Deposition of Environmental Protection Systems from Colloidal Suspension

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ASME Turbo Expo, Power for Land, Sea, and Air

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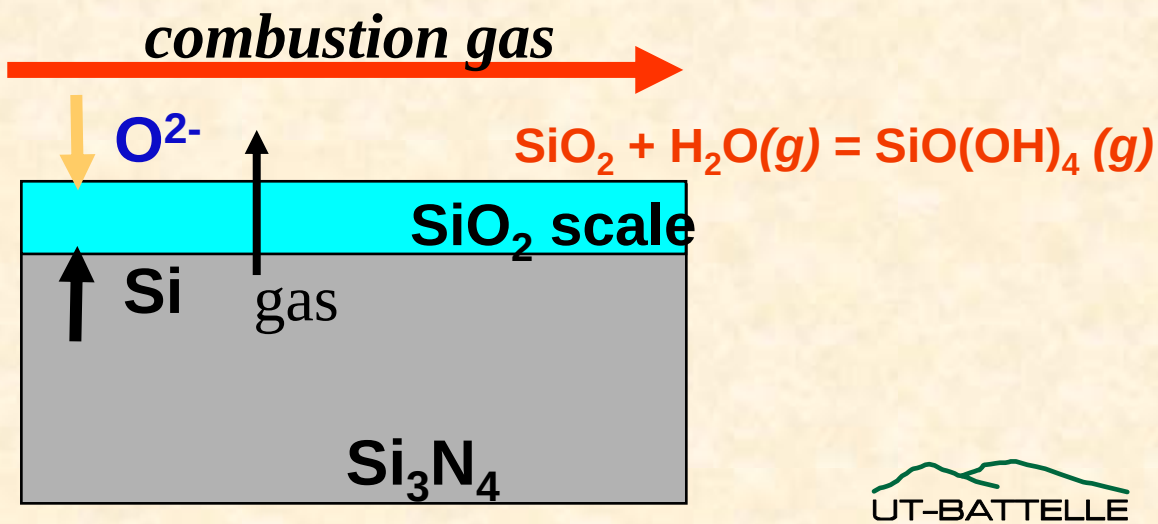
U. S. DEPARTMENT OF ENERGY

Outline

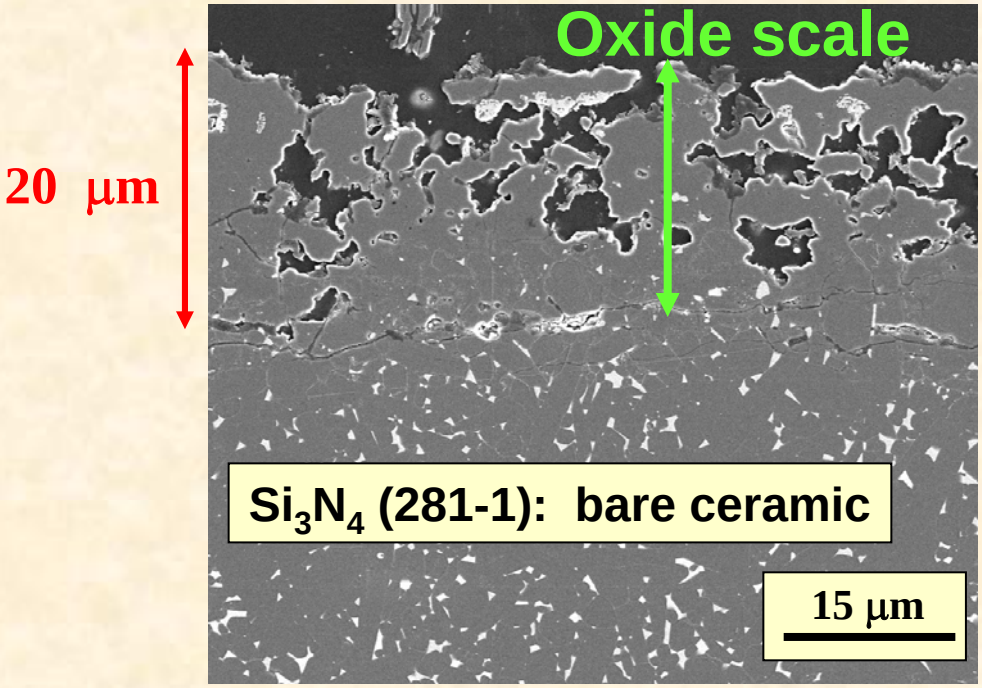
- Background: Advanced ceramics for microturbine applications
- Problem: Corrosion of ceramics in aggressive environments
- Objective: Develop & fabricate low-cost protective coatings
- Slurry processing of protective coating materials
- Research Highlights
- Summary
- Acknowledgements

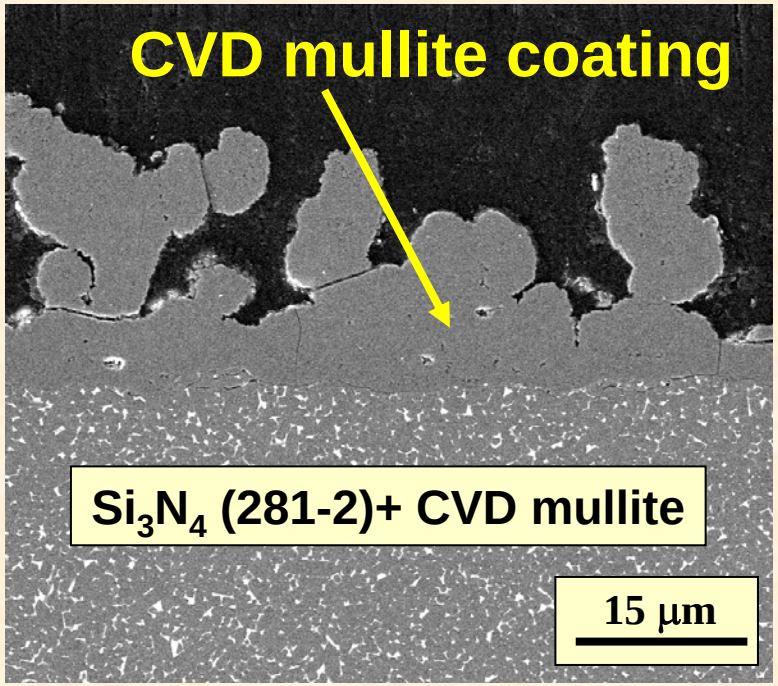
Advanced Ceramics for Microturbine Applications

- Si_3N_4 and SiC/SiC composites are candidate high temperature structural materials for hot section components in microturbine environments.
- Protective SiO_2 scales are the basis for corrosion resistance.
- Silica scales can be rapidly degraded in combustion environments.
  - Hot corrosion by alkali species (Strangman)
  - H_2O vapor & impurities accelerate SiO_2 growth (Deal, Opila, More et al.)
  - SiO_2 is volatile in H_2O (Venable, Opila)
  - Oxidation/volatilization increase w/ gas pressure & velocity (Robinson)



Are Protective Coatings Necessary?





500-h, 1200°C, 10 atm, 15% H_2O

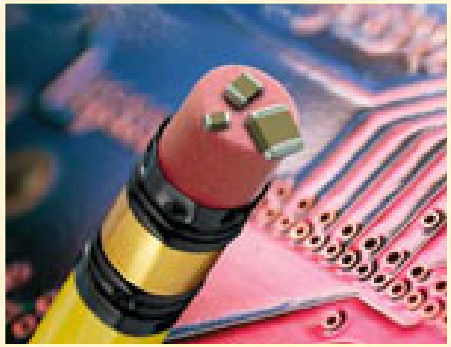
* Micrographs courtesy of J.A. Haynes/Oak Ridge National Laboratory

- **Protective coatings will be necessary to provide adequate ceramic component lifetimes.**
- **Coatings must be adherent, stable and protective in high temperature water vapor, thermal expansion matched with SiC or Si_3N_4, easy to manufacture, and cost effective.**

Coating Performance = *f*(Material + Processing + Environment)

