UT-BATTELLE

Slurry Deposition of Environmental Protection Systems

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Environmental Barrier Coatings Workshop

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OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

ORNL Approach

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

  Utilize colloidal theory and use of additives to develop understanding and design specific properties necessary to dip coating protective systems

- Industrial Collaboration: Apply approach to "real" industrial systems

Factors Influencing Coating Results

- **Processing**
  - **Powder (zeta potential, particle size and morphology, surface area, agglomeration…)**
  - **Additives (dispersant, binders, modifiers = contaminants)**
  - **Slurry (rheology, viscosity)**
- **Interface**

Colloidal Assembly of Ceramic Devices and Coatings

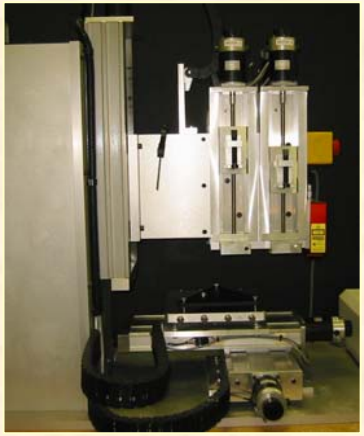
2-D structures

$BaTiO_3$ capacitors

Tape casting

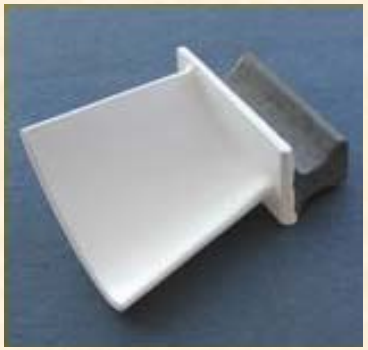
3-D structures

PZT motor arrays



Robotic deposition
3D inkjet printing

Monoliths and Coatings



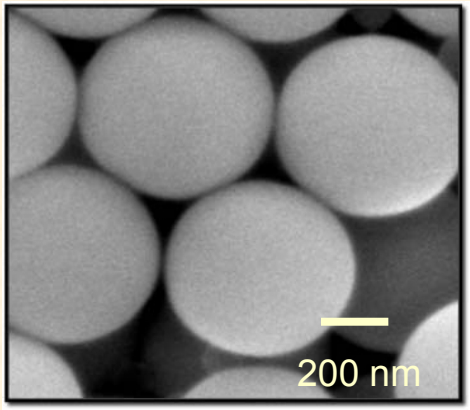
RE-silicate coating on
a Si_3N_4 rotor blade

Gelcasting, slip casting
Dip coating

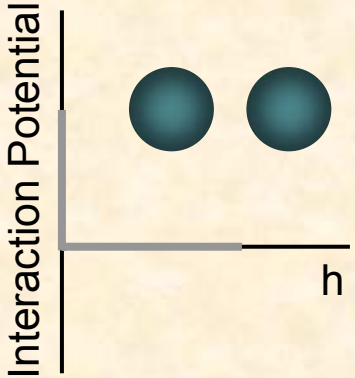
Tailoring Interactions Between Colloidal Particles

Colloidal particles --> basic "building blocks"

- **must control interparticle forces to tailor structure, rheological properties, and drying**

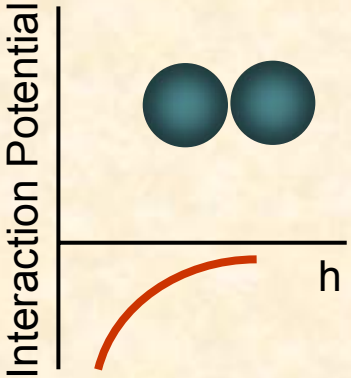


Hard sphere



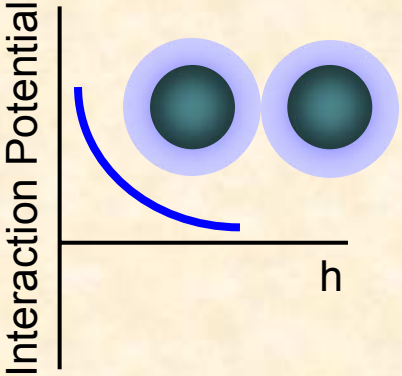
indexed matched
highly screened

Attractive



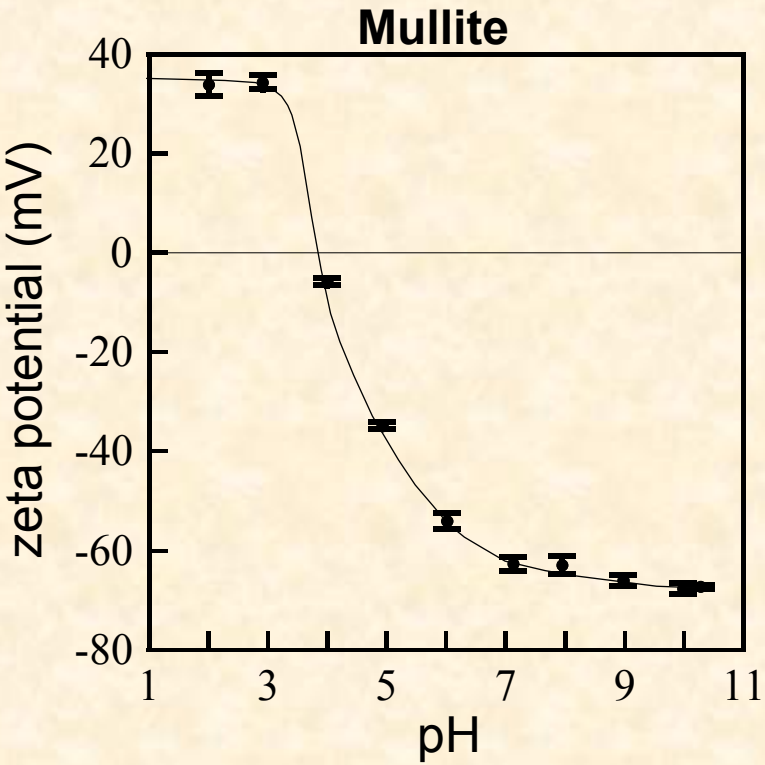
vdw forces
depletion forces

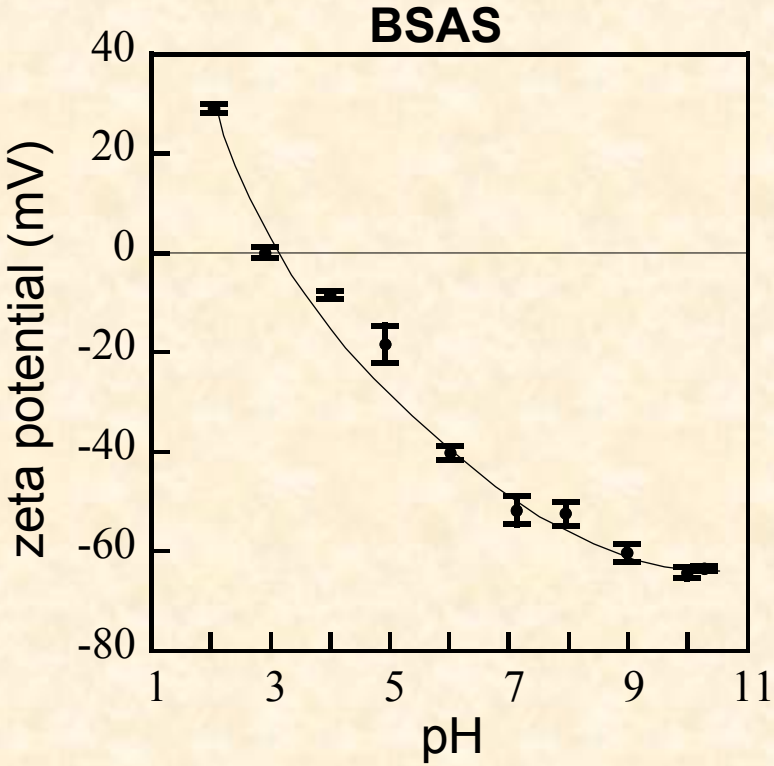
Soft Sphere



charge-stabilized
steric-stabilized

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

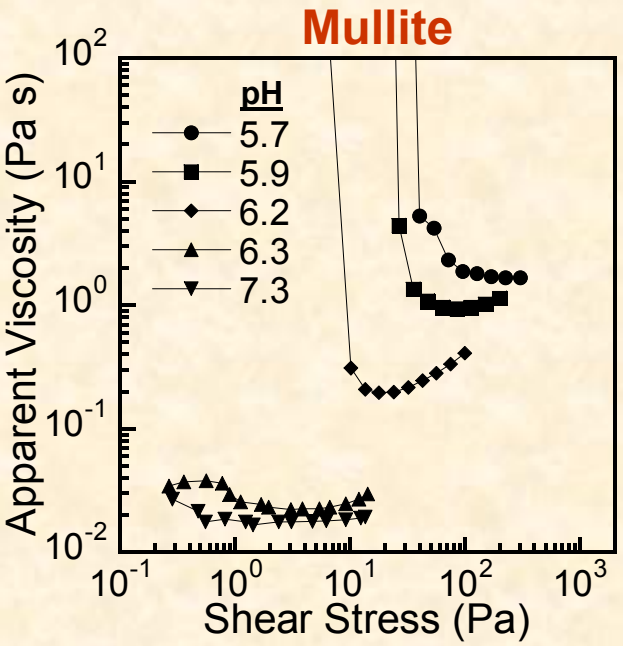


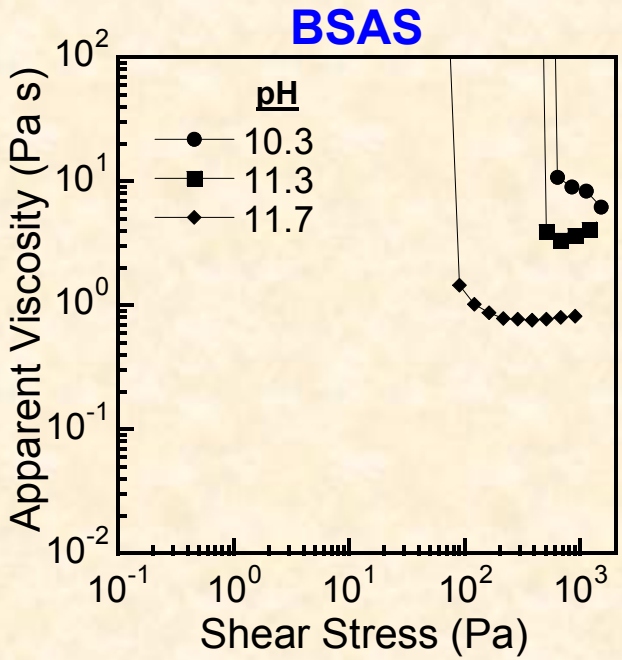


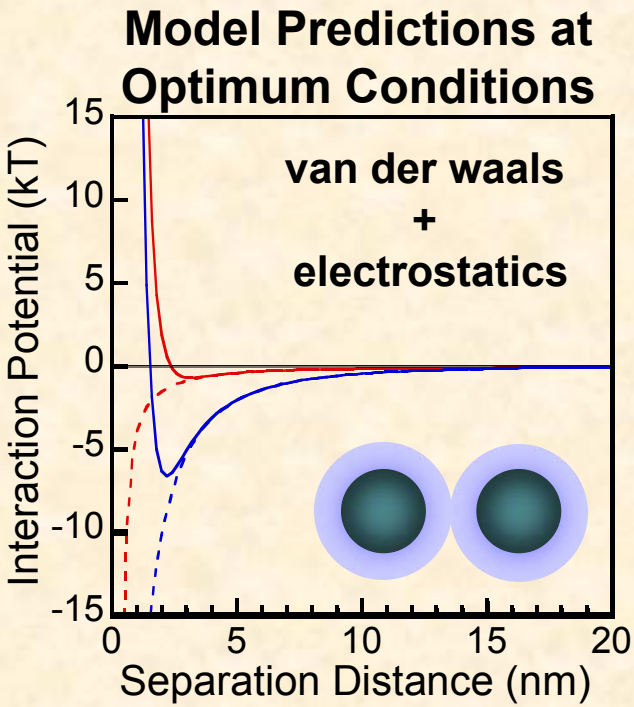
- **The IEP of mullite and BSAS is at pH 3-4**
- **Above the IEP, the zeta potential is negative.**
- **-63 mV achieved at pH 7 and 10 for mullite and BSAS, respectively**

