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High Temperature Ceramic Microstructure and Interface Evolution during Exposure to Particulate Laden Combustion Flows in Gas Turbine Engines

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Overview

- Introduction
  - The sand – CMAS problem
  - Protective Ceramic Coatings

- Ongoing Experimental Efforts
  - TBCs tested in full scale engine tests
  - EBC burner rig testing and characterization
  - CMAS characterization and evolution
  - Model bulk YSZ systems under CMAS attack

- Future Work
  - Advanced Interfacial Studies
  - Computational Studies

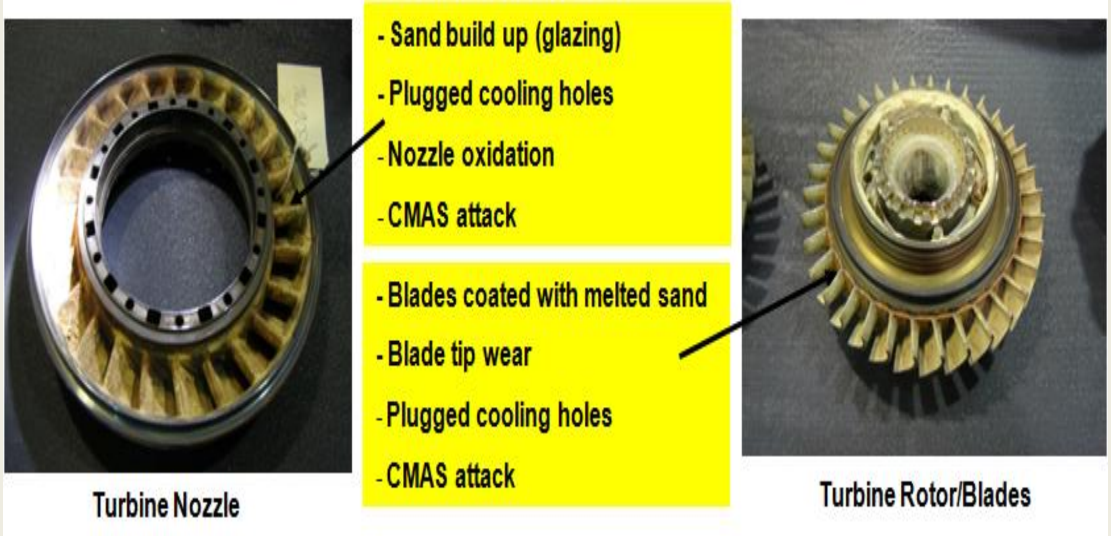
- Summary

OBJECTIVE

To innovate sandphobic coating and surface modification for high temperature turbine blades to resist sand glaze build-up and related Calcia-Magnesia-Alumina-Silicate (CMAS) attack on Thermal/Environmental Barrier Coatings (T/EBCs)

Sand – CMAS Problem

Field returned engine hardware from SWA



- Sand build up (glazing)
- Plugged cooling holes
- Nozzle oxidation
- CMAS attack

- Blades coated with melted sand
- Blade tip wear
- Plugged cooling holes
- CMAS attack

Turbine Nozzle

Turbine Rotor/Blades

Typical build-up on vane

Typical build-up on blade

Typical rotorcraft gas turbine engine nozzle and rotor blades with sand-induced damages

- **Hot section sand glazing / chemical attack is influenced by following parameters:**
  - Particle size and material composition of particle
  - Material properties of airfoil thermal barrier coating systems
  - Fluid flow dynamics and temperature

Problem Statement

- Various empirical methods in research/development to mitigate CMAS damage
- Lacking → quantitative physico-chemical model of the reactions
- This is a complex problem:
  - Impact + adherence
  - Infiltration
  - Glass formation via solidification

All occurring at elevated pressures + high temperatures

- AND, the contaminant adds complexity…
  - Natural sand → compositional variation, different grain sizes, and different morphologies based on the age and location of the desert.
- Synthetic sand developed to create a representative baseline
  - AFRL 02/03 represents the state-of-the-art
    - AFRL 02 → small grains, used for bench-level and component-level testing
    - AFRL 03 → larger grain distribution, used for engine-level testing

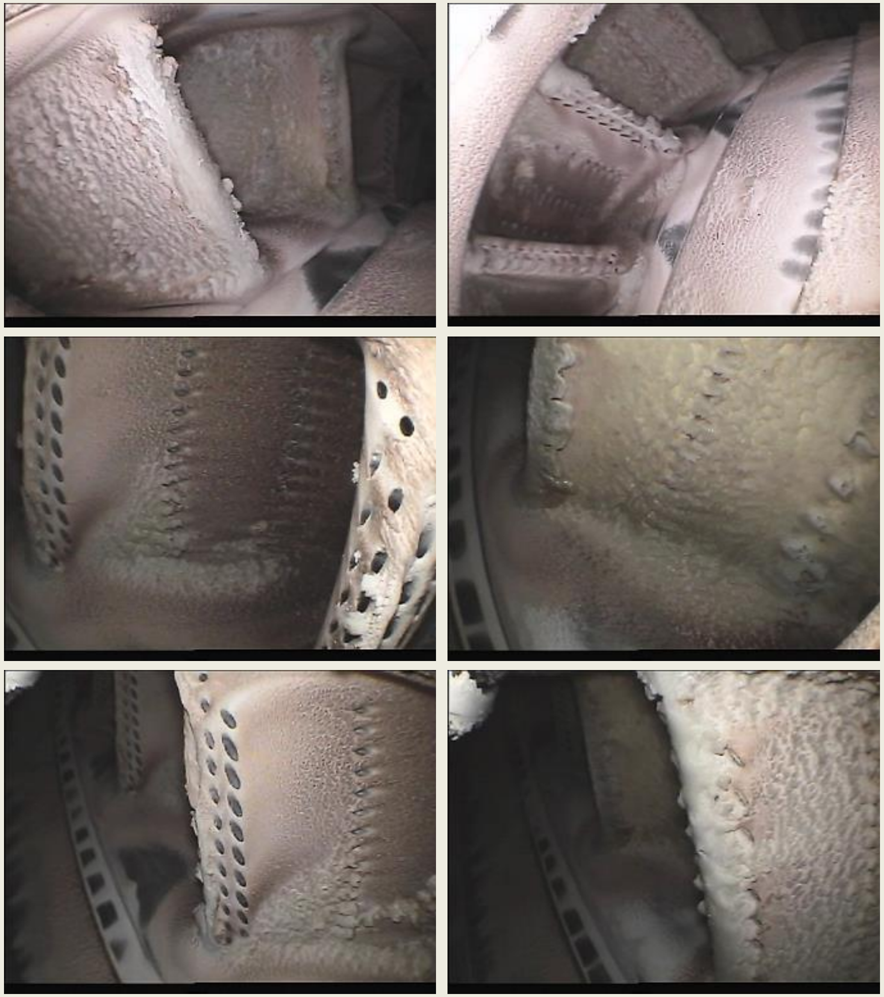
Layered and Composite TBCs Exposed to Full Scale Sand Ingestion Engine Test:

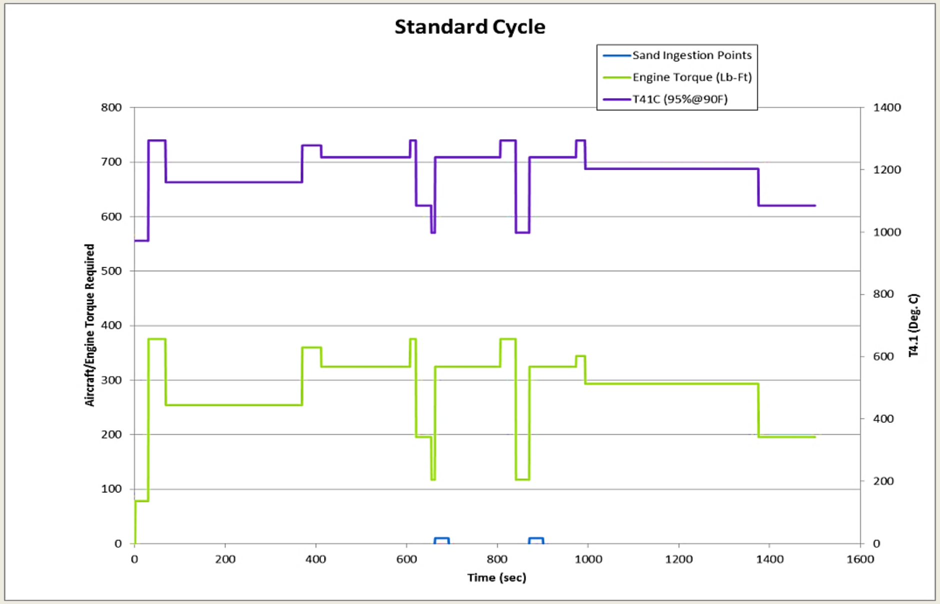
CMAS Adhesion and TBC Microstructural Evolution

Sand Ingestion Jet Engine Test

As-built nozzle ring

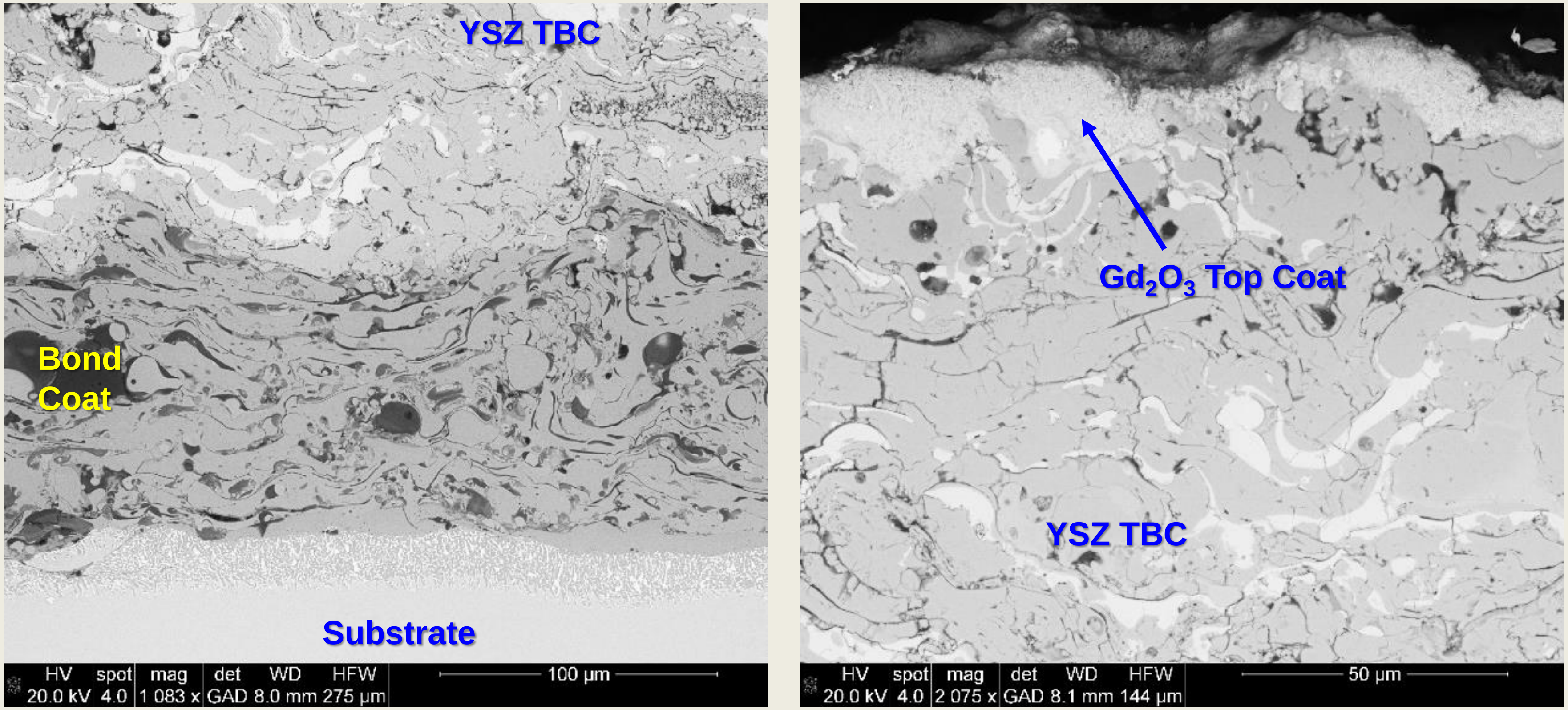
Borescope images from engine run





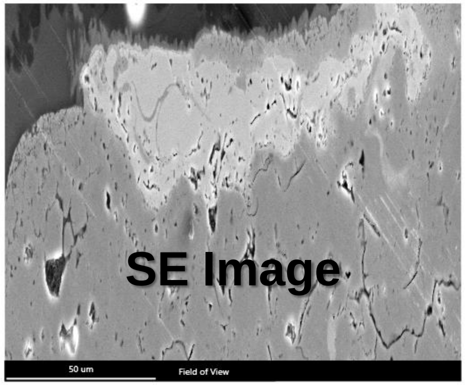
Engine Tested Consisted of Two 25 min Cycles
MAX Temperature of 1240 °C

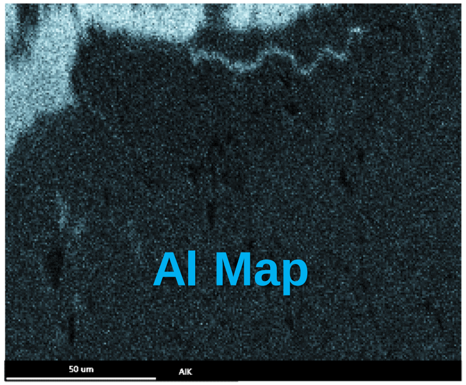
ARL-NASA-02 – Layered and Composite TBC

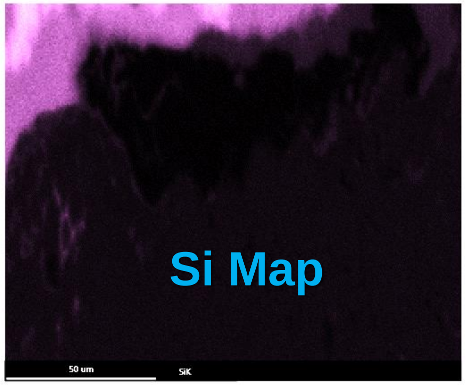


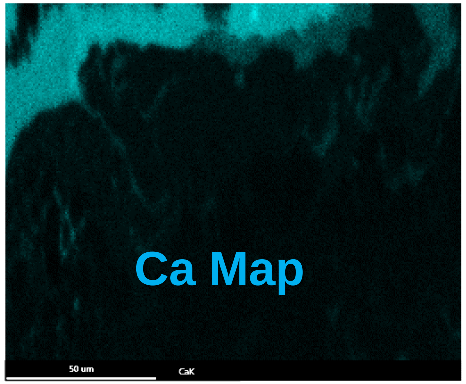
- ➢ No significant damage or chemical degradation observed on ARL-NASA-02
- ➢ Thin segments (10-20 µm) of Gd_2O_3 top coat are found throughout the specimen

