Morphology and High-temperature Stability of Amorphous Alumina Coatings Deposited on Si and CeO_2-Stabilized ZrO_2 by MOCVD

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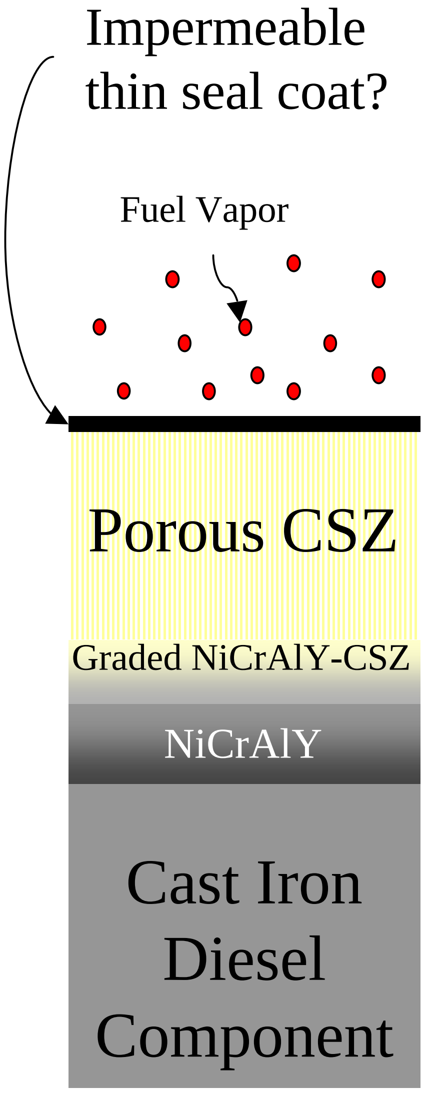
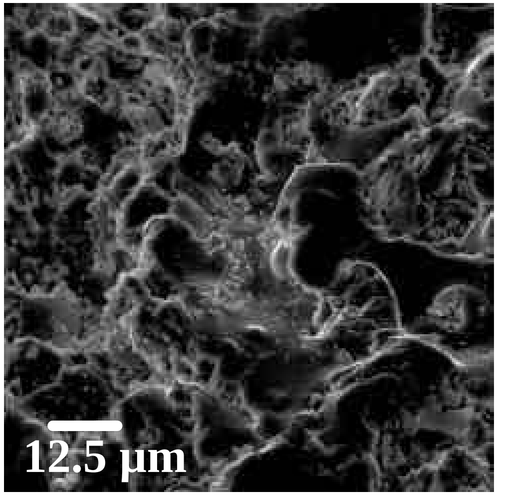
Rationale for Seal Coating

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

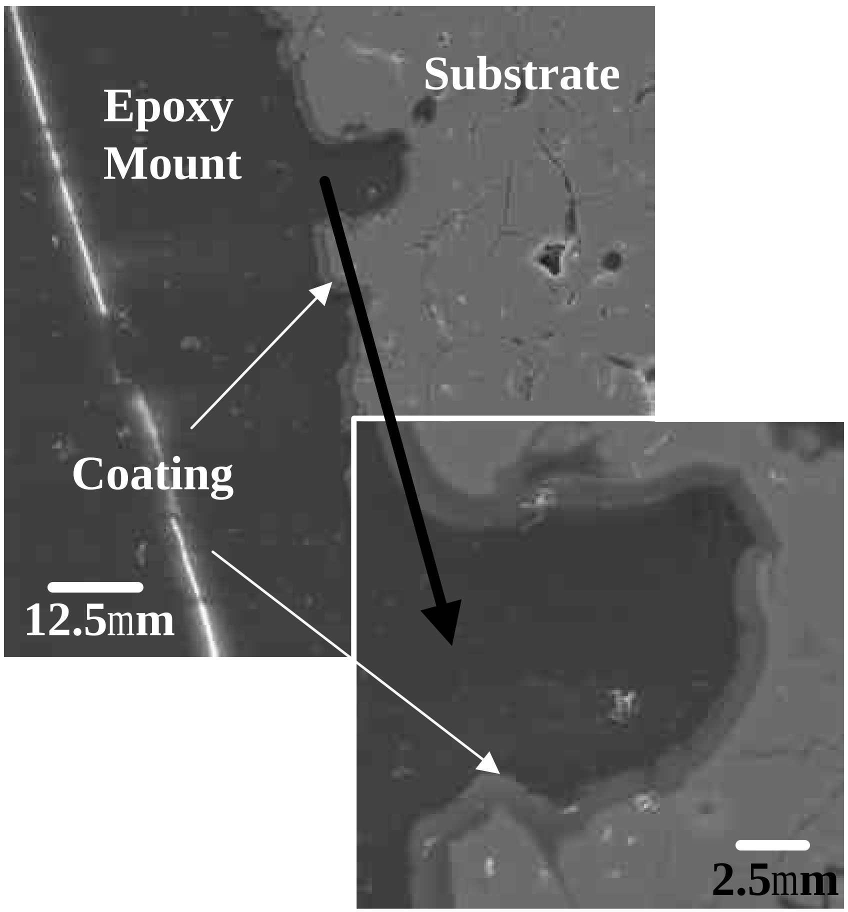
- High-temperature chloride-based CVD processes were used:

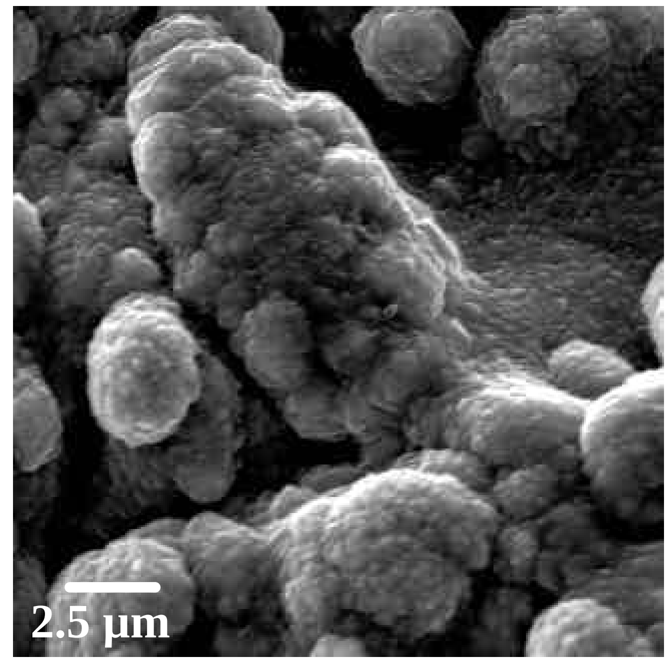
$$2AlCl_3 + 3CO_2 + 3H_2 \rightarrow Al_2O_3 + 6HCl + 3CO \quad (1050°C)$$

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

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

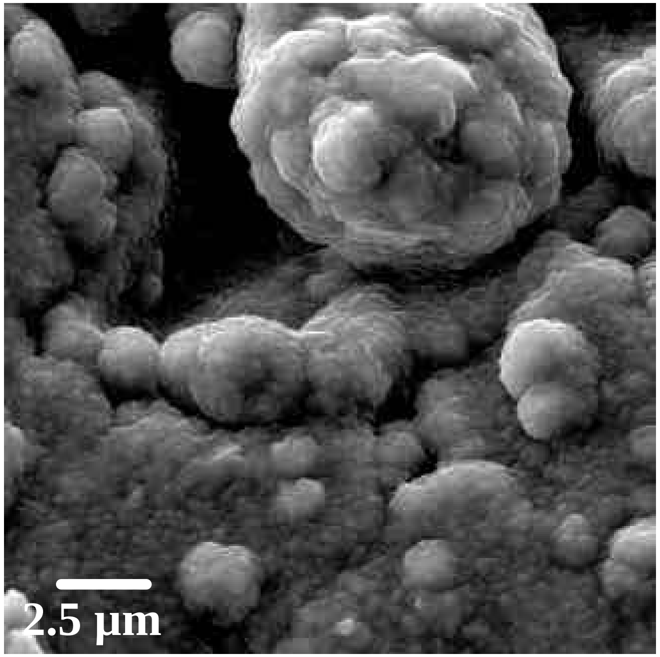
Al_2O_3 Seal Coating (from Chloride Process) Was Uniform and Conformal