Charge Stabilization of Ceramic Suspensions

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





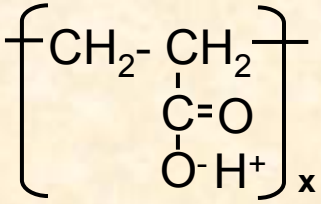


- **Mullite suspensions are stable (Newtonian) just above pH 6.3**
- **BSAS suspensions cannot be stabilized by bare surface charge modification**
- **Results agree with model predictions.**

Bergstrom, *Adv. Colloid Interface Sci.* **70** (1997) pp 125-169
Bergstrom *et. al.*, *J. Am. Ceram. Soc.* **79** [2] (1996) pp 339-348
Prieve & Russel, J. Colloid Interface *Sci.* **125** [1] (1988) pp 1-13
Benzing & Russel, *J. Colloid Interface Sci.* **83** [1] (1981) pp 178-190
Hough & White, *Adv. Colloid Interface Sci.* **14** (1980) pp 3-41
Hunter, *Foundations of Colloid Science*, **1&2** (1995)

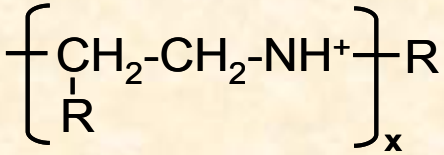
Polyelectrolyte Dispersants

Anionic

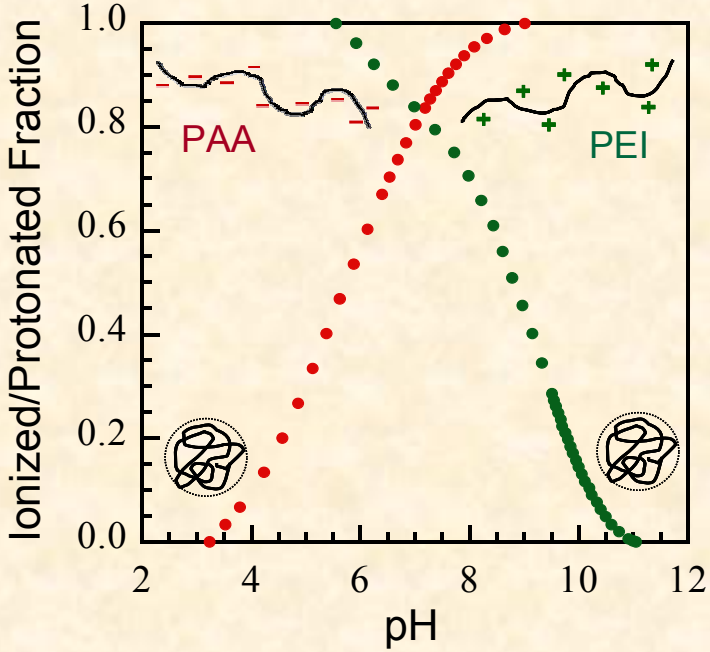


Poly(acrylic acid) (PAA)

Cationic



Poly(ethylene imine) (PEI)



Guidelines for Adsorption

IEP < 6 PEI

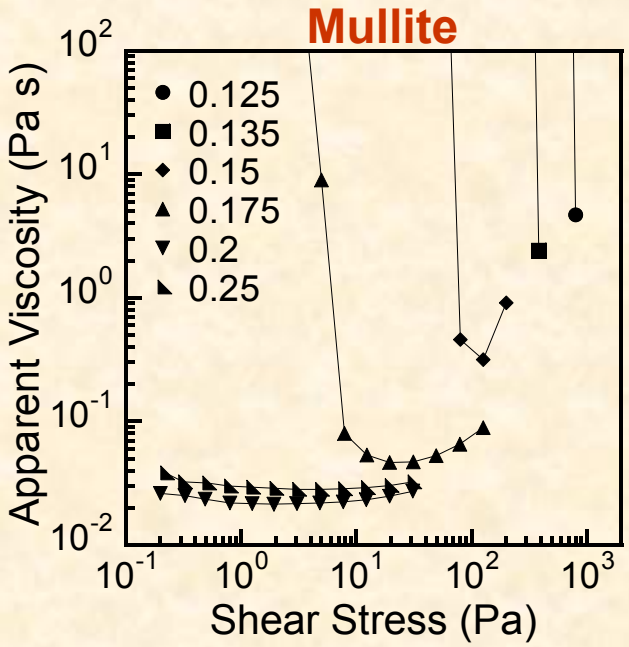
IEP 6-8 PAA or PEI

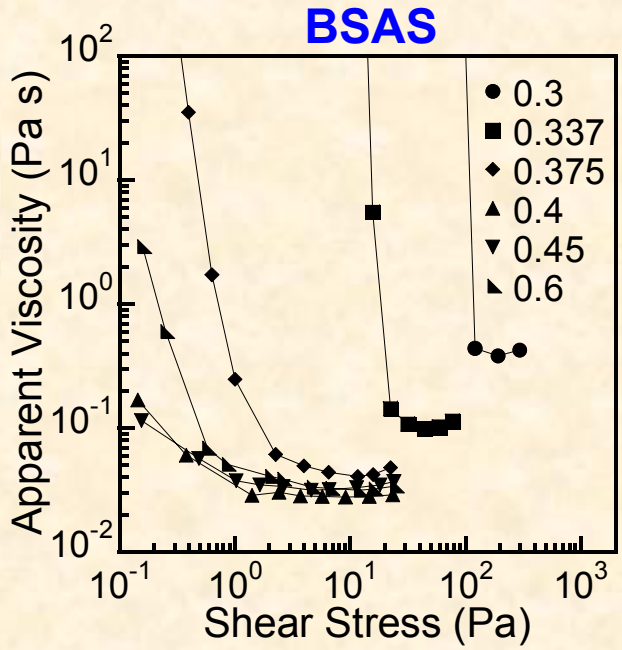
IEP > 8 PAA

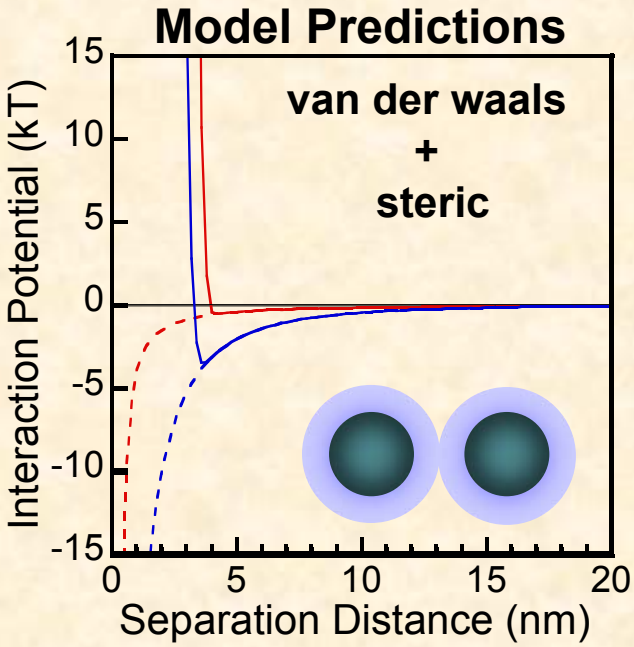
Ceramic Material	IEP	Dispersant
SiO_2	3-4	PEI
SiC	3-4	PEI
Si_3N_4 (E10)	3-4	PEI
BSAS	3-4	PEI
Mullite	3-4	PEI
RE-silicates	3-6	PEI
Al_2O_3	8-9	PAA
Y_2O_3	8-9	PAA
MgO	12-13	PAA

Polyelectrolyte Stabilization of Ceramic Suspensions

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





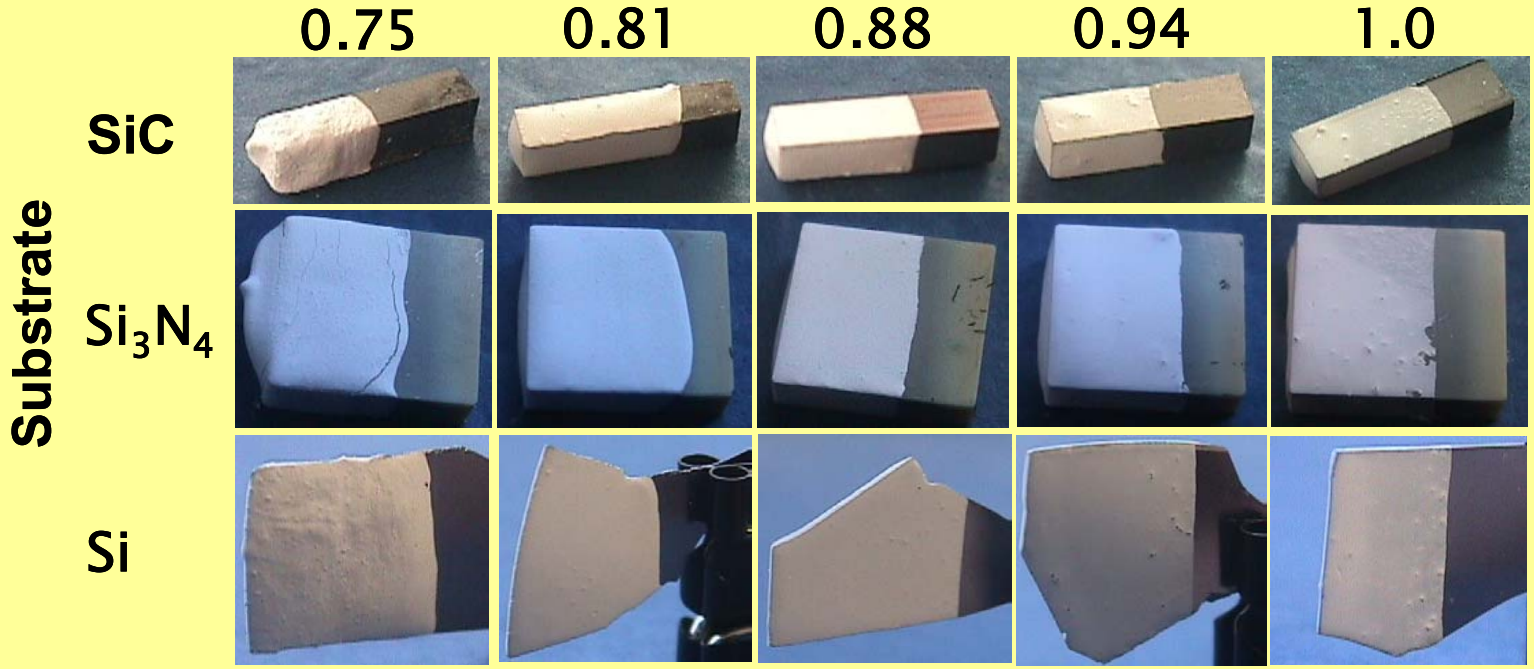


- **Newtonian and near-Newtonian flow behavior achieved with the addition of 0.2 mg PEI/m² mullite and 0.4 mg PEI/m² BSAS, respectively**
- **Results agree with model predictions:**

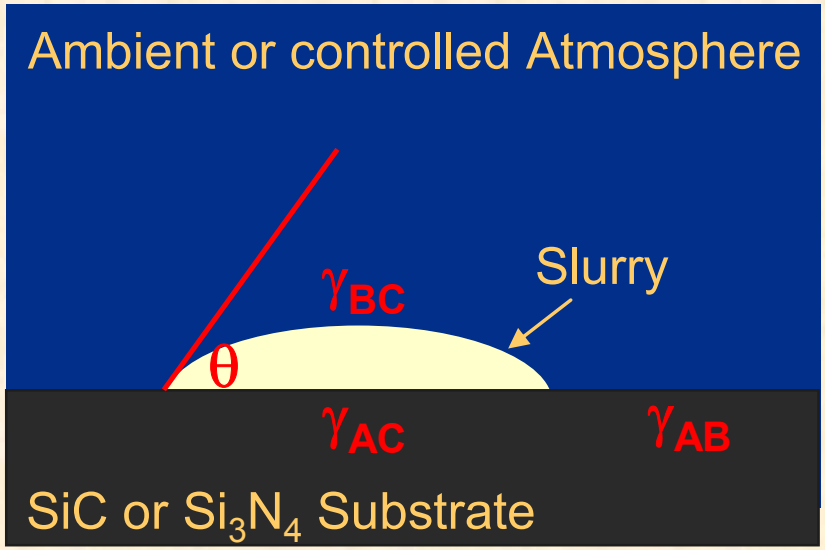
Bergstrom, *Adv. Colloid Interface Sci.* **70** (1997) pp 125-169
Bergstrom *et. al.*, *J. Am. Ceram. Soc.* **79** [2] (1996) pp 339-348
Prieve & Russel, J. Colloid Interface *Sci.* **125** [1] (1988) pp 1-13
Benzing & Russel, *J. Colloid Interface Sci.* **83** [1] (1981) pp 178-190
Hough & White, *Adv. Colloid Interface Sci.* **14** (1980) pp 3-41
Vincent, *Colloids Surf.*, **18** (1986) pp 261-281

