Materials and Processing Issues Associated With Seal Coating Development

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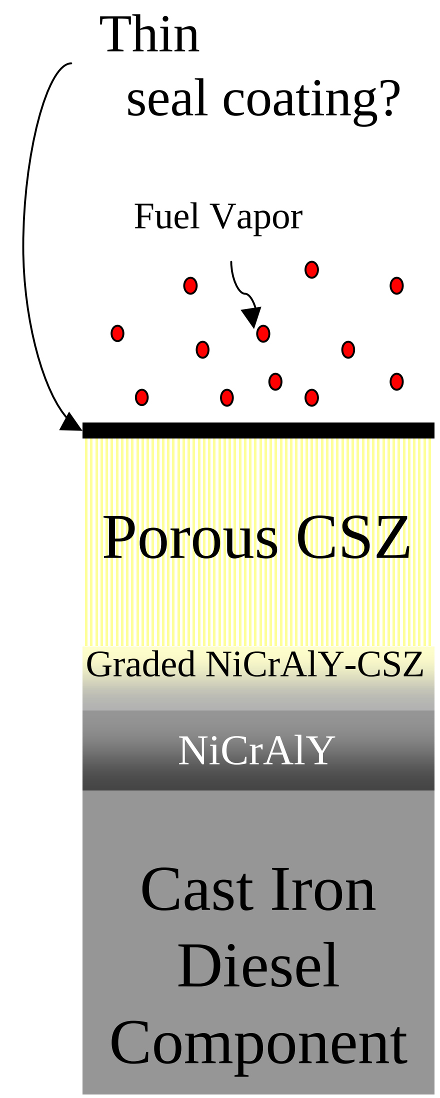
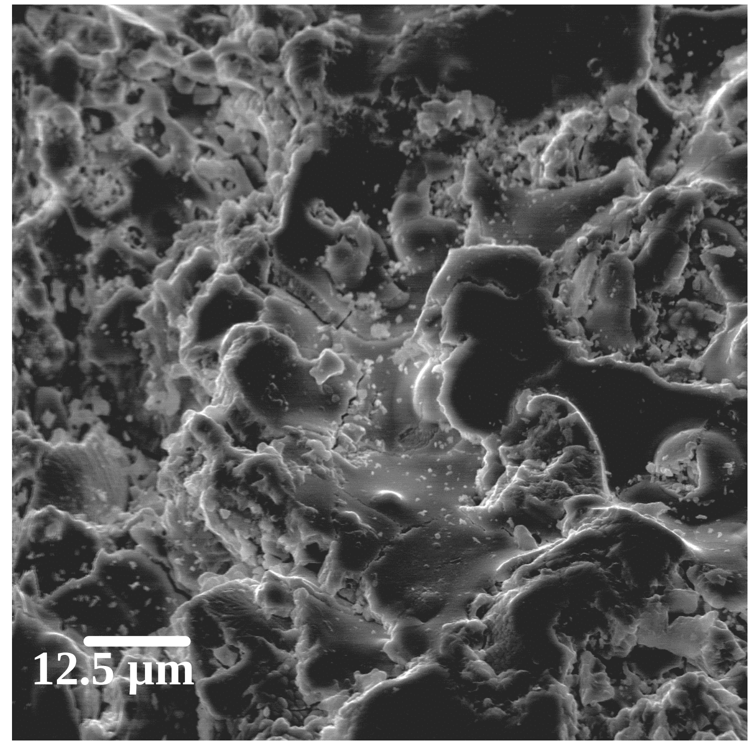
Rationale for Seal Coating

- Thermal Barrier Coatings (TBCs) are being considered to improve diesel engine efficiency
  - CeO_2-stabilized ZrO_2 (CSZ) prepared by air plasma spray (APS) provides thermal insulation of diesel components
  - APS-CSZ 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]



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

- 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)

Coating Material Selection

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_2O_3	8	380
$3Al_2O_3 \cdot 2SiO_2$	6	145
SiO_2 (fused)	0.5	70
CSZ (substrate)	~10	~200
Si (substrate)	3	163