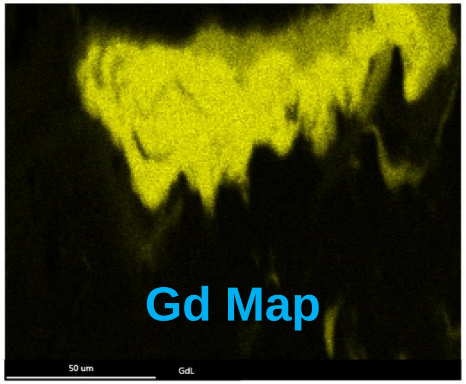
ARL-NASA-02 EDS

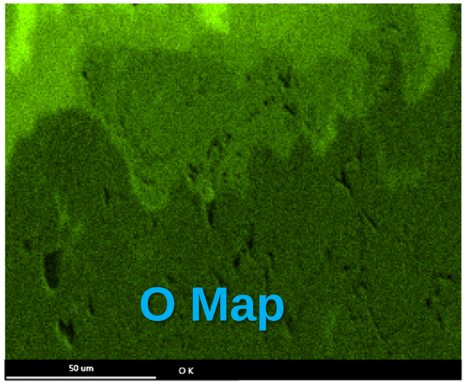


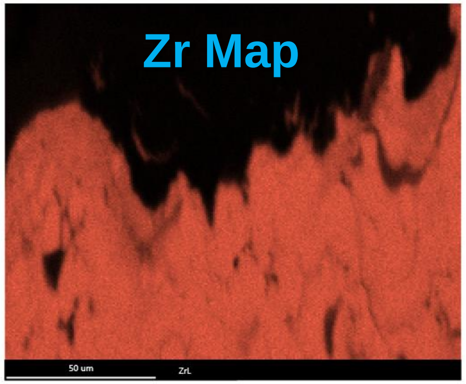


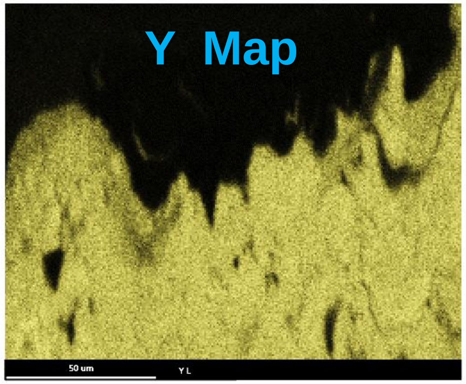




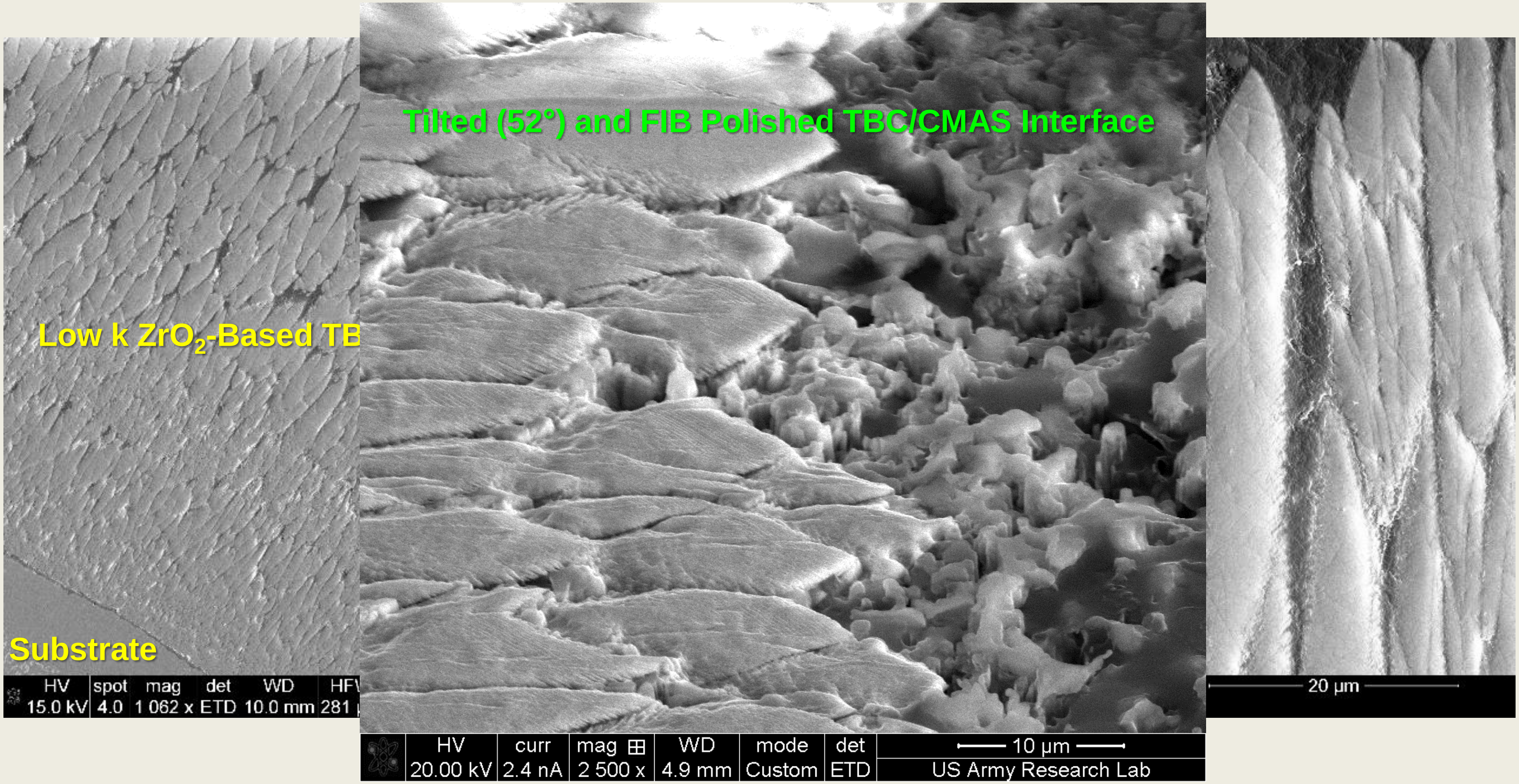






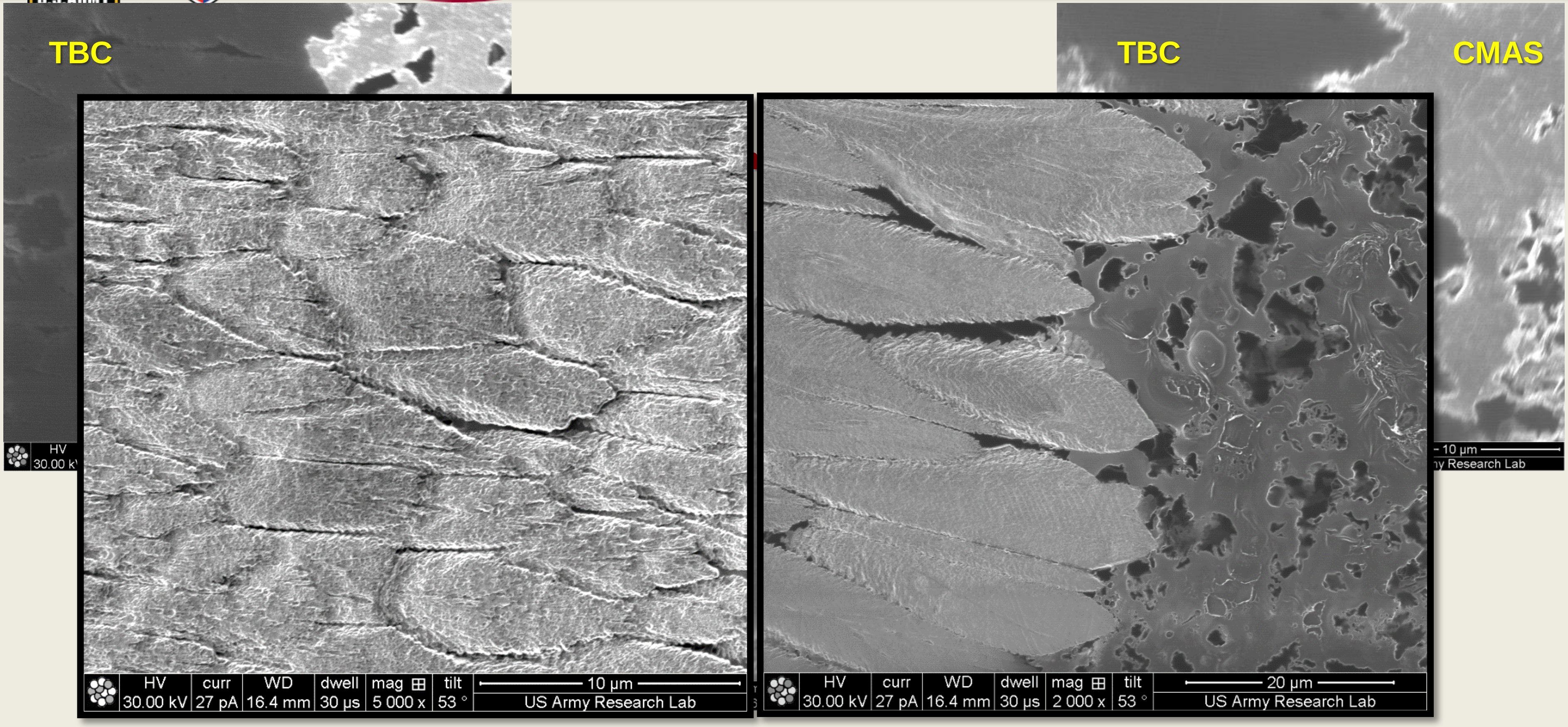


ARL-NASA-06 – Doped TBC



- ARL-NASA-06 exhibits minimal signs of structural damage
- Porous columnar structure does not lead to CMAS infiltration

ARL-NASA-06 – FIB Imaging



- ➢ **FIB ion milling and imaging provides distinct contrast between TBC & CMAS**
  - **CMAS infiltration can be assessed *w/out EDS mapping***

- ➢ **FIB polishing removes surface artifacts due to mechanical preparation (e.g., debris, polishing media)**

Environmental Barrier Coatings (EBC) under Sand Laden Combustion Flows

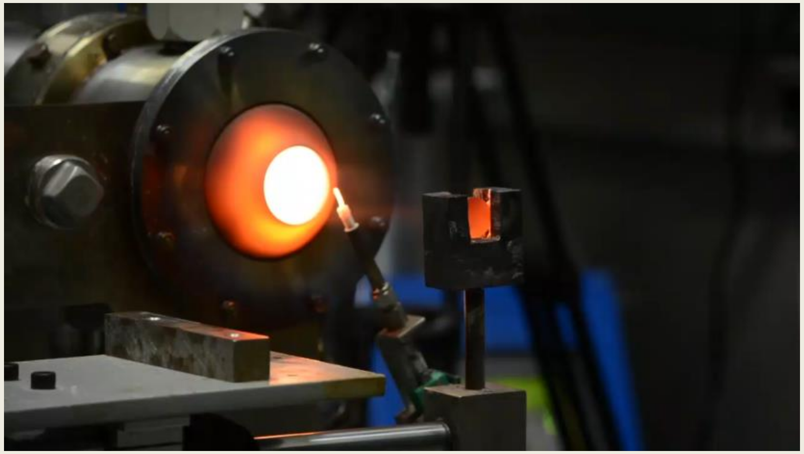
Burner Rig Testing and Microstructural Evolution

EBC Infiltration Kinetics

- Burner Rig testing with sand ingestion will be conducted on several promising EBCs to evaluate resistance to CMAS infiltration

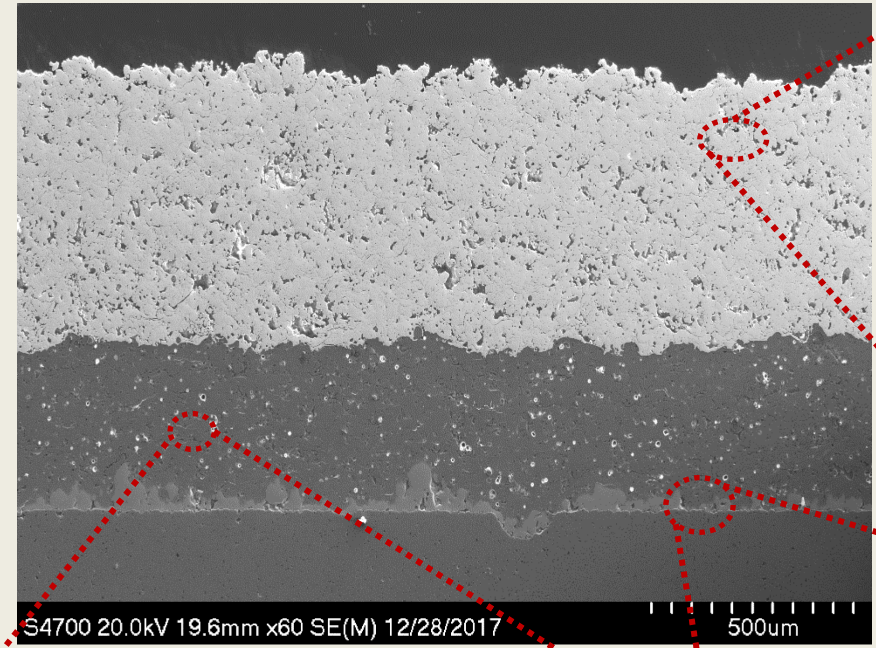
- EBCs will be held under continuous exposure to sand laden combustion flow at ~0.5 Ma and ~1550 °C, for set time intervals (5 – 60 min)
  - Times can be adjusted based on CMAS infiltration behavior and EBC durability

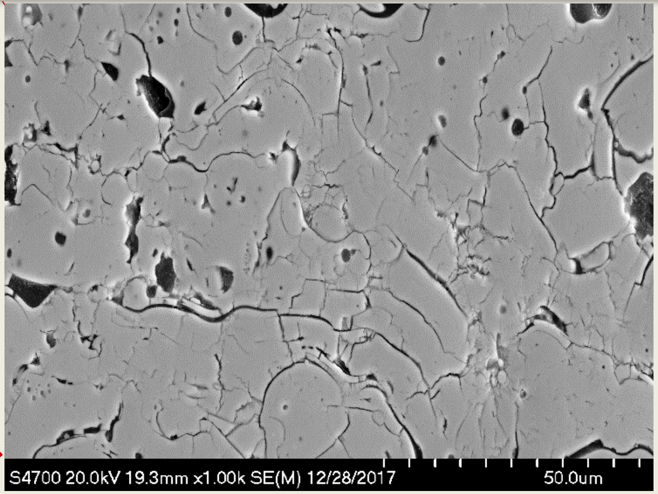
- Objective is to quantify the CMAS infiltration kinetics on different EBC systems, and if possible, within individual layers of the EBC



