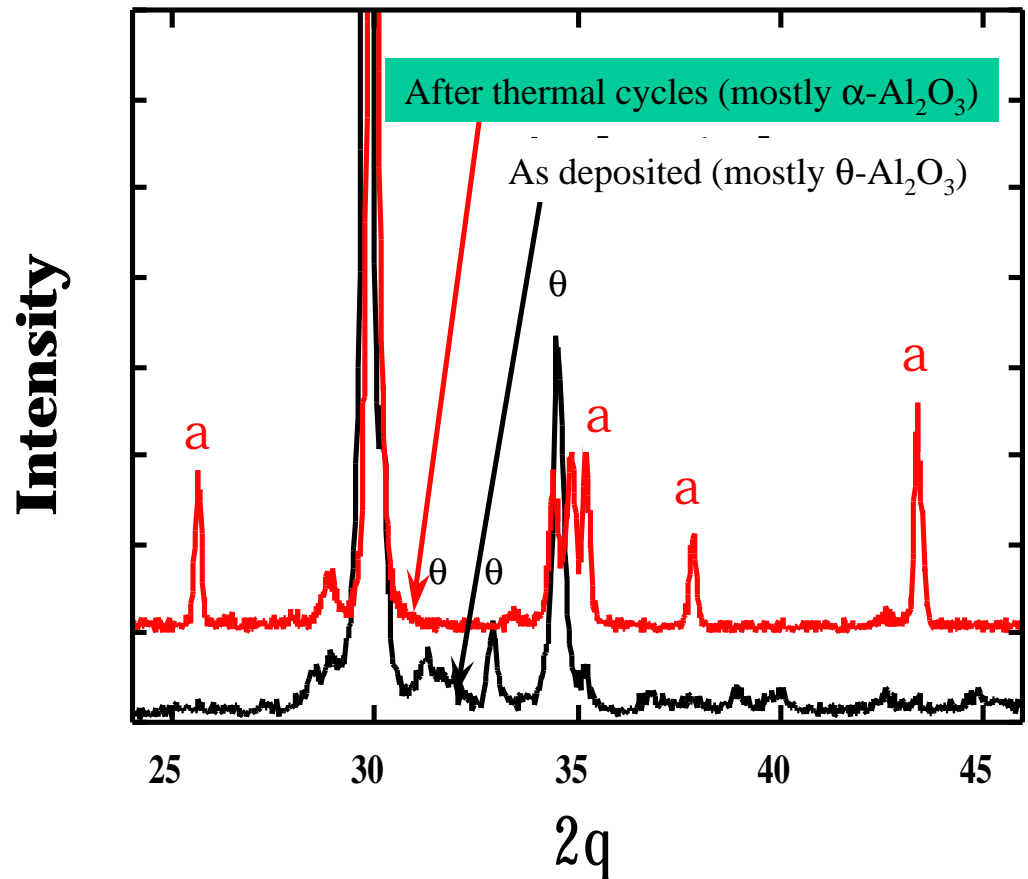


As coated

Al₂O₃ Seal Coating (from Chloride Process) Was Stable upon Thermal Cycling



After 49 1-hr. Cycles
to 1150°C



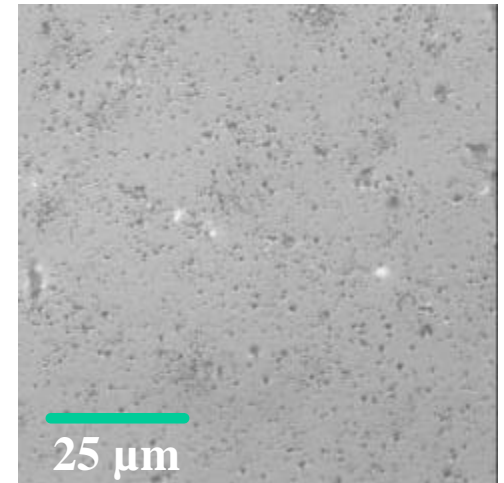
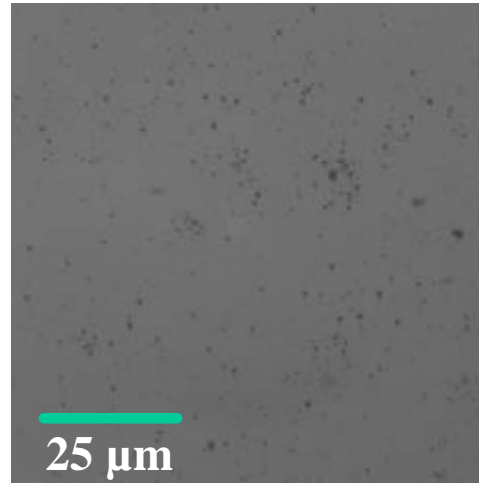
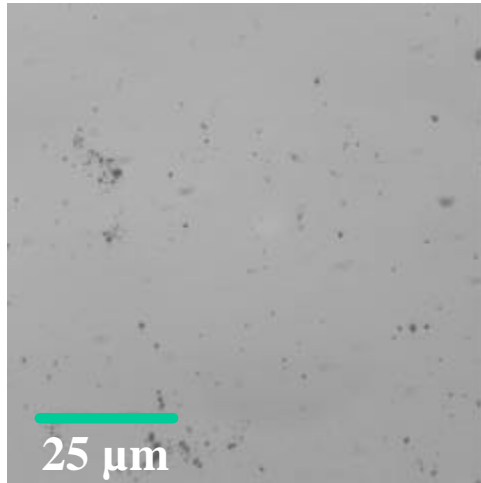
Micro-Cracking Falls With Coating Thickness