Colloidal Assembly of Ceramic Devices and Coatings

2-D structures



$BaTiO_3$ capacitors

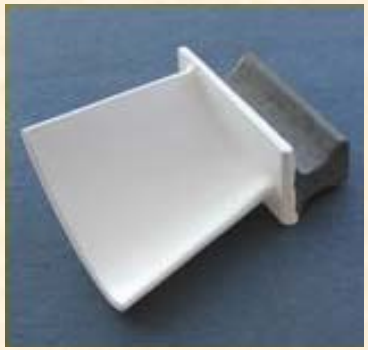
Tape casting

3-D structures

PZT motor arrays

Robotic deposition
3D inkjet printing

Coatings and Monoliths

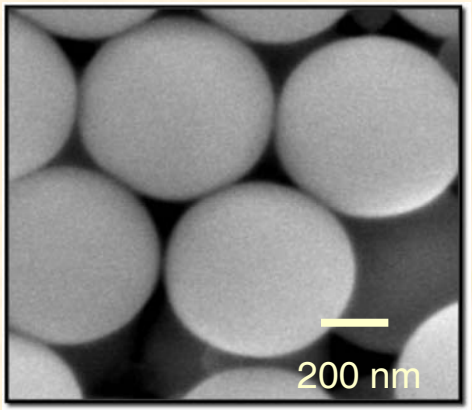


RE-silicate coating on
a Si_3N_4 rotor blade

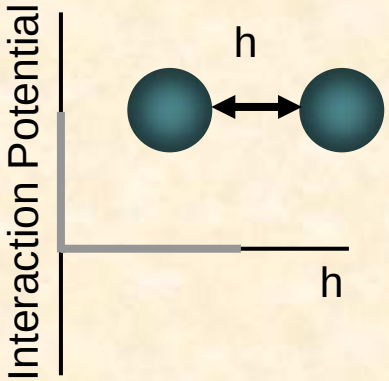
Gelcasting, slip casting
Dip coating

Interparticle Forces Must be Controlled to Tailor Suspension Rheological Behavior

Colloidal particles --> basic "building blocks"

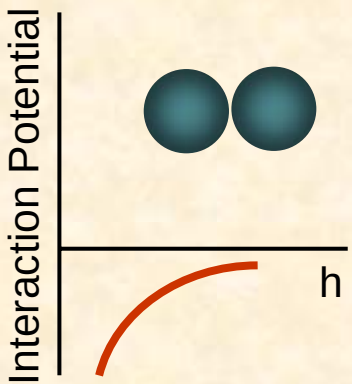


Hard sphere



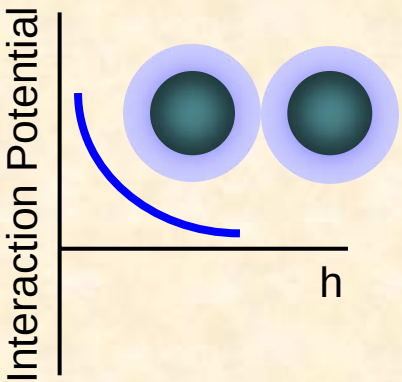
indexed matched
highly screened

Attractive



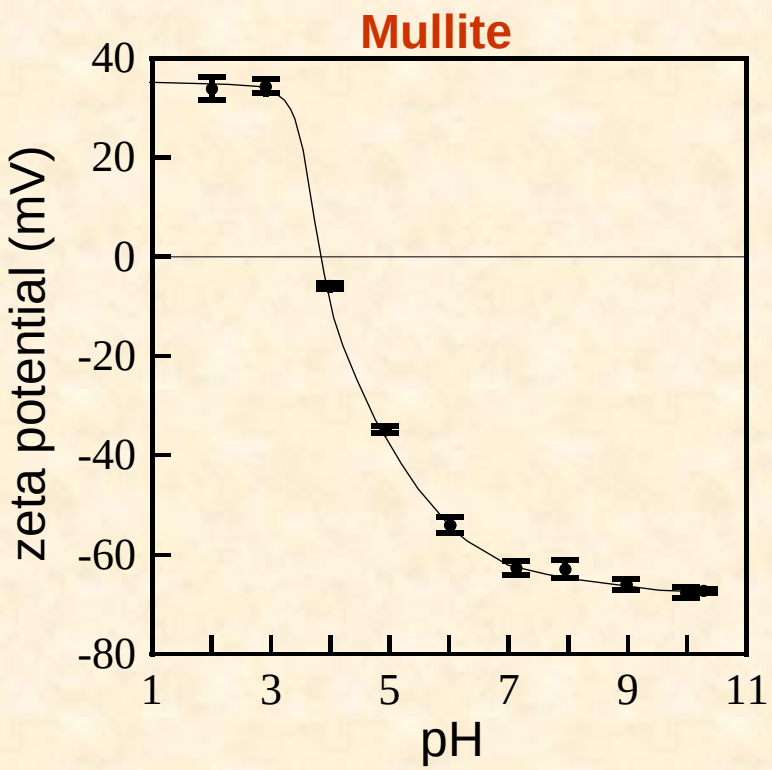
vdw forces
depletion forces

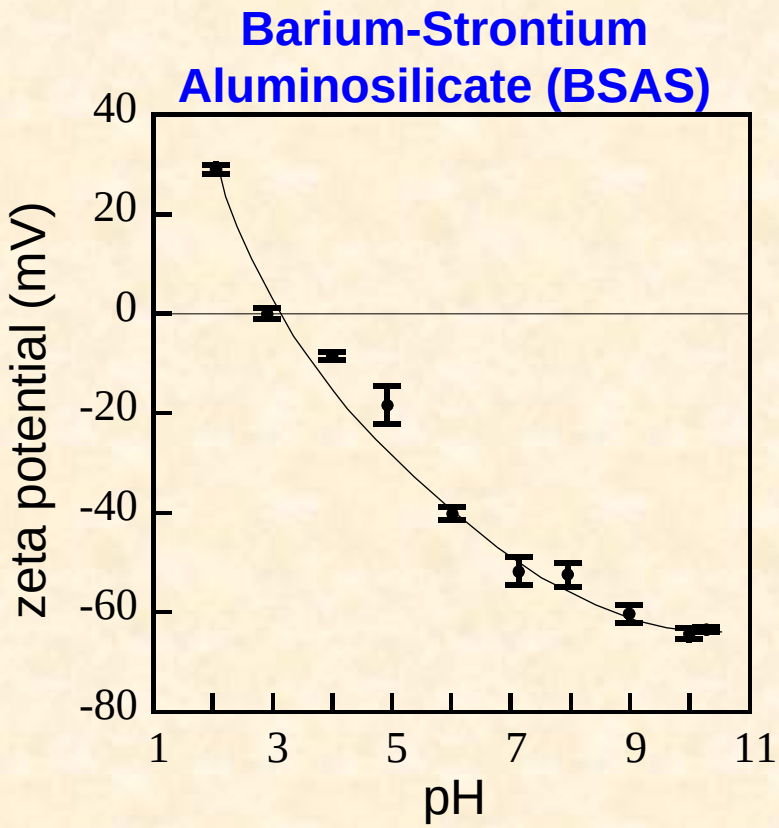
Soft Sphere



charge-stabilized
steric-stabilized

Surface (Zeta) Potential of Ceramic Particles in Aqueous Media
(Dilute Suspensions, 10^{-3} vol%)