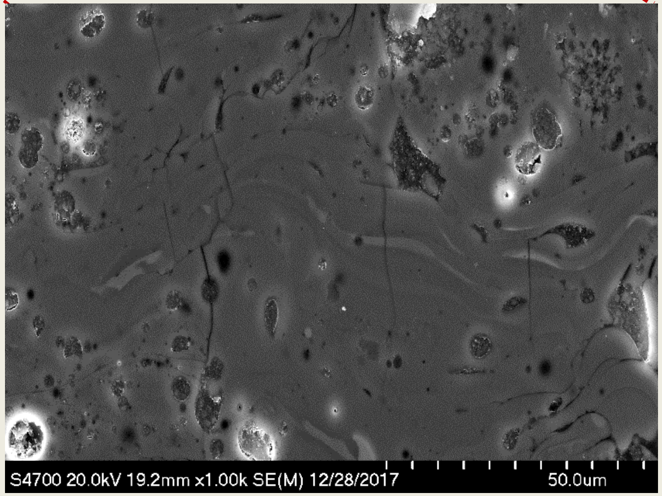
ZrO_2-Y_2O_3 based EBC Systems: As Sprayed

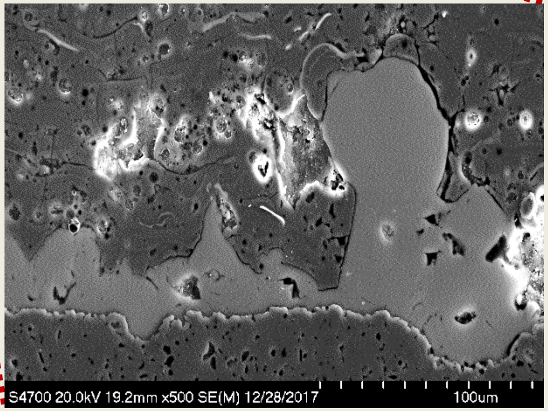
APS ZrO_2-Y_2O_3 based top coat provides low thermal conductivity a good damage tolerance





Alumina-rich Mullite Layer





Si Layer serves as oxygen barrier for Substrate

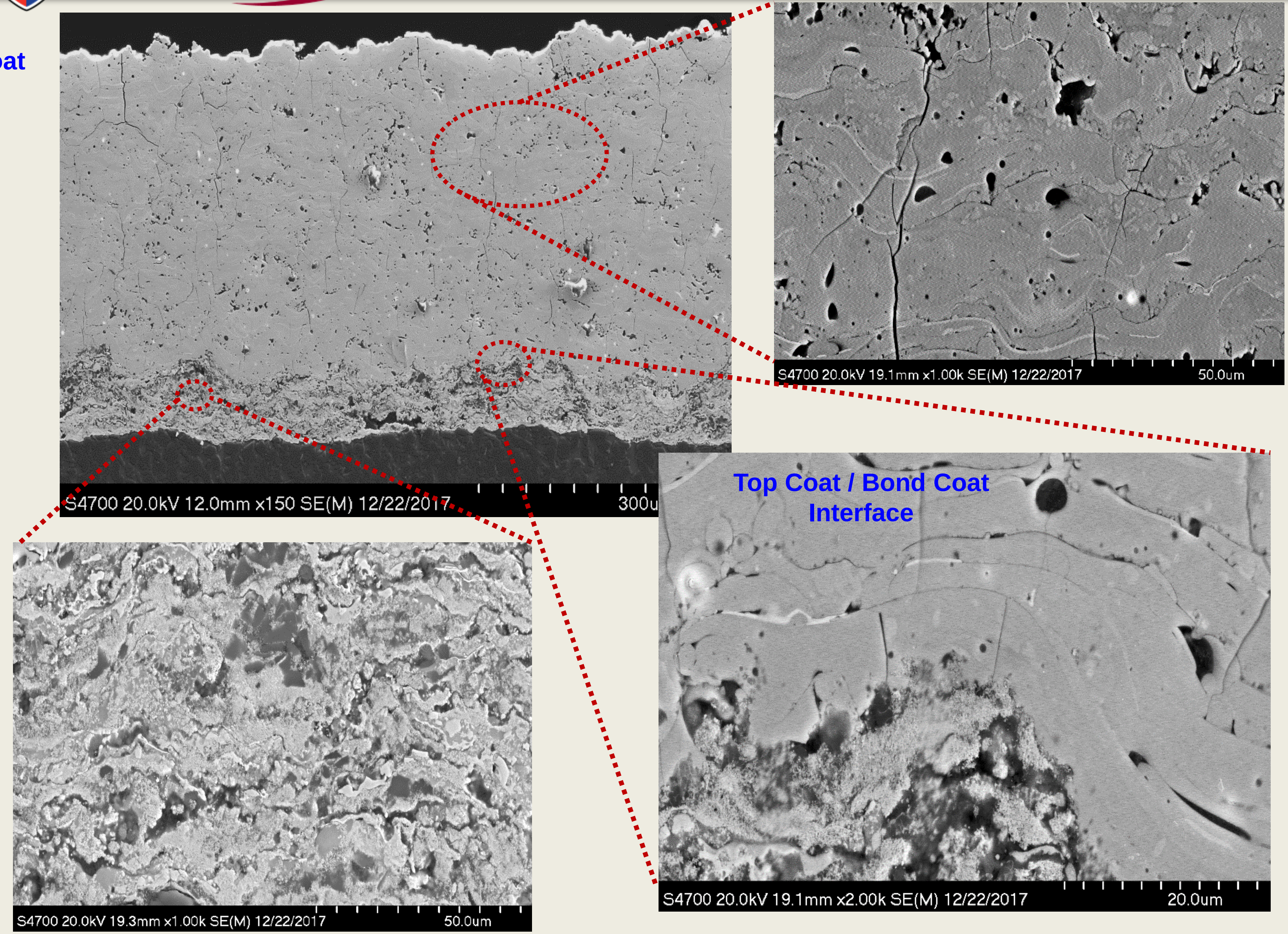
-Sensitive to surface roughness

-Uneven thickness

RE DS on HfO_2-Si Bond Coat EBCs: As Sprayed

RE DS Top coat w/ Vertical Cracks for Improved Damage Tolerance

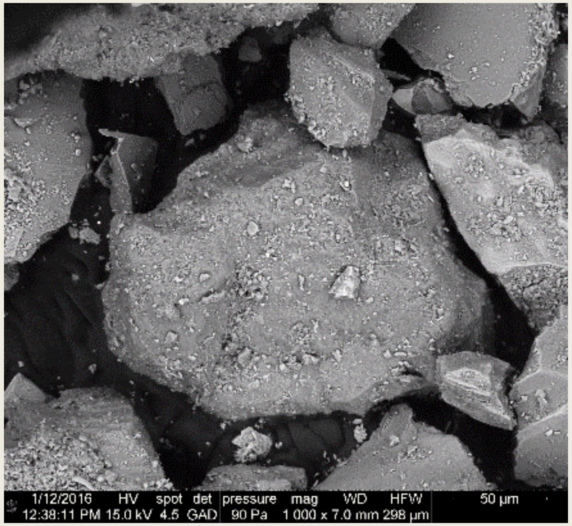
HfO_2-Si bond coat for reduced CTE mismatch with SiC-SiC CMCs



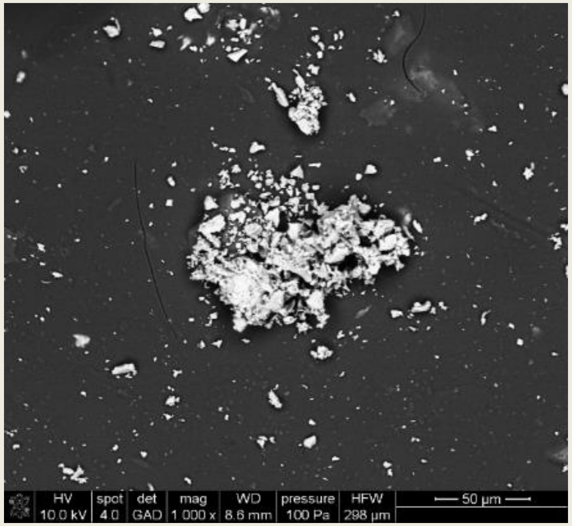
Characteristics and Chemical / Microstructural Evolution of Sand/CMAS

Sand Morphology

Natural Sand

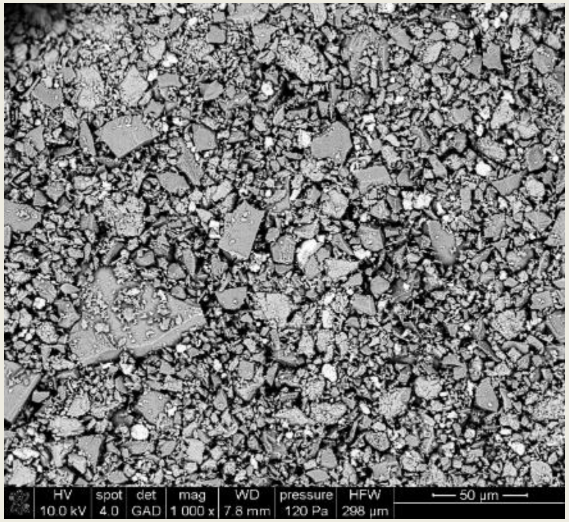


AFRL 02 Sand

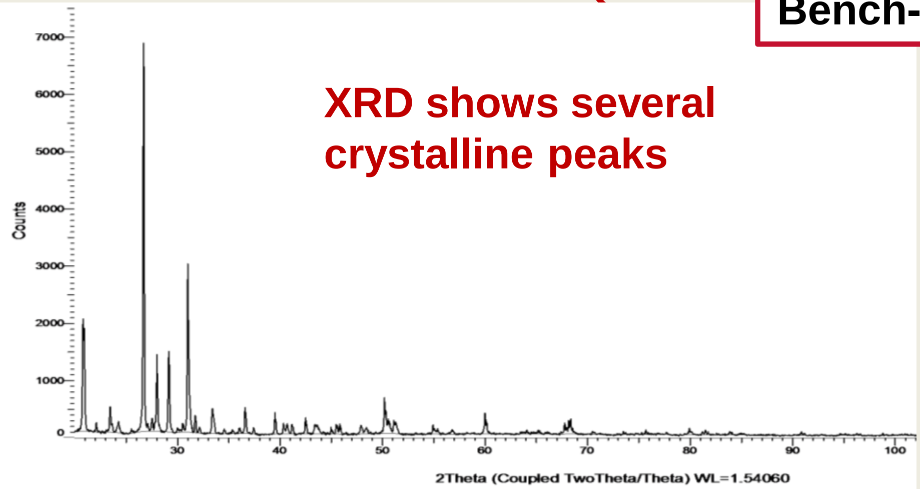


Bench-level

AFRL 03 Sand



Engine-level



XRD shows several crystalline peaks

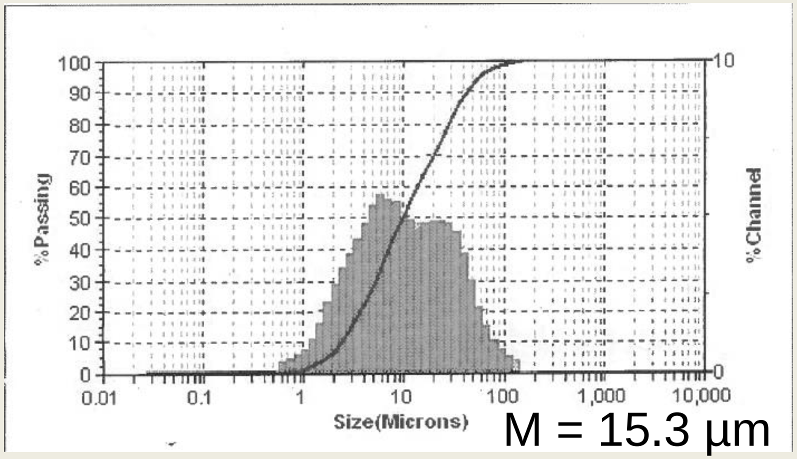
AFRL synthetic sand

- 34 % quartz (SiO_2)
- 30 % gypsum ($CaSO_4 \cdot 2H_2O$)
- 17 % aplite (SiO_2 + $KAlSi_3O_8/NaAlSi_3O_8/CaAl_2Si_2O_8$)
- 14 % dolomite ($CaMg(CO_3)_2$)
- 5 % salt (NaCl)

