Low Thermal Conductivity, High Durability Thermal Barrier Coatings for IGCC Engines

(DE-FE-0007382, 10/1/12-12/30/14)

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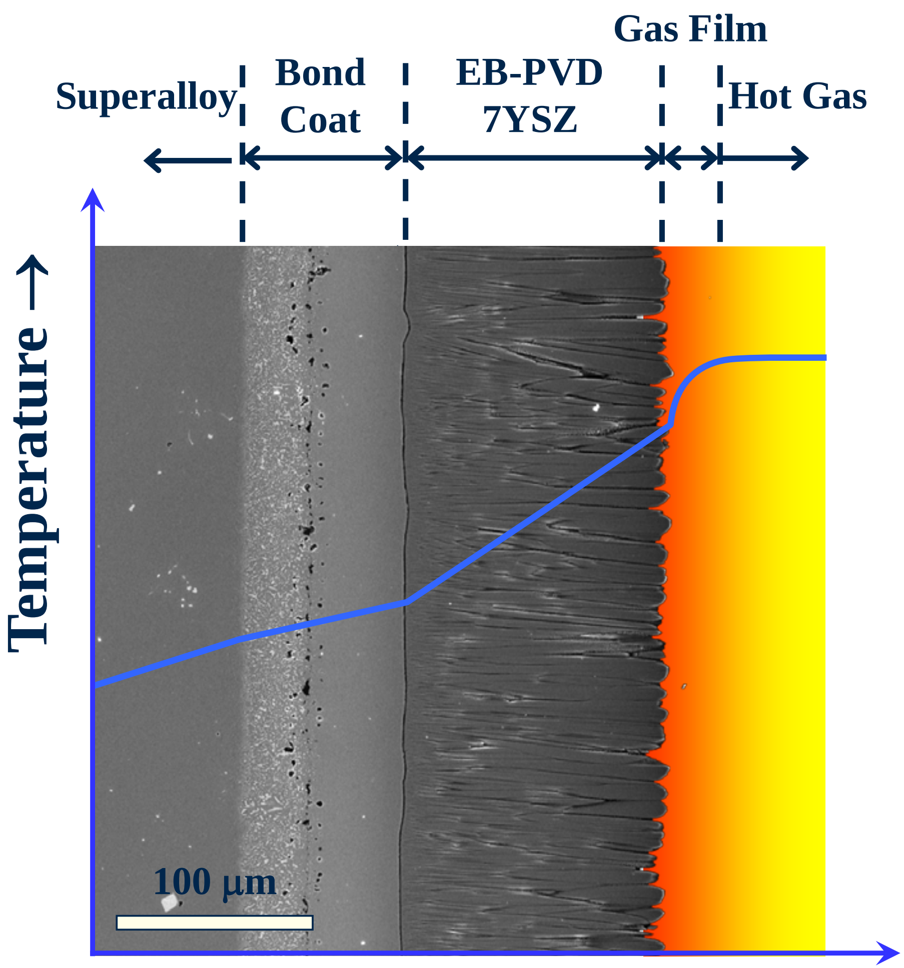
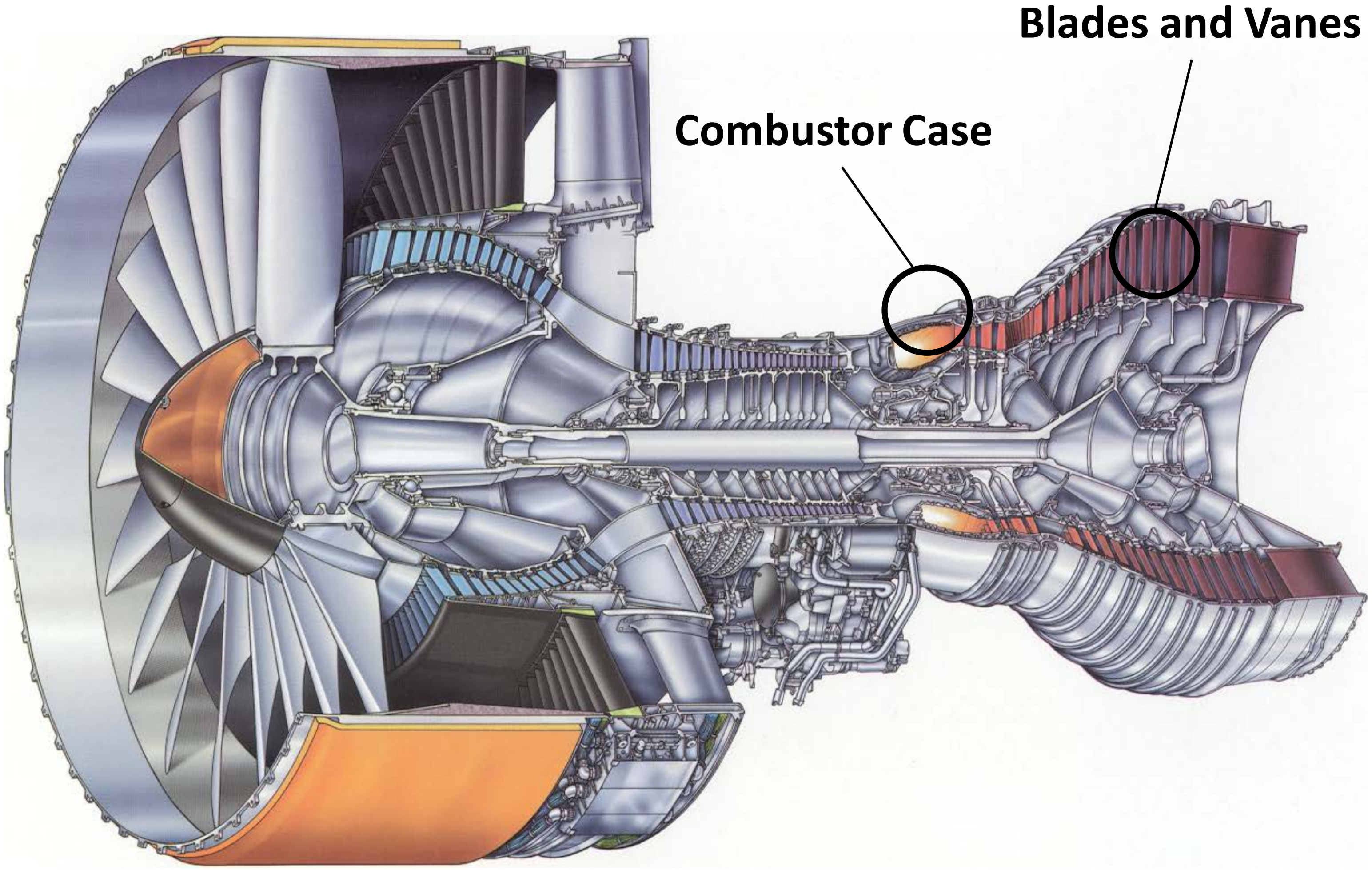
Microstructure & Requirements



Topcoat requirements:

- **Low thermal conductivity,**
- **High use temperature,**
- **High durability:**
  - ➢ **Toughness**
  - ➢ **Strain tolerance**

TBC Applications



Objectives

- Reduce the thermal conductivity of TBCs to 0.6 $Wm^{-1}K^{-1}$ by optimal porosity structuring;
- Increase the allowable surface temperature of the TBC from the current approximately 1200 ^{o}C for YSZ to 1300 ^{o}C by a more stable top layer;
- Improve the durability of the TBC in the face of contaminants (CMAS) and moisture compared to current YSZ coatings.

Accomplishments

- **SPPS Process with IPBs reduces YSZ thermal conductivity to half of normal values;**
- **Thermal conductivity of ~0.6 $Wm^{-1}K^{-1}$ attained;**
- **SPPS YSZ TBCs can replace advanced low K TBCs with expensive rare earth content;**
- **Successfully added a top Gadolinium layer**
- **Created a YSZ layer with metastable Al for CMAS resistance**

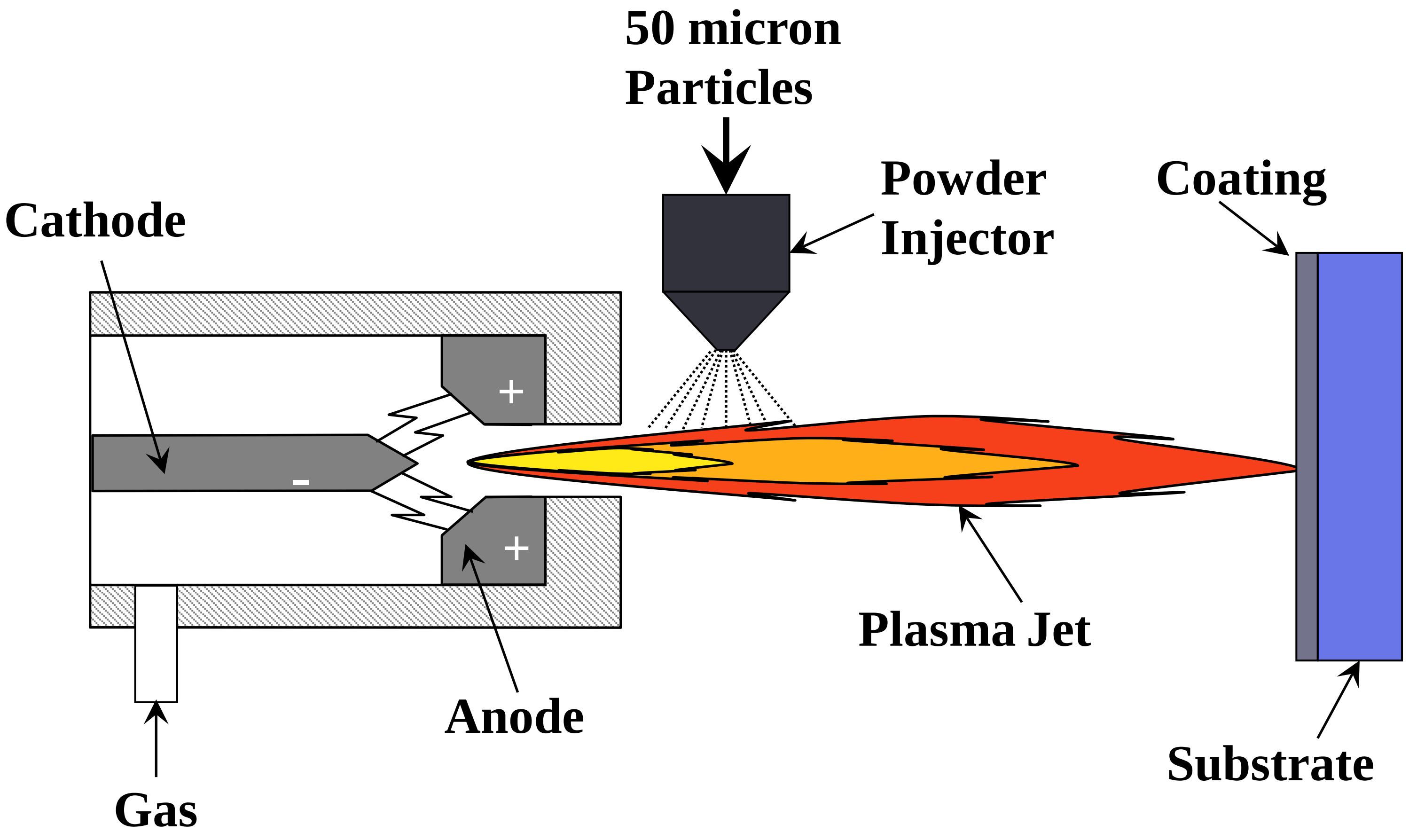
Goals will be accomplished by making and testing TBC systems using:

- **Solution Precursor Thermal Spray in UConn thermal spray facility;**
- **TBC testing facility;**
- **High temperature moist environment testing rig (built for this program).**

Program Plan

	YEAR 1				YEAR 2				YEAR 3			
TASK	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
1. Manage/Plan/Report												
2. SPPS of Low K TBC												
3. Test Low K TBC												
4. Fabricate GdZr Layer												
5. Fab. Al/Ti-doped TBC												
6. Fab. $CaSO_4$ Additive												
7. CMAS Testing												
8. Moisture Testing												
9. Define Mechanism												
10. Gradient Cyclic Testing												