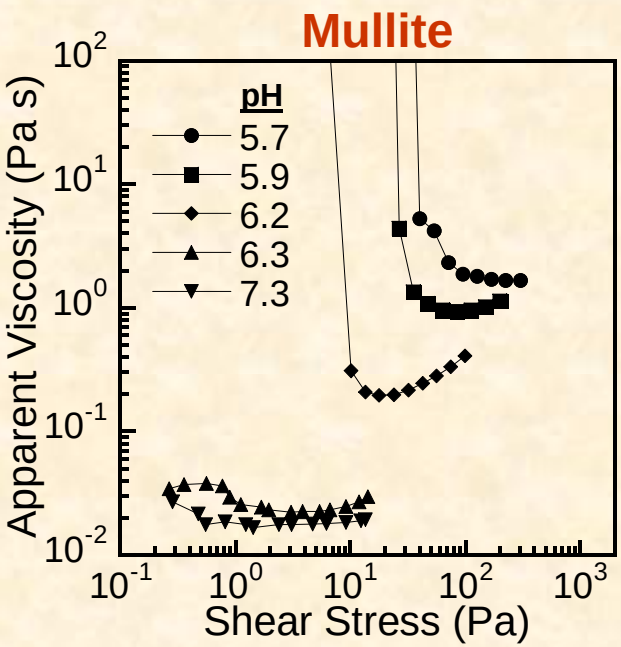


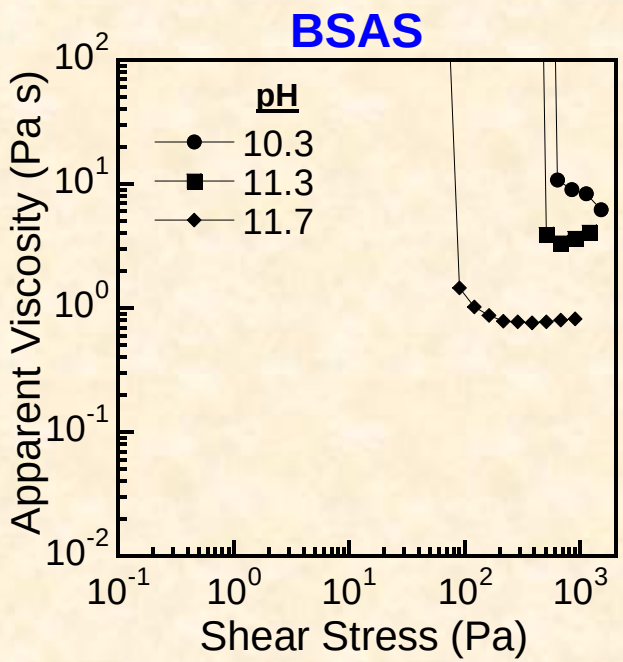


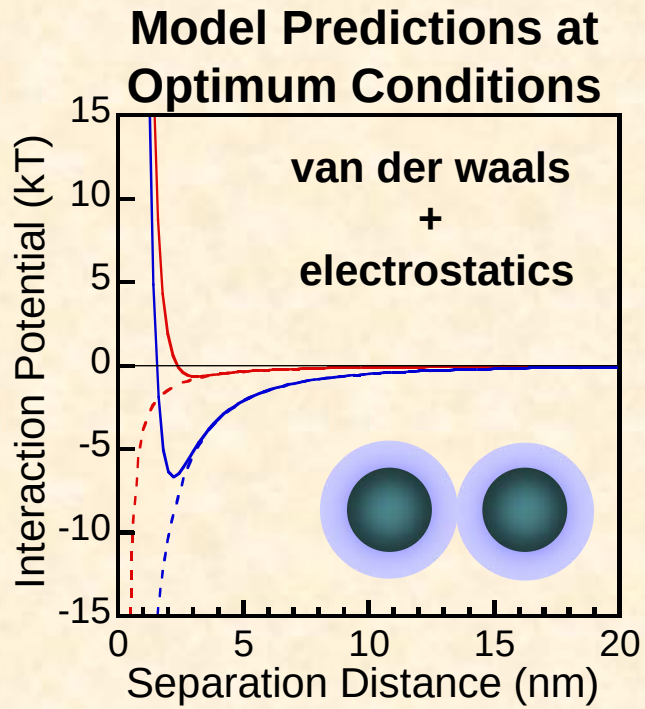
- **The isoelectric point (IEP) of mullite and BSAS is at pH 3-4.**
- **Above the IEP, the zeta potential is negative.**
- **-63 mV achieved at pH 7 and 10 for mullite and BSAS, respectively.**

Charge Stabilization of Ceramic Suspensions

(45 vol%, pH adjusted with 1 *M* HNO_3 and 1 *M* NH_4OH)



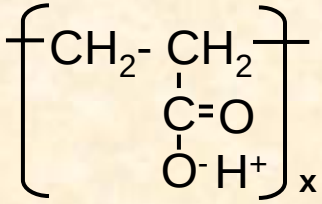




- **Mullite suspensions are stable (Newtonian) just above pH 6.3.**
- **BSAS suspensions cannot be stabilized by bare surface charge modification.**
- **Results agree with model predictions.**

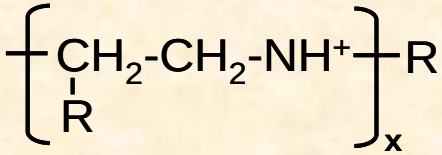
Polyelectrolyte Dispersants

Anionic

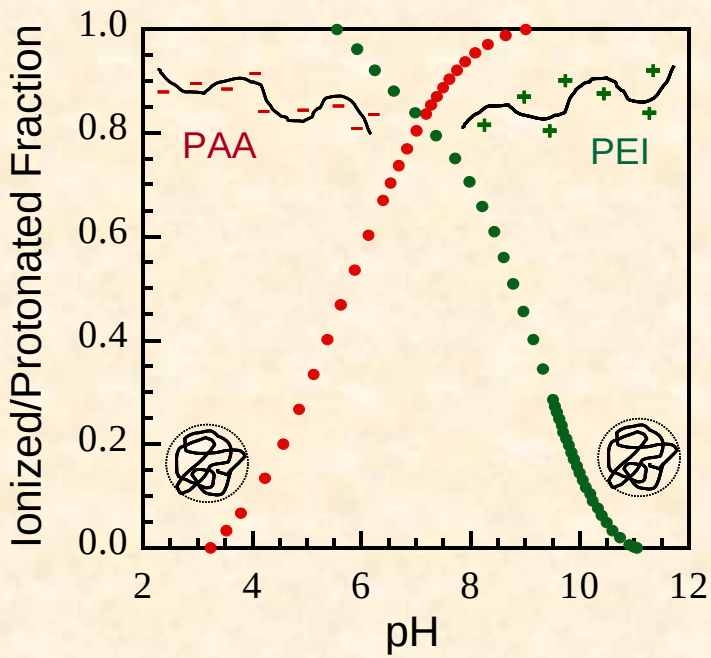


Poly(acrylic acid) (PAA)

Cationic



Poly(ethylene imine) (PEI)



Guidelines for Adsorption

IEP < 6 cationic

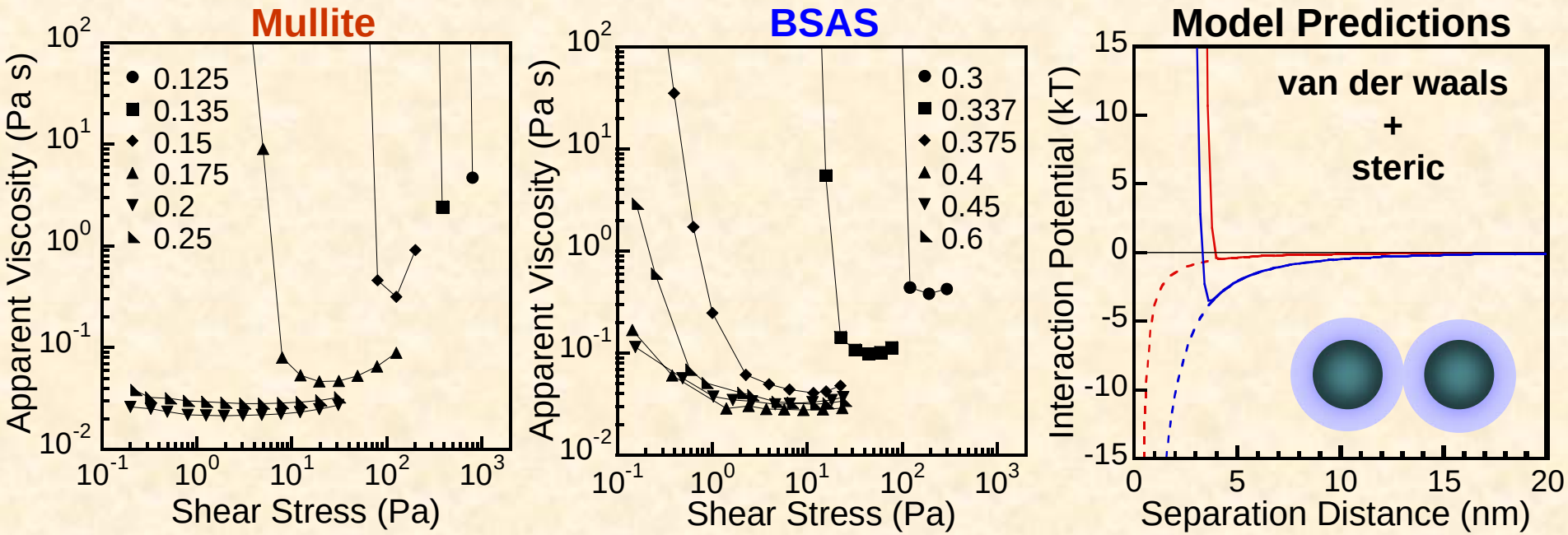
IEP 6-8 anionic or cationic

IEP > 8 anionic

Ceramic Material	IEP	Dispersant
SiO_2	3-4	PEI
SiC	3-4	PEI
Si_3N_4 (E10)	3-4	PEI
BSAS	3-4	PEI
Mullite	3-4	PEI
RE-silicates	3-6	PEI
Al_2O_3	8-9	PAA
Y_2O_3	8-9	PAA
MgO	12-13	PAA