Sand size distribution

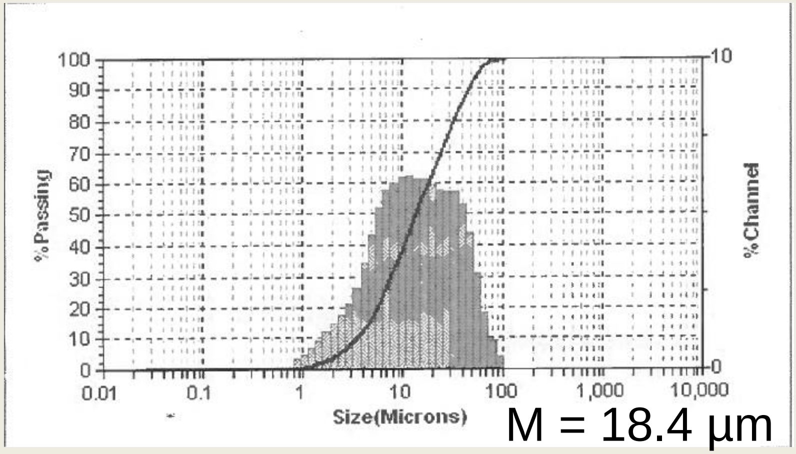
PTI Information

AFRL 02



M = 15.3 µm

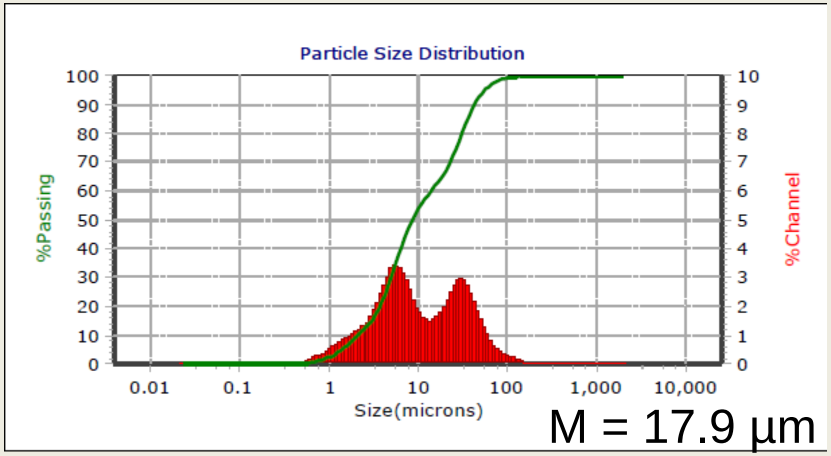
AFRL 03



M = 18.4 µm

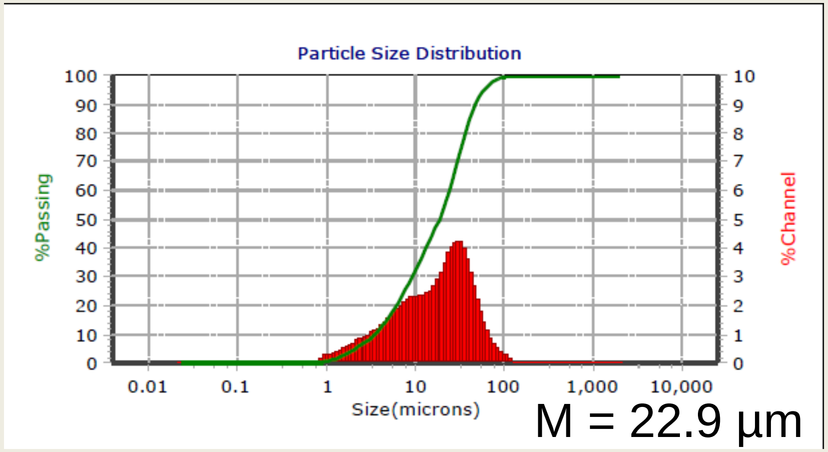
ARL Demonstration

AFRL 02



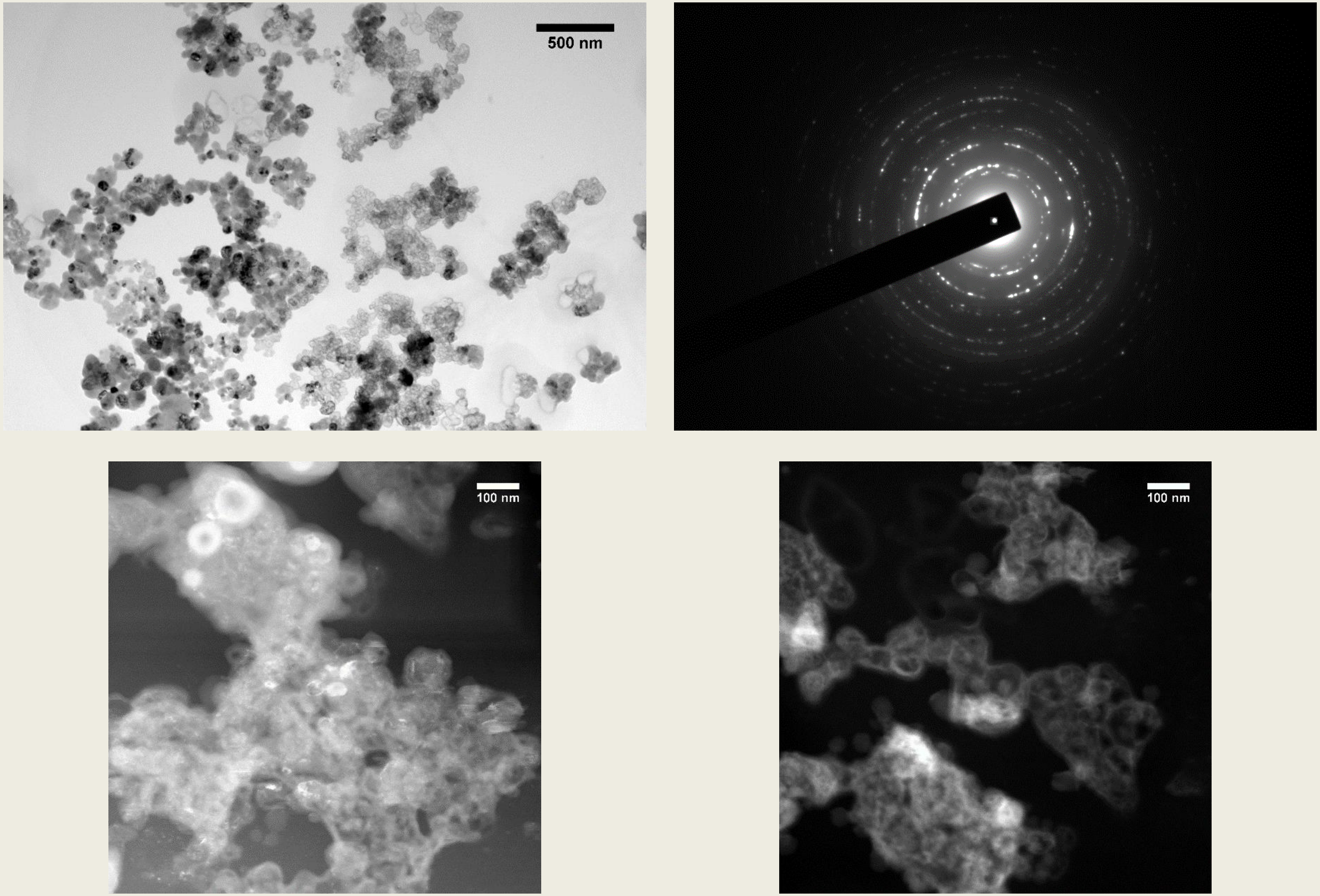
M = 17.9 µm

AFRL 03

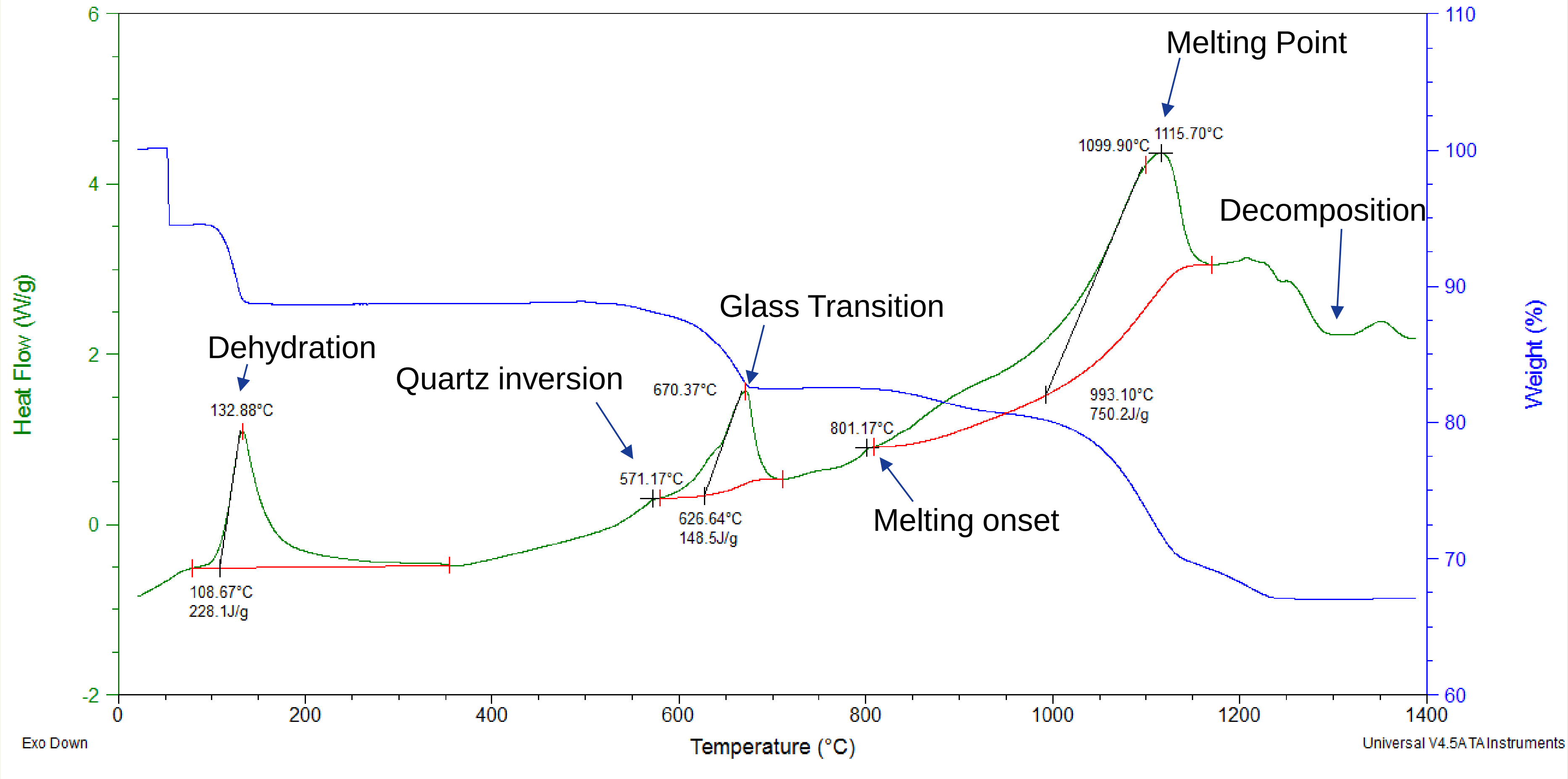


M = 22.9 µm

TEM of Nanometric Crystals in AFRL-02



Differential Scanning Calorimetry
AFRL-02

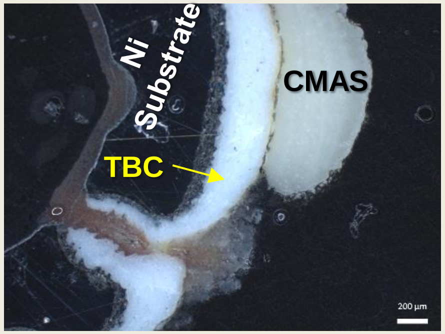


under Ar gas flow

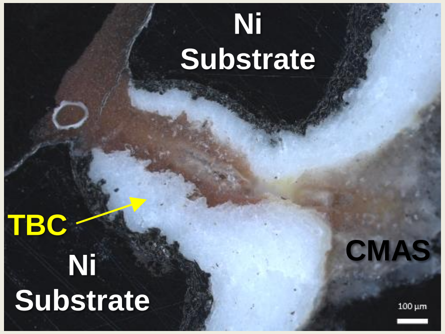
Optical Microscopy (OM) - Nozzle Cross-Sections

ARL-NASA-02

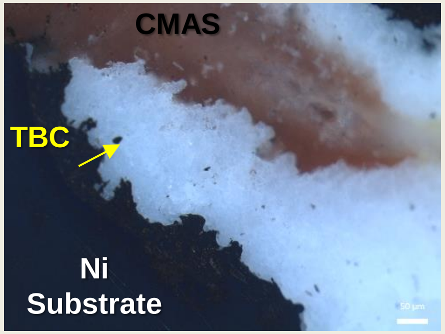
50x Dark Field



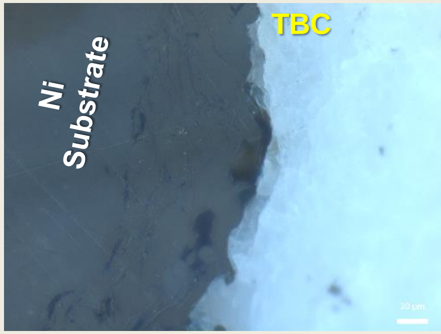
100x Dark Field



200x Polarized



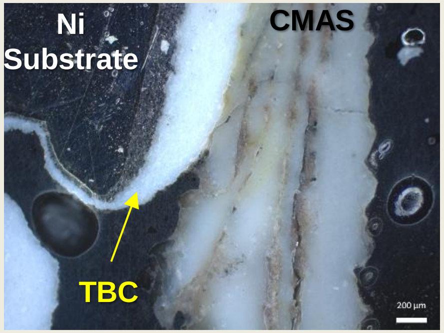
500x Polarized



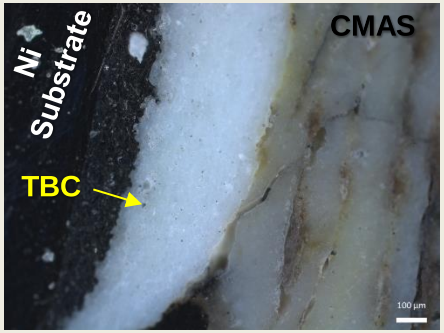
Leading Edge (LE)