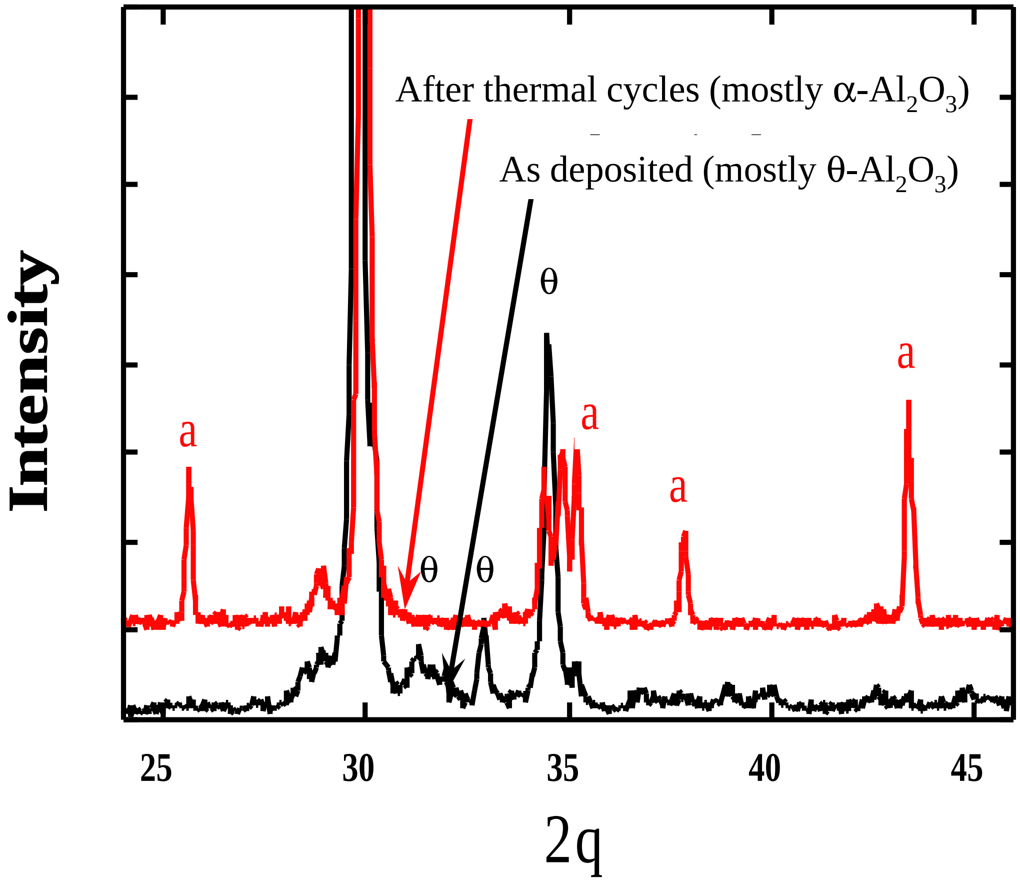


As coated

Al_2O_3 Seal Coating (from Chloride Process) Was Stable upon Thermal Cycling



After 49 1-hr. Cycles
to 1150°C



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

- Al_2O_3 was able to seal the porous CSZ surface
  - Although it transformed from θ- to α-Al_2O_3

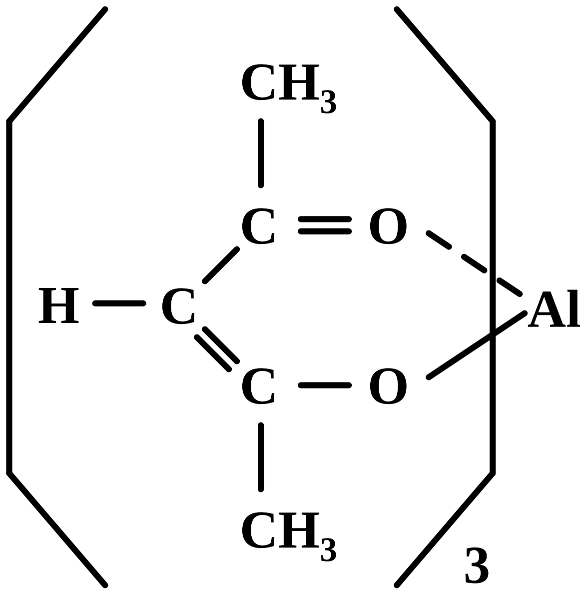
Free-standing CSZ without seal coating:

Free-standing CSZ coated and annealed:

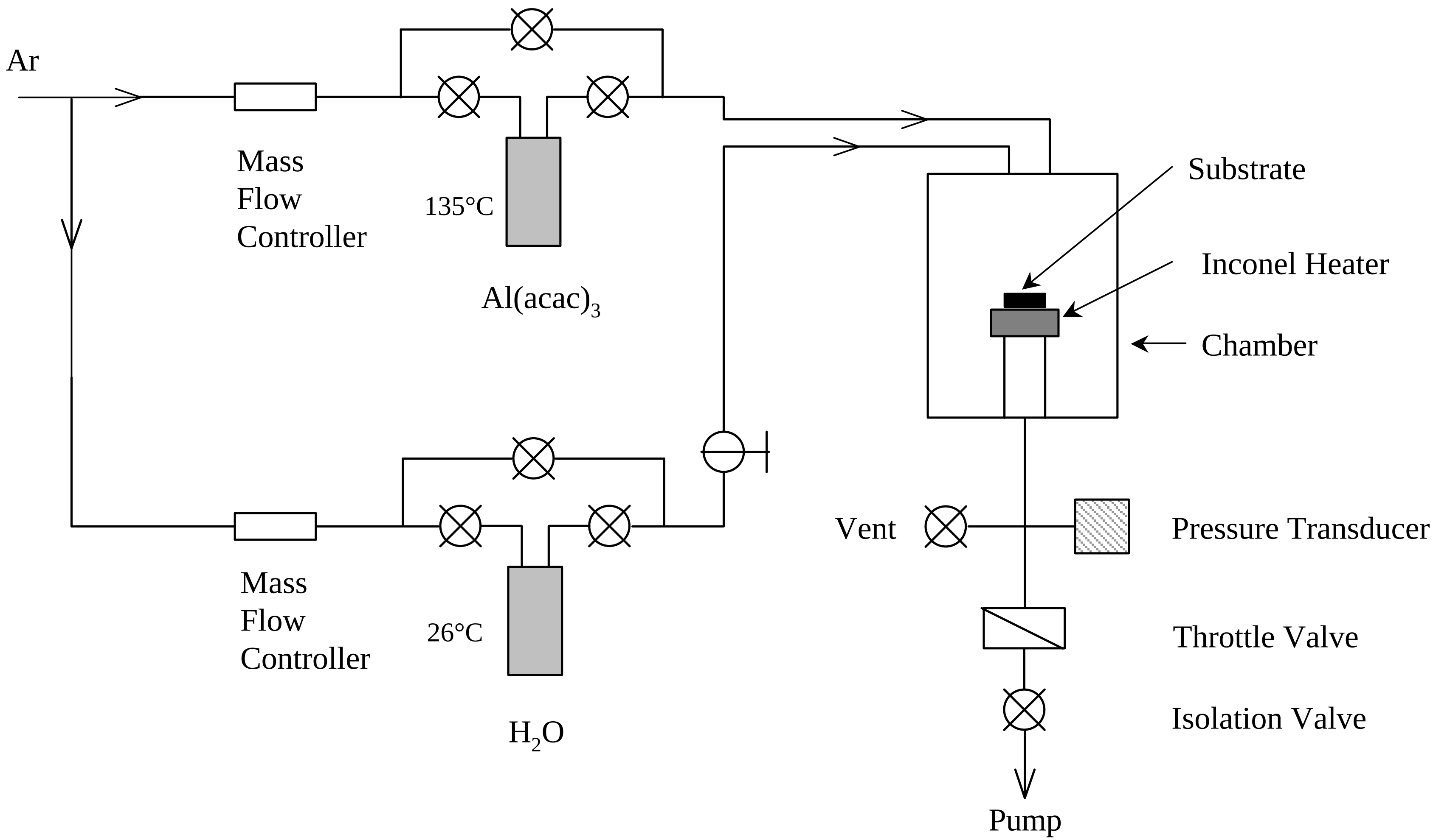
- $3Al_2O_3{\cdot}2SiO_2$ and SiO_2 spalled during thermal cycling, probably due to CTE mismatch with respect to CSZ

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]

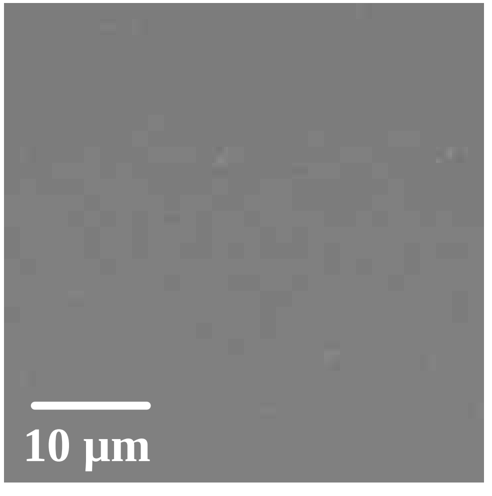


Cold-wall Al_2O_3 MOCVD System Constructed

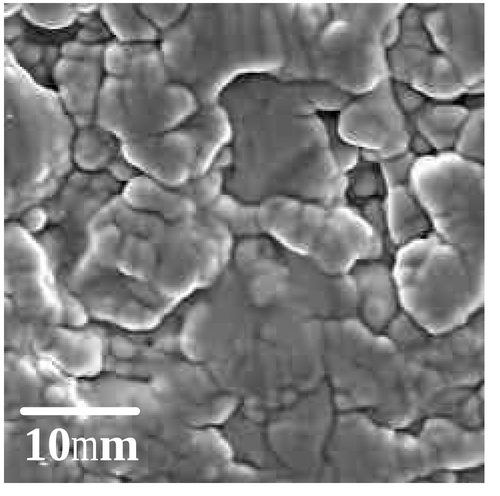


MOCVD Al_2O_3 Seal Coating Process Parameters Were Optimized

Substrate temperature	505 ±5°C
Total pressure	1.33 kPa
Argon supply rate ($Al(acac)_3$ / H_2O)	120 / 20 cm^3/min
Effective flow rate ($Al(acac)_3$ / H_2O)	0.43 / 0.67 cm^3/min
$Al(acac)_3$ vaporization temperature	130-135°C