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



- The contact angle (θ) depends on the surface tension/charge of the substrate and coating material
- The contact angle decreases with use of latex additives

Mullite-Latex

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

ϕ_{latex}	SiC θ	Si_3N_4 θ
0	55.0	71.5
0.034	49.5	50.5
0.076	40.0	40.5
0.201	45.5	47.5

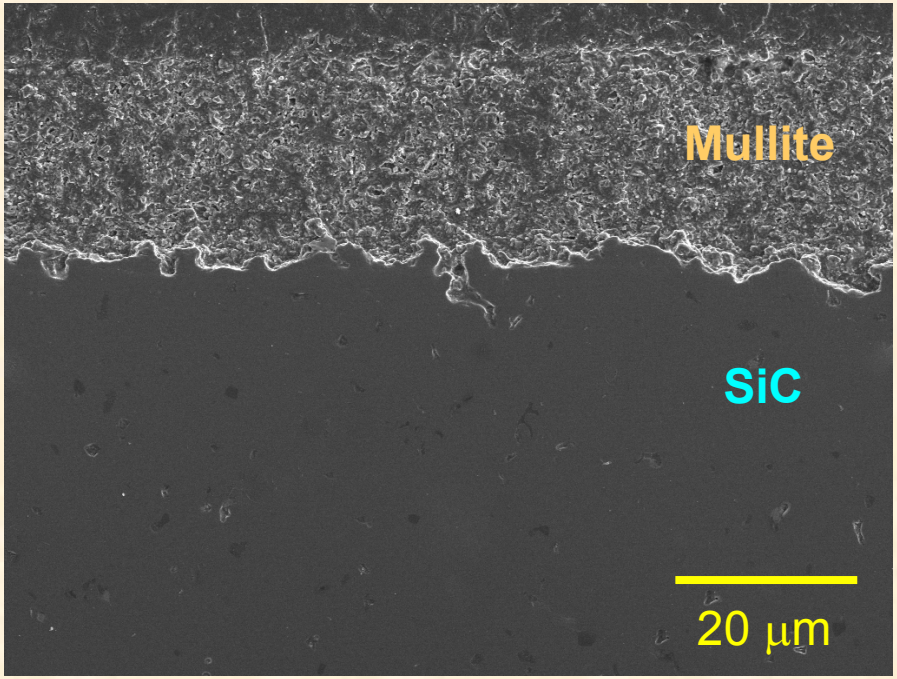
BSAS-Latex

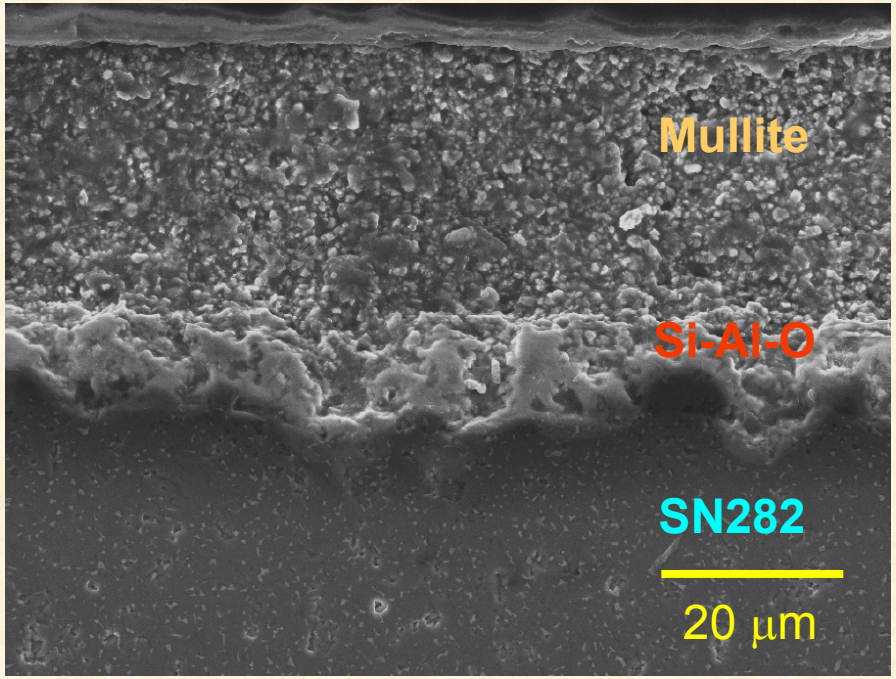
ϕ_{BSAS} = 0.25, pH 10

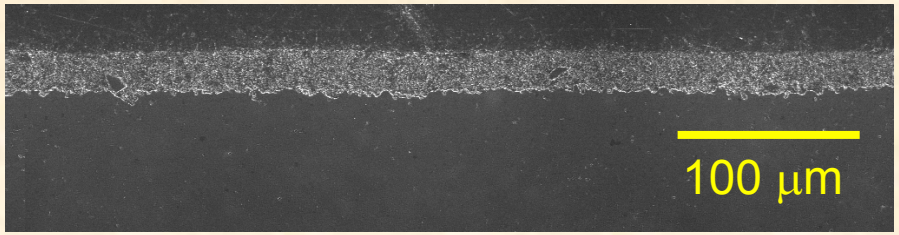
ϕ_{latex}	SiC θ	Si_3N_4 θ
0	53.0	85.5
0.034	48.0	49.0
0.076	44.5	41.5
0.201	*	*

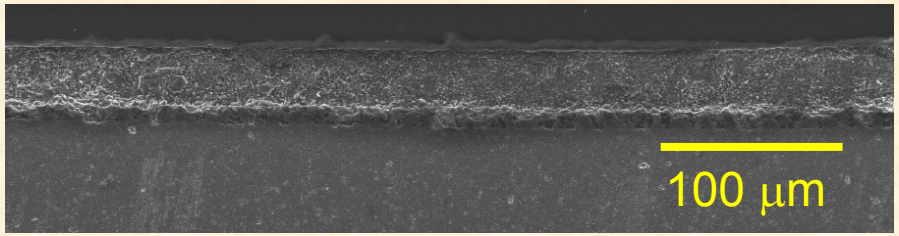
Formation of Thin, Uniform Mullite Coatings

Coating applied from 25 vol% mullite suspension w/ 5 vol% latex







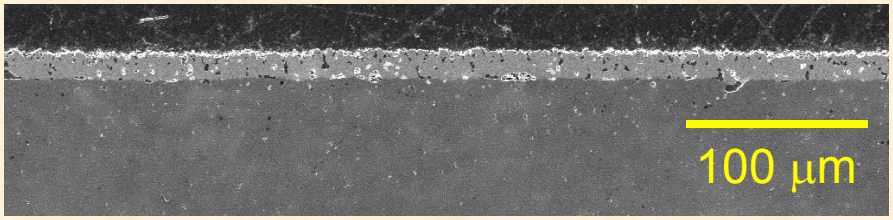


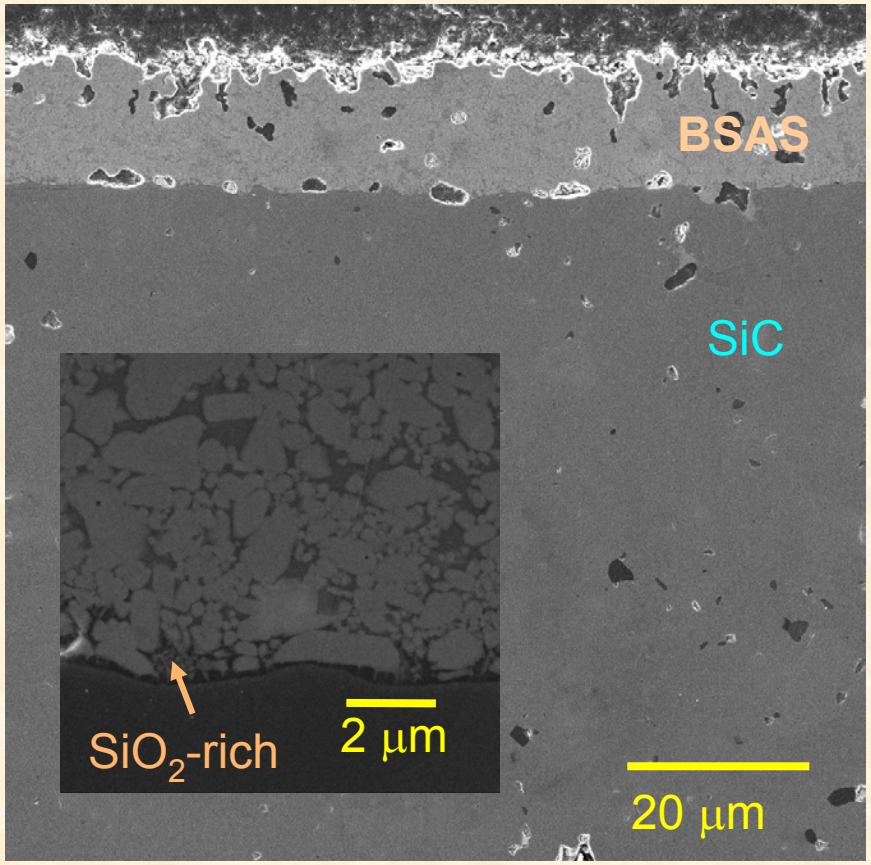
Sintered in air, 1400 °C

Formation of Thin, Uniform BSAS Coatings

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

Sintered in air, 1300 °C

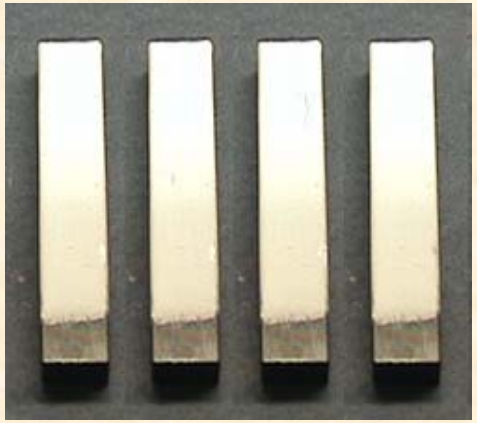




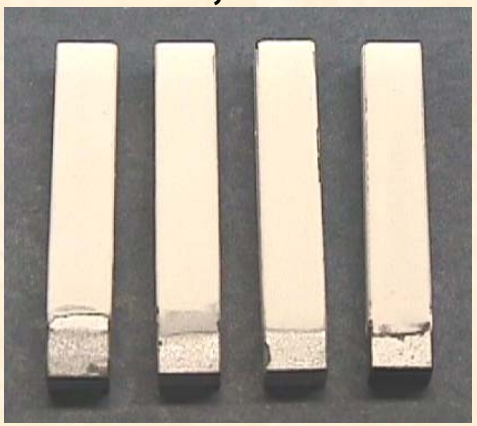
Exposure of Mullite Coated SiC and SN282 Test Bars

(500h Steam Exposure at 1200°C, 100% RH, 1 atm)