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

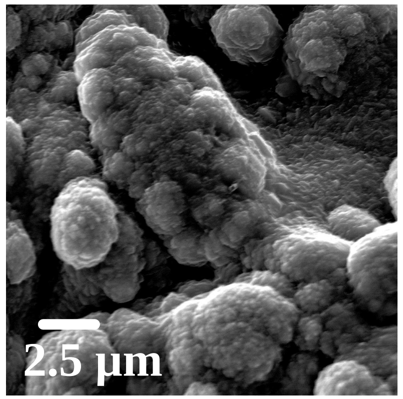
$$2AlCl_3 + 3CO_2 + 3H_2 \rightarrow Al_2O_3 + 6HCl + 3CO \quad (1050°C)$$

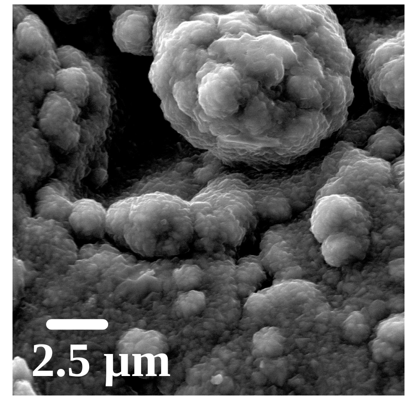
$$SiCl_4 + 2CO_2 + 2H_2 \rightarrow SiO_2 + 4HCl + 2CO \quad (1050\ °C)$$

- Thermally cycled to 1150°C in air to assess seal coating/CSZ stability
- $3Al_2O_3 \cdot 2SiO_2$ and SiO_2 spalled during thermal cycling, probably due to CTE mismatch with respect to CSZ

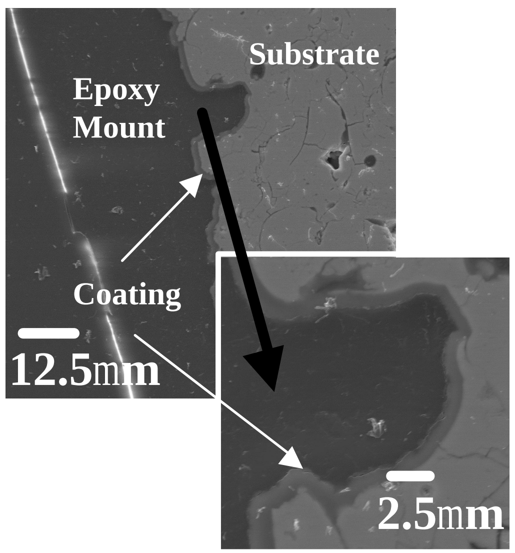
Al_2O_3 *Seal Coating (from Chloride Process) Was Uniform, Conformal, and Thermally Stable*

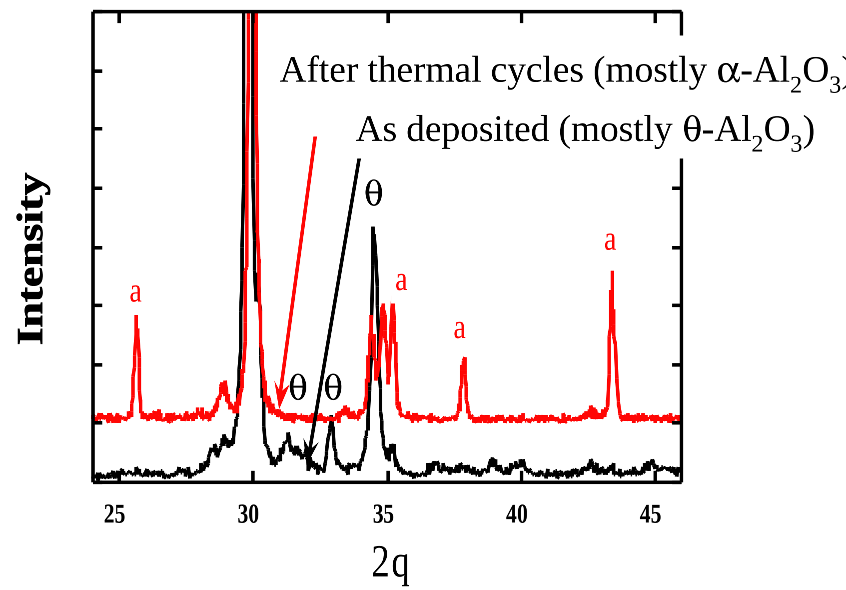
As coated:





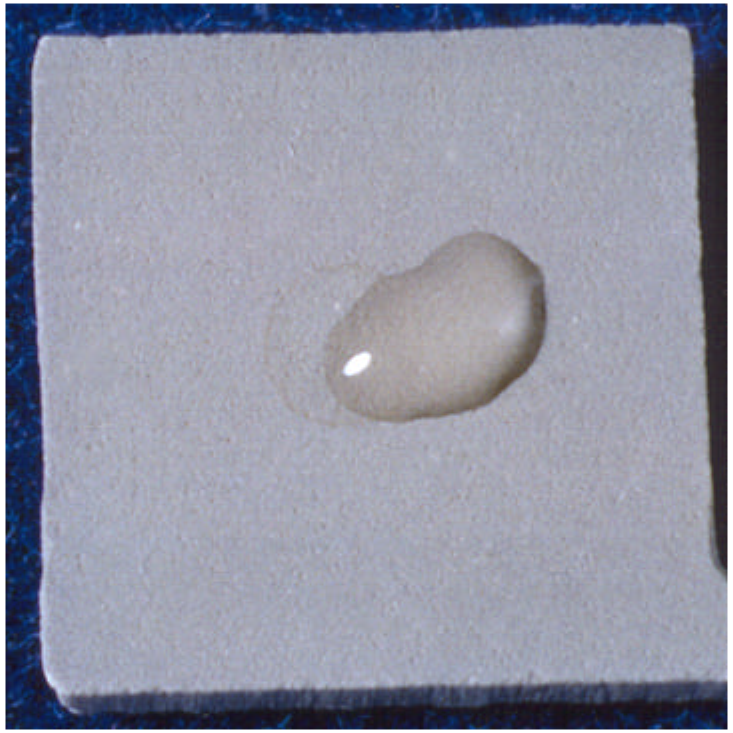
After 49
1-h. Cycles
to 1150°C.





Screening Results Suggest That Metastable Al_2O_3 Seal Coating May Be Useful If It Can Be Prepared at T < 500°C