Polyelectrolyte Stabilization of Ceramic Suspensions

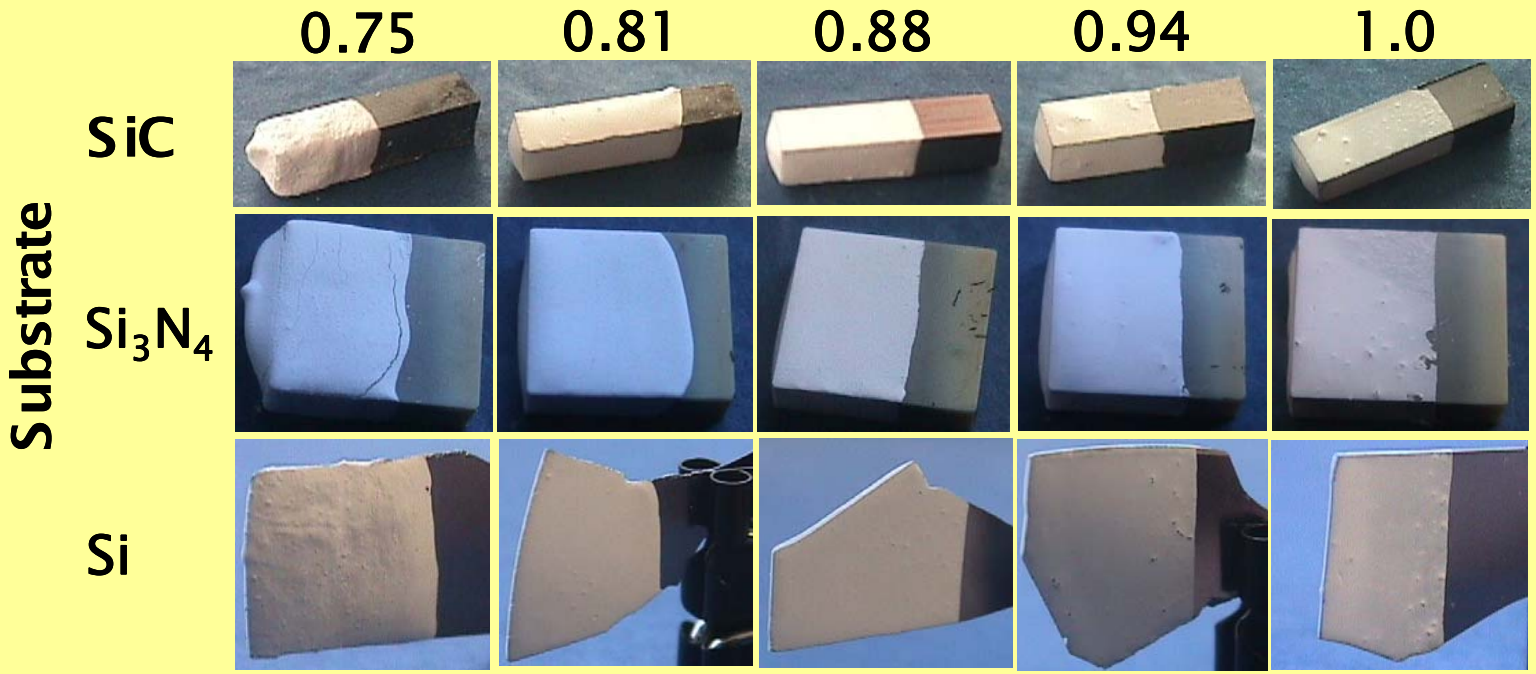
(45 vol%, pH 7, 10,000 g/mole PEI)



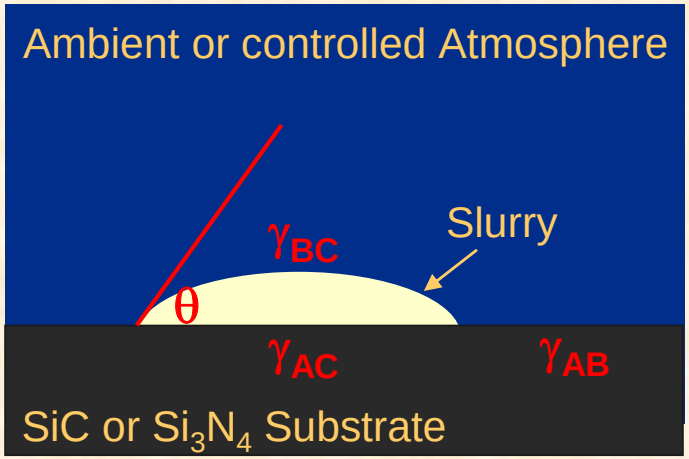
- **Newtonian and near-Newtonian flow behavior achieved with the addition of 0.2 mg PEI/m^2 mullite and 0.4 mg PEI/m^2 BSAS, respectively.**
- **Results agree with model predictions.**

Resulting Coating Quality Depends Upon Slurry Rheology

Coatings formed by dipping substrates into mullite slurries (45 vol%) of varying PEI Concentration, $[PEI]/[PEI]_{crit}$