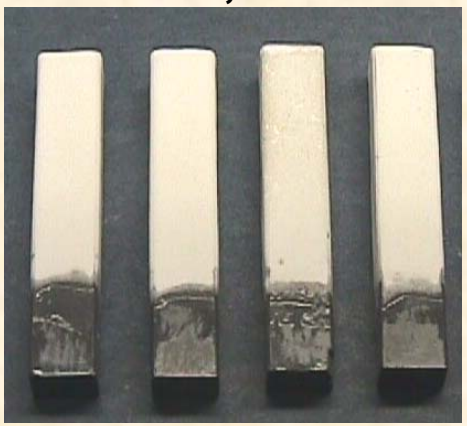
SiC, before



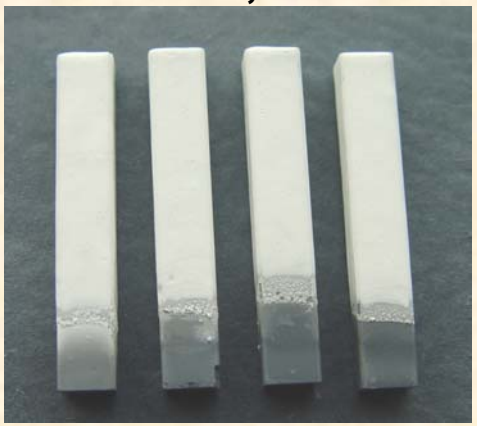
SiC, after



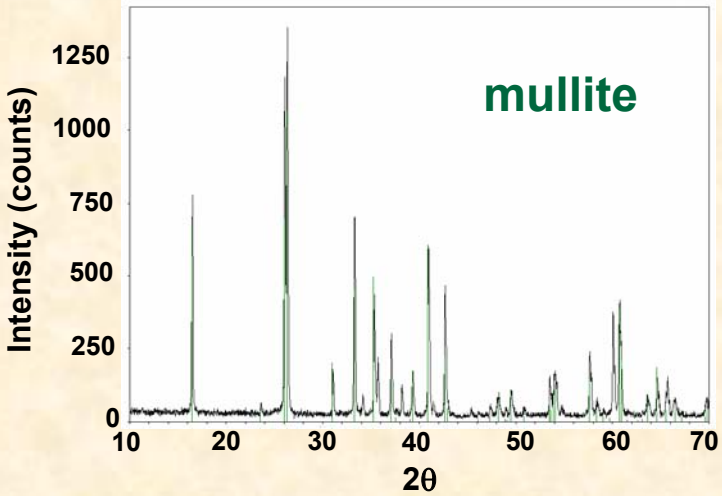
SN282, before

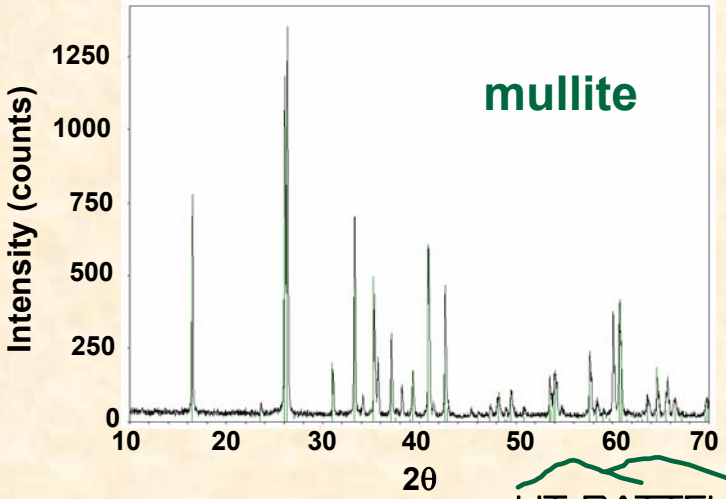


SN282, after

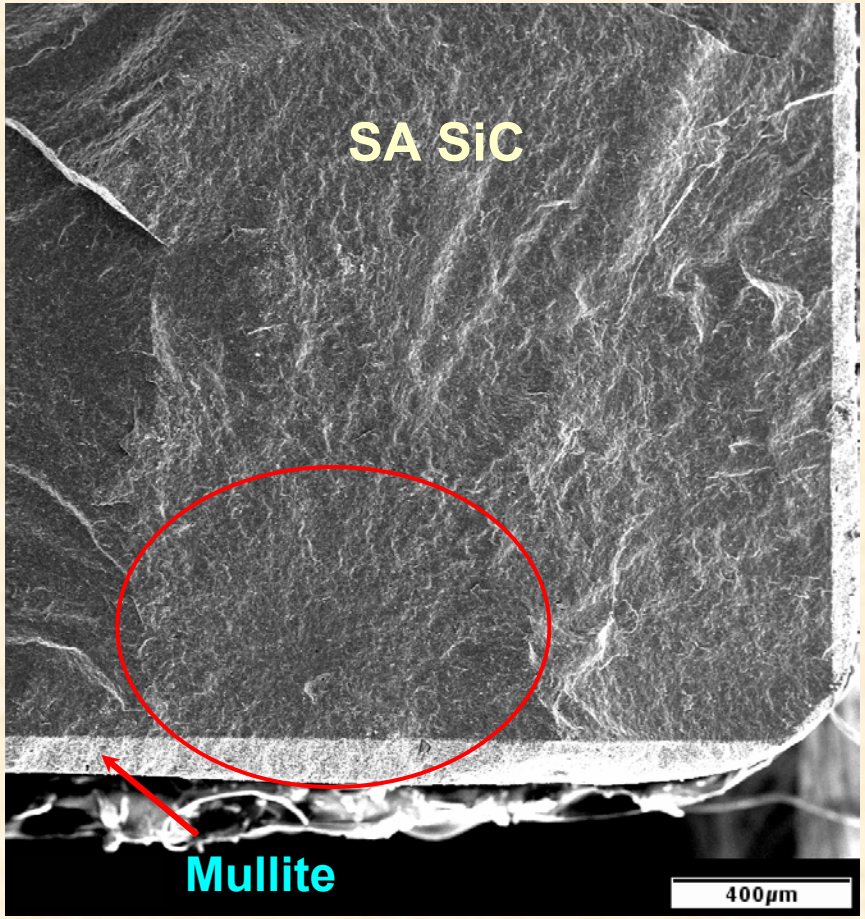


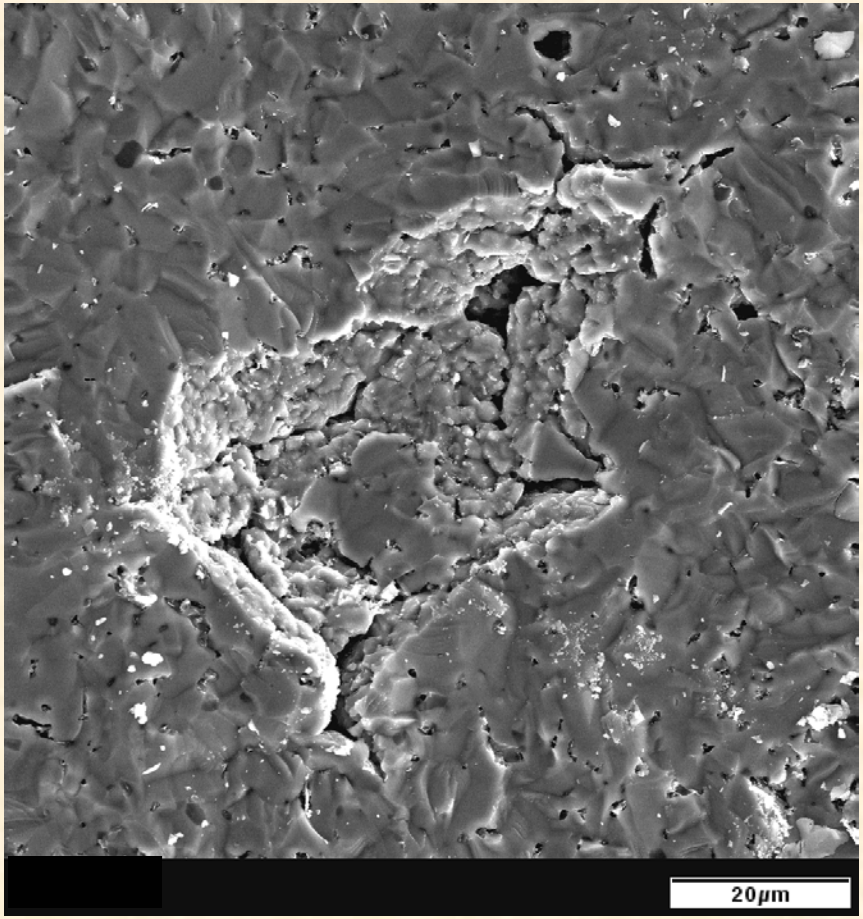
Diffraction Pattern After Exposure



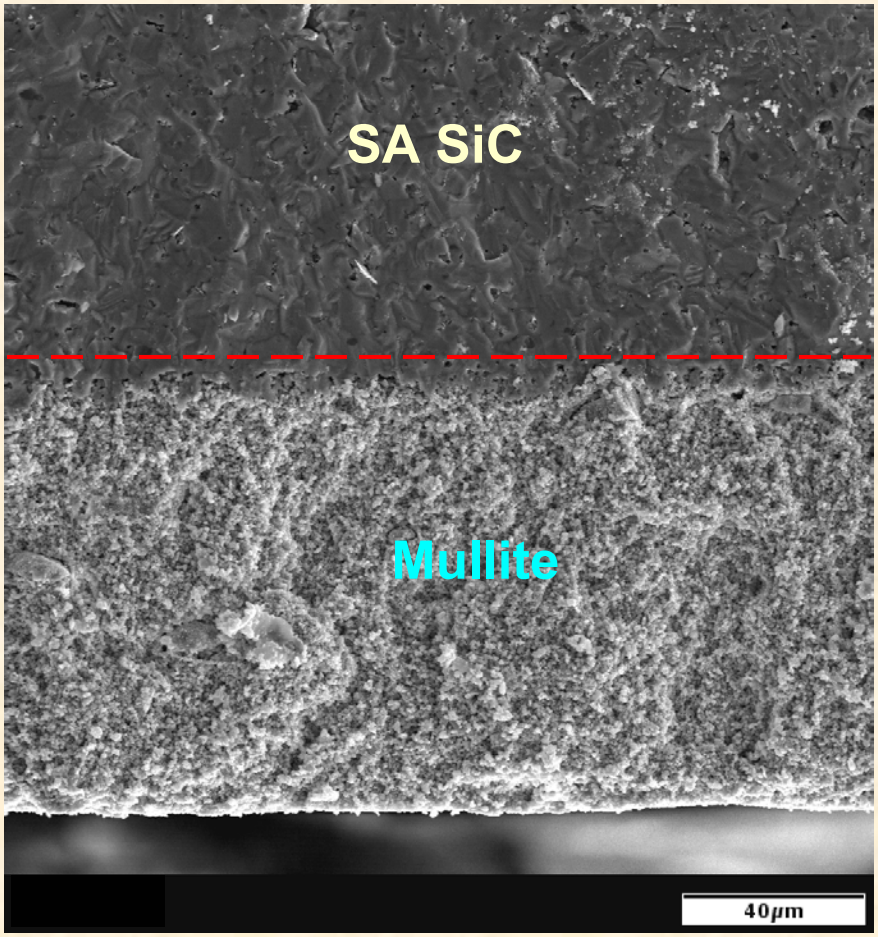


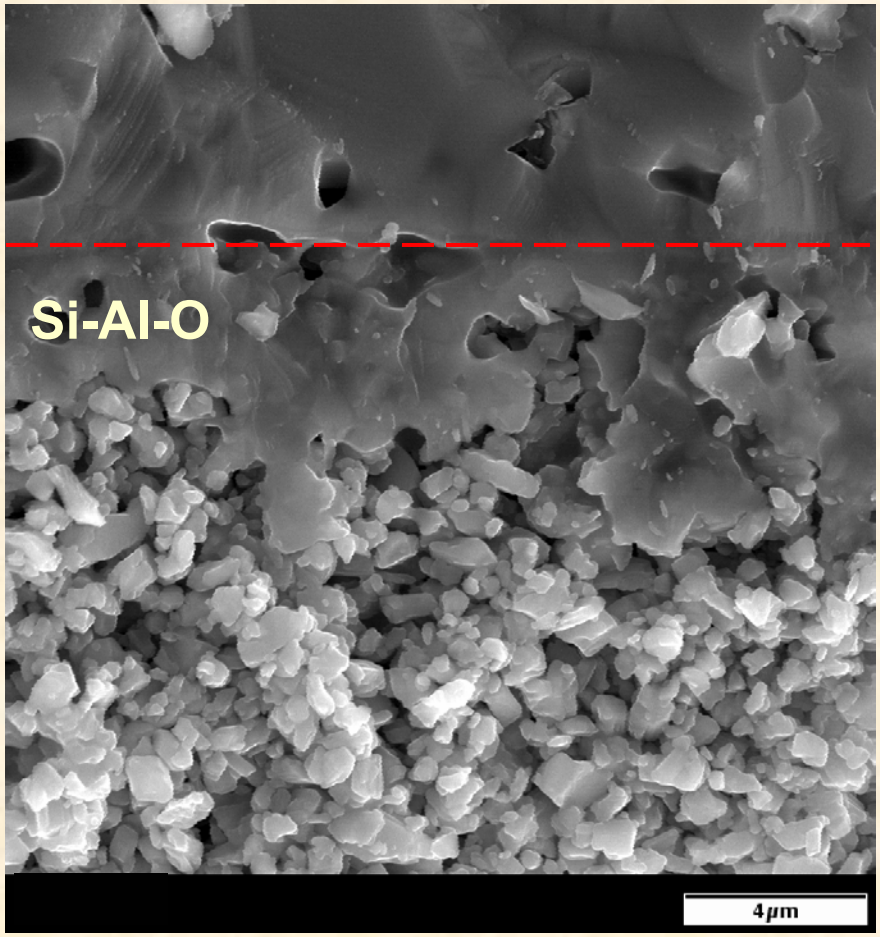
As-Coated Strength Governed by Intrinsic Processing Flaws in SA SiC Substrate