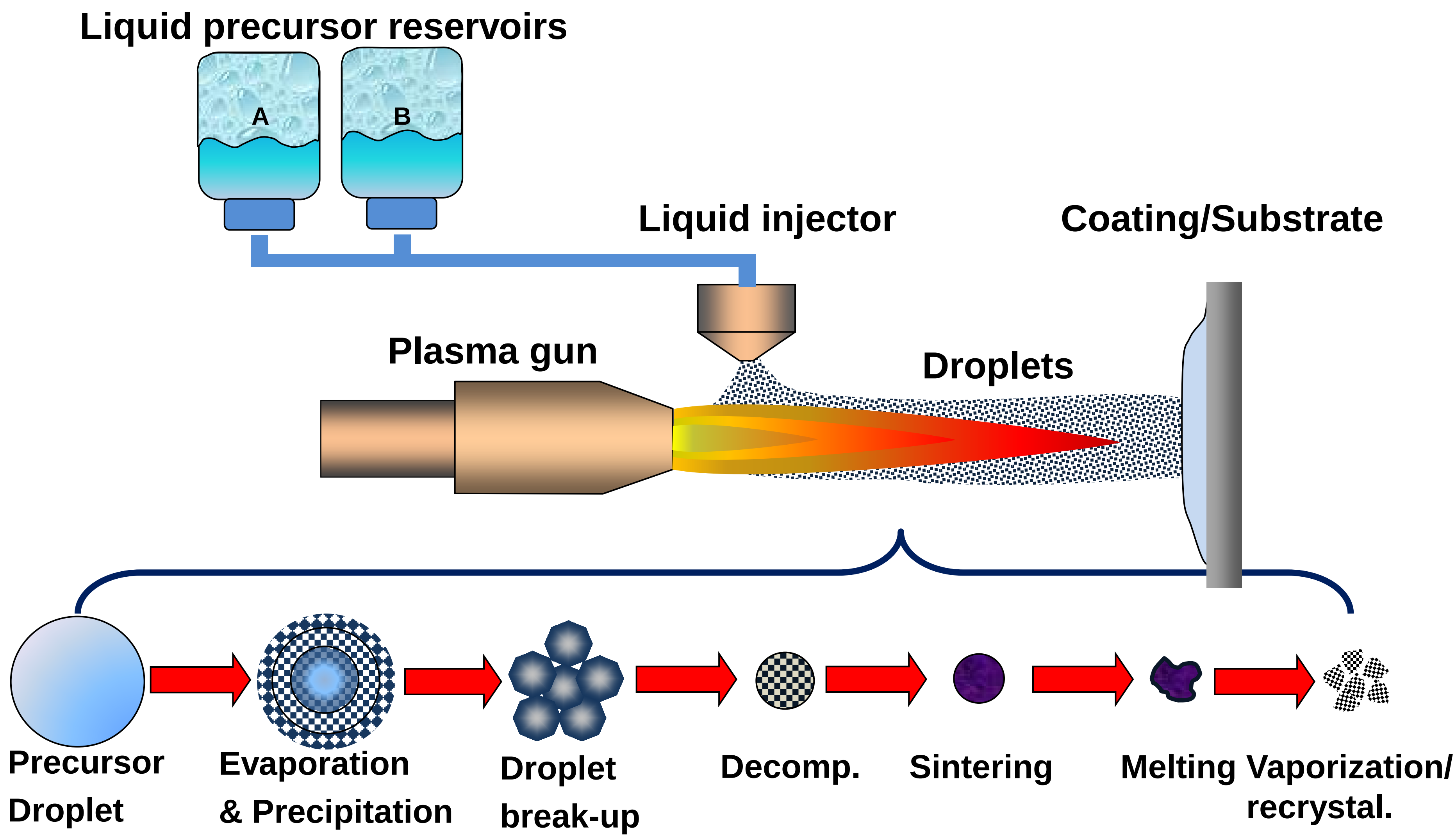
Air Plasma Spray (APS)



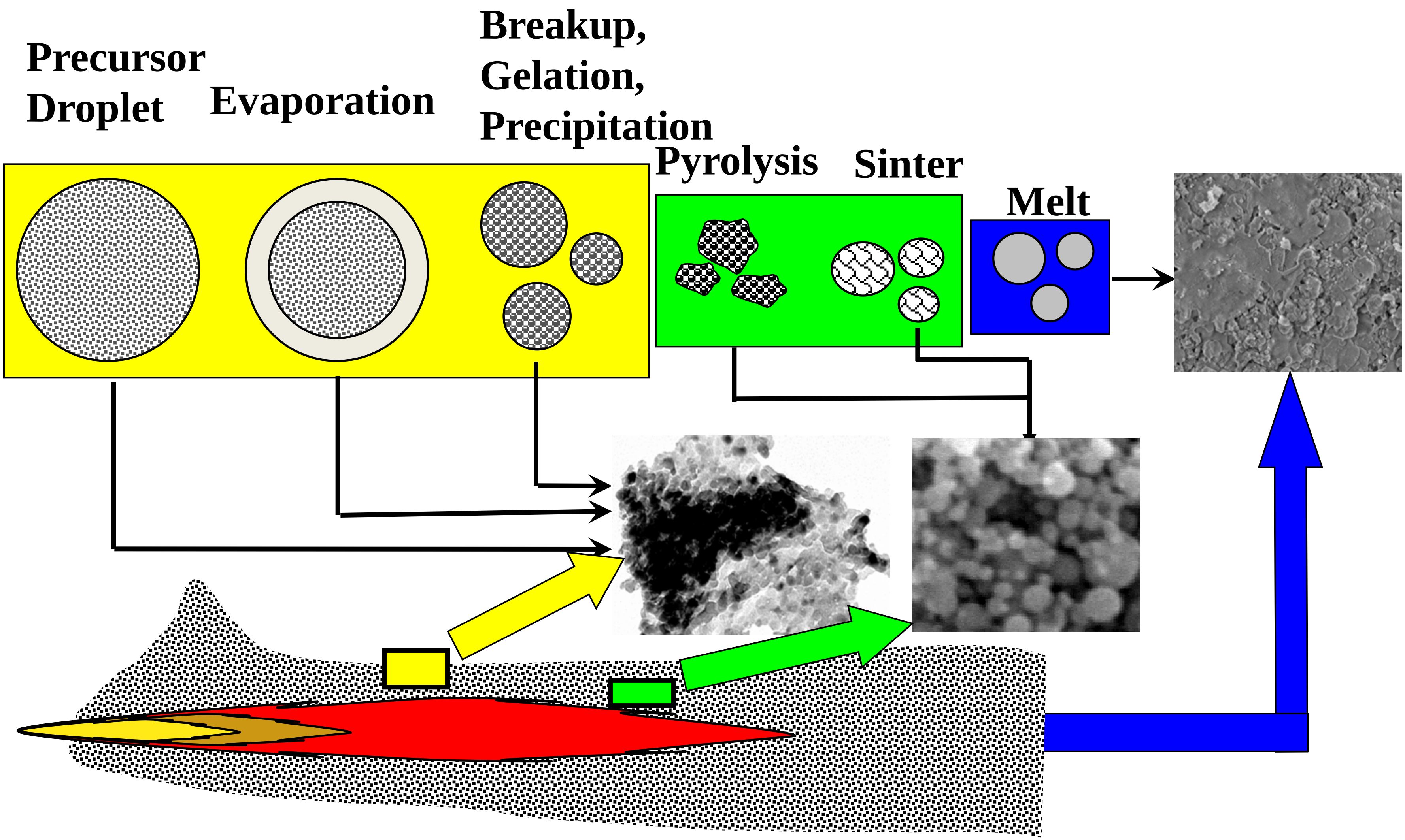
Particles melt and form splat structures → 7YSZ

Solution Precursor Plasma Spray

Process schematics



SPPS Deposition: Process Flexibility



Spray pyrolysis

UConn Thermal Spray Facility

Liquid Delivery Options

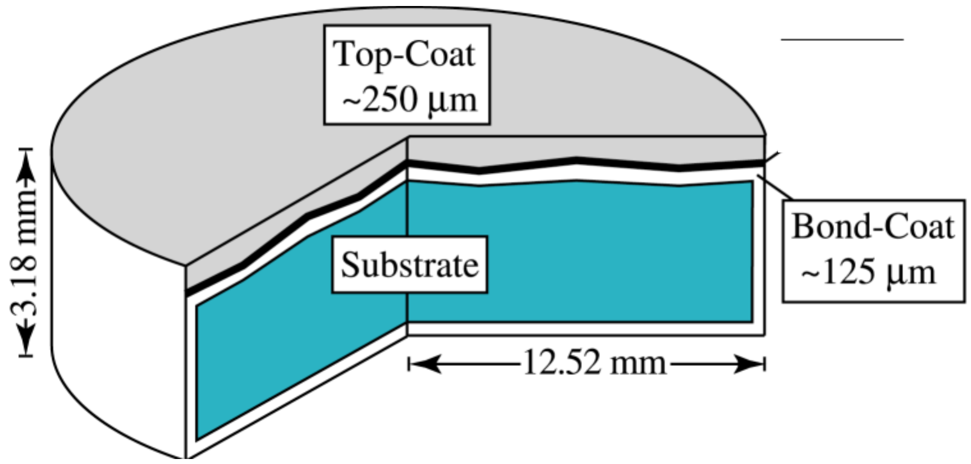
Standard Liquid Delivery System

Unique High Pressure System (33 atm)