Al_2O_3 on Si

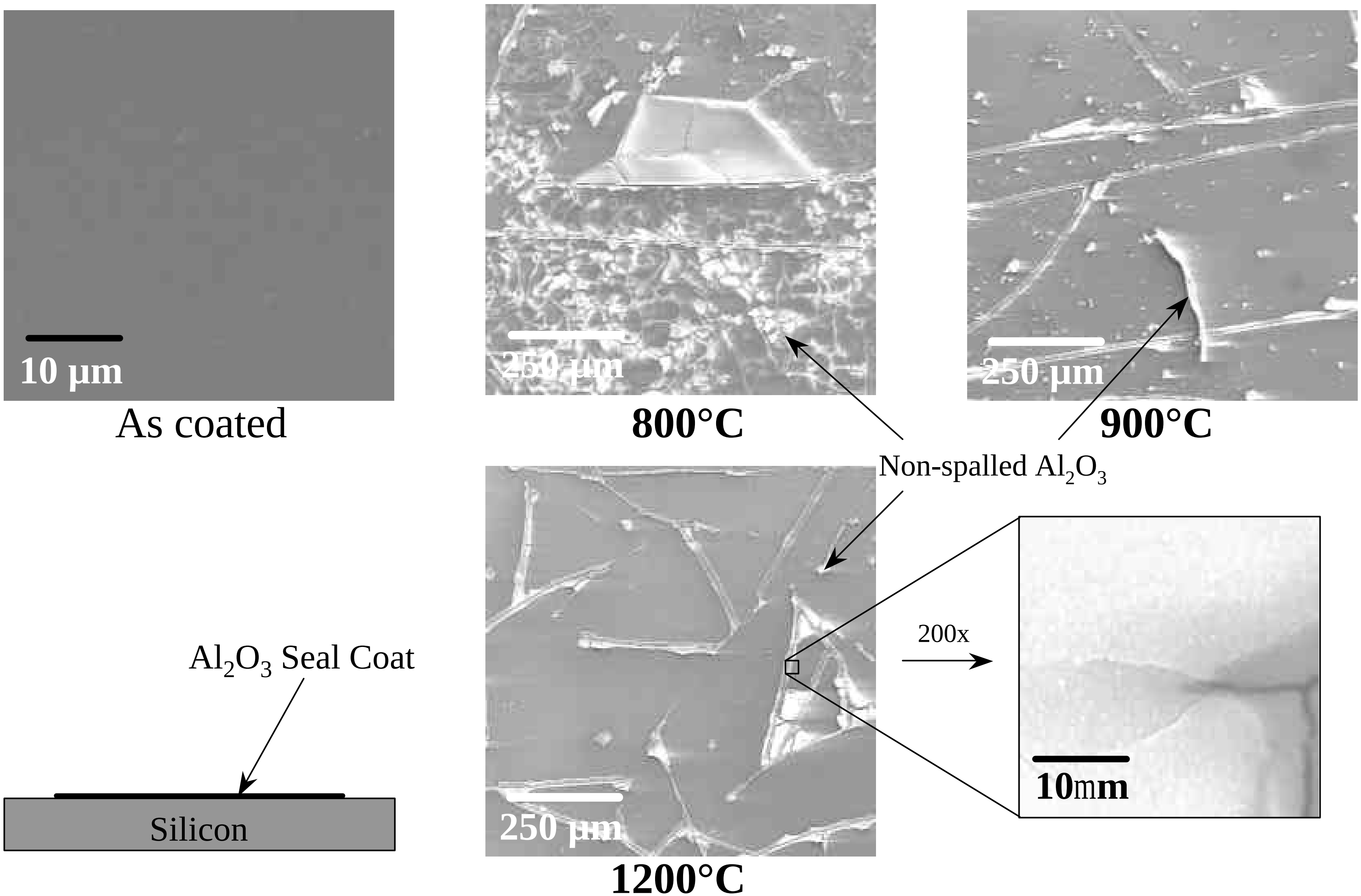


Al_2O_3 on CSZ

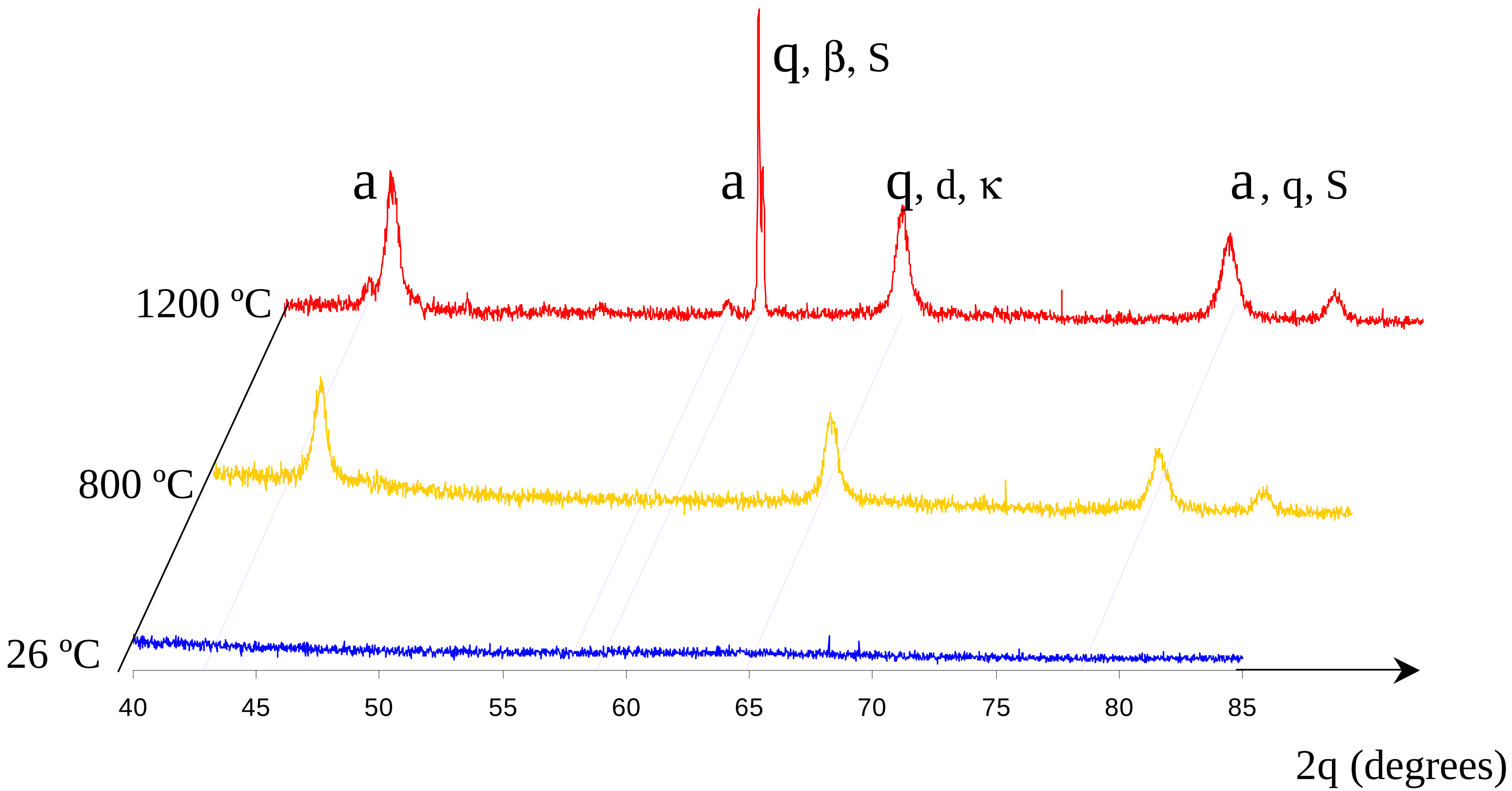
Experimental Approach to Testing MOCVD Al_2O_3 Seal Coating

- Potential problems with MOCVD Al_2O_3 coating:
  - Amorphous Al_2O_3 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.

MOCVD Al_2O_3 on Silicon Spalled upon Annealing



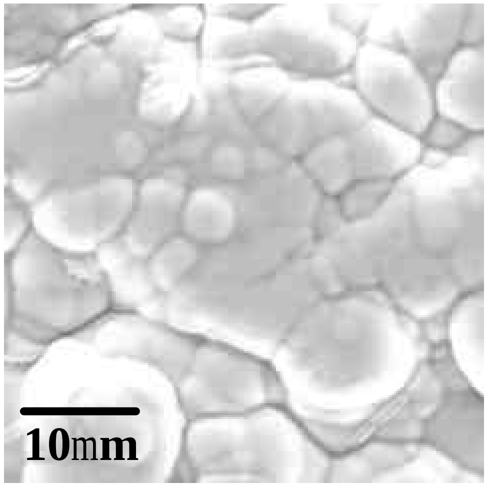
Crystallization of MOCVD Al_2O_3 Occurs Relatively Rapidly (20 Hours) at 700°C to 1200°C