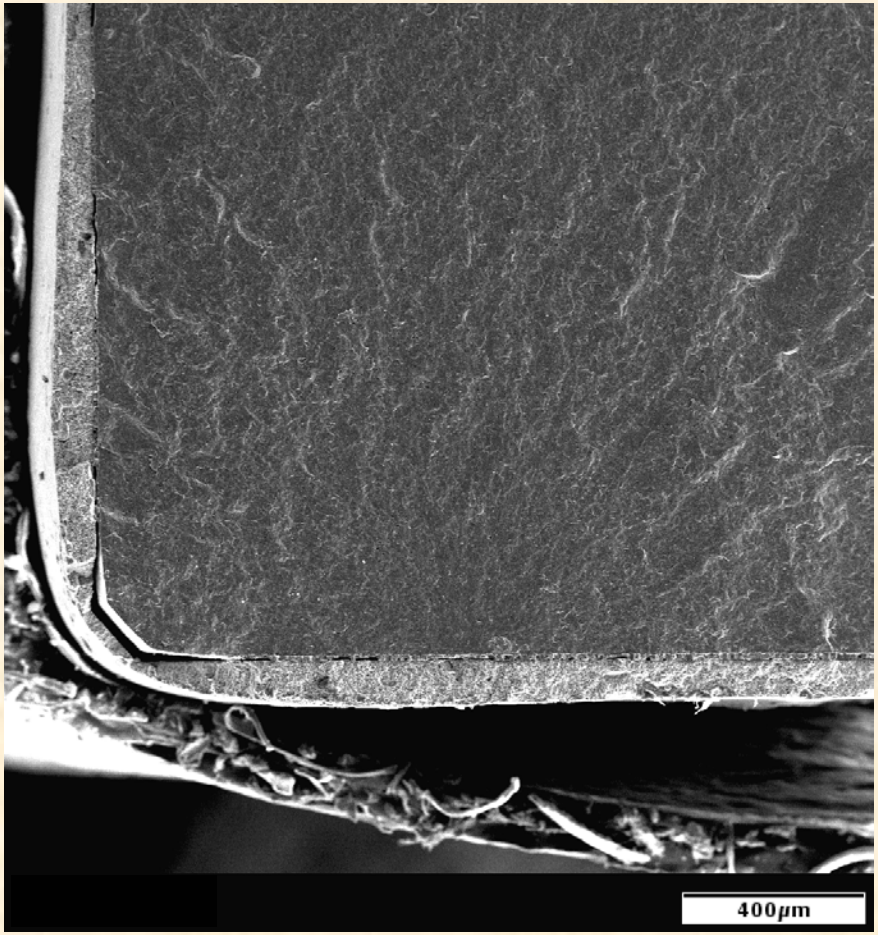
Minor Reaction Occurred Between Mullite and SASiC Substrate During the Sintering

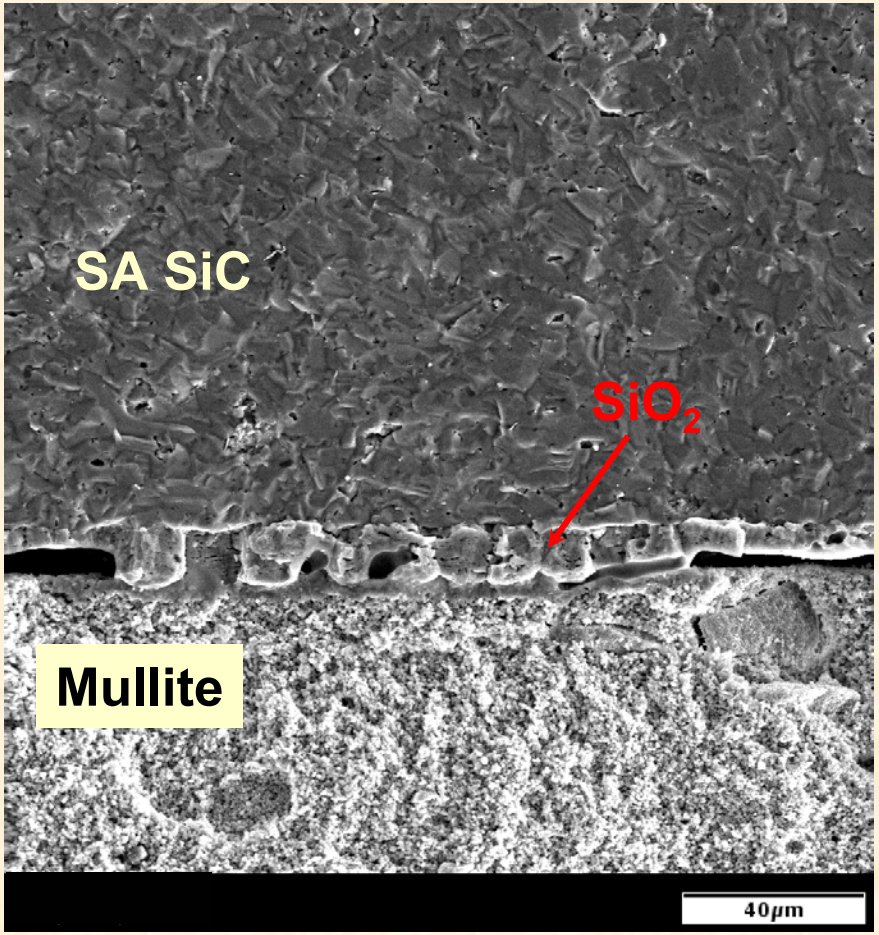




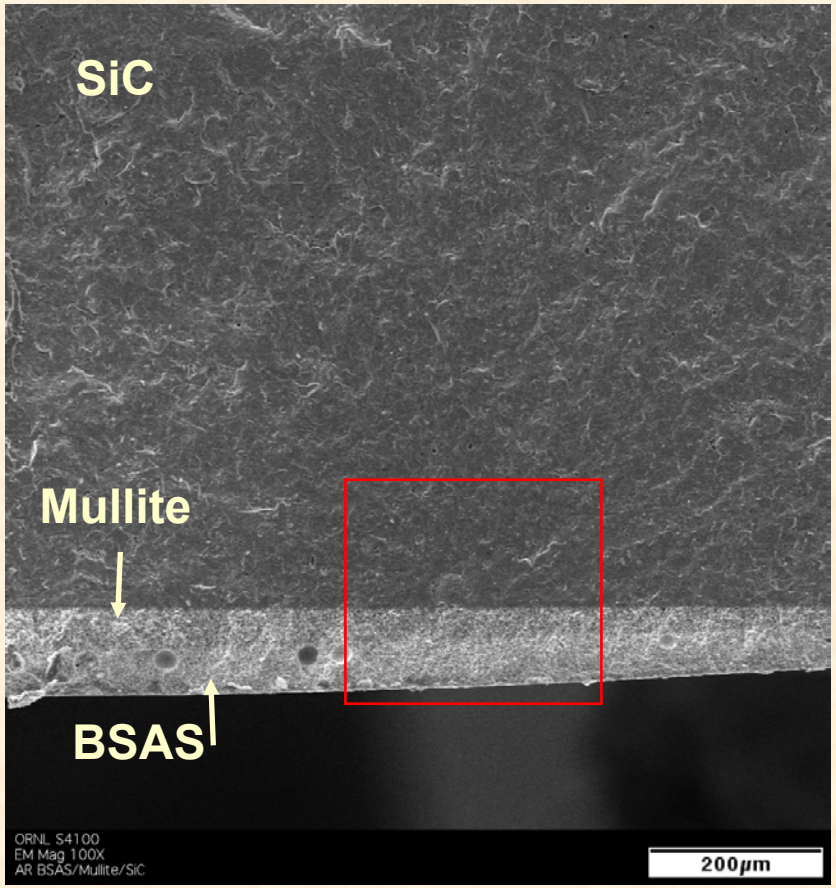
Interaction at the interface promotes adhesion

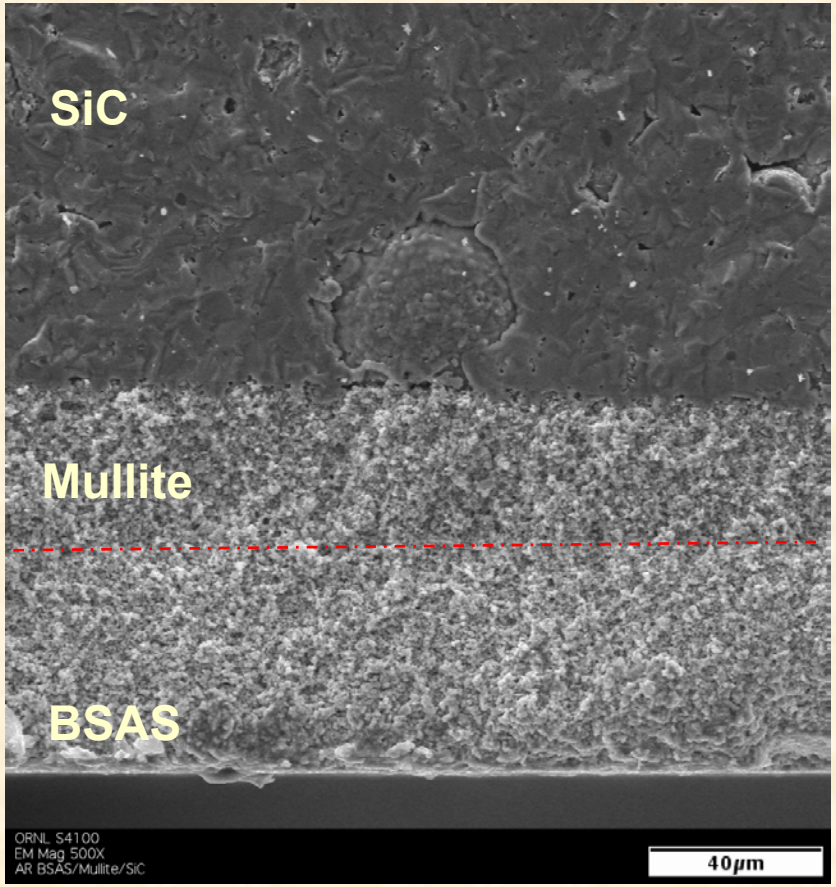
Silica Formation Occurs Due to Conduction of O_2 Through the Porous Mullite Layer