Wetting Behavior Controlled Through Use of Additives



Sessile Drop Measurements:
10 μL mullite suspension droplet on SiC

Mullite-Latex

$\phi_{mullite}$ = 0.25, pH 10

ϕ_{latex}	SiC	Si_3N_4
	θ	θ
0	55.0	71.5
0.034	49.5	50.5
0.076	40.0	40.5

BSAS-Latex

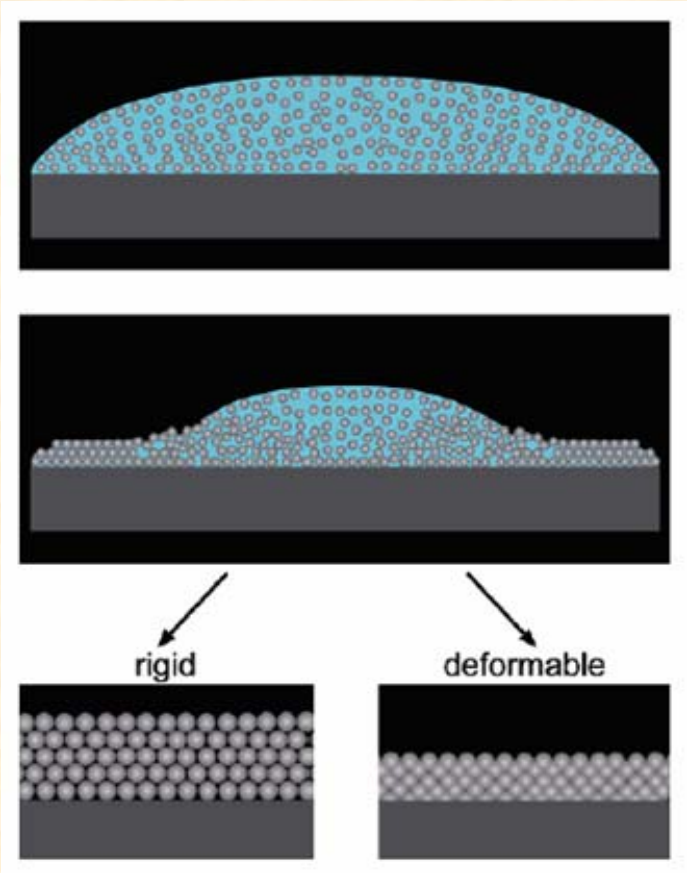
ϕ_{BSAS} = 0.25, pH 10

ϕ_{latex}	SiC	Si_3N_4
	θ	θ
0	53.0	85.5
0.034	48.0	49.0
0.076	44.5	41.5

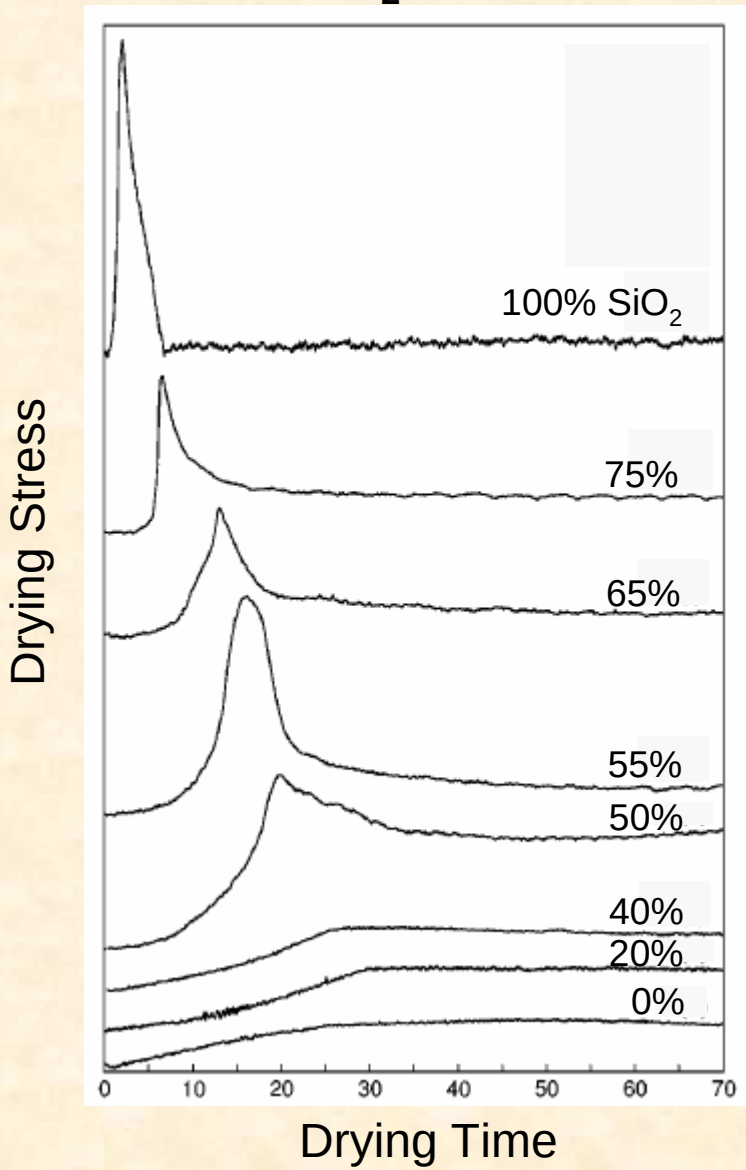
- **The contact angle (θ) depends on the interfacial energy between the coating and substate, the substrate and atmosphere, and the coating and atmosphere.**
- **The contact angle decreases with use of latex additives.**

Drying Stresses Reduced with Additives

Ceramic-Latex Binary Suspensions



SiO_2-Latex

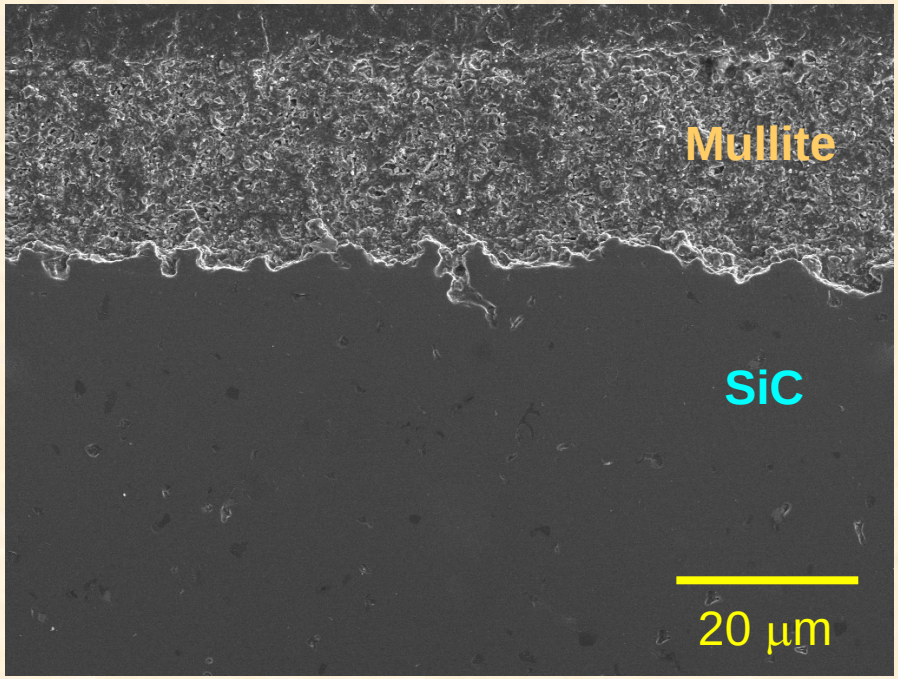


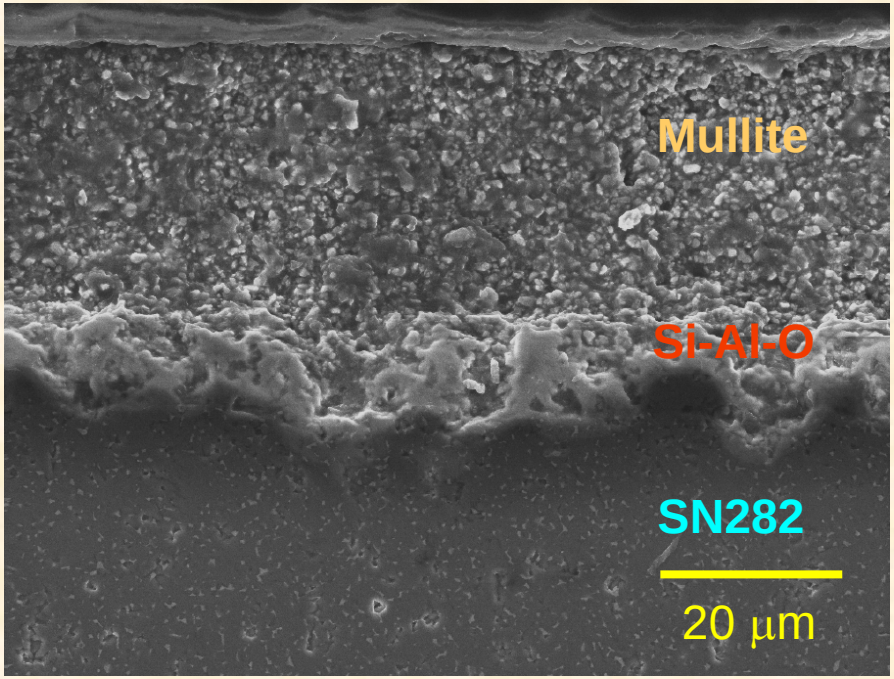
Deformable latex particles promote uniform,
Crack-free drying of slurry coatings

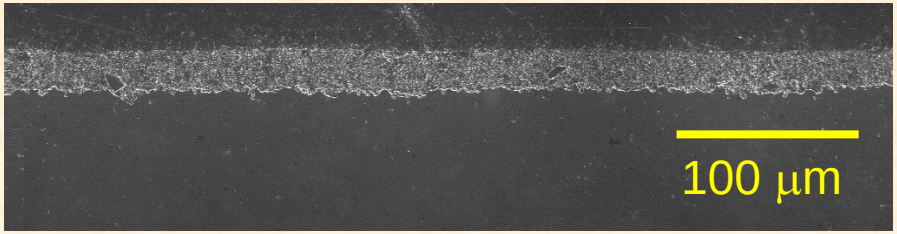
C. J. Martinez and J. A. Lewis, *Langmuir*, **18** [12] 2002

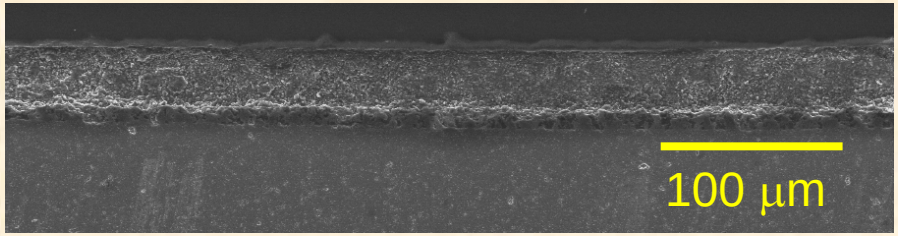
Formation of Thin, Uniform Mullite Coatings