ARL-NASA-03

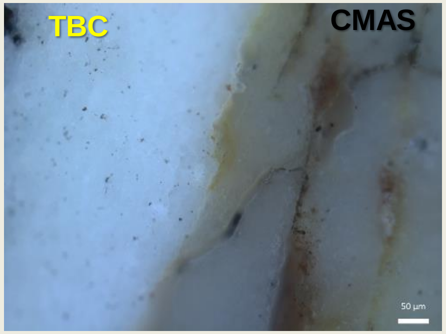
50x Dark Field



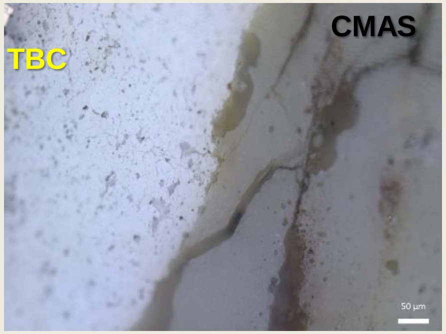
100x Dark Field



200x Polarized

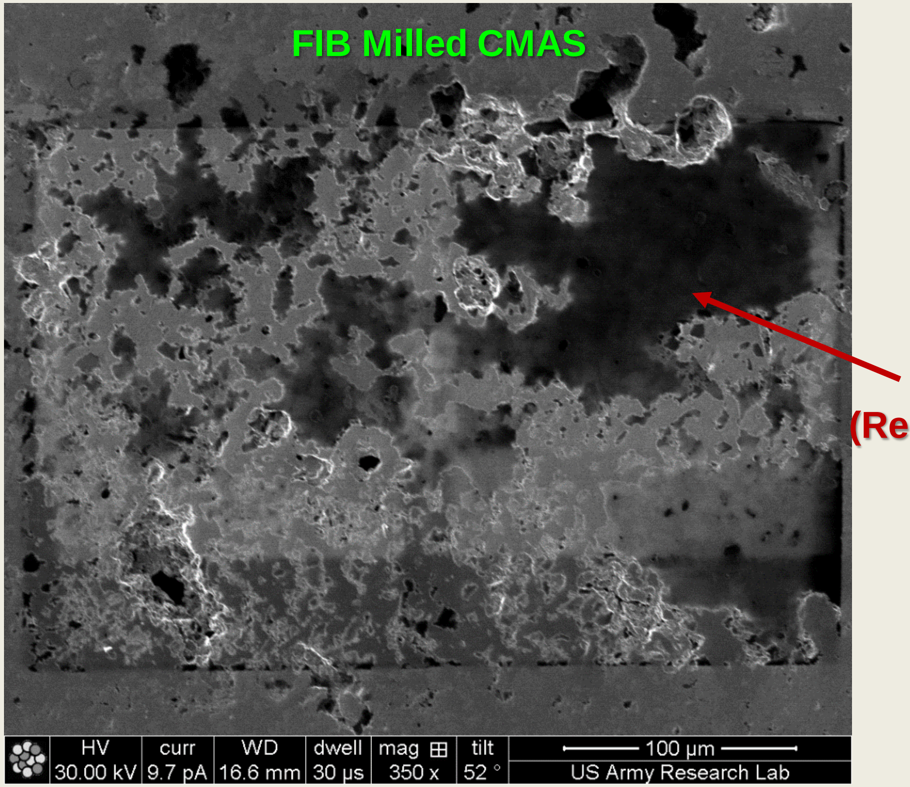


200x Bright Field

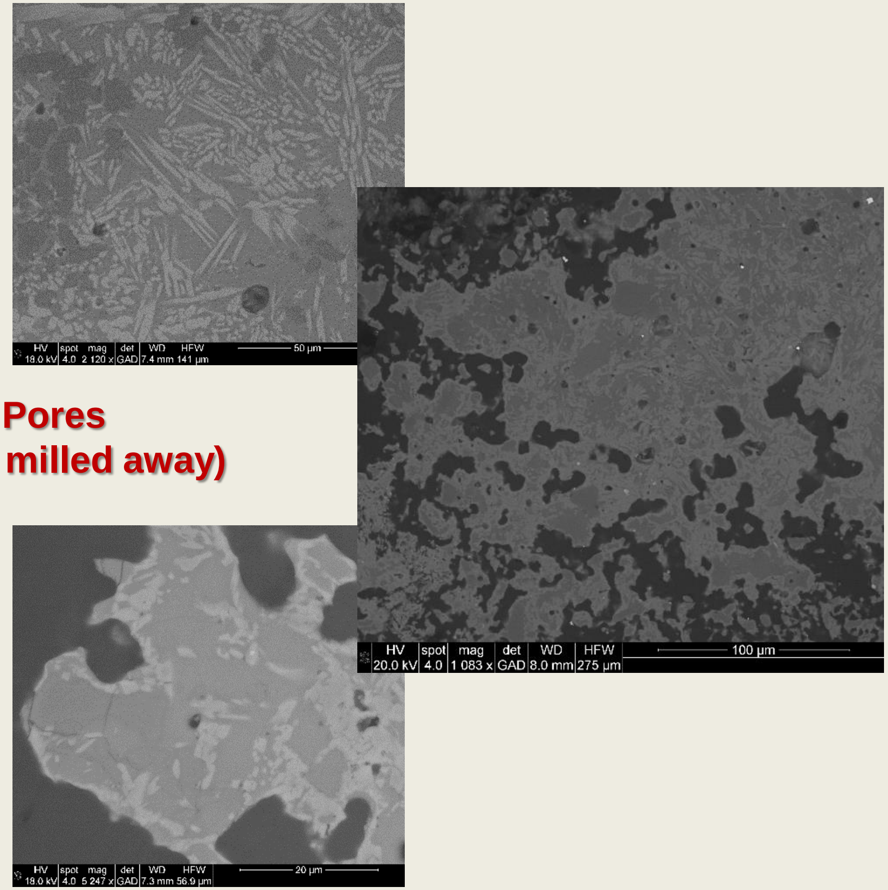


Pressure Side (PS) - Near TE

CMAS Characterization



Pores
(Resin milled away)



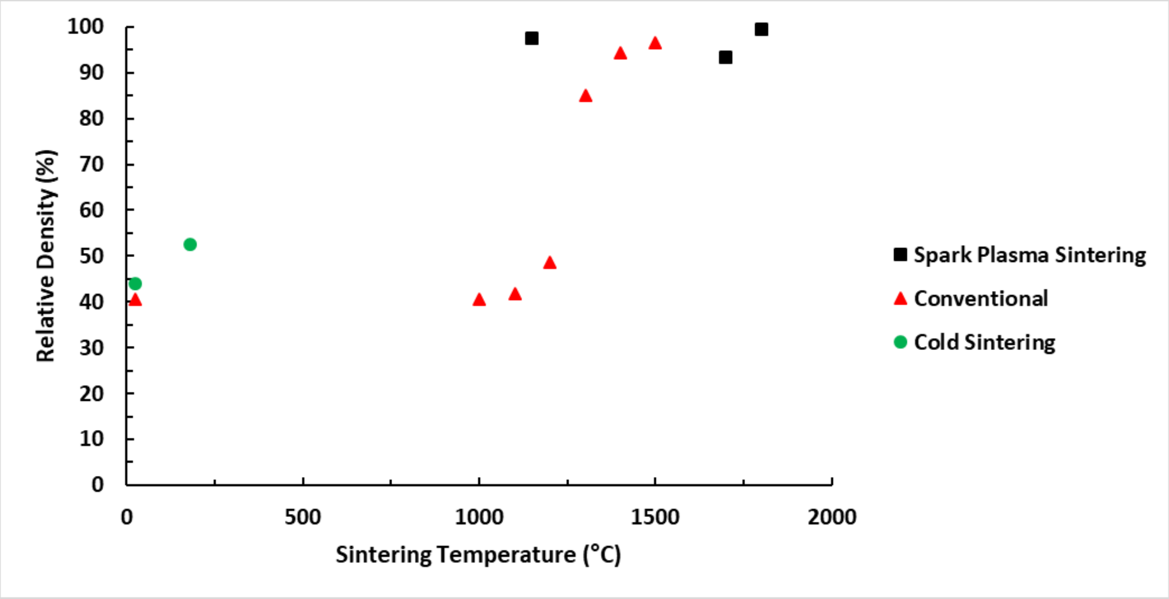
- **CMAS deposits exhibit chemical and microstructural variances**
- **Complex environment coupled with complex CMAS chemistry leads to a range of material responses and behaviors**

Model YSZ-based Sintered Compacts under Controlled CMAS Attack:

Effect of Porosity on CMAS Infiltration and YSZ/CMAS Interactions

YSZ Pellet Synthesis

- Approximately 25 pellets synthesized
  - 3 mol%, 8 mol%, 7 wt% (~4 mol%)
  - Conventional (pressureless), spark plasma, and cold sintering
- Cold Sintering: ~50% relative density
- Spark Plasma Sintering: ~95-99.5% relative density
- Conventional Sintering: ~40-95% relative density

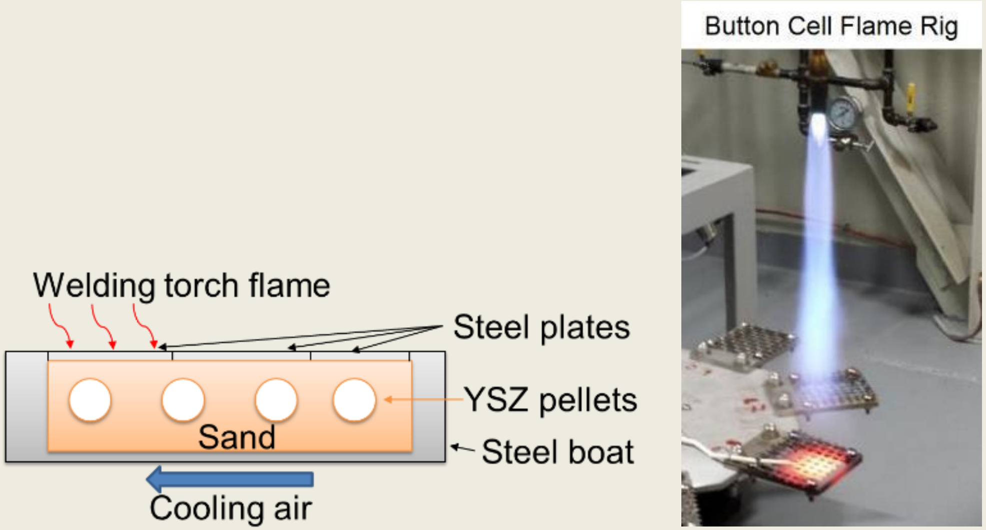


Comparison of relative densities achieved through varying sintering methods

CMAS Attack Testing

Button Cell Flame Test Rig

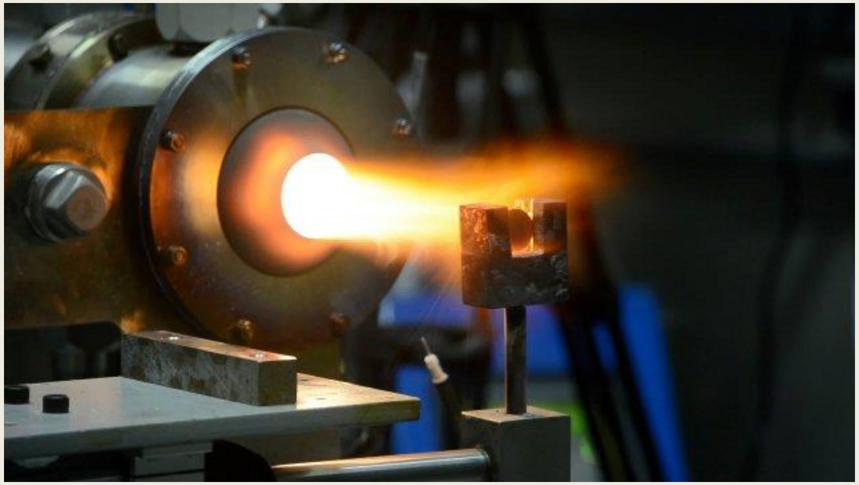
- Pellets buried in sand
- 1300°C
- 15 min exposure time
- Stationary contact



Schematic of the button cell flame rig along with the actual set-up

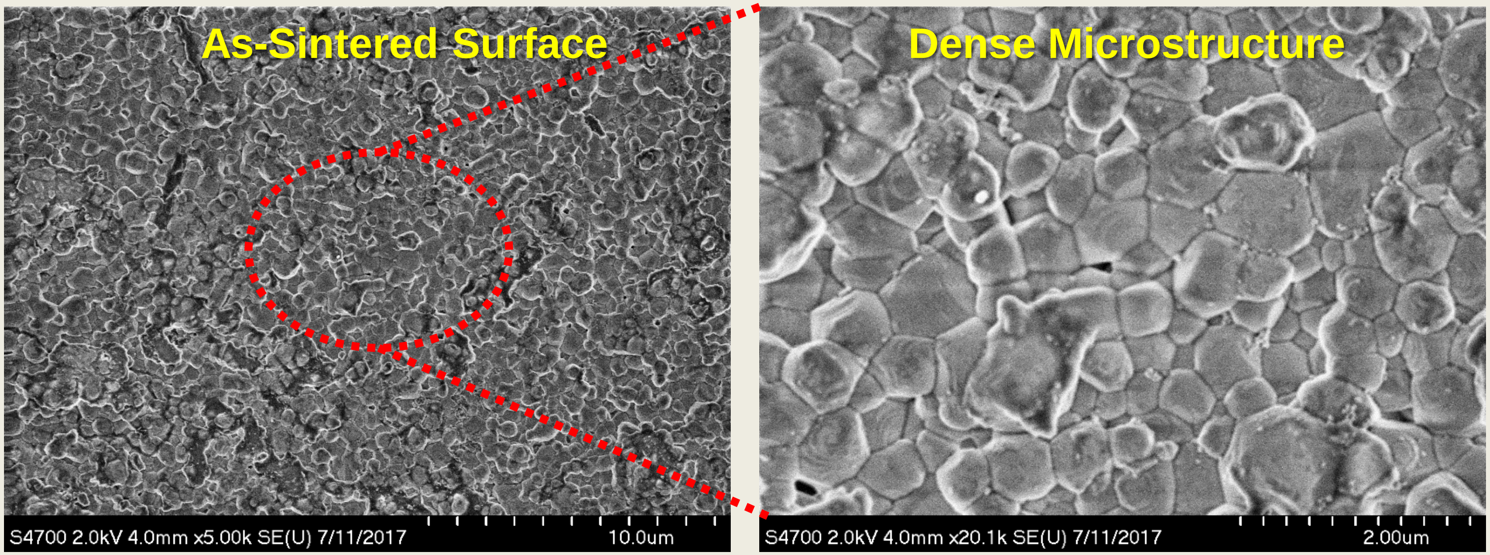
Hot Particulate Ingestion Rig

- Replicates temperature and velocity conditions of a jet engine
- Settings:
  - 1300°C
  - 0.3 M
  - 1 g of sand/min,
  - 3 cycles of 5 min exposure; 15 min total
- Dynamic CMAS Contact

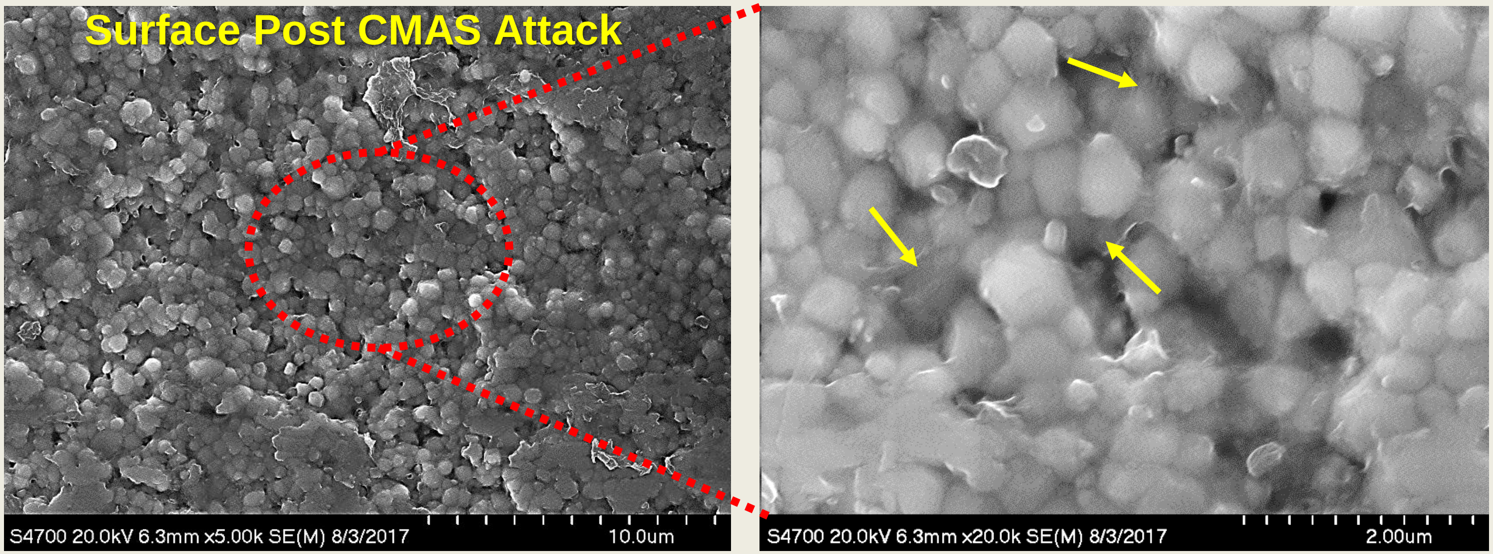


Hot particulate ingestion rig in operation

Surface Morphology – Dense SPS'd Compact



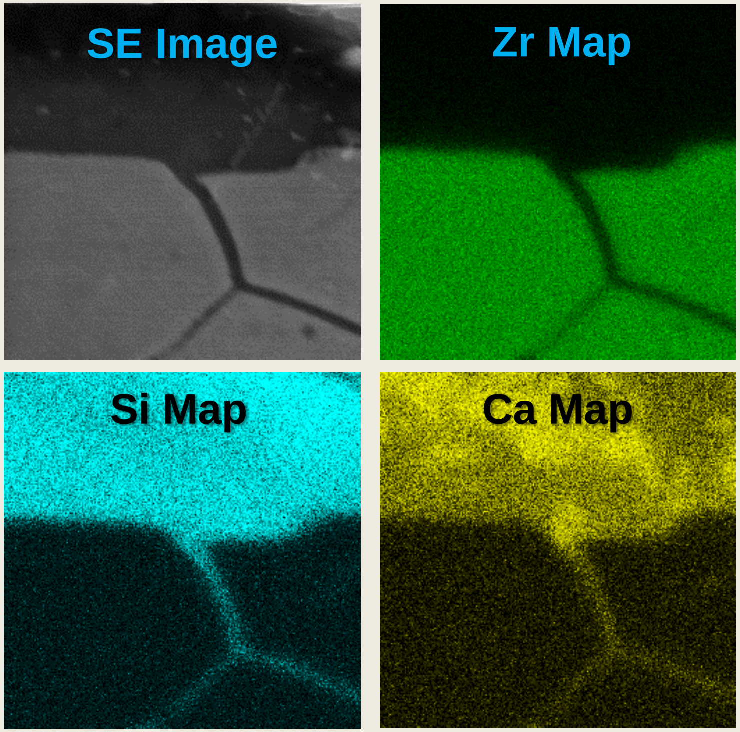
- SPS consistently produced densest pellets
  - 97% Dense pellet exhibits dense microstructure on as-sintered surface
  - Grain structure is relatively fine (~ 1 – 2 µm)