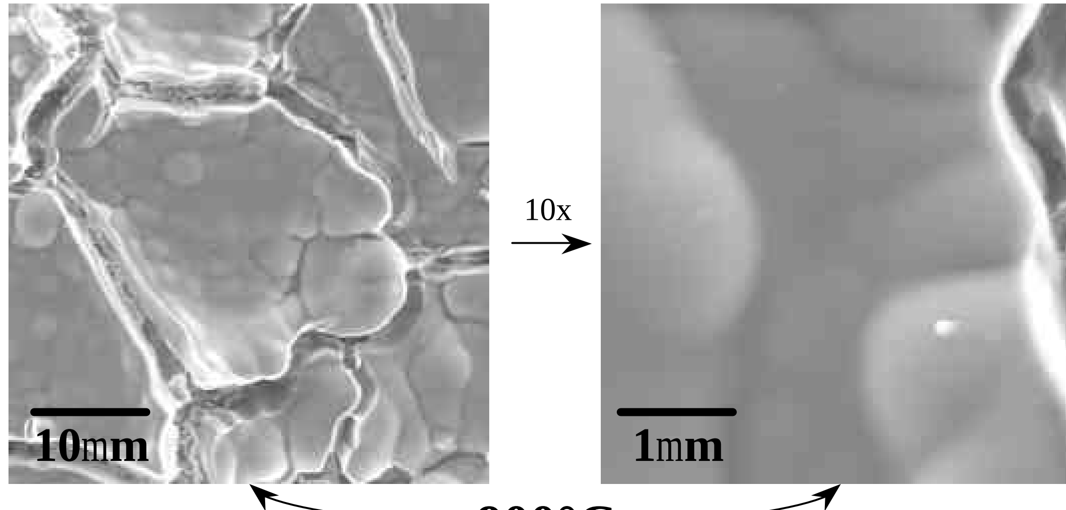
a: α-Al_2O_3 **S**: $Al_2Si_4O_{10}$

Not much Al_2O_3 remained on the substrate for XRD analysis

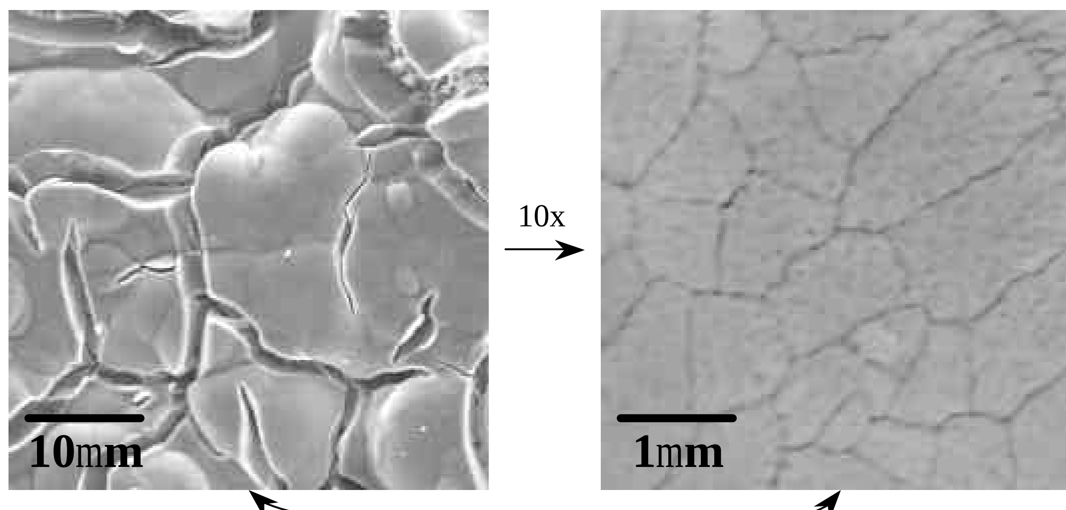
MOCVD Al_2O_3 on Constrained CSZ/Iron Cracked Upon Annealing



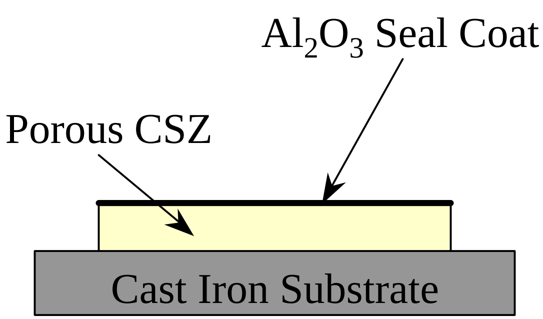
As coated.