Free-standing CSZ without seal coating

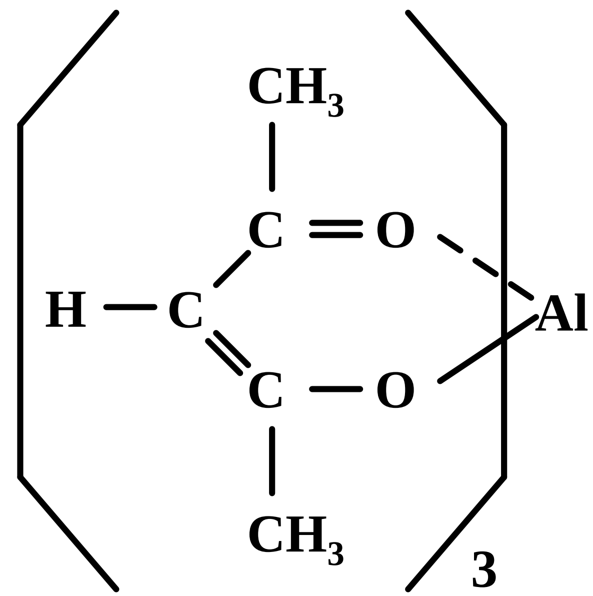


Free-standing CSZ coated and cycled

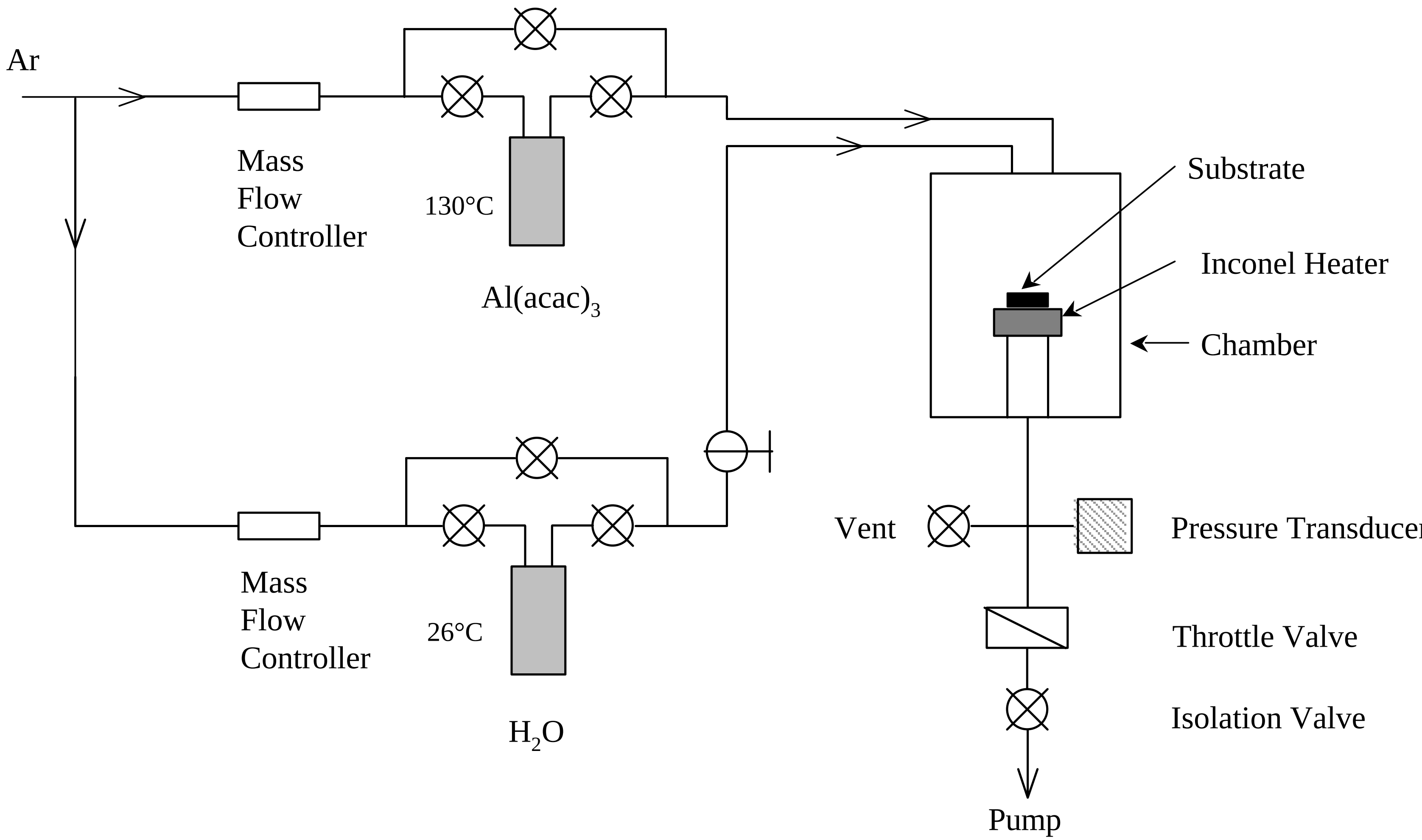
MOCVD Al_2O_3 Coating Synthesis

$Al(acac)_3$ and H_2O Were Selected to Prepare Low-temperature Al_2O_3 Seal Coating

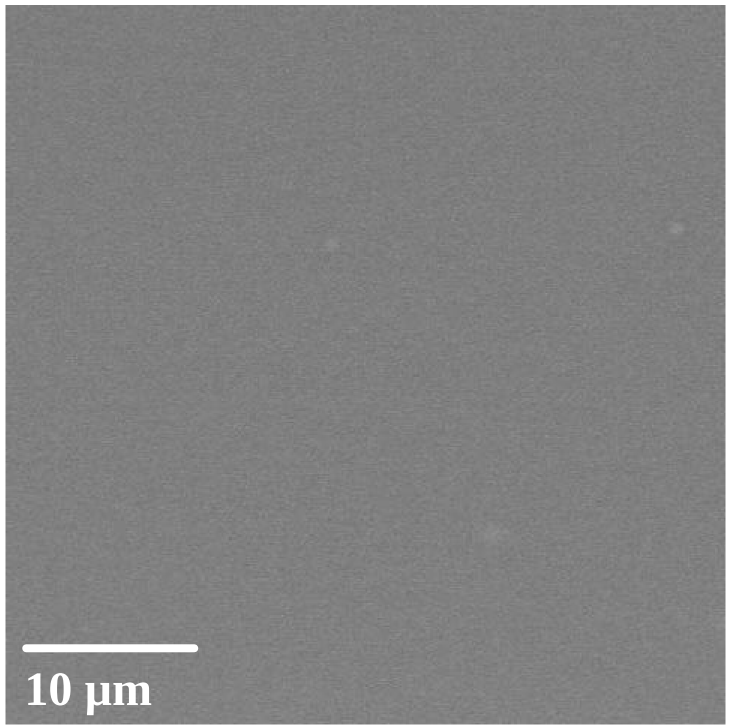
- Major reasons:
  - Decomposes readily (well below 500°C)
  - Low toxicity and cost
  - Relatively moisture-insensitive
  - Stable compound at room temperature
  - Some carbon contamination observed
- Inclusion of water vapor appears to help eliminate carbon contamination [J.S. Kim *et al*., 1993]