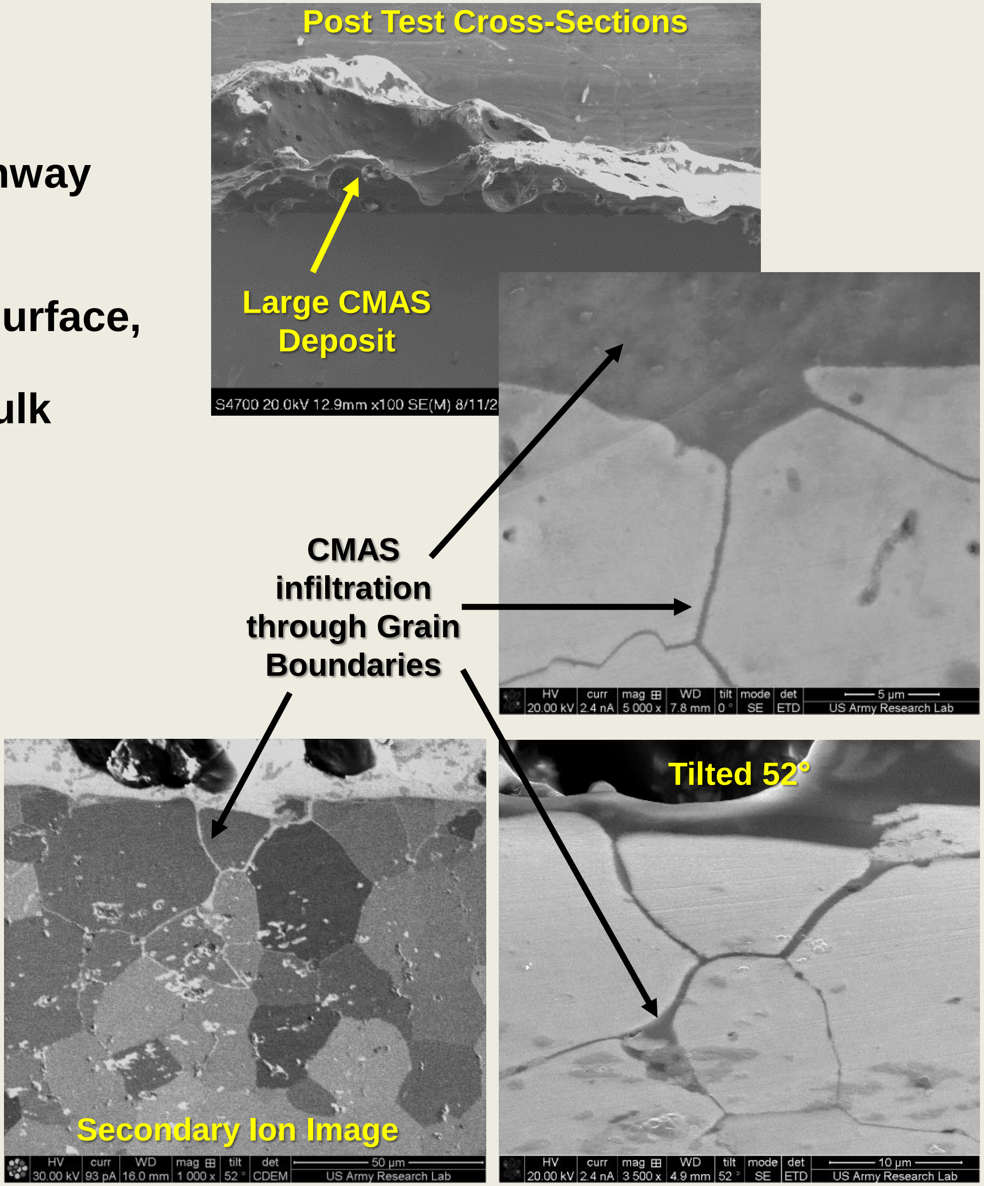


- Post CMAS attack grains appear to be covered in CMAS 'glaze'
  - Thin, transparent CMAS strands seen
  - Thin deposits not seen via visual inspection
  - Grains appear to be less faceted, suggesting possible dissolution

CMAS Attack on 99.5% Dense SPS Pellet

- Highly dense pellets were expected to mitigate CMAS attack by preventing infiltration
  - Lack of pores eliminates facile pathway for infiltration
- CMAS infiltration is observed on near surface, adjacent to surface deposits
  - Infiltration depth over 50 µm into bulk




Post Test Cross-Sections

Large CMAS Deposit

CMAS infiltration through Grain Boundaries

Secondary Ion Image

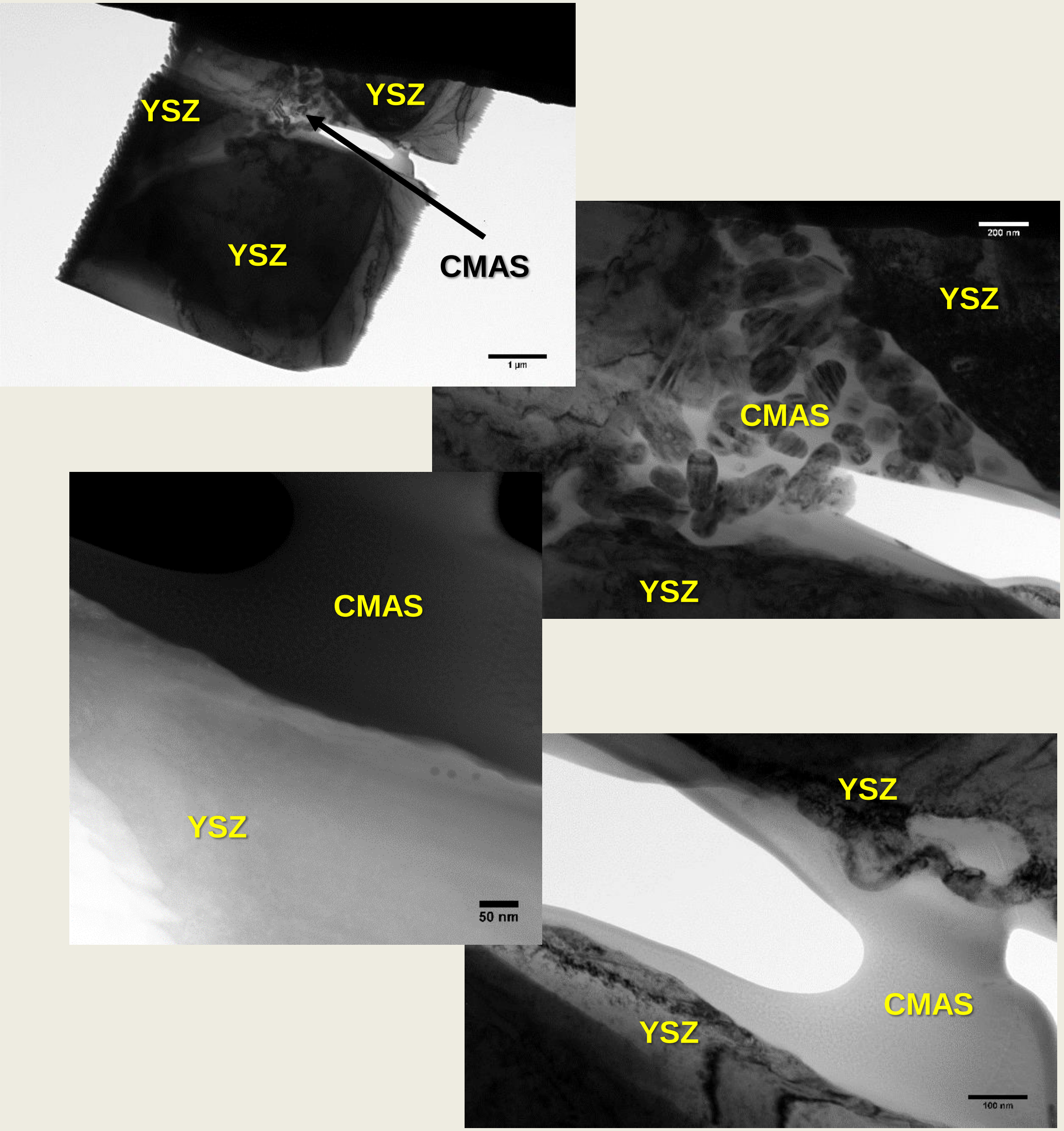
Tilted 52°

Infiltrated YSZ Grain Boundary Characterization

- TEM studies underway to elucidate CMAS infiltration mechanism in the absence of porosity

- Nanometric YSZ particles at triple junction exhibit severe twinning
  - Not seen in YSZ grains away from CMAS
  - Deformation twinning suggests CMAS induced strains play a role in infiltration/dissolution/reaction mechanisms

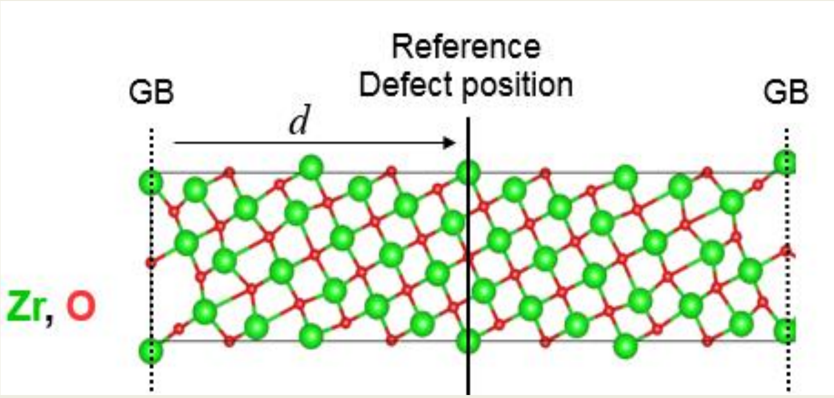
- STEM/EDS/EELS analysis will attempt to determine atomic scale diffusion mechanisms at CMAS/YSZ interface

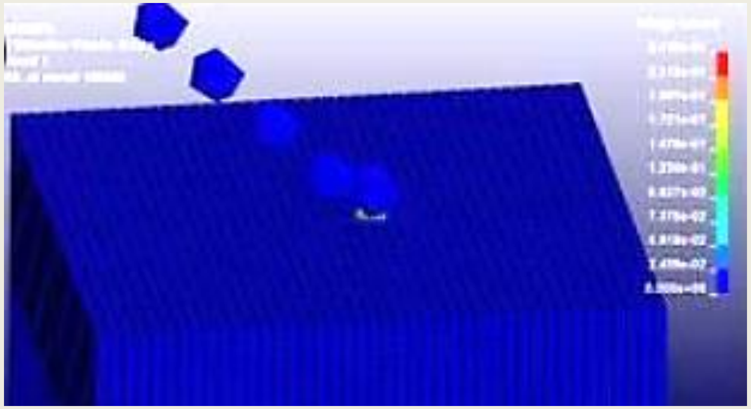


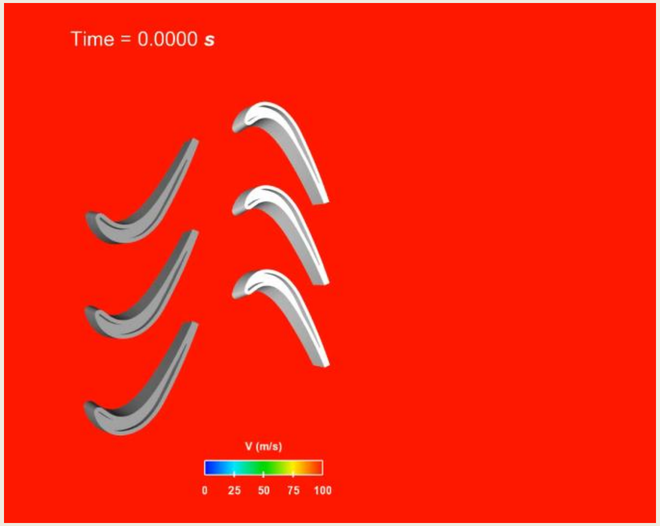
Future Work

Computational Materials Modeling

- Flow field modeling in gas turbine engine to determine regions in components exposed to most severe CMAS attack and accumulation conditions
- Molecular dynamics (MD) simulations on CMAS constituent element segregation on YSZ boundaries, with Prof. Kesong Yang at University of California San Siego
- Particle impact/adhesion simulations on EBC/CMC systems





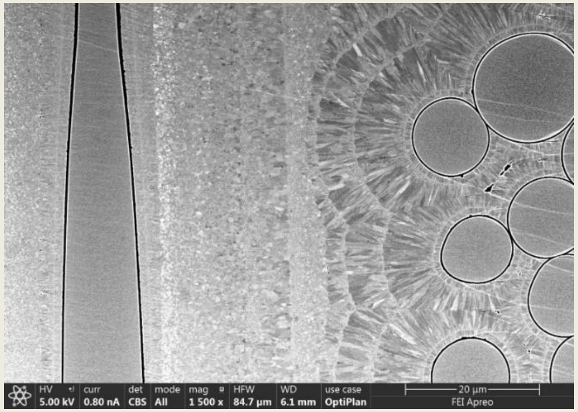


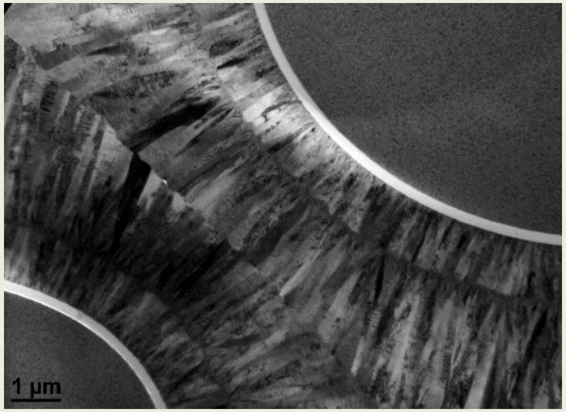
Future Work

Nanoscale Interfacial Characterization

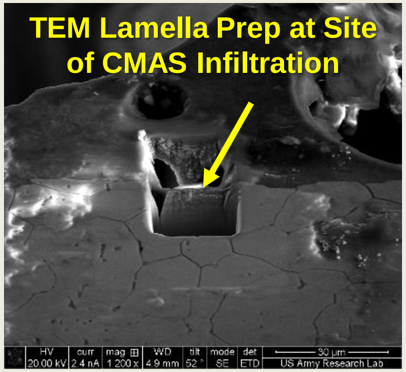
- Evaluation of CMAS kinetics in RE silicate / disilicate EBCs on SiC and CMC substrates will be conducted at ARL under engine relevant conditions
- Site specific TEM studies (EELS, SAD) will be conducted at CMAS/TBC/EBC/CMC interfaces and on CMAS phases.
- Evaluation of microstructure and properties of various commercially available CMCs and ceramic fibers.