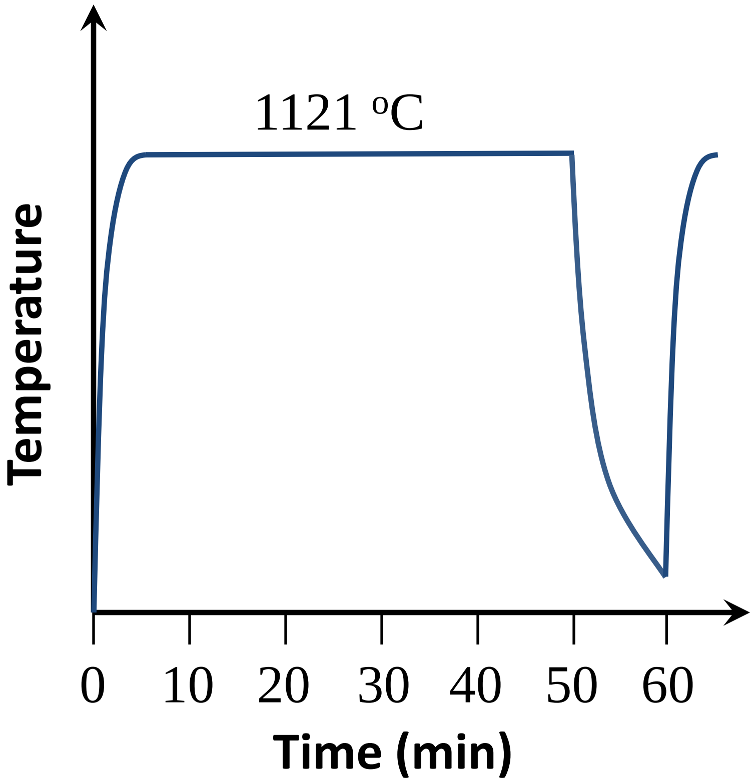
Cyclic Furnace Test Facility

Specimen Shape & Furnace Cycle

Disk-shape samples

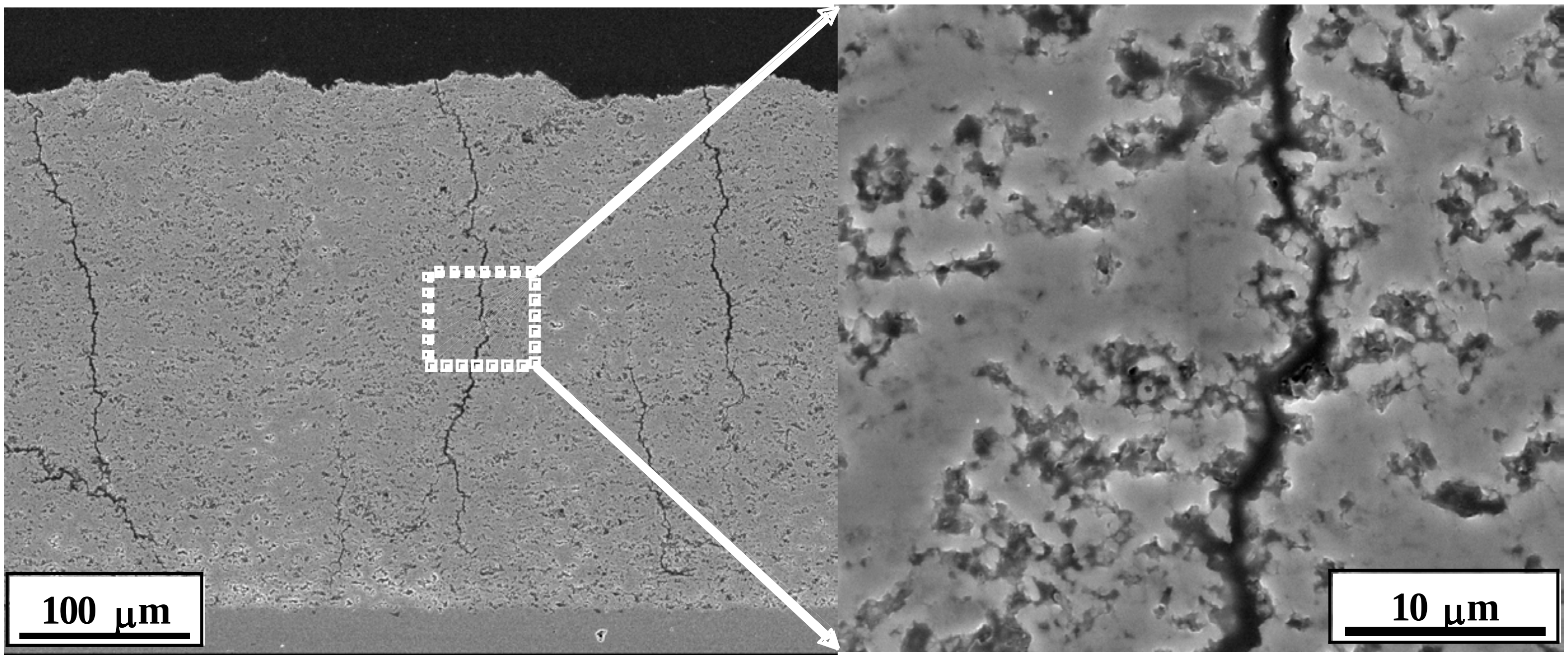


Thermal cycling life test



(1) Put the T/C on the sample; furnace T/C is 20 °C low;
(2) Rotate sample to average hot spots.

SPPS TBCs Have Unique Features



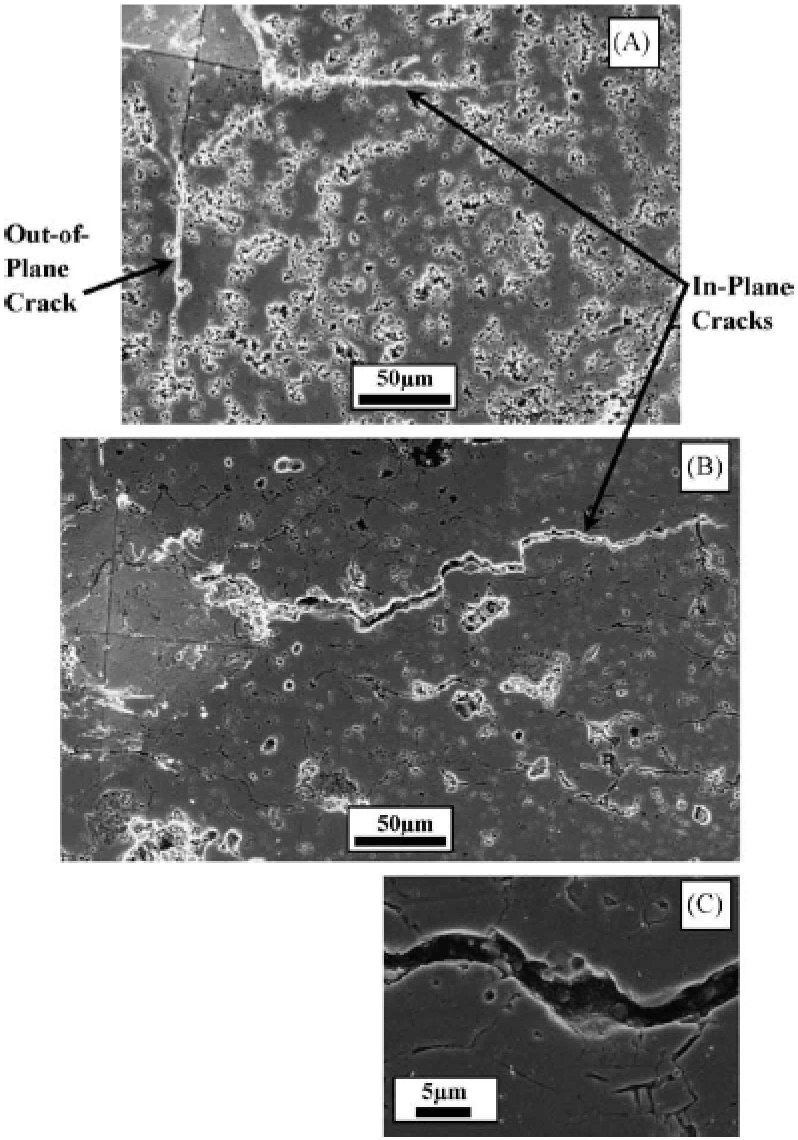
Unique Features:

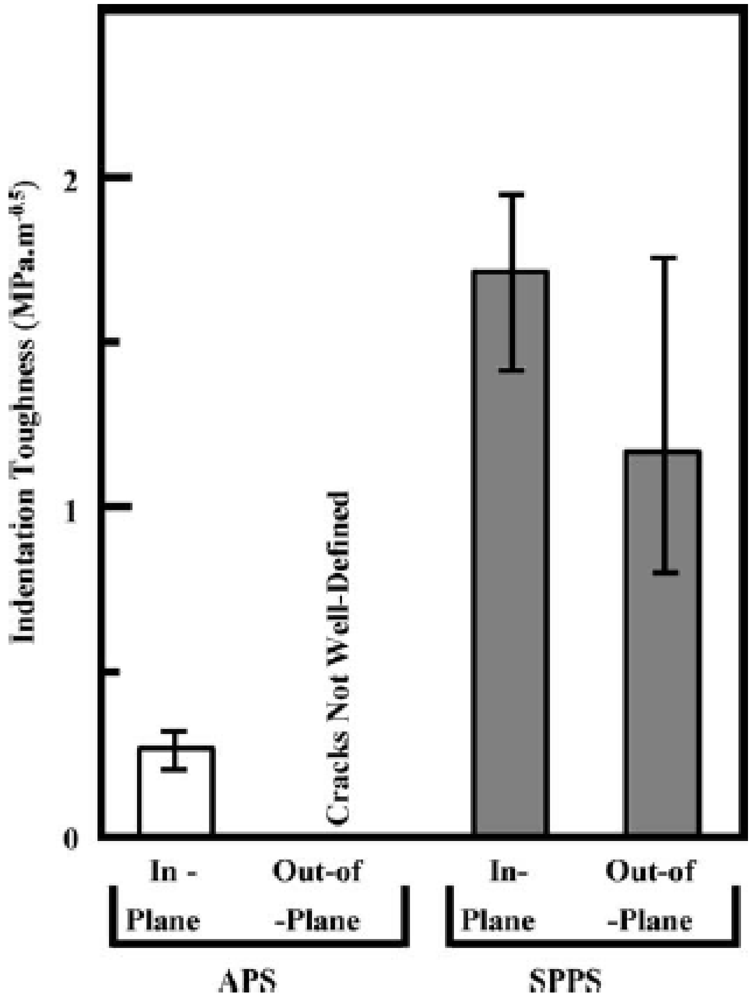
- 3D nano & micron scale porosity;
- Through-thickness vertical cracks;
- Smooth coating surfaces;
- Ultra-fine splats.

Vertical Cracks Relive Stress

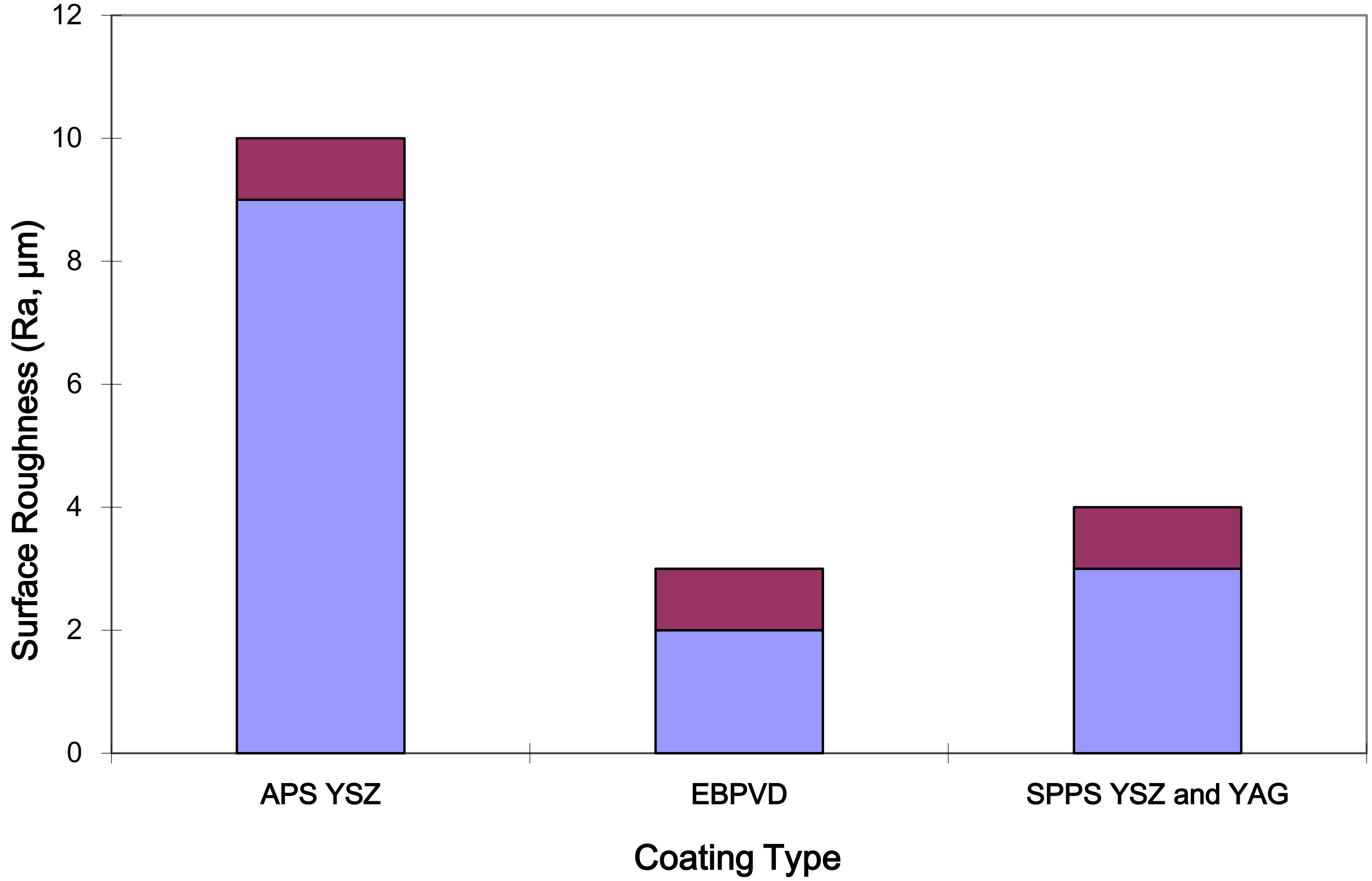
- Zero stress in synchrotron
- Will allow materials with worse CTE Mismatch to be Used—YAG
- No issues with very thick TBCs. Otherwise thicker TBC has more strain energy and give reduced durability.