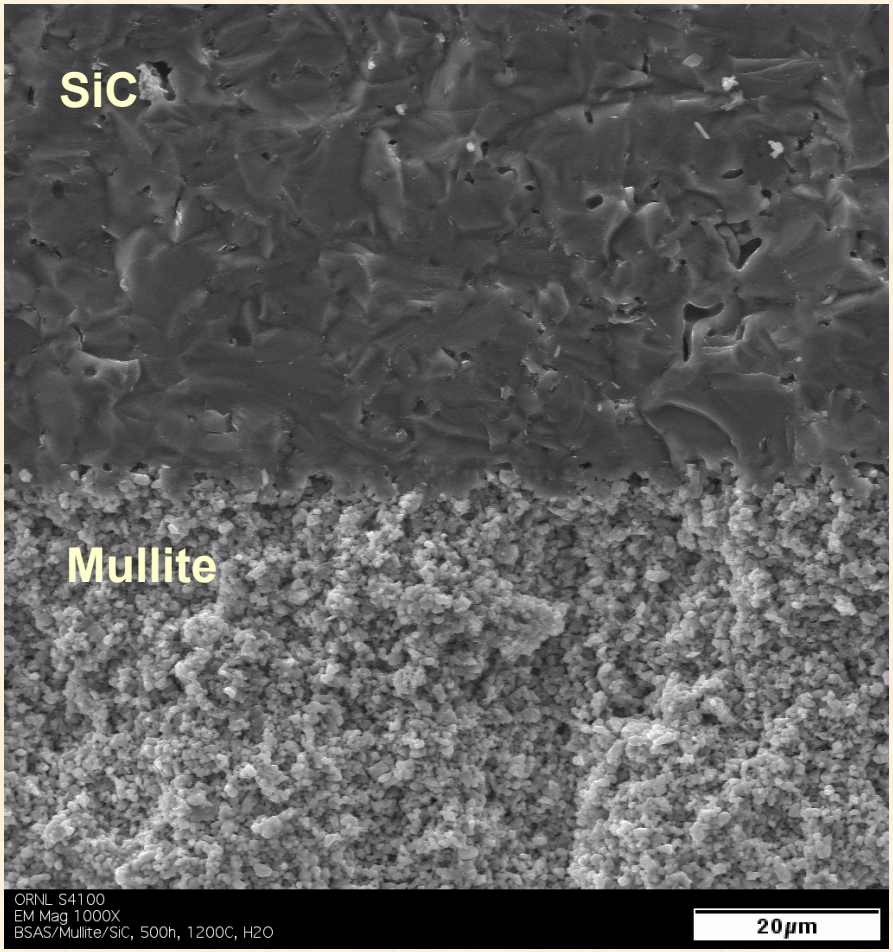
What Happens to Coating Integrity with Introduction of Second Layer?

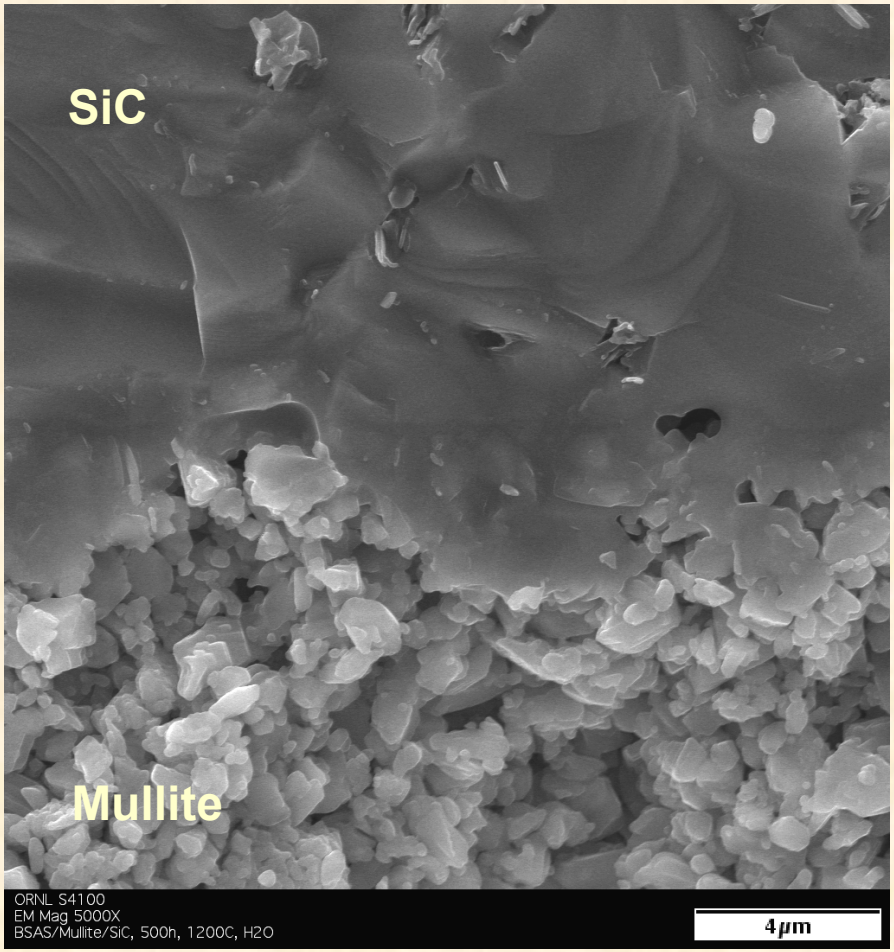




Coated SASiC with mullite and BSAS before testing

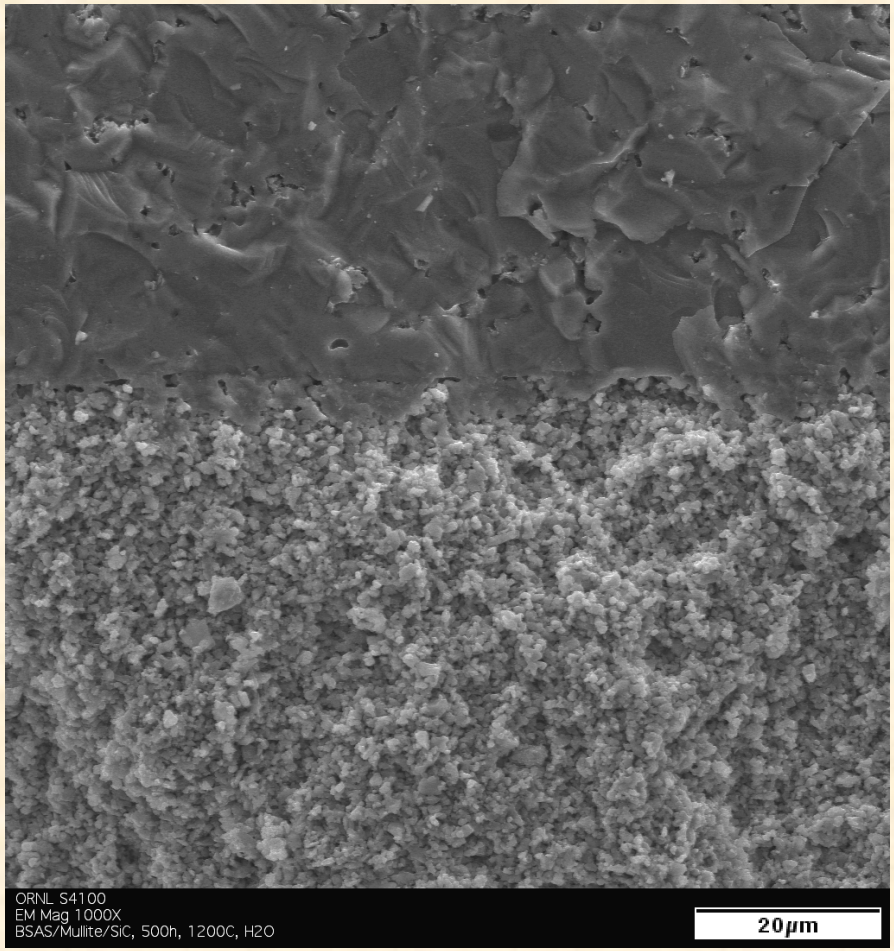
Adhesion at Interface Promoted by Alumino-silicate Formation

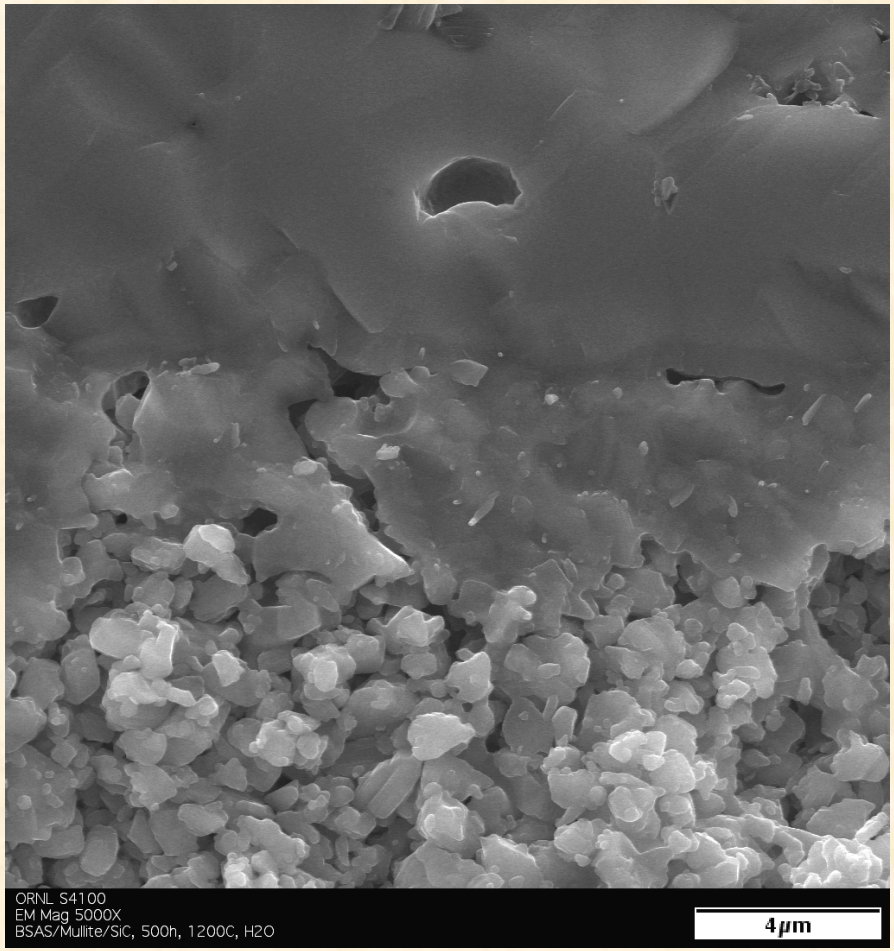




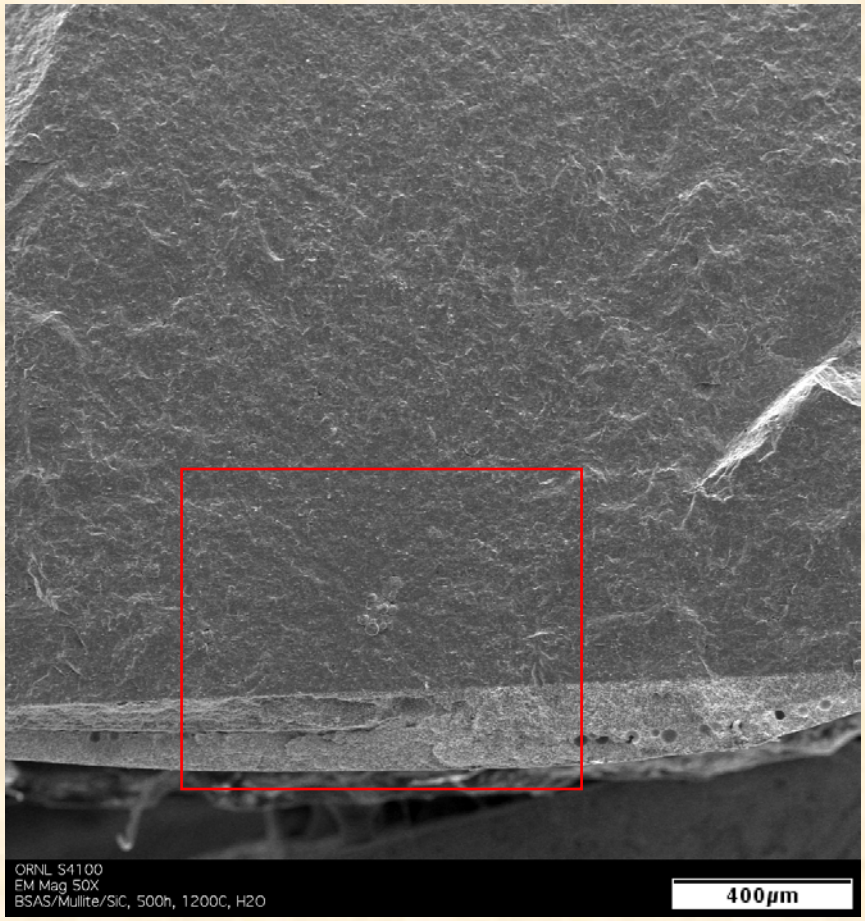
Coated SASiC with mullite and BSAS before testing