CMC Cross Section





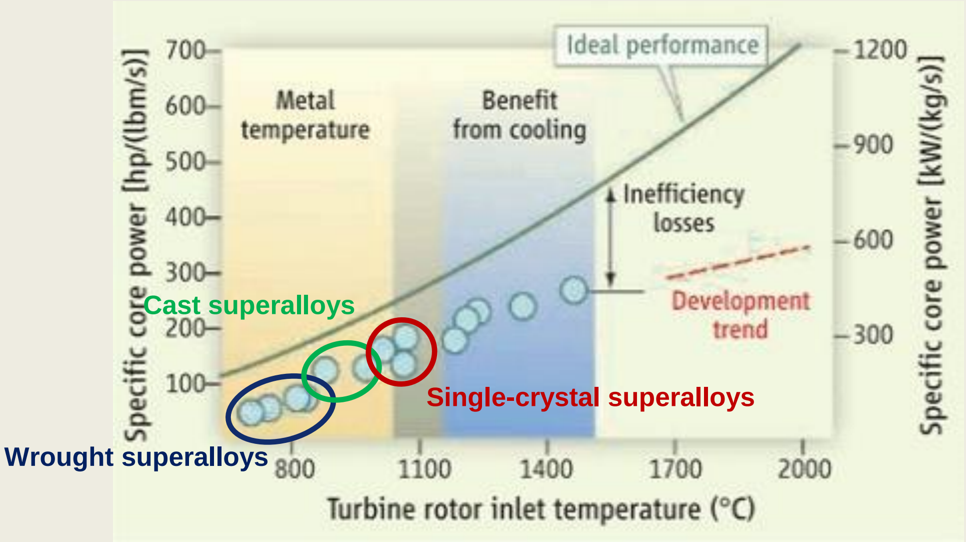
Site Specific TEM Characterization via FIB


TEM Lamella Prep at Site of CMAS Infiltration

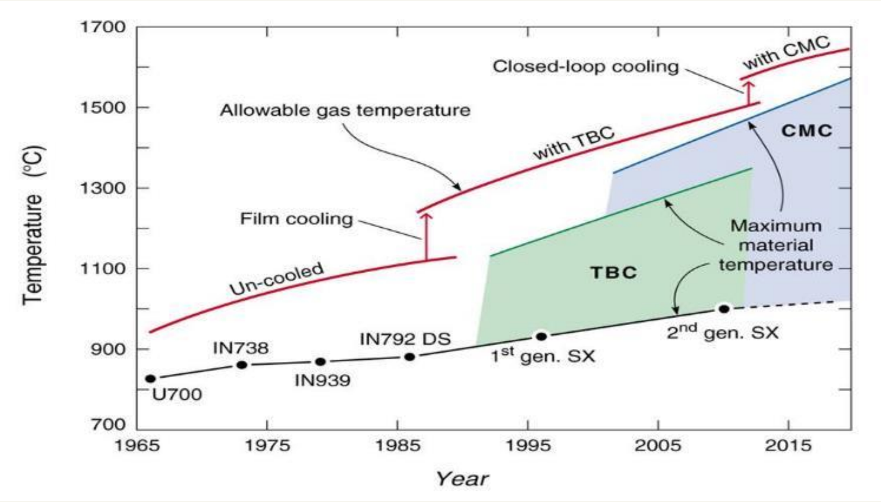

Ion Milled Infiltrated Grain Cross Section

Back-up

Protective ceramic coatings



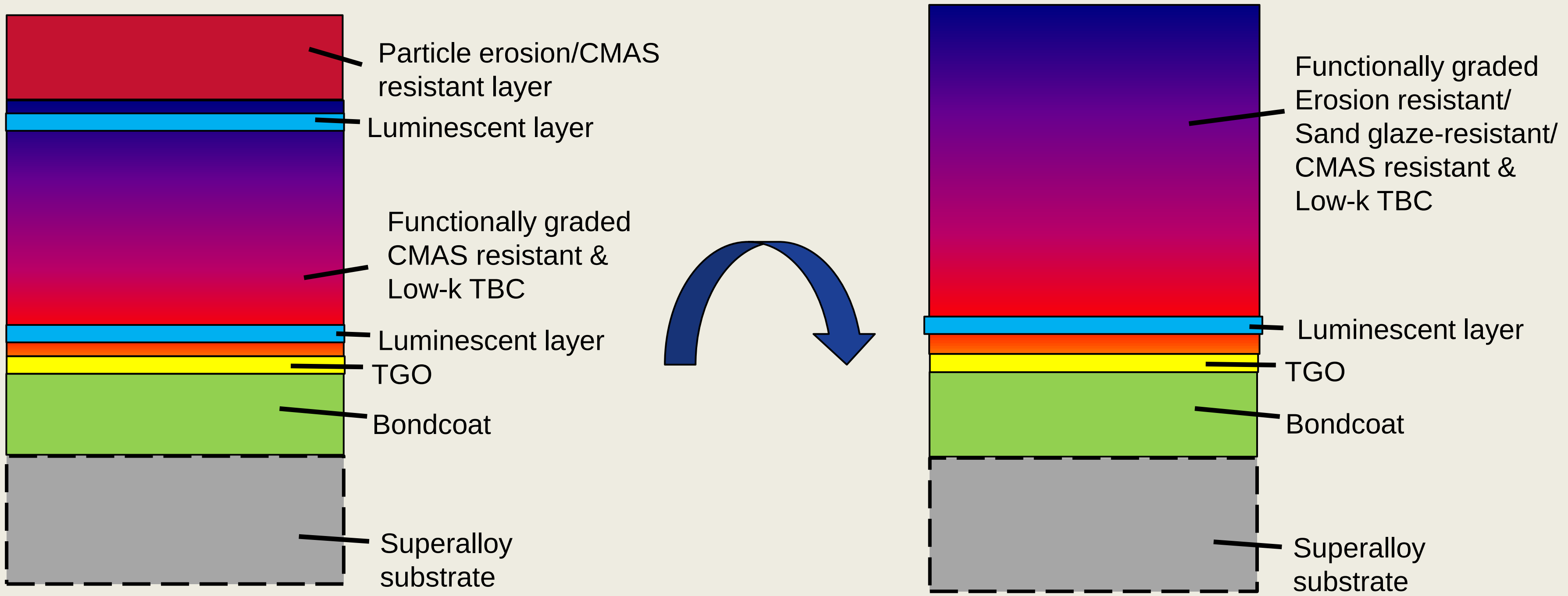
J.H. Perepezko, Science 326, 1068 (2009); used with permission



Source: http://www.virginia.edu/ms/research/wadley/high-temp.html

- **Current state-of-the-art turbine nozzles & blades:**
  - **Single-crystal Ni superalloy blades**
  - **Metal bond-coat: (Pt, Pd)Al**
  - **Ceramic thermal barrier coating (TBC): 7 wt % Y_2O_3: ZrO_2**
- **Other hot section components (such as shrouds and combustor liners):**
  - **Polycrystalline, cast Ni superalloys**
  - **M-CrAlY (NiCo-CrAlY) bond-coats**
  - **Ceramic TBC: 7 wt % Y_2O_3: ZrO_2**

Proposed Sandphobic TBC System – Ni-Superalloy Turbine Blade



Particle erosion/CMAS resistant layer

Luminescent layer

Functionally graded CMAS resistant & Low-k TBC

Luminescent layer

TGO

Bondcoat

Superalloy substrate

Hybrid Approach (Layered & Graded)

Functionally graded Erosion resistant/ Sand glaze-resistant/ CMAS resistant & Low-k TBC

Luminescent layer

TGO

Bondcoat

Superalloy substrate

Functionally Graded Approach

- ❖ Luminescent layers will provide self-aware coating capability
- ❖ Functionally graded layer has multifunctional capability

Accumulation and Infiltration

Identification of Primary Mechanism(s) for Sand Accumulation and its abatement include:

- Surface finish improvement
- Surface debris ‘wetting’ reduction/repellant
- Ablative
- Limit infiltration through microstructural tuning

Primary Mechanism(s) for Sand Melt/ CMAS Infiltration depth, glassification and mitigation:

- Viscosity and surface tension of the melt
- Operational temperature and surface temperature of the substrate
- Shape of the inter-columnar gaps
- Thermal conductivity and Porosity of TBC
- Size and shape of original sand particulate (spherical vs nonspherical)

Button cell tests

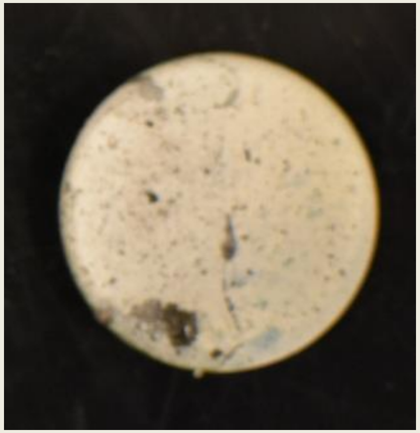
- Oxy-propane torch
- Motorized rotary stage
- Temperature measurement → Optical pyrometer
- Test parameters
  - Surface temperature ~ 1300 °C
  - 3 cycles – IN/OUT: 3 min/3 min
  - AFRL-02 sand → slurry deposited on surface, and allowed to dry before test