SPPS Coatings Have 7X Higher In-plane Toughness



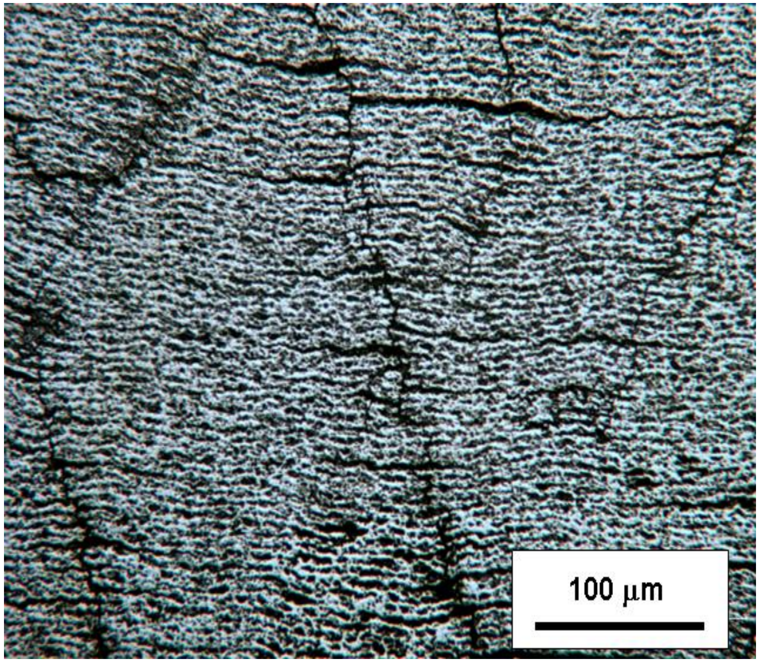


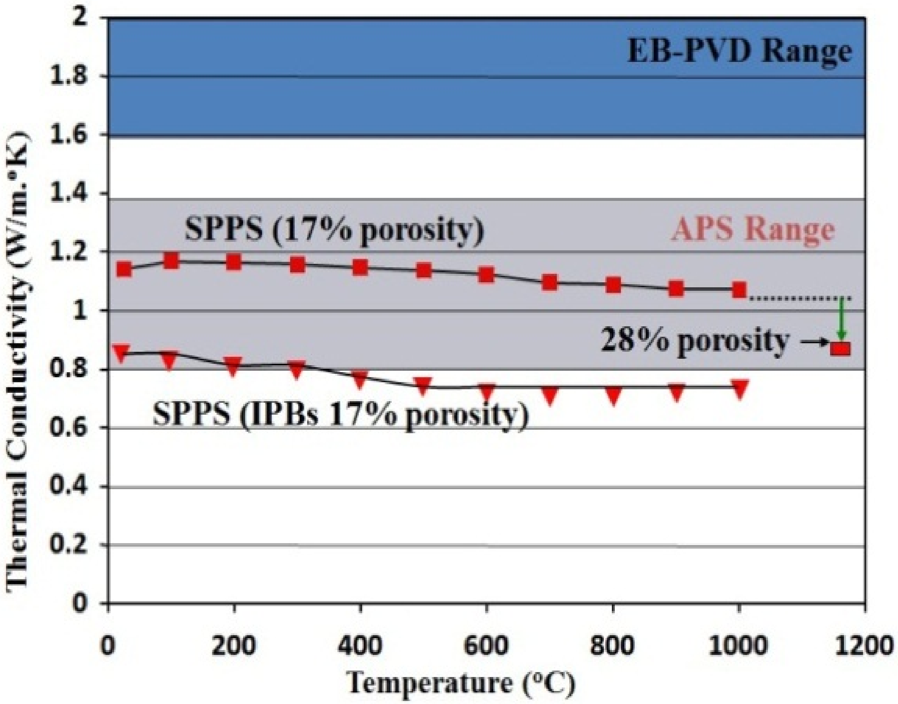
Surface Roughness of TBCs



- **A smoother surface provides aerodynamic, heat transfer and erosion resistance benefits.**

Structured Planar Porosity (IPBs) Leads to Lower Thermal Conductivity





Advantages of Solution Precursor Plasma Spray

- Vertical stress relieving cracks;
- Higher fracture toughness;
- Smooth coating surface finish;
- Rapid composition exploration (100X);
- Structured porosity (IPBs) leading to low K coatings;

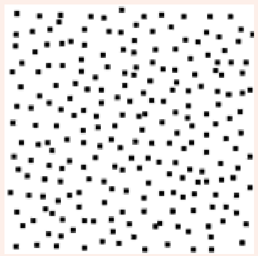
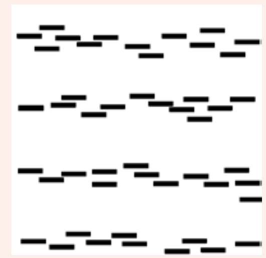
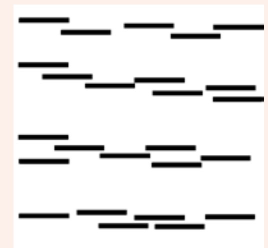
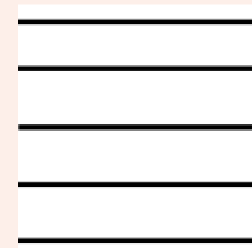
Initial SPPS Trials/Thermal Conductivity Measurements

- **Taguchi DOE Spray Trials to optimize IPBs for minimum thermal conductivity (0.6 $Wm^{-1}K^{-1}$).**
- **Access outcome using image-based finite element (OOF) calculated thermal conductivity.**
- **Image-based thermal conductivity determination (OOF) was not RELIABLE for this application.**

Development of Heuristics Needed to Make Optimal IPBs

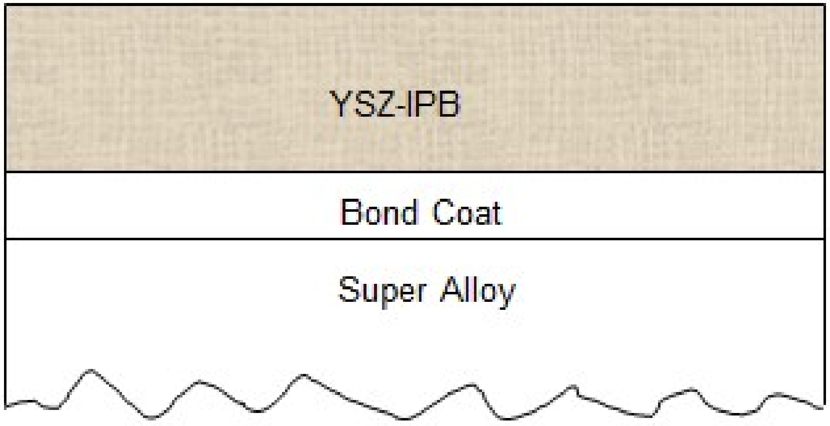
By Modeling and Testing

Structured Planar Porosity (IPBs) Leads to Lower Thermal Conductivity

Artificial Porosity Image					
Simulated Thermal Conductivity ($Wm^{-1}K^{-1}$)	1.942	1.876	1.256	0.800	0.176

FEA (OOF2, NIST) of coating thermal conductivity as a function of porosity geometry, ~10% porosity.

Baseline Systems

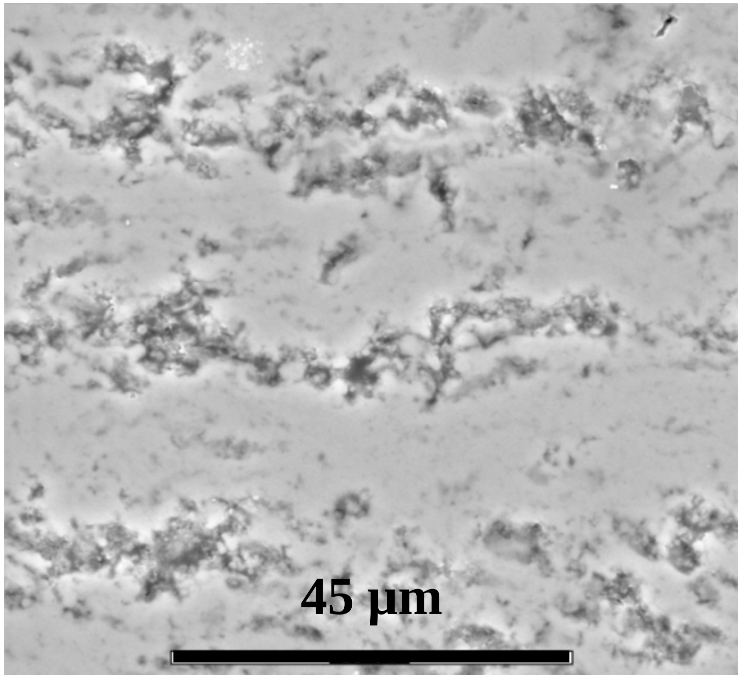


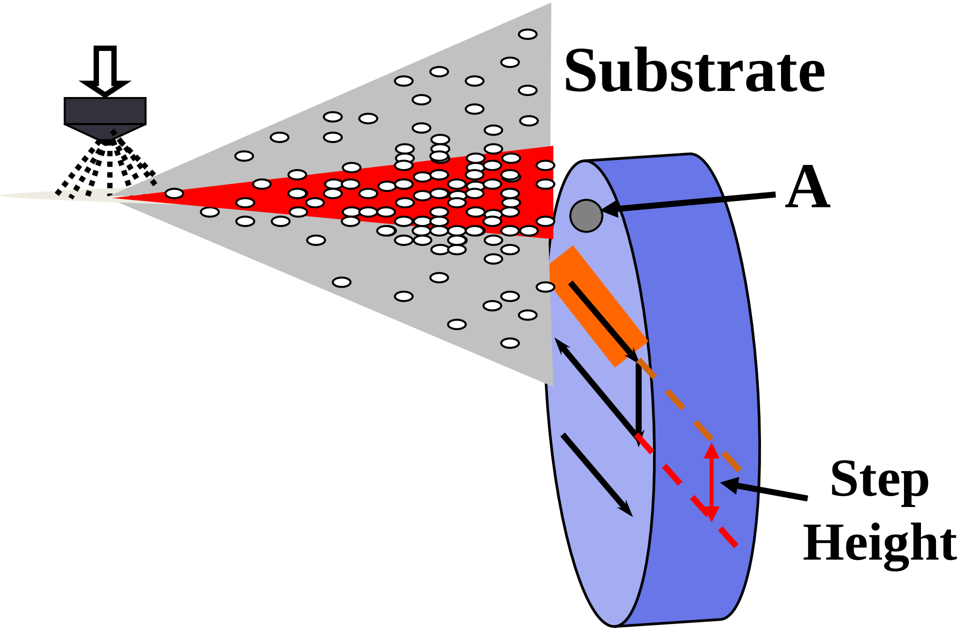
TBC #1, a low K SPPS YSZ TBC using layered porosity (IPBs)

Effects of Processing Variables on IPB Formation

- **Precursor Injection Method**
- **Spray Distance**
- **Precursor Feed Rate**
- **Raster Scan Step Height**
- **And etc.**