Coating applied from 25 vol% mullite suspension w/ 5 vol% latex
Sintered in air, 1400 ^{o}C





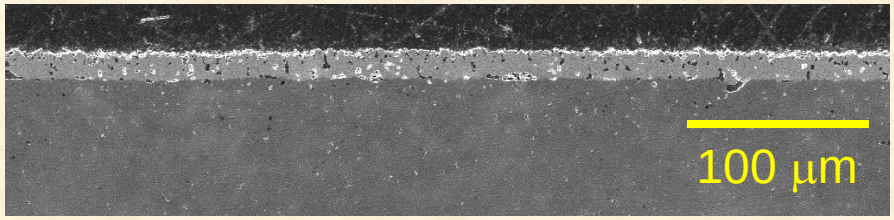


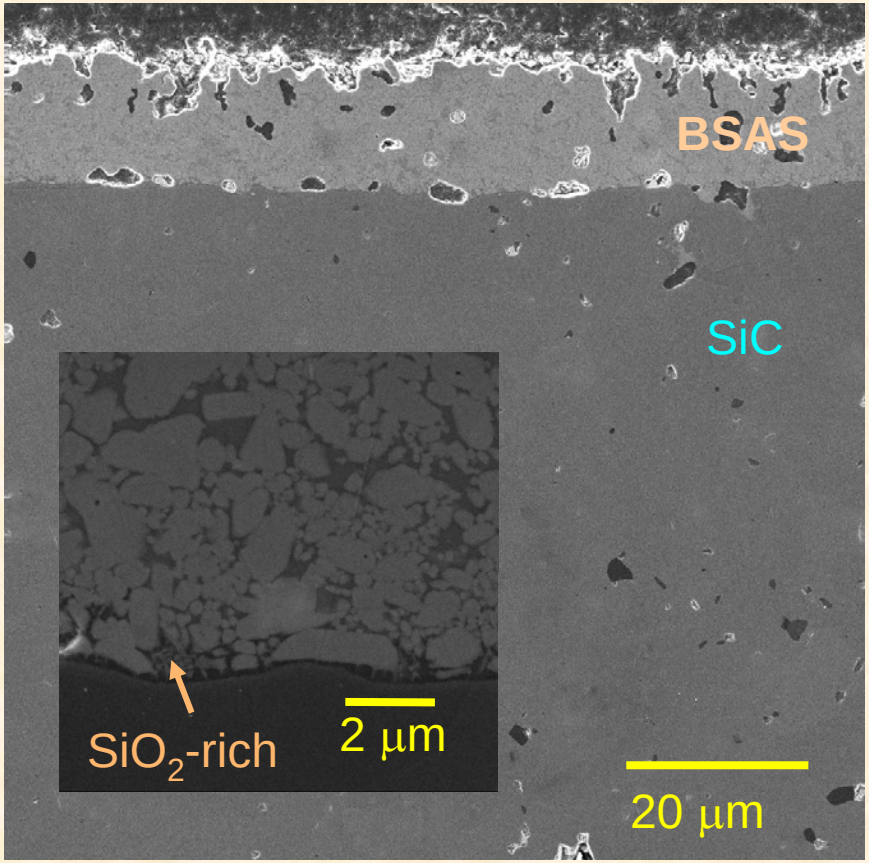


Formation of Thin, Uniform BSAS Coatings

Green coating, from 25 vol% BSAS suspension w/ latex

Sintered in air, 1300 ^{o}C

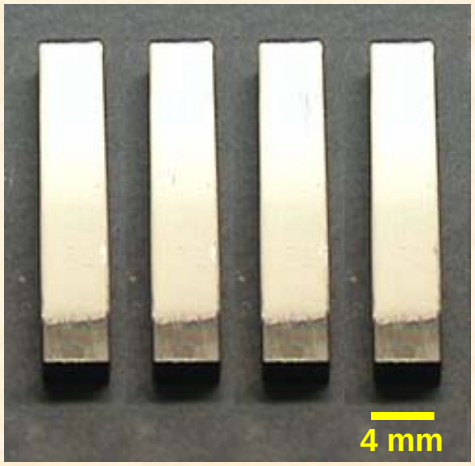




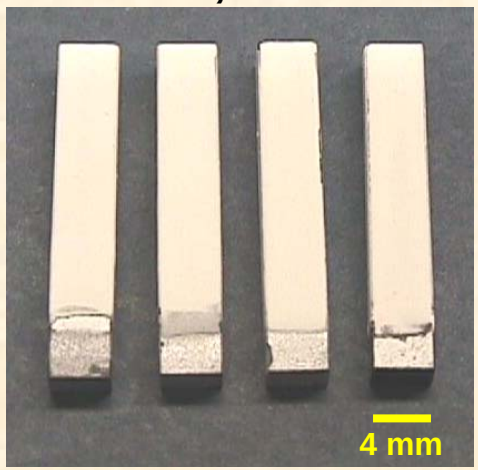
Exposure of Mullite Coated SiC and SN282 Test Bars

(500h Steam Exposure at 1200°C, 1 atm)