Visual Inspection

Button cell Flame Test Rig

Pre-test
YSZ, topped with YSZ-GdO

Post-test
YSZ, topped with GdO



Post-test
YSZ, topped with YSZ-GdO

Hot Particulate Ingestion Rig

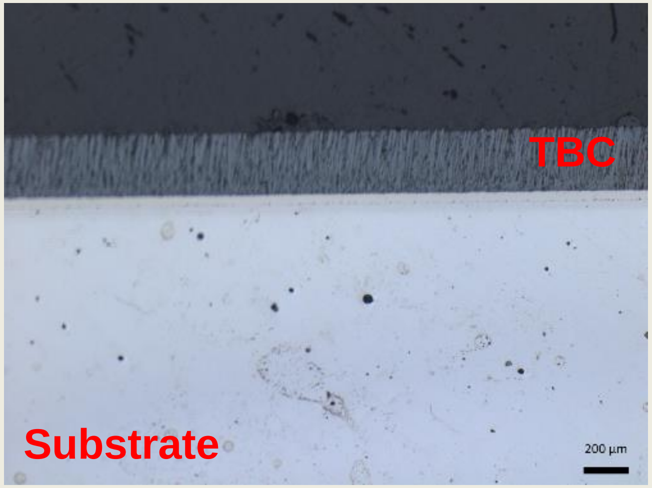
Pre-test
MAX-phase: Ti2AlC

Post-test
Low-k ZrO2-based

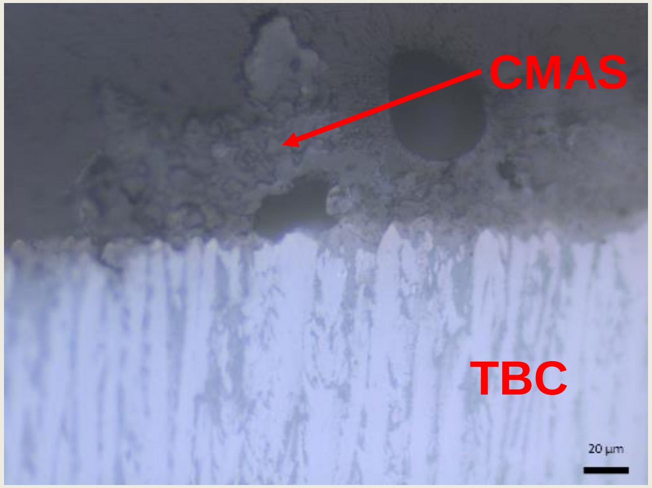
Post-test
MAX-phase: Ti2AlC

Optical Microscopy (OM)
HM-3848

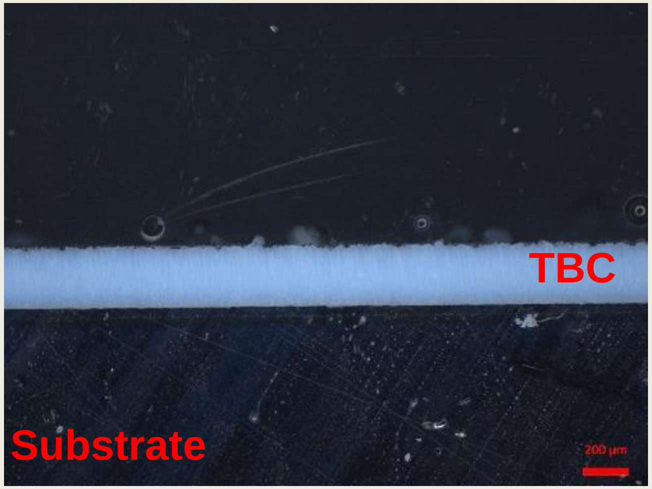
BF @ 5X



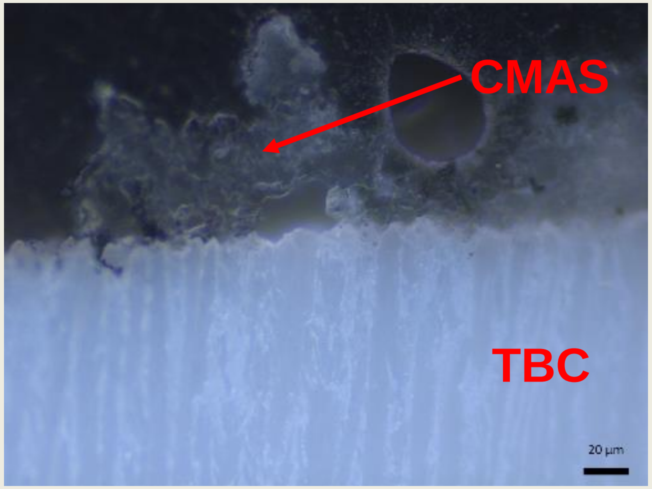
BF @ 50X



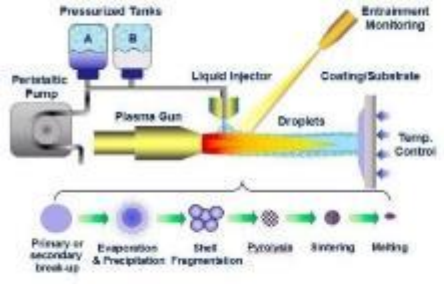
DF @ 5X

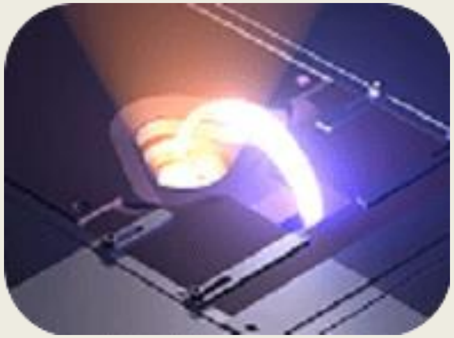


DF @ 50X



Down-selected Compositions

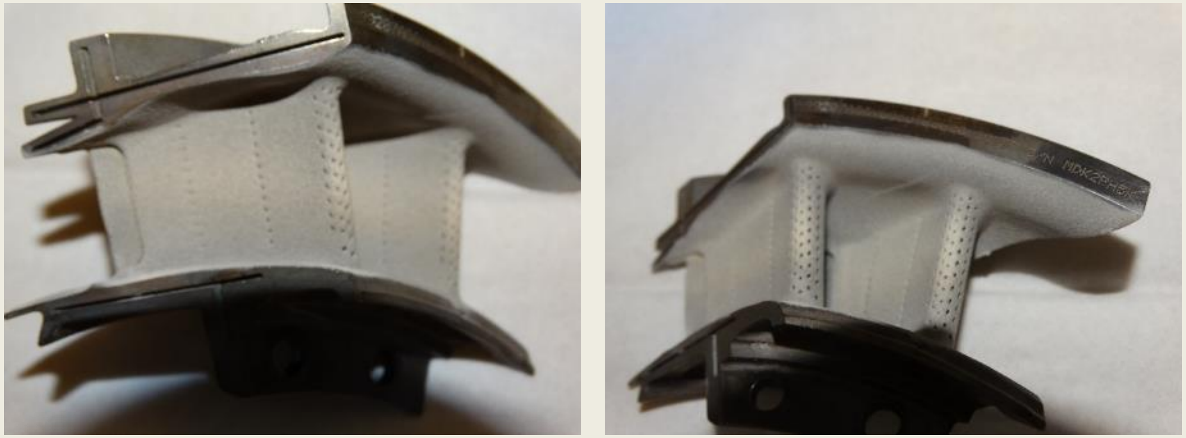




ID	Processing	Coating Architecture	Post-deposition treatment	Suspected Mitigation Mechanism
1	SPPS	8YSZ	None	Finer microstructure, with limited infiltration paths
2	APS	7YSZ / Gd2O3	None	Reduced wetting by debris
3	APS	(7YSZ+Gd2O3 blend) / GZO	None	Crystallization of deposits
4	APS	7YSZ / GZO	None	Crystallization of deposits
5	APS	7YSZ / (7YSZ + Gd2O3 blend)	None	Reduced wetting by debris
6	EB-PVD	Low-k ZrO2-based	None	Reduced wetting by debris
7	EB-PVD	low-k HfO2-based	None	Reduced wetting by debris

Process Optimization – Nozzles

Nozzle 1 – 7YSZ via APS



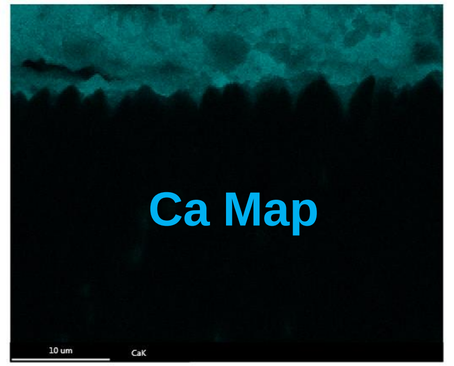
- Leading Edge Holes are largely clear
- Clogging increases as you approach the vane's trailing edge

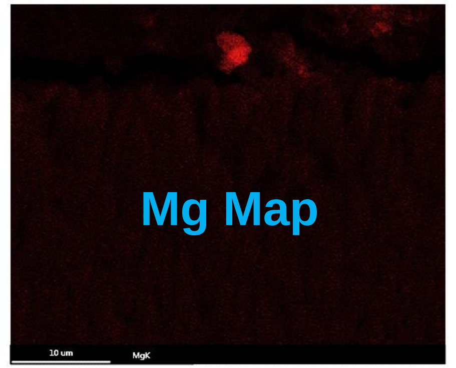
NOTE: Samples were grit-blasted for coating adhesion

Nozzle 2 – 8YSZ via SPPS

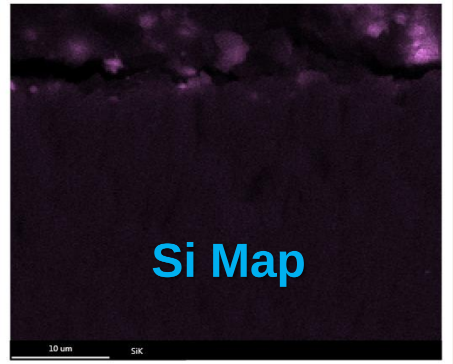
- Cooling hole row at the peak of the leading edge is clogged
- Trailing edge shows less clogging than Nozzle 1, despite identical spray path
- Finer Coating Droplets (Solution Plasma Topcoat) appear to bridge cooling holes more easily/thoroughly, despite increased bleed air inlet pressure/flow.

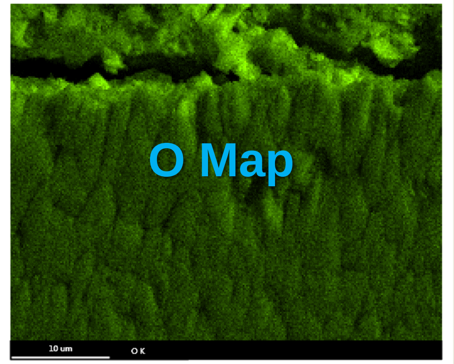
ARL-NASA-06

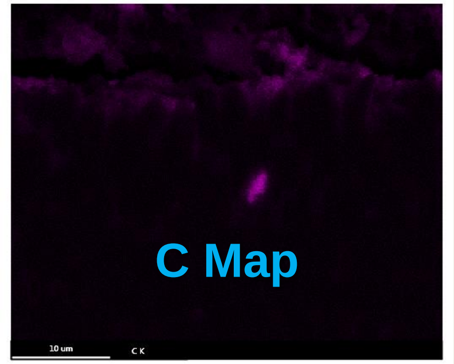

Ca Map
10 um
CaK

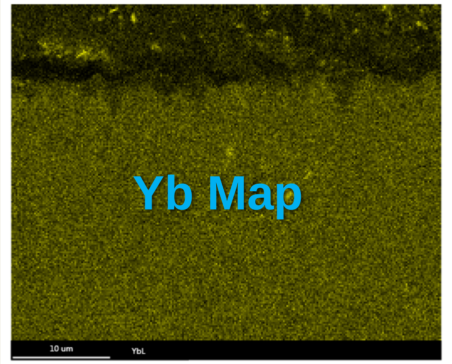

Mg Map
10 um
MgK

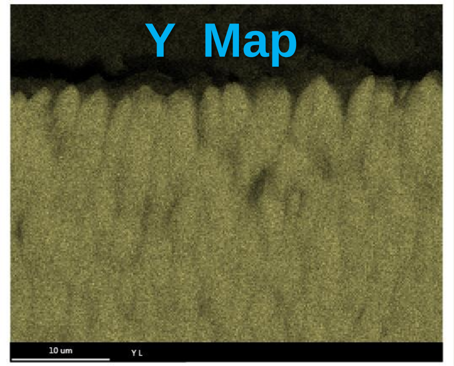

S Map
10 um
S K

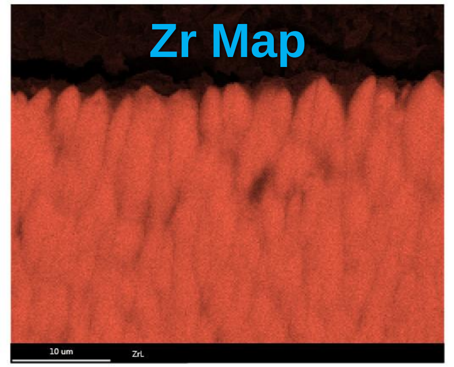

Si Map
10 um
SiK


O Map
10 um
O K

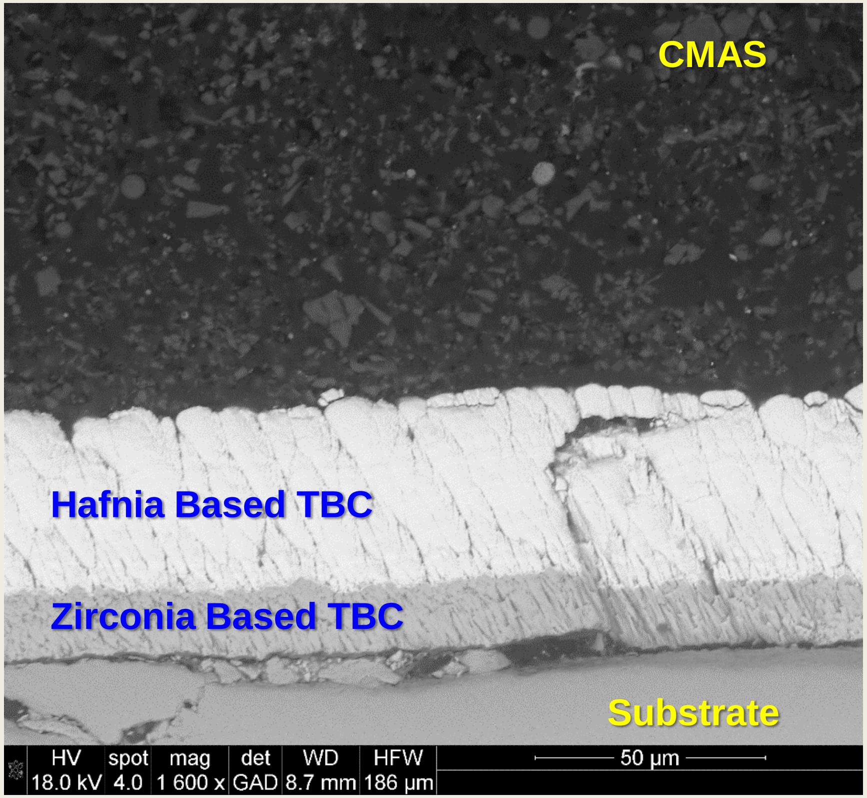

C Map
10 um
C K

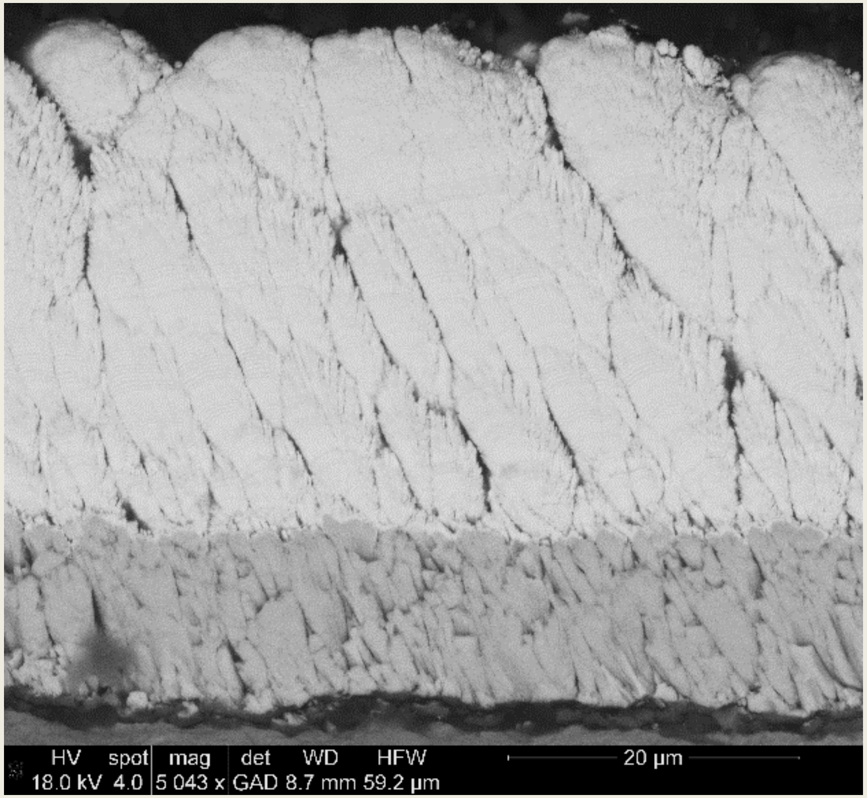

Yb Map
10 um
YbL


Y Map
10 um
Y L


Zr Map
10 um
ZrL

ARL-NASA-07





- ARL-NASA-07 shows signs of delamination from the substrate, as well as significant cracking on TBC itself (*aside from columnar structure*)
- Columnar structure of hafnia based EB-PVD TBC is significantly different from that of 5YSZ EB-PVD TBC (*ARL-NASA-07 is also much thinner*)

ARL-NASA-05

- CMAS constituents exhibit rich variety of morphologies and microstructures

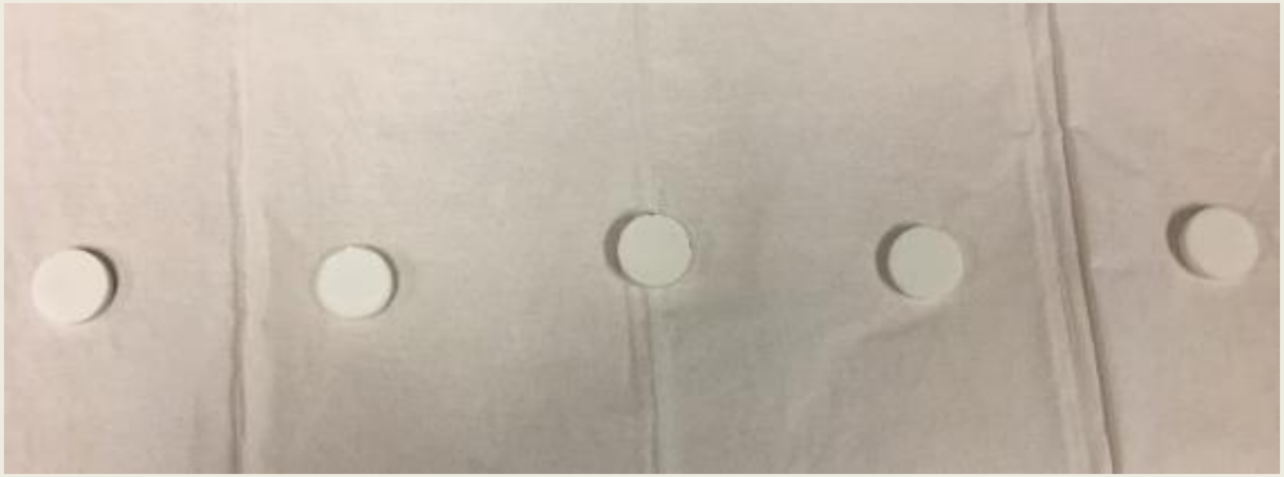
- Different CMAS constituents will have distinct reactions to high temperatures and different interactions w/ TBCs

- Most CMAS deposits are very rough and porous

- CMAS deposits can be white, red, or both.

CMAS deposits Post CMAS Attack Testing

As-Sintered Pellets



Pellets Post CMAS Attack Testing

Adhesion, morphology, and size of CMAS deposits can be seen to vary significantly