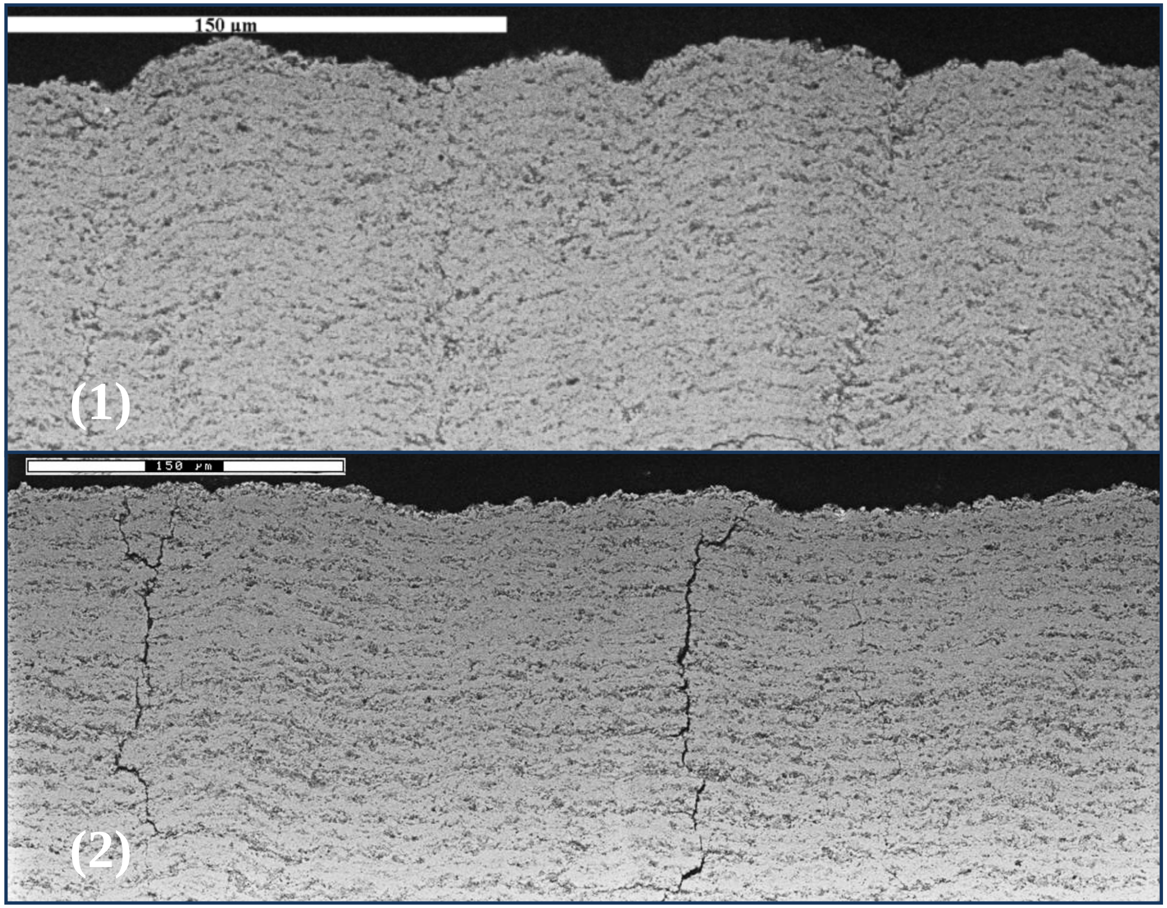
Formation of Inter-Pass Boundaries

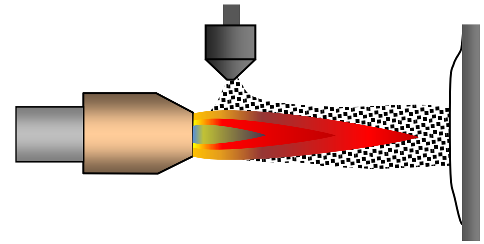




Precursor Injection Methods

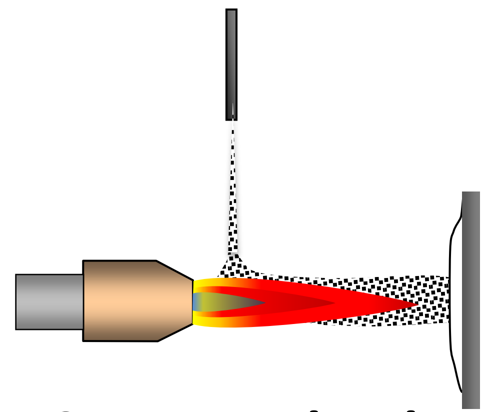
Atomization: manageability and porosity





Atomization

(1)

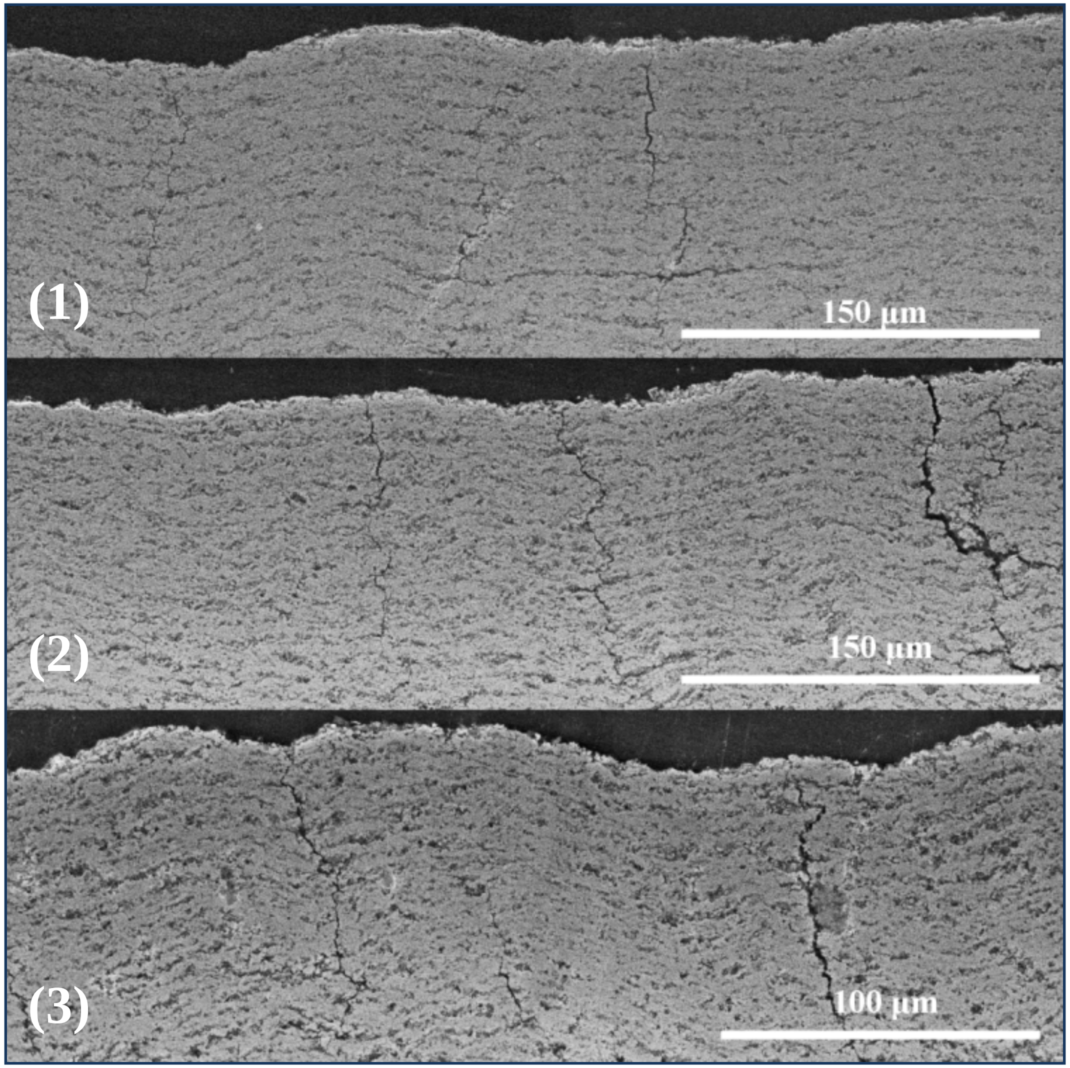


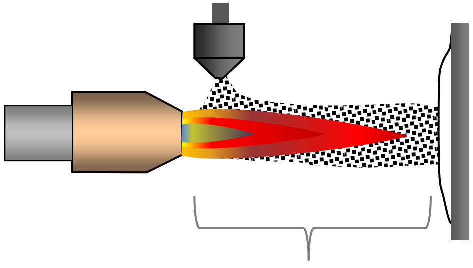
Stream Injection

(2)