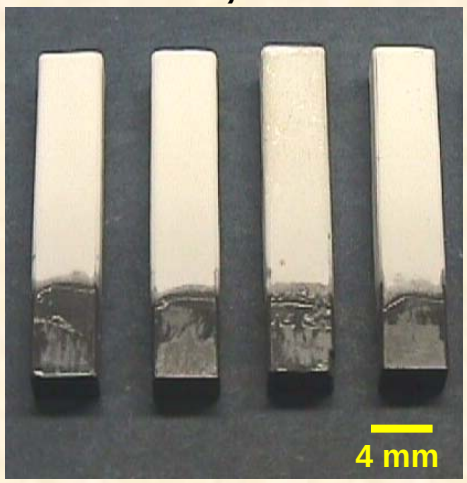
SiC, before



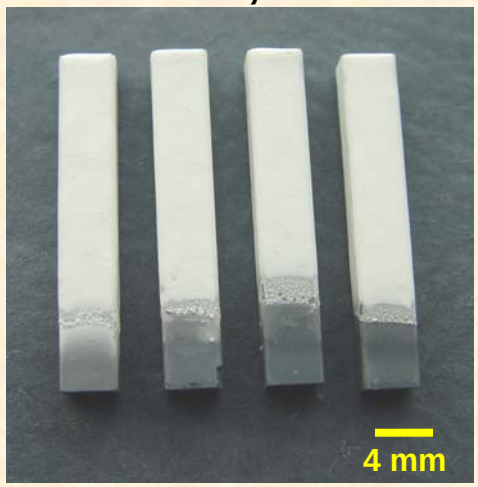
SiC, after



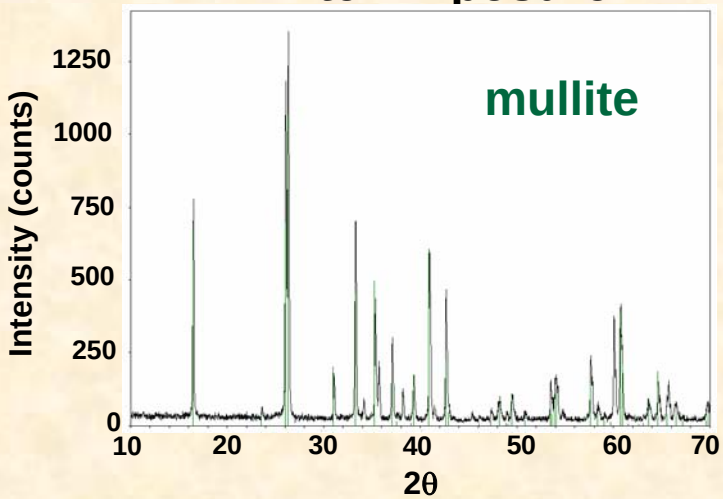
SN282, before

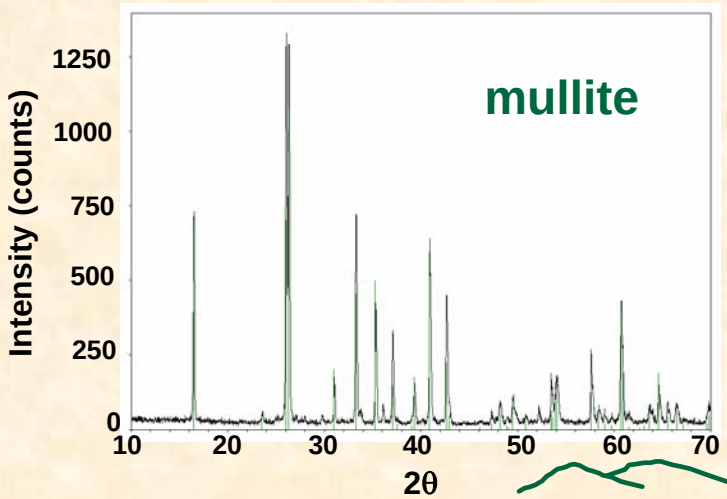


SN282, after

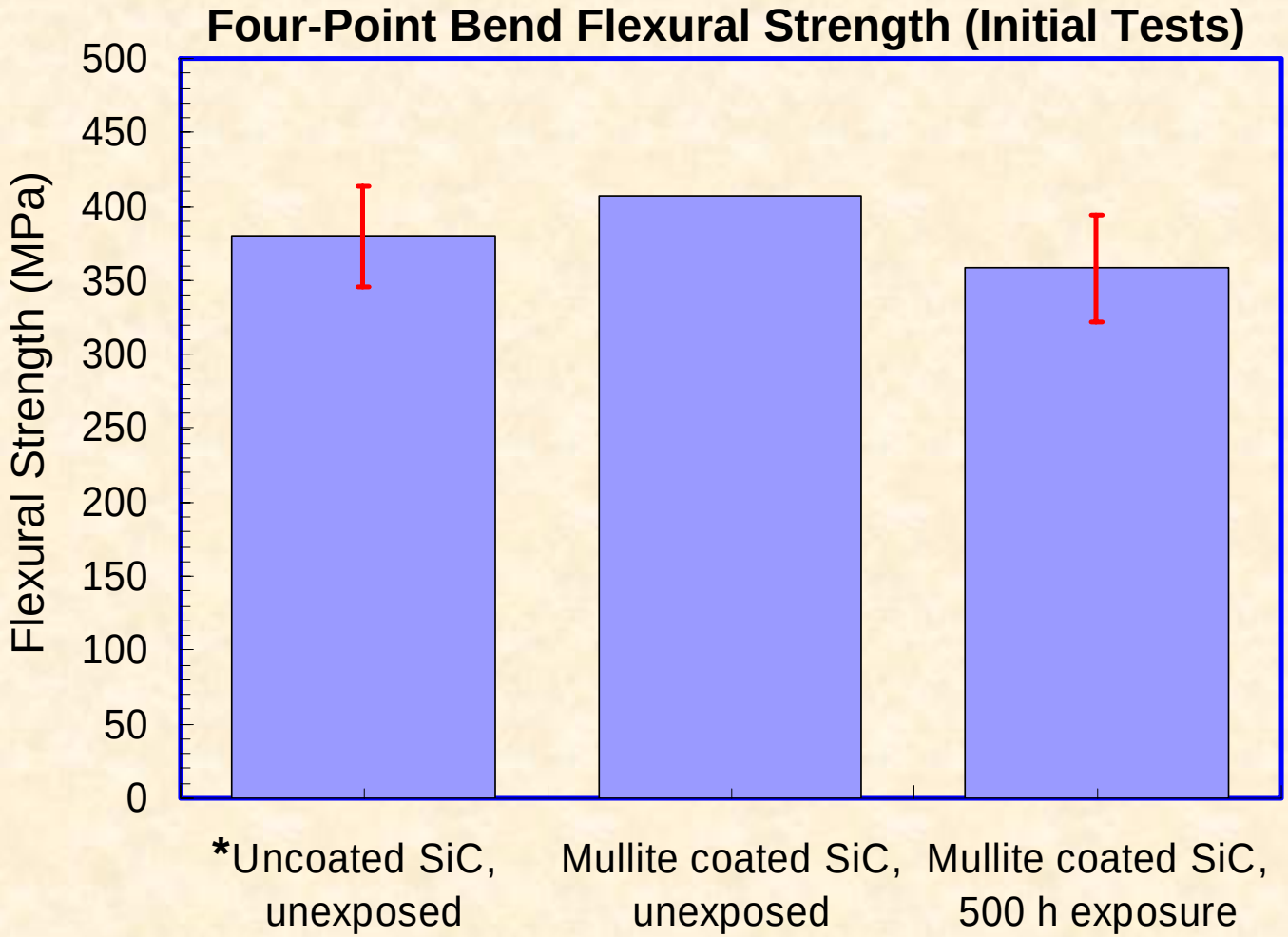


Diffraction Pattern After Exposure





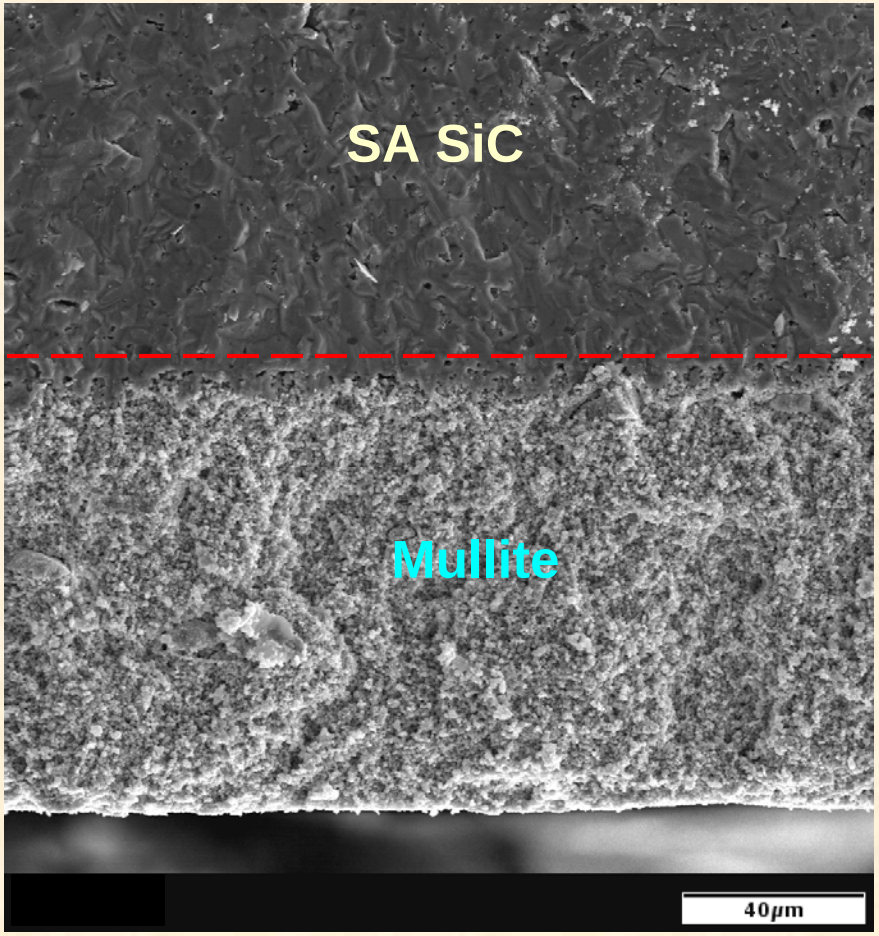
Strength Can Be Influenced by Coating Properties