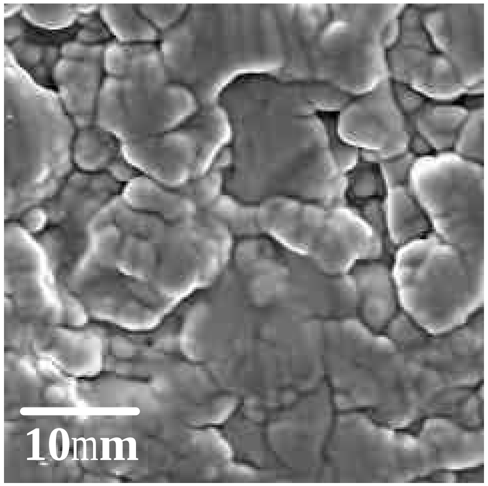
900°C



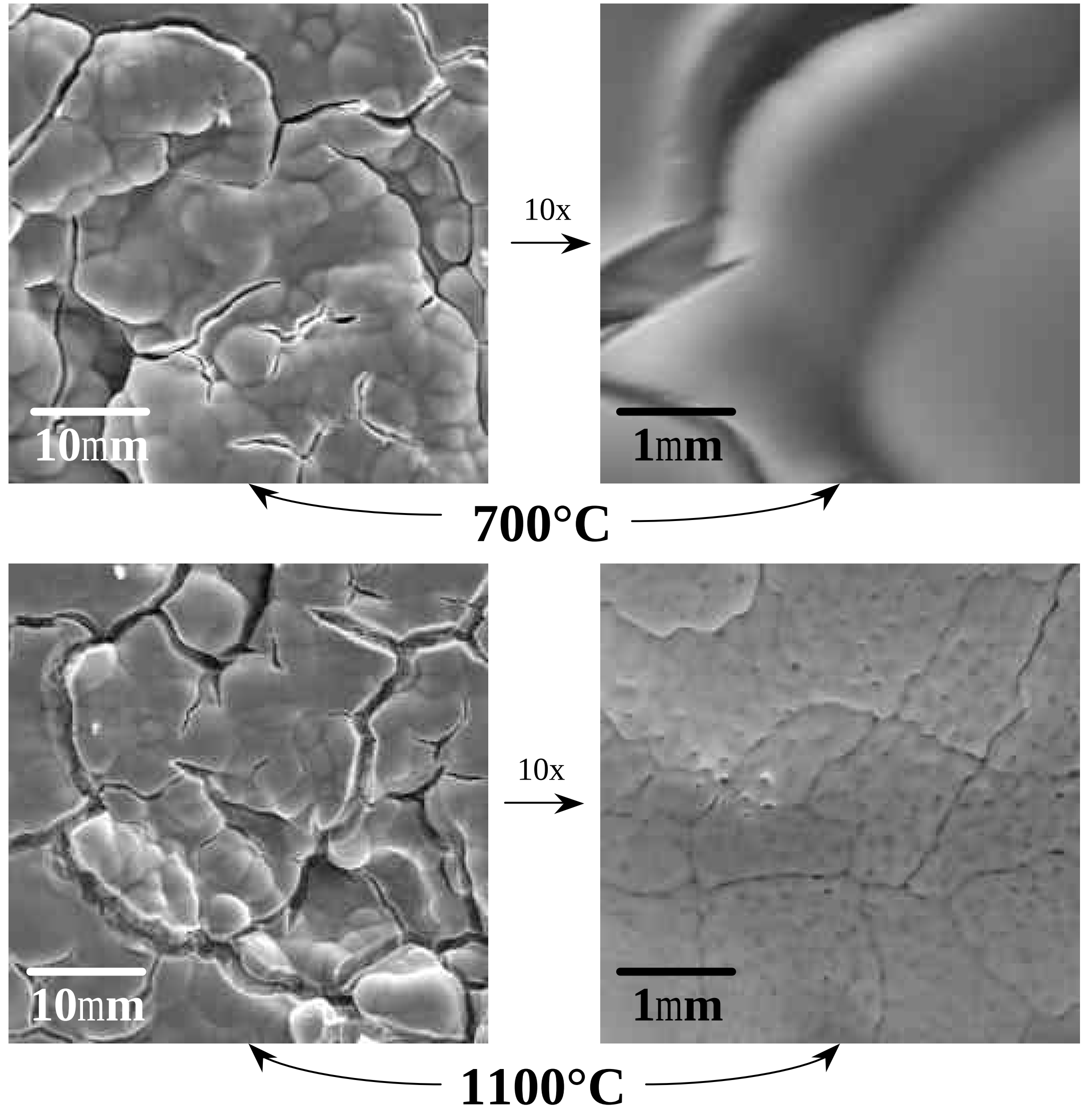
1000°C

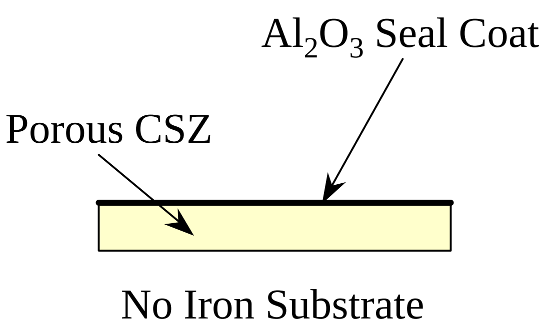


Metallic Substrate Had No Discernable Effect on Coating Behavior



As coated.





Annealing of MOCVD Al_2O_3 Leads to Inadequate Adhesion and Sealing

- Considerable spallation on silicon
  - CTE mismatch
  - Volume shrinkage due to crystallization
- 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 & structural integrity	Severe cracking, despite adhesion
Crystallization:	θ-Al_2O_3 $\rightarrow$ α-Al_2O_3 ($\Delta V < -9\%$)	Amorphous $\rightarrow$ 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 contained significant amounts of θ-Al_2O_3.
- MOCVD Al_2O_3 coating could be prepared at 500°C, but was entirely amorphous.
- Metastable Al_2O_3 coating (θ-Al_2O_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.

Acknowledgments

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