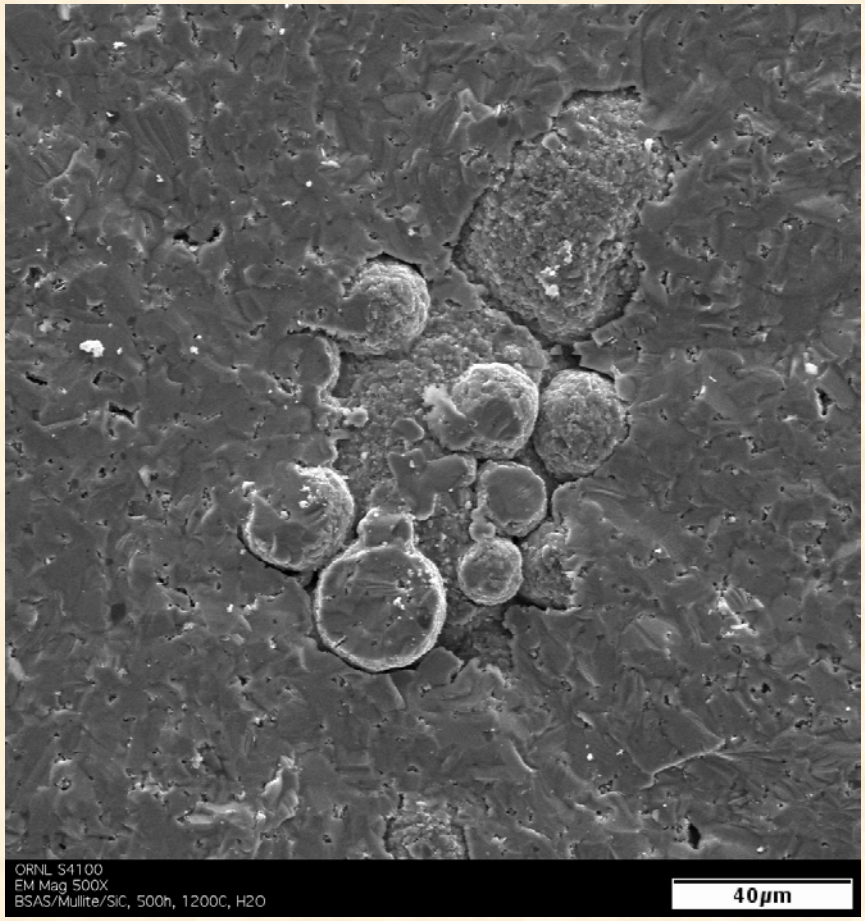
Formation of Alumino-Silicate Phase at Interface of Mullite and SASiC After 500 Hour Exposure at 1200°C in Steam





Formation of Defects at Interface of Mullite and BSAS Layers After 500 Hour Exposure at 1200°C in Steam





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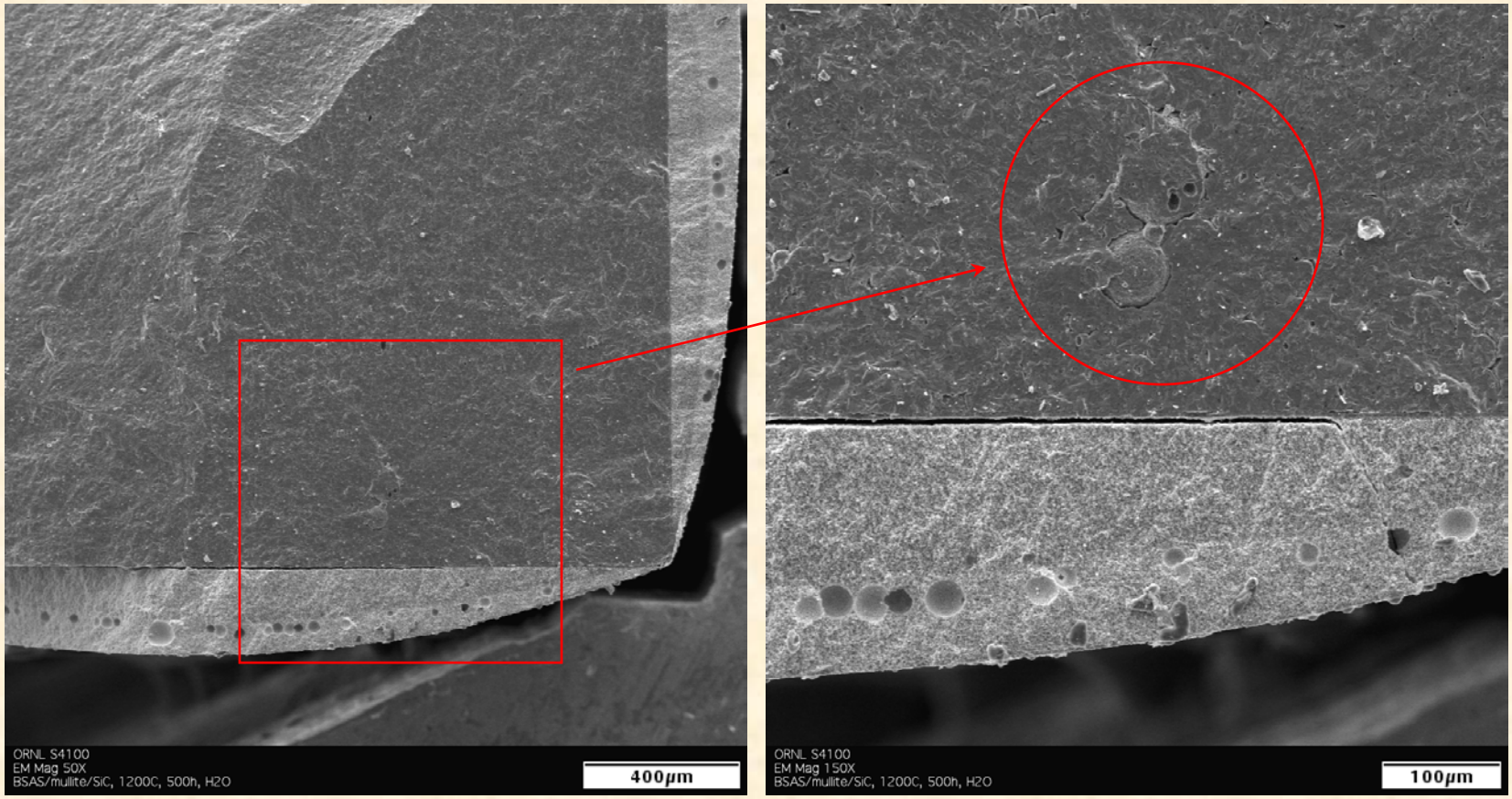
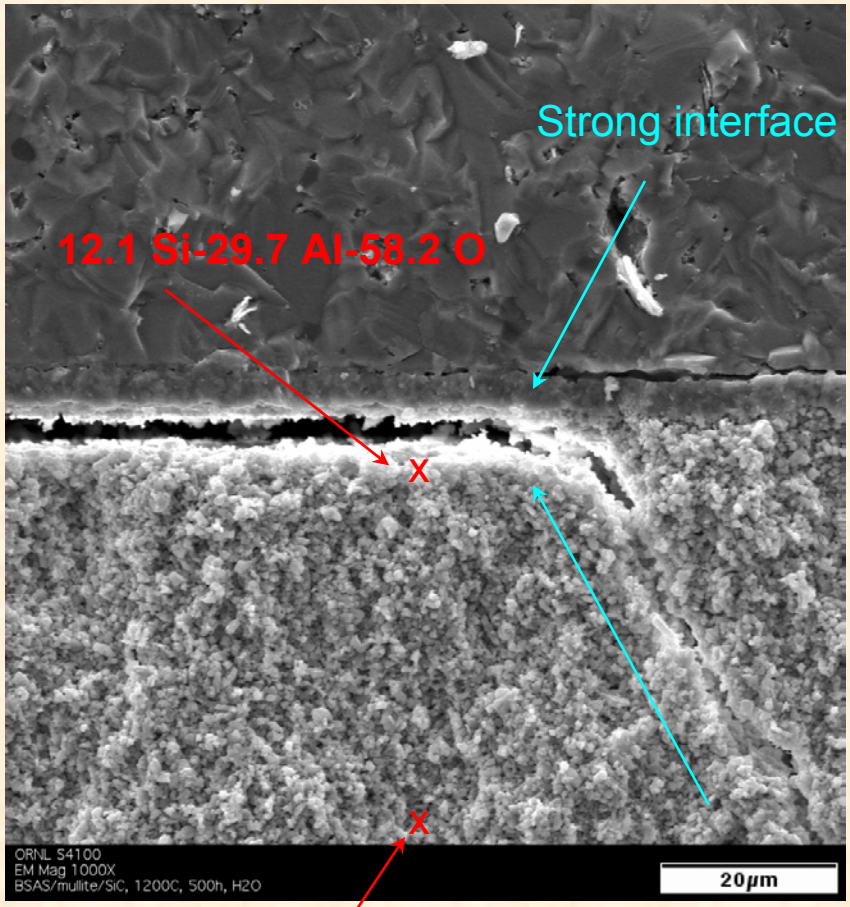
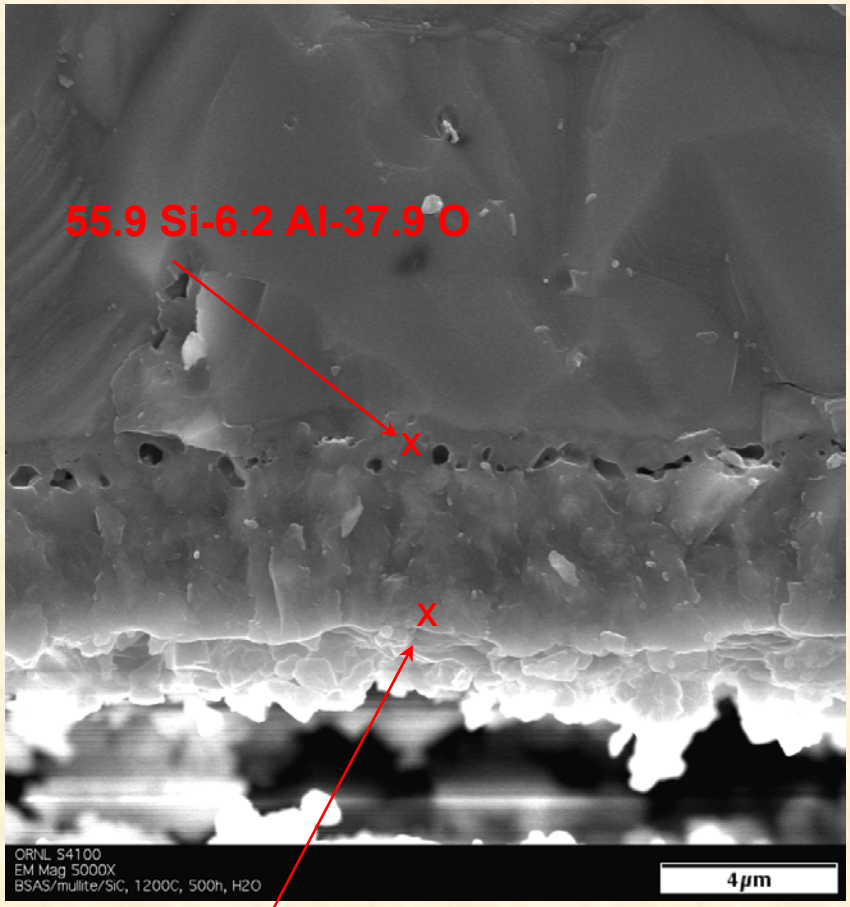


Formation of Interface of Mullite and SASiC After 500 Hour Exposure at 1200°C in Steam