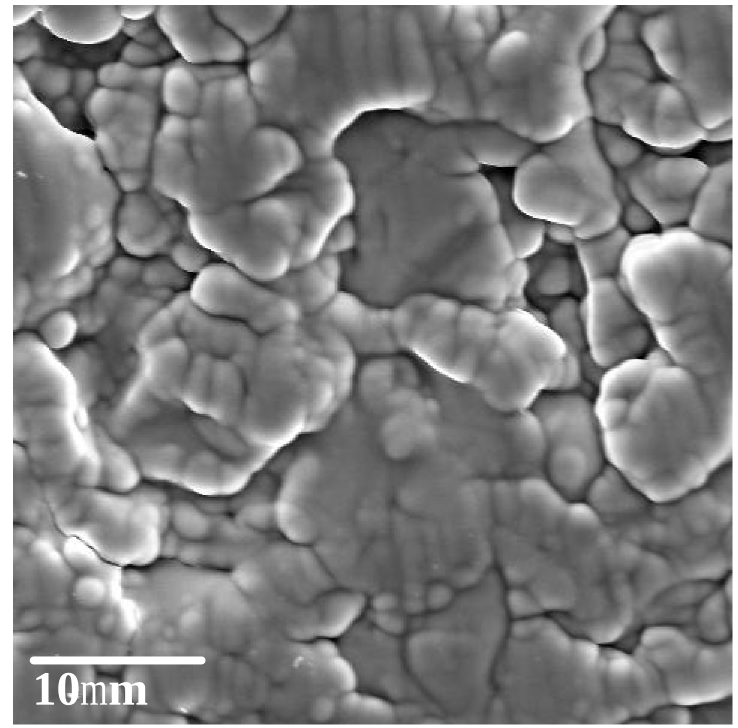
Cold-wall Al_2O_3 MOCVD System Constructed