Process Variables Study on IPBs

Closer spray distance





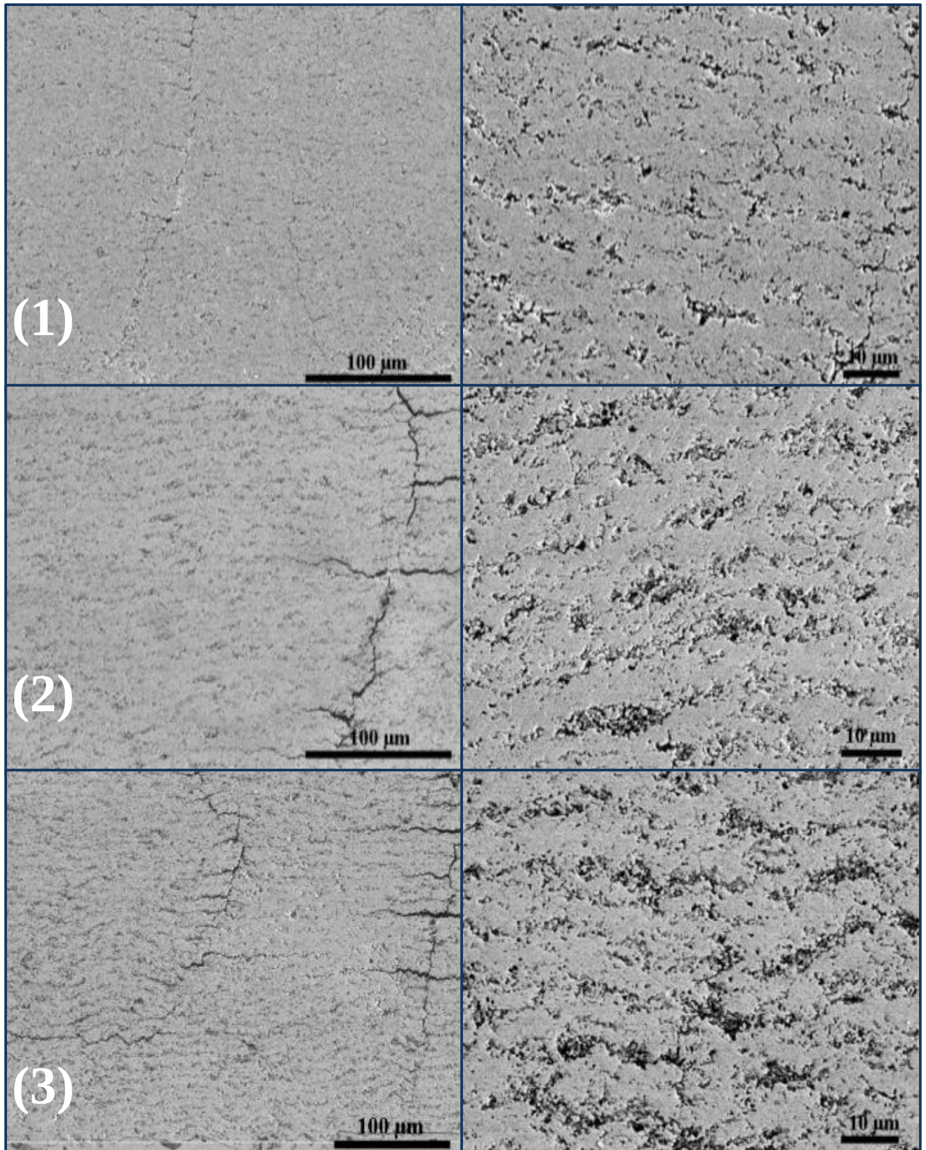
(1) 4.13 cm SD

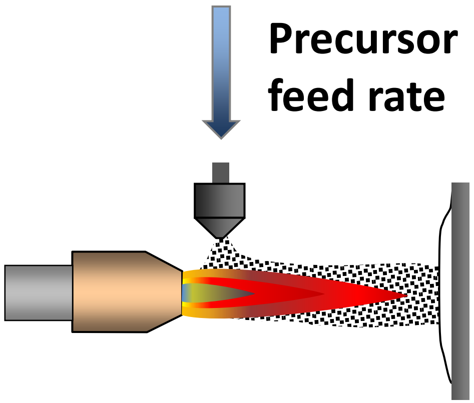
(2) 4.44 cm SD

(3) 4.76 cm SD

Process Variables Study on IPBs

Moderately higher feed rate





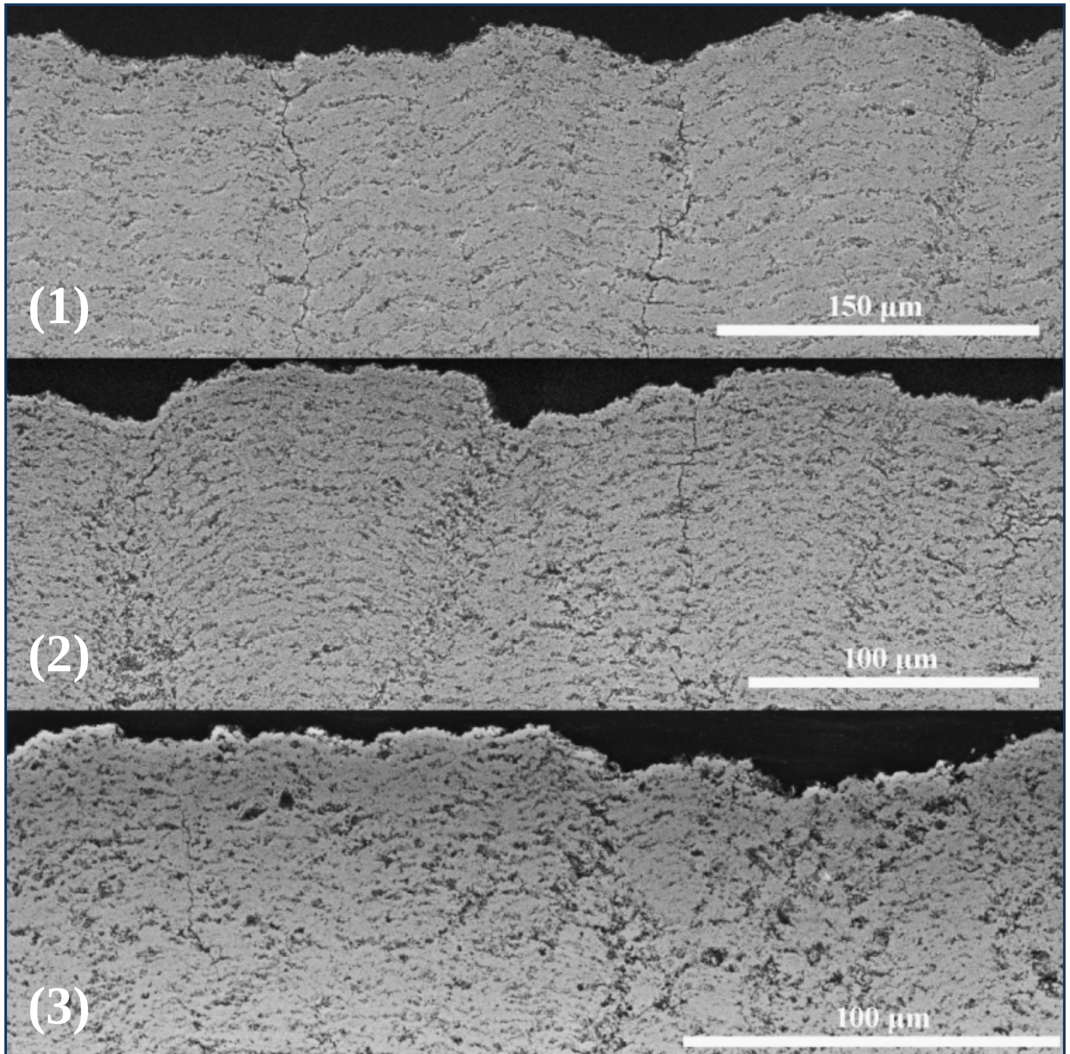
(1) 24 mL/min

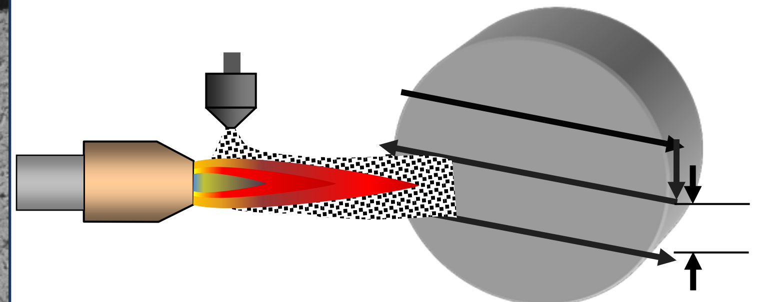
(2) 36 mL/min

(3) 50 mL/min

Process Variables Study on IPBs

Smaller raster scan step height





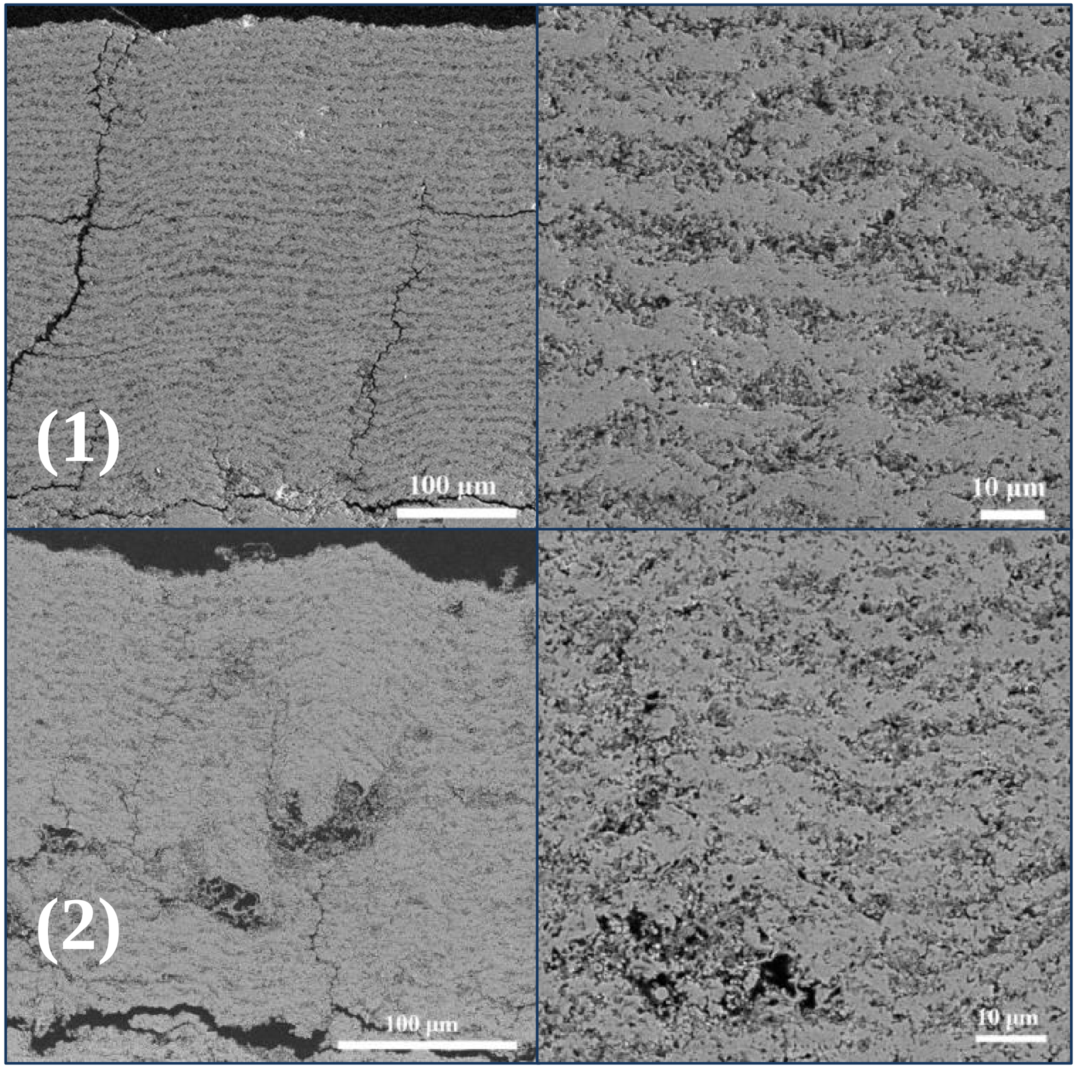
(1) 1 mm index

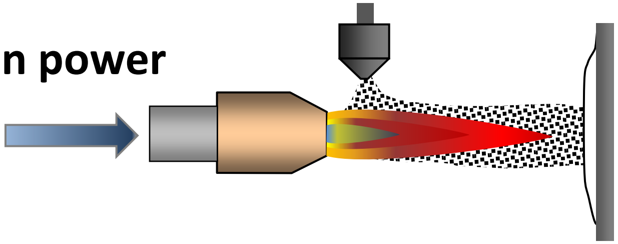
(2) 2 mm index

(3) 3 mm index

Process Variables Study on IPBs

Enough (maximum) gun power



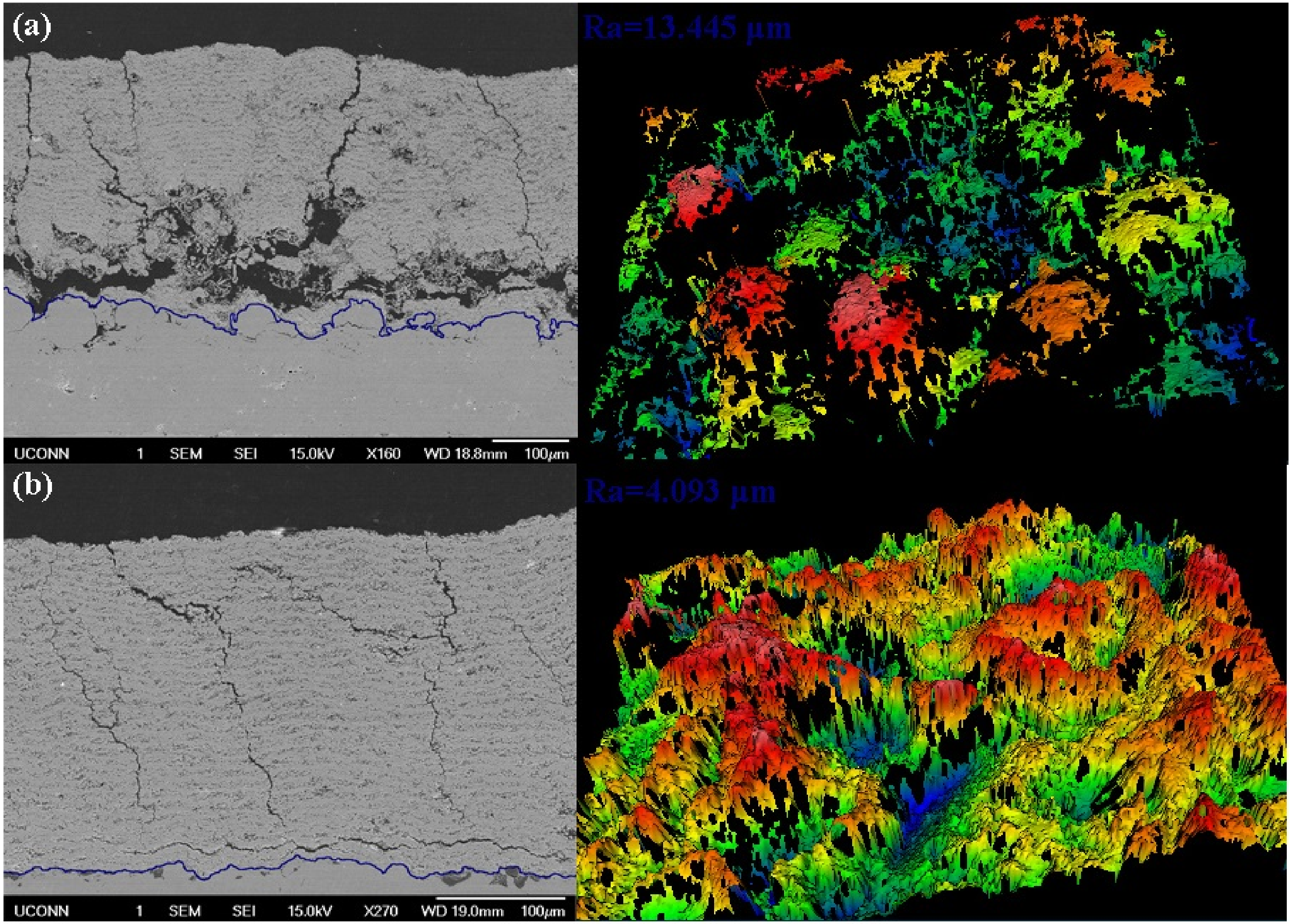


(1) 45 kW

(2) 40 kW

Process Variables Study on IPBs

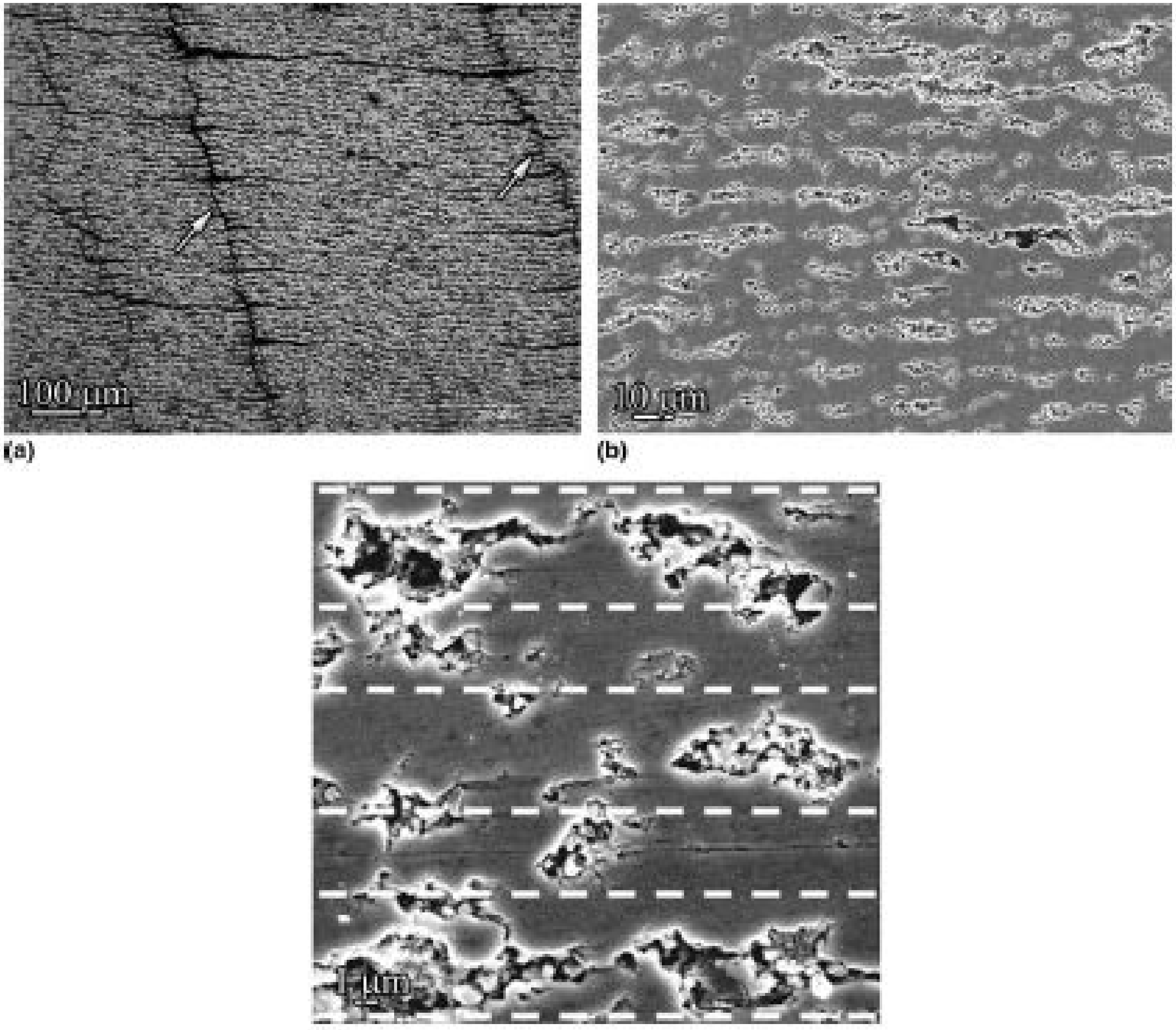
Substrate roughness MATTERS



Characterizing TBCs with Low Thermal Conductivity

Calculating Thermal Conductivity

A.D. Jadhav et al. / Acta Materialia 54 (2006) 3343–3349



(a) (b) (c)

Finite Element Mesh Generated from Micrograph Using OOF Program

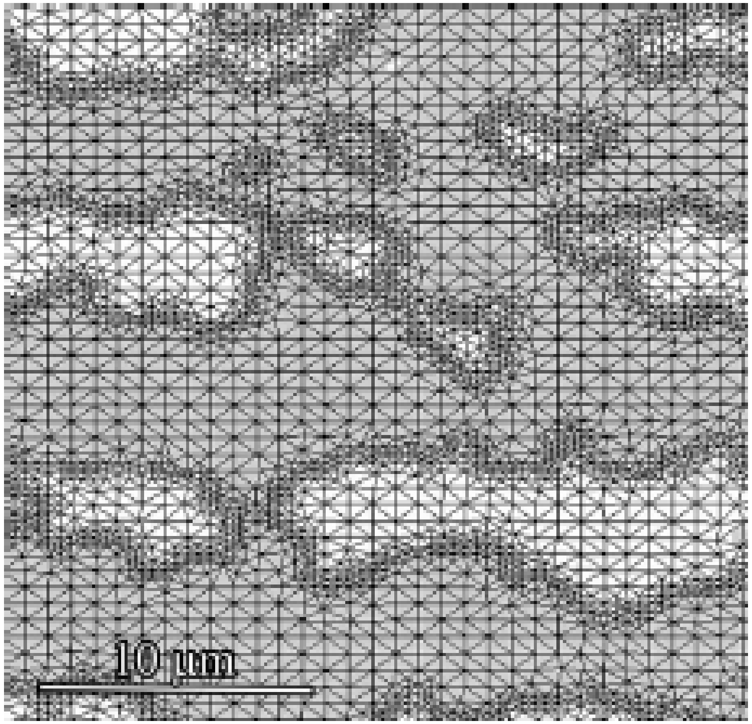


Image Based (OOF) Conductivity

NOT Reliable

Sample	LFA		OOF		Note
	Temp	Thermal Conductivity	Temp	Thermal Conductivity	
Stainless steel substrate	100 C	16.5			Single-layer model, 3mm substrate, 6mm piece
IPB#042412-C	150 C	0.72	150 C	0.919	Two-layer model, 3mm substrate, 6mm piece
IPB#042412-D	150 C	0.99	150 C	1.13	Two-layer model, 3mm substrate, 6mm piece
IPB#060412-G	150 C	0.55	150 C	1.216	Two-layer model, 2mm substrate, 1" disk
IPB#060412-I	150 C	0.32	150 C	1.235	Two-layer model, 3mm substrate, 1" disk

Table 1. Thermal conductivity of YSZ TBCs with interpass boundaries determined by laser flash analysis (LFA) vs. finite element calculations using SEM images and OOF software.

Limitation of 2D Calculation

- **The reliability of the 2D calculation highly depends on the representativeness of the input images of the microstructure. But determination of the *representative* image can be subjective.**

- **Voids smaller than resolution limits in the SEM image are in most cases neglected in binarized images, yet they still affect the overall thermal conductivity.**

- **Even if there is no obvious path of conduction in the shown cross-sectional images, other 3D paths can exist.**