290 nm

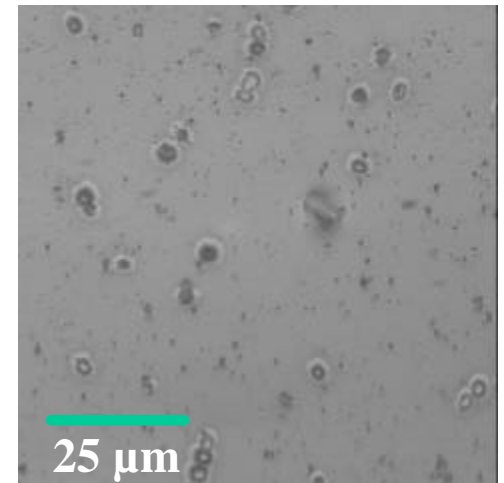
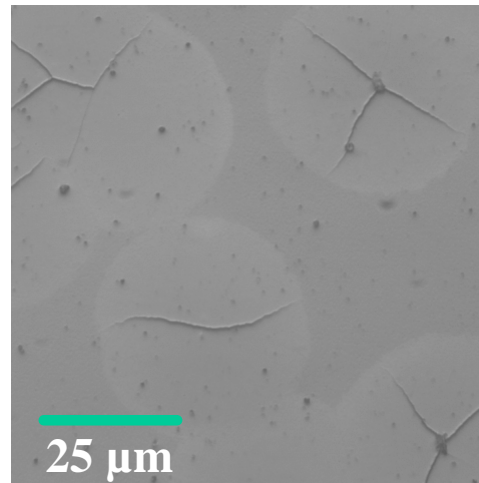
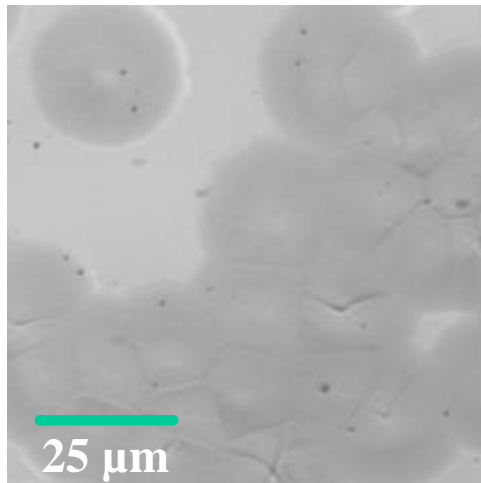
260 nm

160 nm

700°C



1100°C



Comparison of Chloride-based Al_2O_3 vs. MOCVD Al_2O_3

	<i>Chloride-based Al_2O_3</i>	<i>MOCVD Al_2O_3</i>
<i>As prepared:</i>	Conformal, mostly metastable (θ)	Conformal, amorphous
<i>Thermally annealed:</i>	Retained adhesion & structural integrity	Severe cracking, despite adhesion
<i>Crystallization:</i>	$\theta-Al_2O_3 \rightarrow \alpha-Al_2O_3$ ($\Delta V < -9\%$)	Amorphous \rightarrow metastable, $\alpha-Al_2O_3$ ($\Delta V > -9\%$)
<i>Possible C & H impurities:</i>	Highly unlikely	Possible, but minimized
<i>Quality of sealing:</i>	“Sufficient”	Insufficient

Primary Phase Nucleation Mechanisms

- Surface of substrate, leading to a “rising front” as phase boundary migrates upwards
- Grain boundary nodes
- Coating crack edges