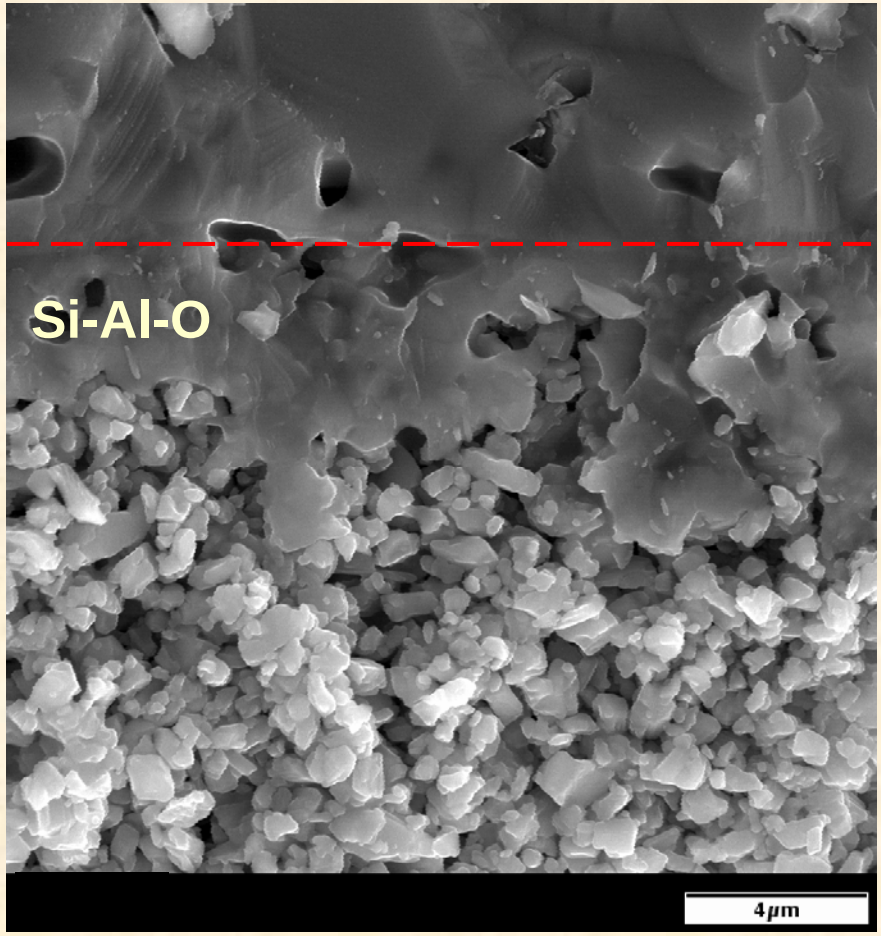


Minor Strength Degradation Observed After 500h Steam Exposure at 1200°C, 1 atm

*** Hexaloy specifications for four-point bend flexural strength with standard deviation from Kim & Moorhead, *J. Am. Ceram. Soc.*, 73 [7] (1990) pp 1868-72.**

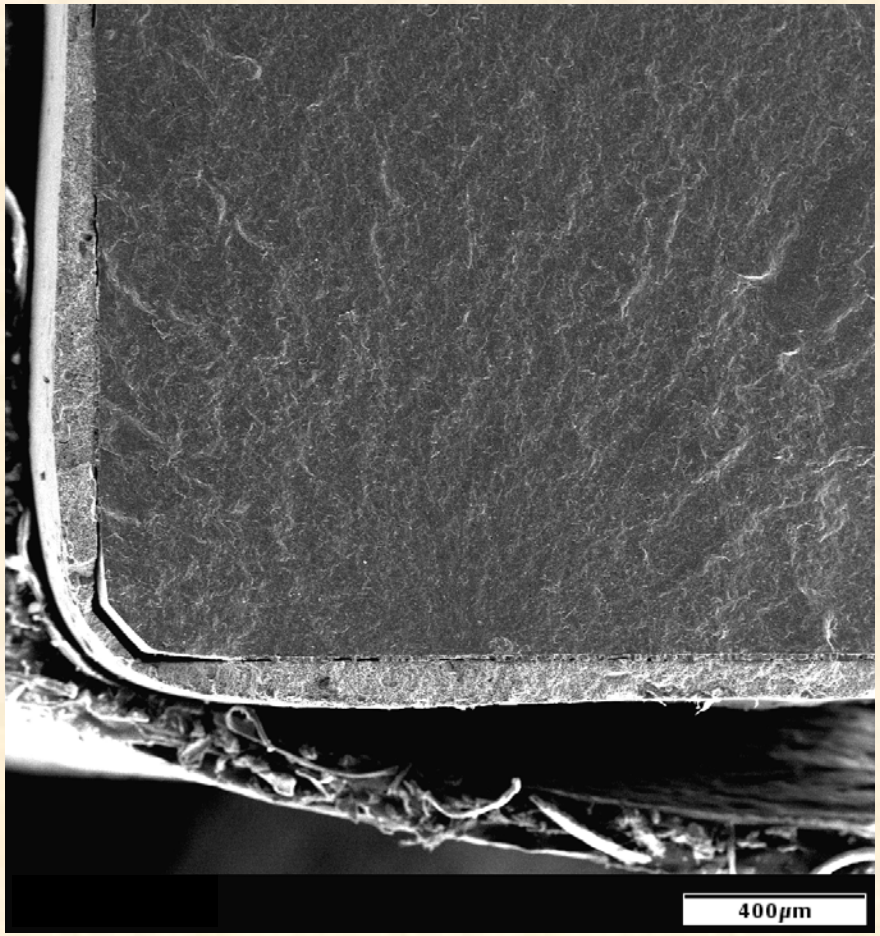
Minor Reaction Occurred Between Mullite and SASiC Substrate During the Sintering

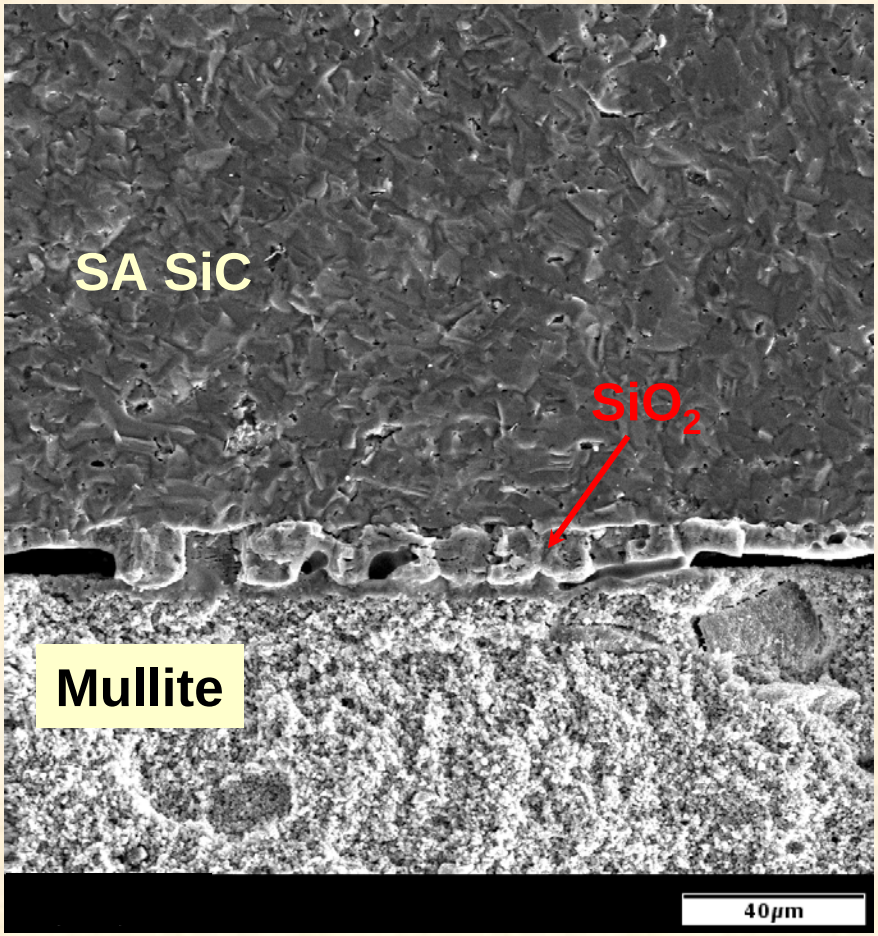




Interaction at the interface promotes adhesion

Silica Formation Occurs Due to Conduction of O_2 Through the Porous Mullite Layer





Summary

- By applying the principles of colloidal processing, the rheological behavior of ceramic suspensions can be tailored for the ORNL dip-coating process.
- Uniform coatings have been formed on complex-shaped components. Uniform coatings do not result in a significant strength debit to the component.
- The coatings must be dense (i.e., no open porosity) to prevent O_2 conduction to the substrate and ultimately, the formation of porous SiO_2 at the interface.
- The substrate/coating interface is strongly influenced by the test environment and material selection. Reactions that occur at the interface will likely dictate the service life of a coated component.

Acknowledgements

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Questions?