Uniform and Conformal MOCVD Al_2O_3 Seal Coating Was Prepared at 500°C



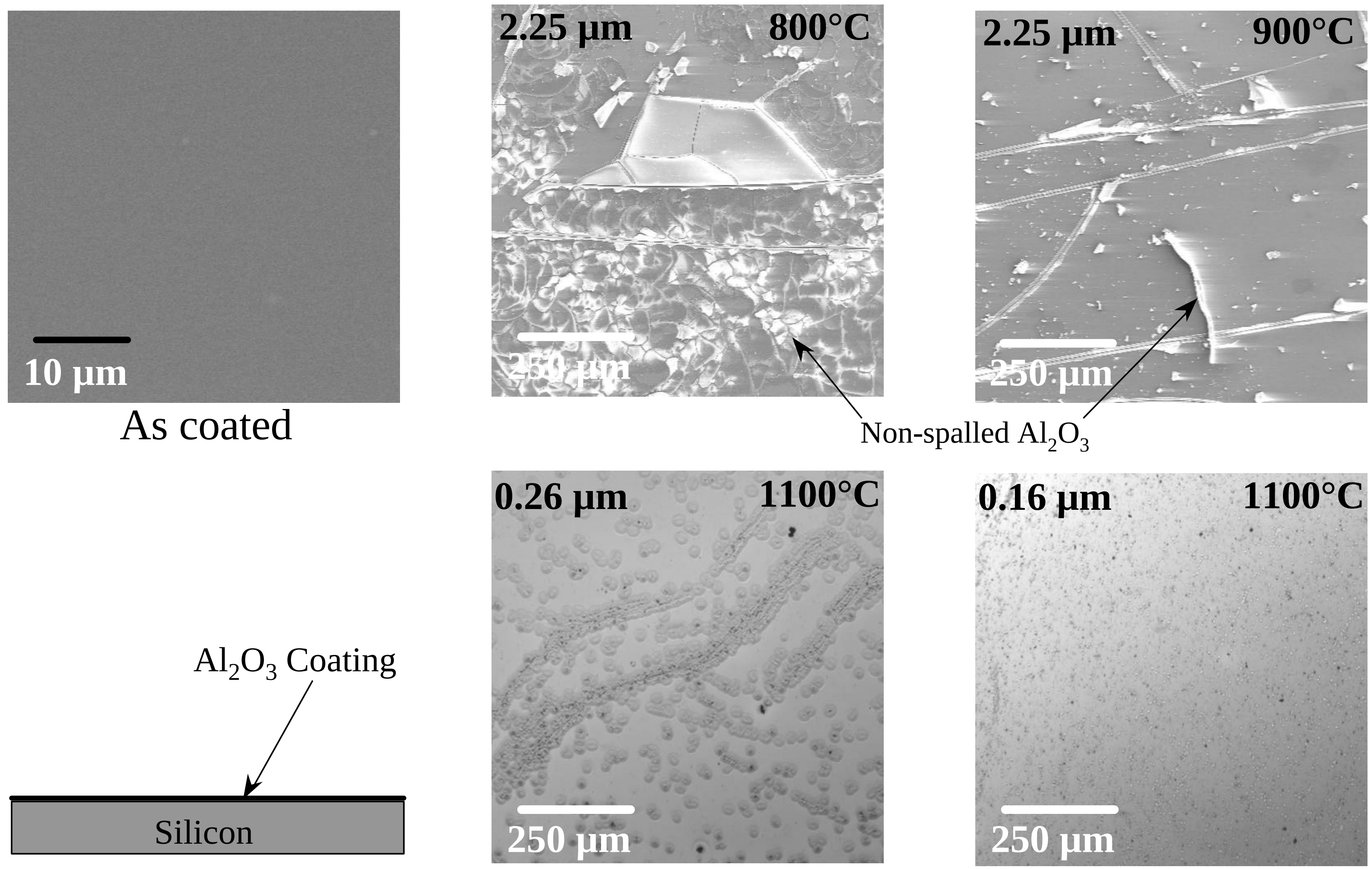
Al_2O_3 on Silicon



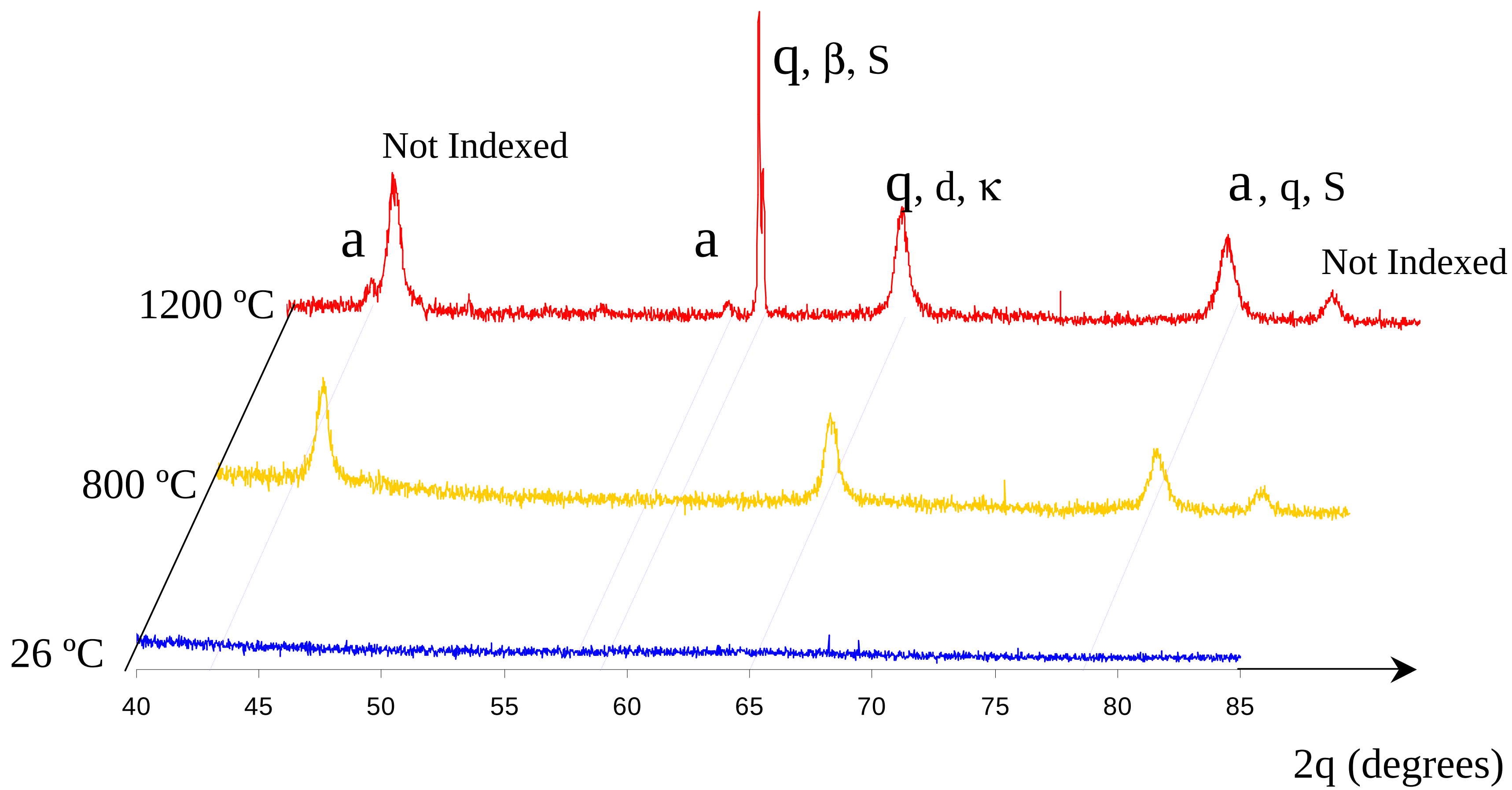
Al_2O_3 on CSZ

Thermal Stability of MOCVD Al_2O_3 Coating

Thinner Al_2O_3 Coating on Silicon Did Not Spall upon Annealing



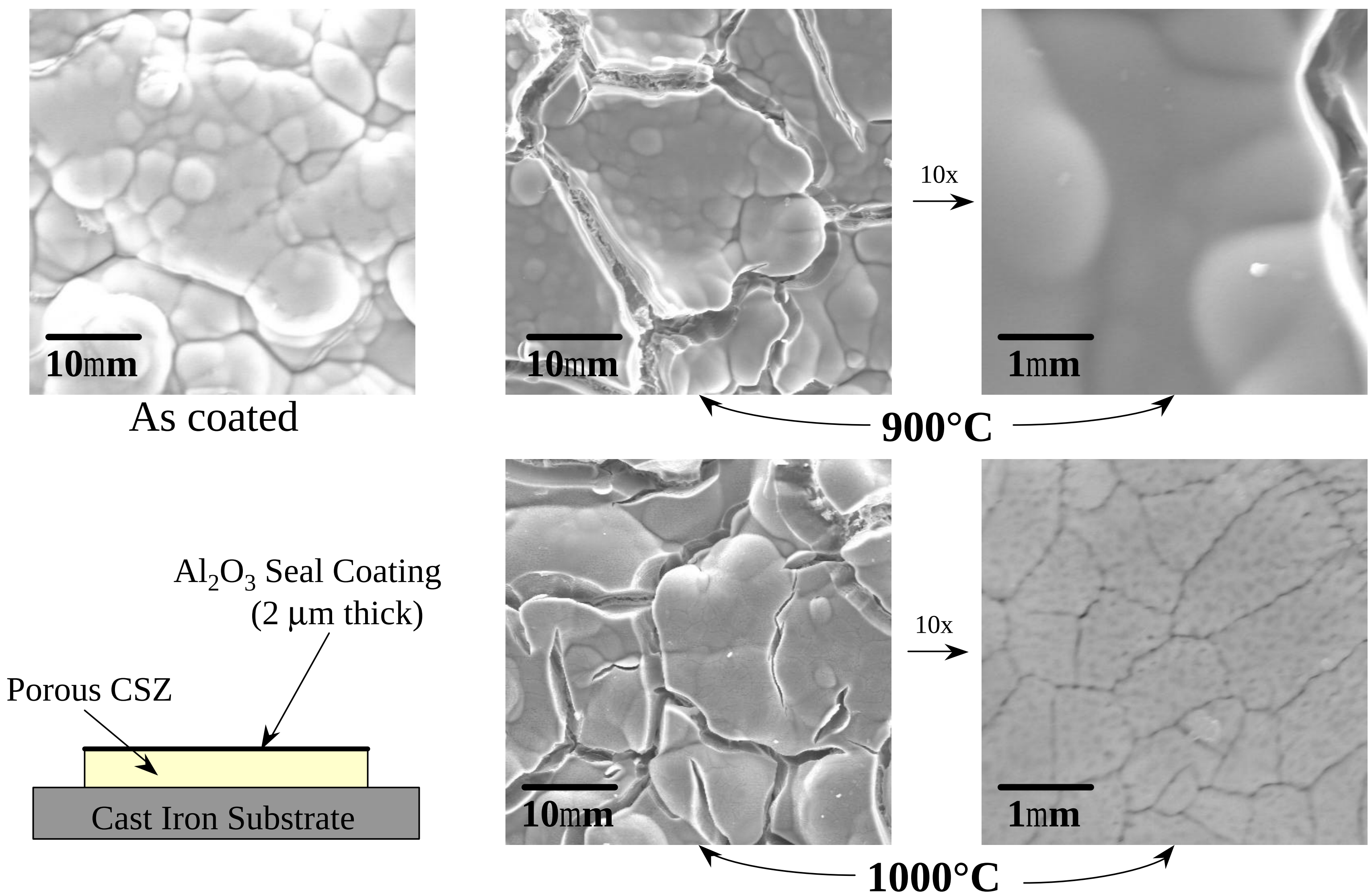
Crystallization of Al_2O_3 Occurred Relatively Rapidly (<20 Hours) at 700°C to 1200°C



a: α-Al_2O_3 **S**: $Al_2Si_4O_{10}$

Not much Al_2O_3 remained on the substrate for XRD analysis

Al_2O_3 on Constrained CSZ/Iron Substrate Cracked Upon Annealing



Comparison & Summary

Annealing of MOCVD Al_2O_3 Leads to Inadequate Adhesion and Sealing