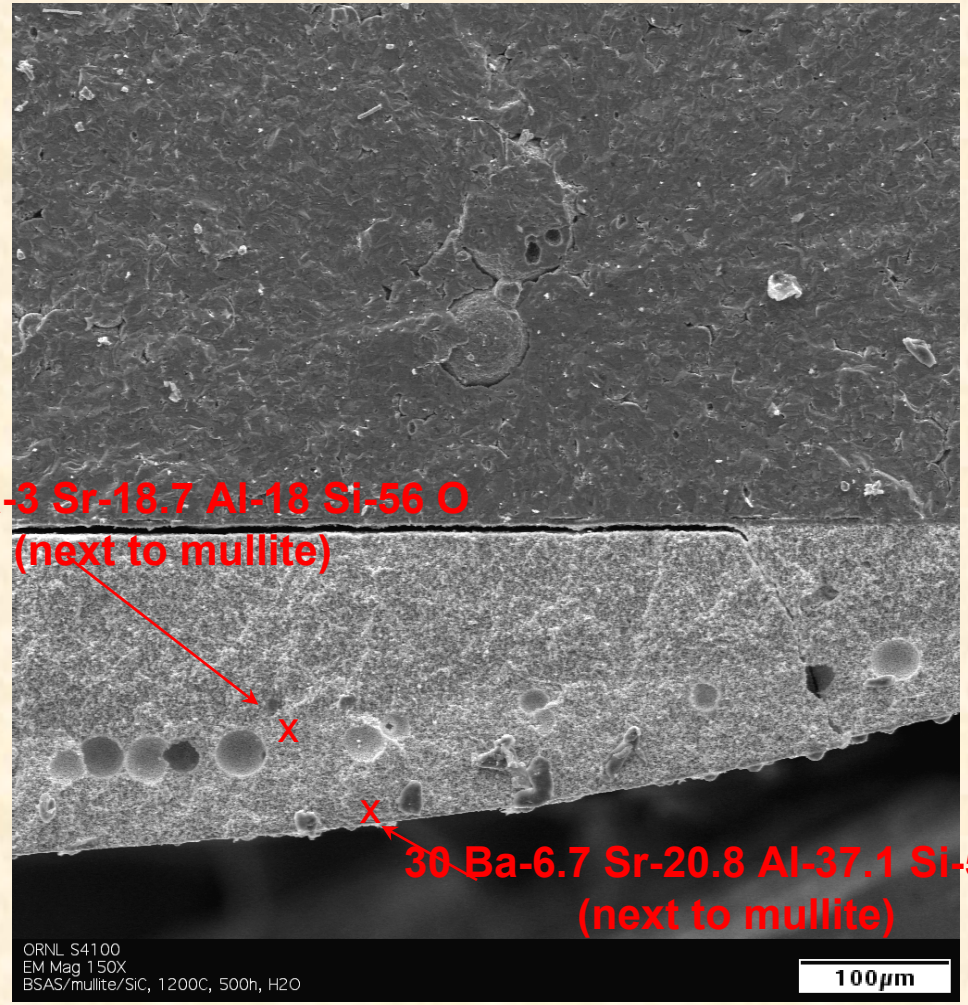




14.2 Si-36.5 Al-(0.6 Ba)-48.8 O (point next to BSAS)

35.8 Si-28 Al-36.2 O

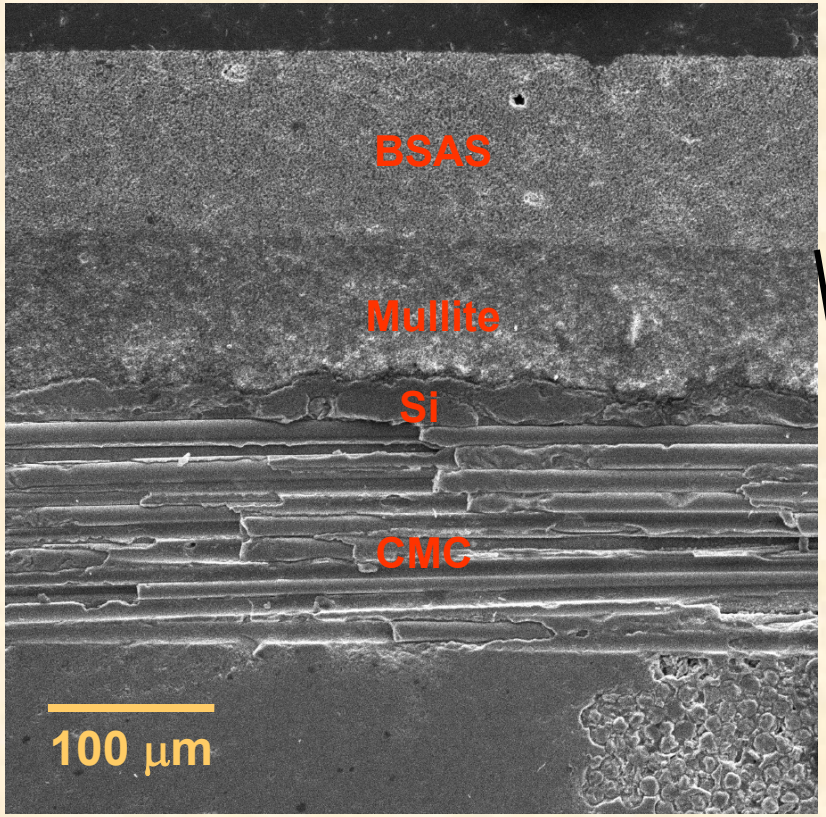
Cause of Defects at Interface of Mullite and BSAS Layers After 500 Hour Exposure at 1200°C in Steam?



Sintered Mullite-BSAS Coatings on CMC's

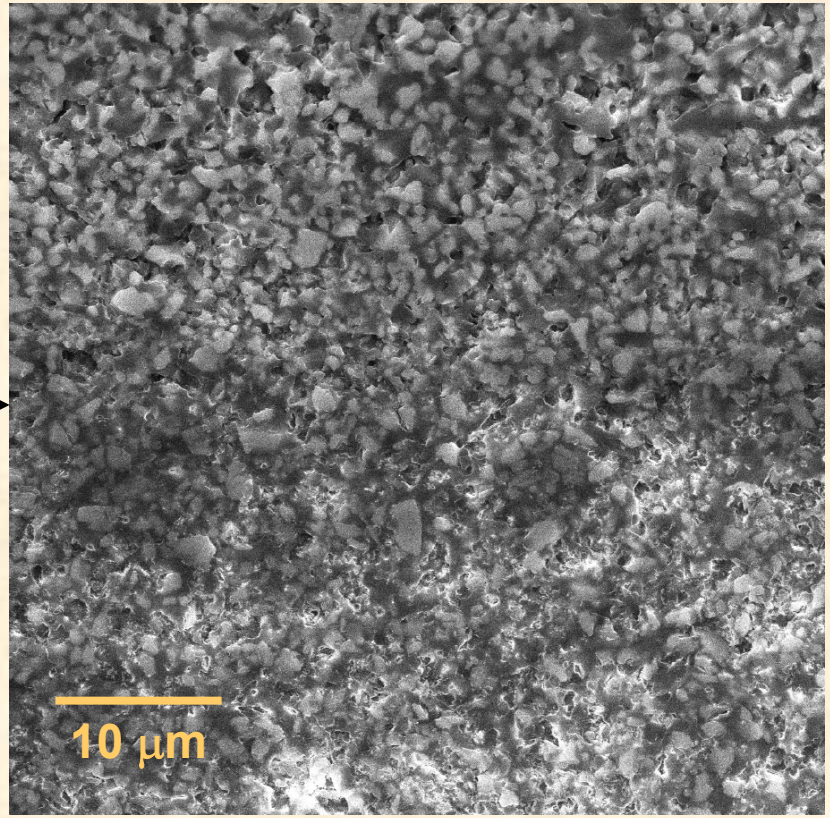
- **Note that the each layer was sintered independently**

Mullite-BSAS Layers on Si-Coated CMC's



?

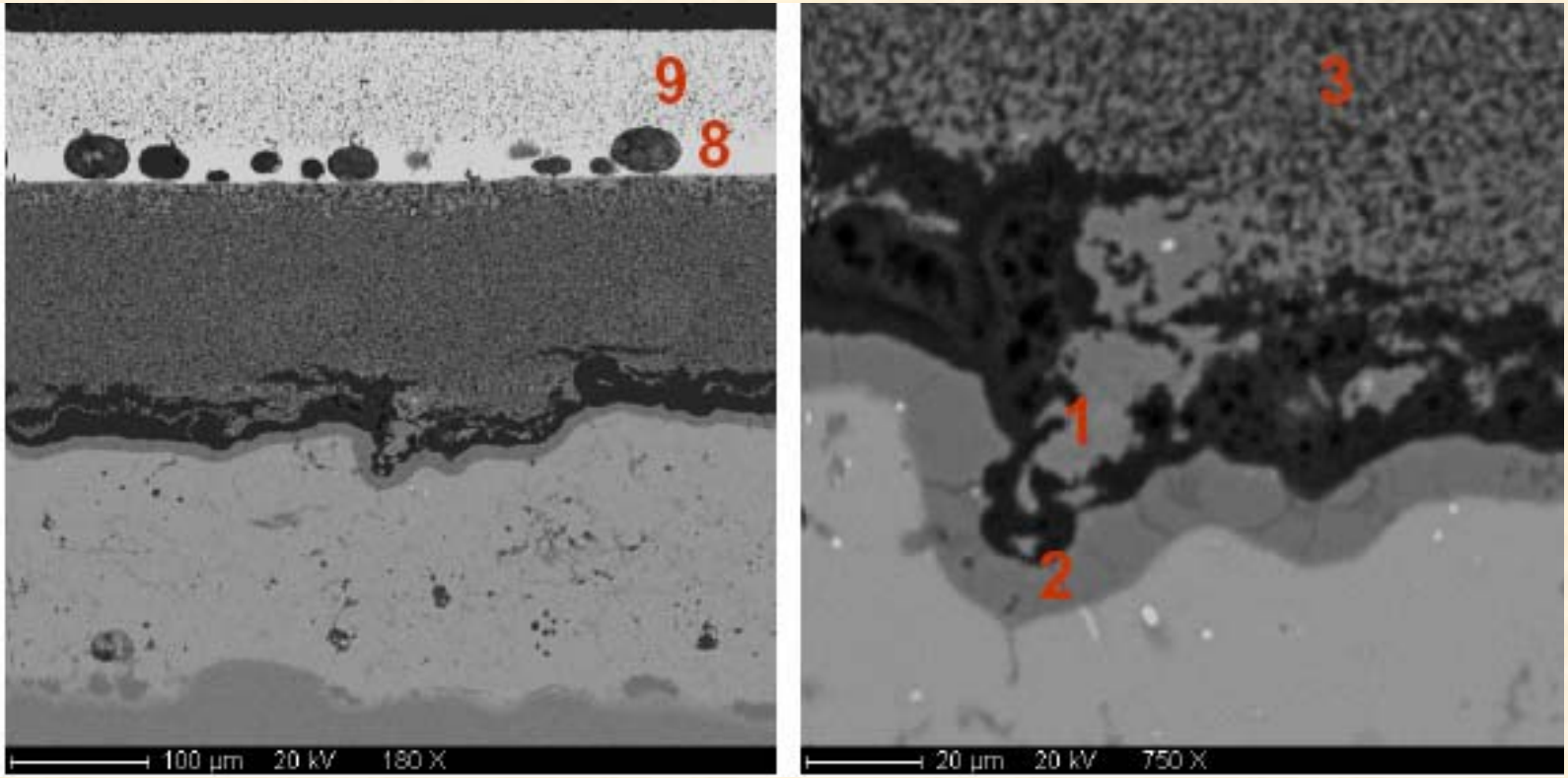
The BSAS-Mullite Interface



- The knit line is not obvious at higher magnification
- Can density of layers affect resulting test successes?

Mullite-BSAS Layers on Si-Coated CMC's

After 500 hour Exposure at 2400 F (1315 C)



1: High SiO_2 aluminosilicate, 2: SiO_2, 3: High Al_2O_3 mullite, 8,9: BSAS

Silica layer results typical of APS coated equivalent system

Summary

- The understanding of colloids are a useful tool to promote the success of slurry applied barrier coatings through control of
  - Coating thickness (solids loadings and rheology)
  - Coating structure, i.e, flatness, density, defects (additives)
  - Coating adhesion (wetting)
  - Coating composition
- Strength limiting flaws are in the substrate

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*Now currently at GE Aviation, Cincinnati, OH

Questions?