- Considerable spallation on silicon with 2.25 μm coating
  - CTE mismatch
  - Volume shrinkage due to crystallization (> ~9%)
- Sub-micron coatings on silicon were less susceptible to spallation
- Adhered on CSZ, but coating cracked as crystallization occurred
  - Less CTE mismatch with CSZ than with Si
  - Better adhesion may be due to mechanical interlocking at CSZ/coating interface
  - Volume shrinkage still significant (> ~ 9%)

Comparison of Chloride-based Al_2O_3 vs. MOCVD Al_2O_3

	Chloride-based Al_2O_3	***MOCVD Al_2O_3***
As prepared:	Conformal, mostly metastable (θ)	Conformal, amorphous
Thermally annealed:	Retained adhesion & no cracking	Severe cracking, despite adhesion
Crystallization:	θ-Al_2O_3 → α-Al_2O_3 ($\Delta V \sim -9\%$)	Amorphous → metastable, α-Al_2O_3 ($\Delta V > -9\%$)
Possible C & H impurities:	Highly unlikely	Possible, but minimized
Quality of sealing:	“Sufficient”	“Insufficient”

Conclusions

- Chloride-based Al_2O_3 coating deposited at 1050°C was mostly θ-Al_2O_3
  - Sealed the porous surface, although it transformed from θ- to α-Al_2O_3
- MOCVD Al_2O_3 coating could be prepared at 500°C, but was amorphous
  - Adhered to CSZ upon annealing, but cracked extensively
- Metastable Al_2O_3 coating (*e.g.*, θ-Al_2O_3) and appropriate processing modifications may be required