Laser Flash Apparatus

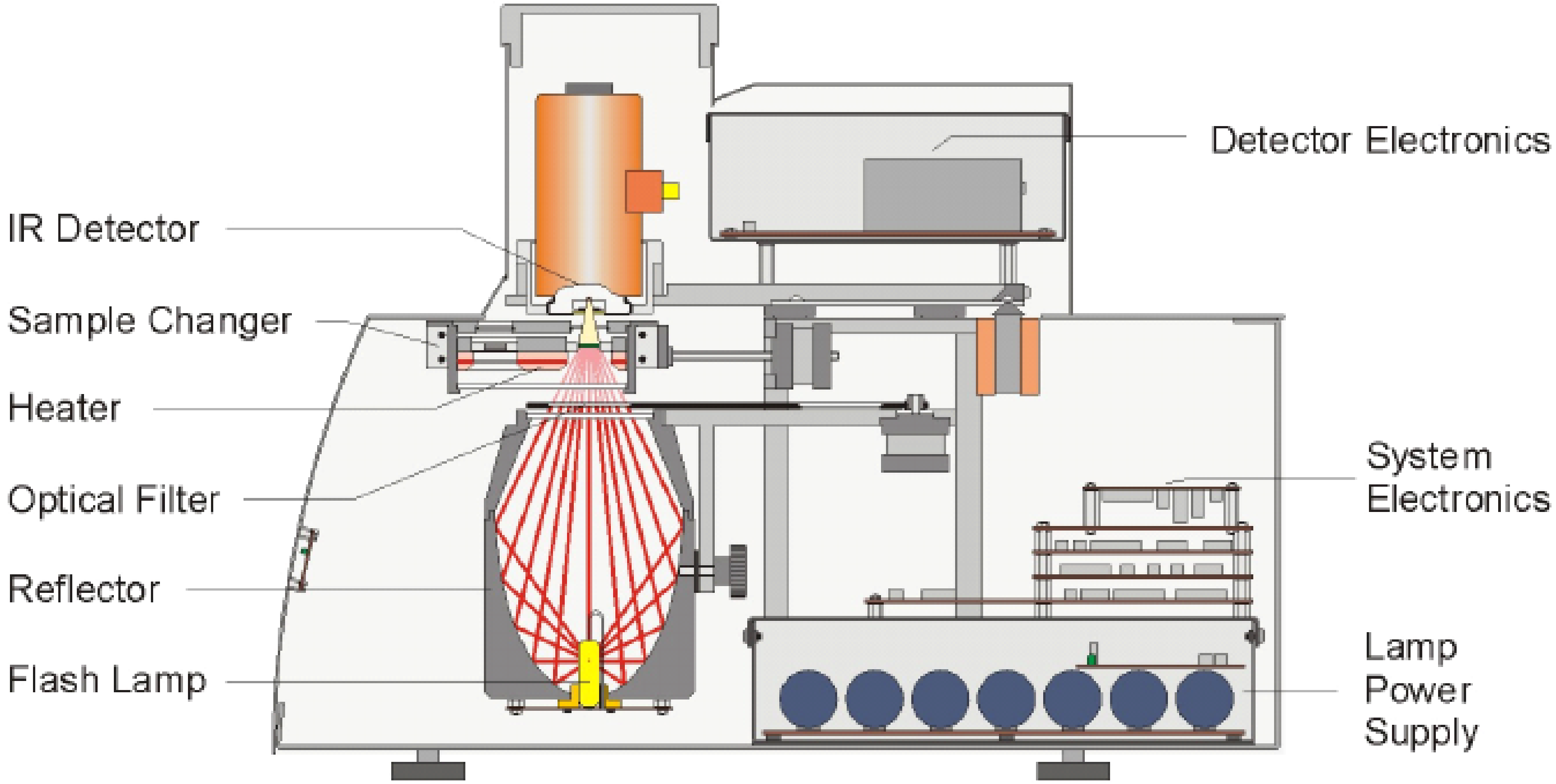


Figure 2: Schematic of the NETZSCH LFA 447

Flash Method Schematic

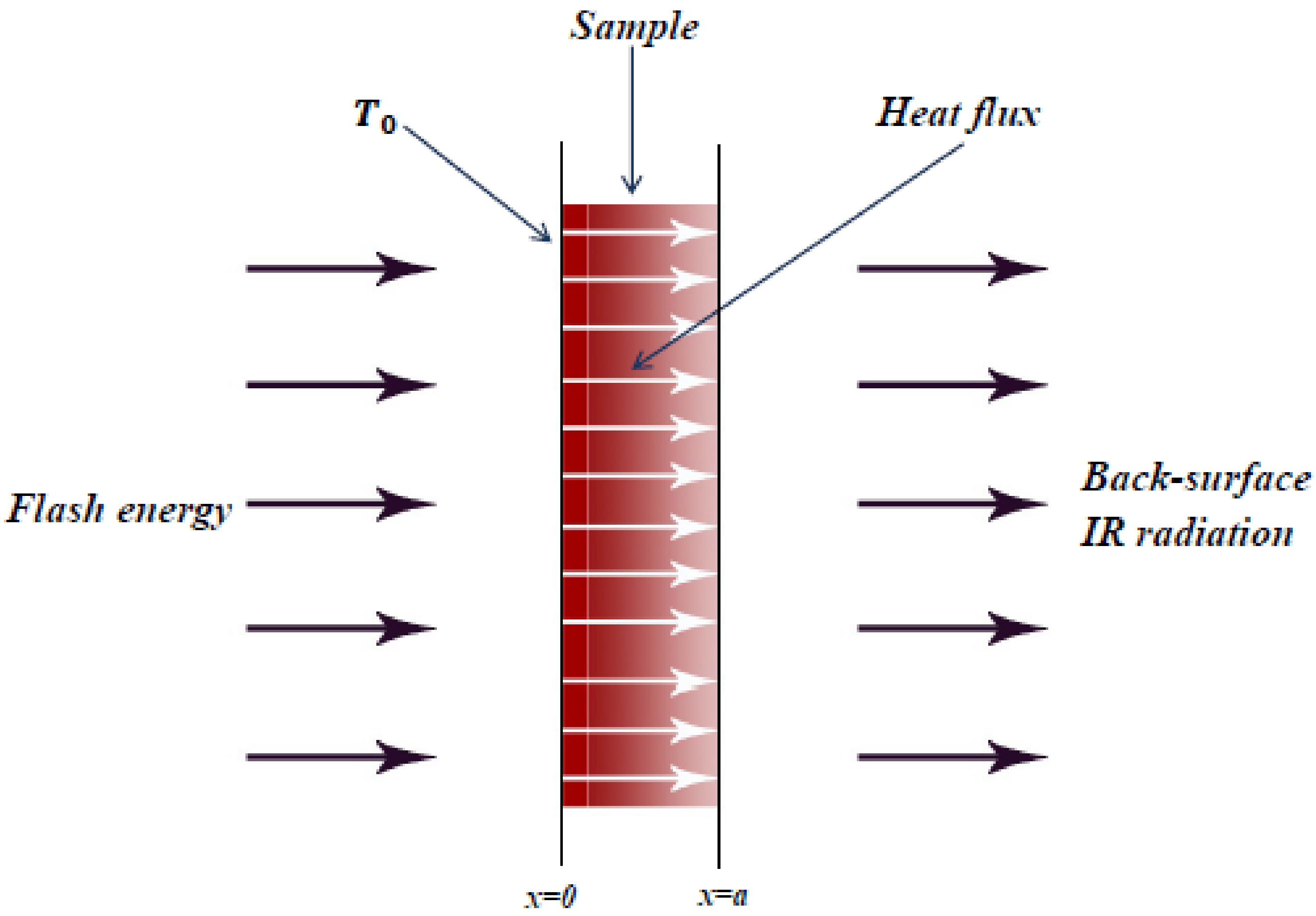
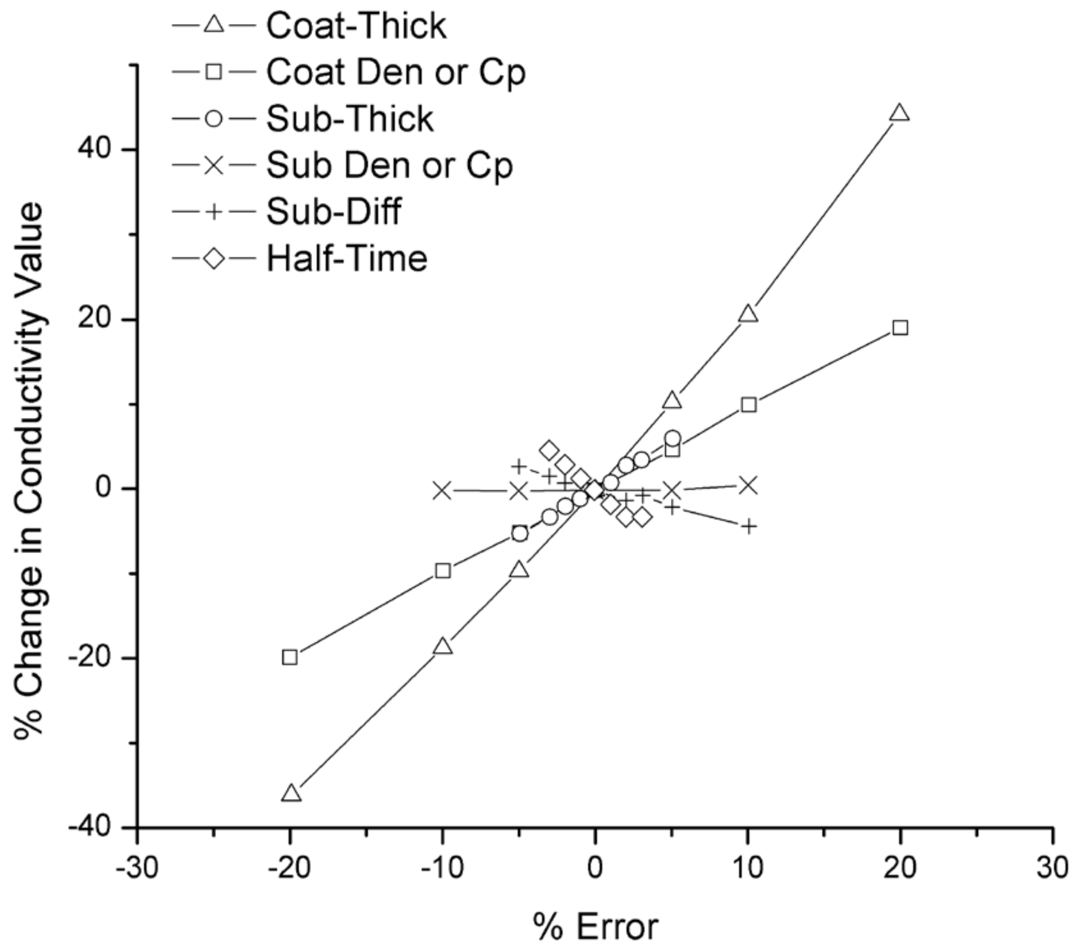


Figure: Diagram of the flash method for measuring thermal diffusivity.

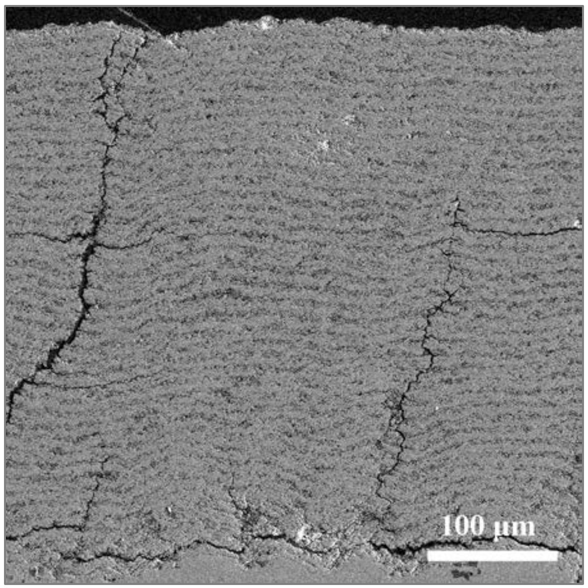
Flash Method
Error

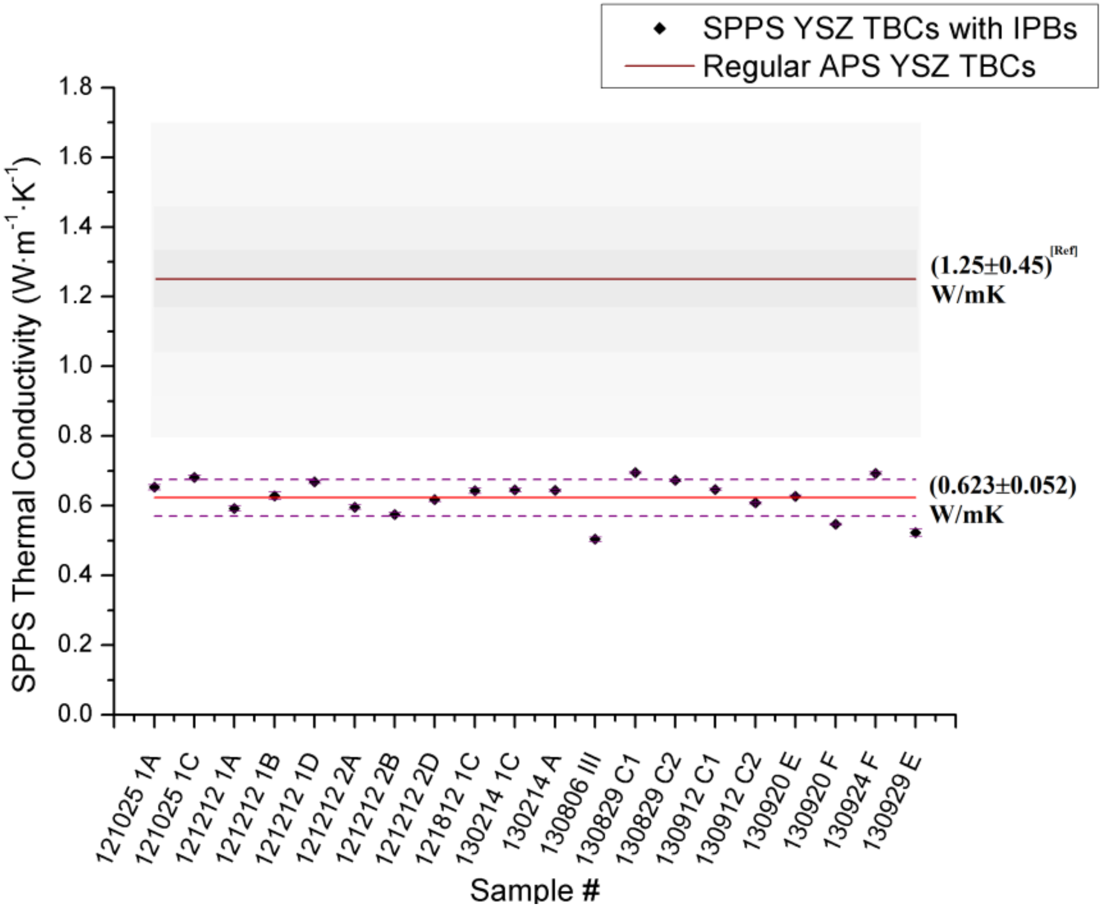


[4] Taylor RE. Thermal conductivity determinations of thermal barrier coatings. *Materials Science and Engineering A*245.1998: 160–167

Performance of TBCs with IPBs

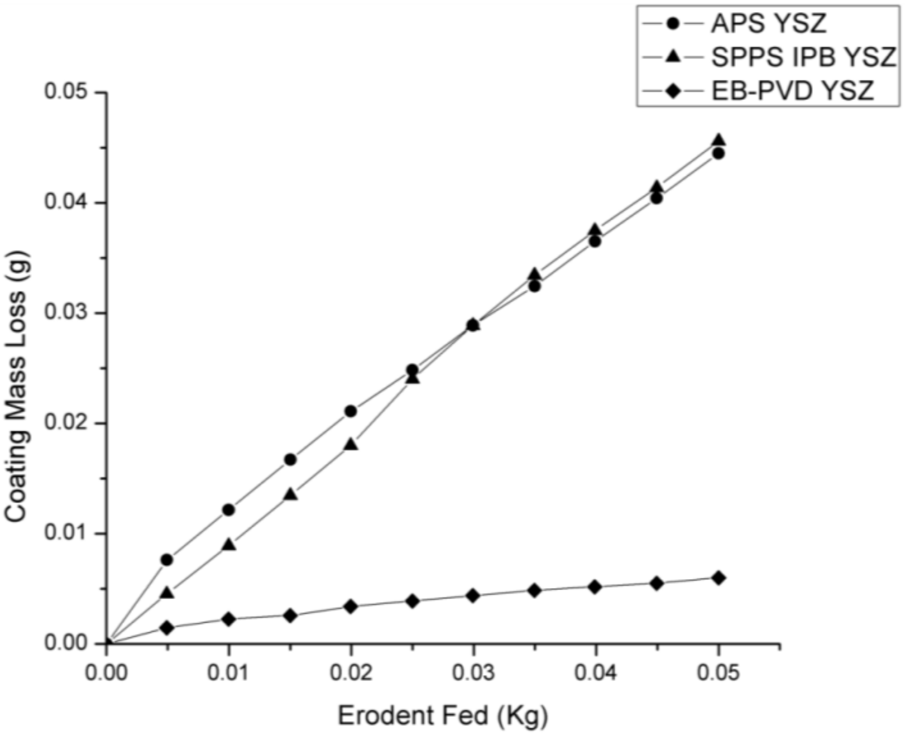
Low thermal conductivity, ~50% reduction



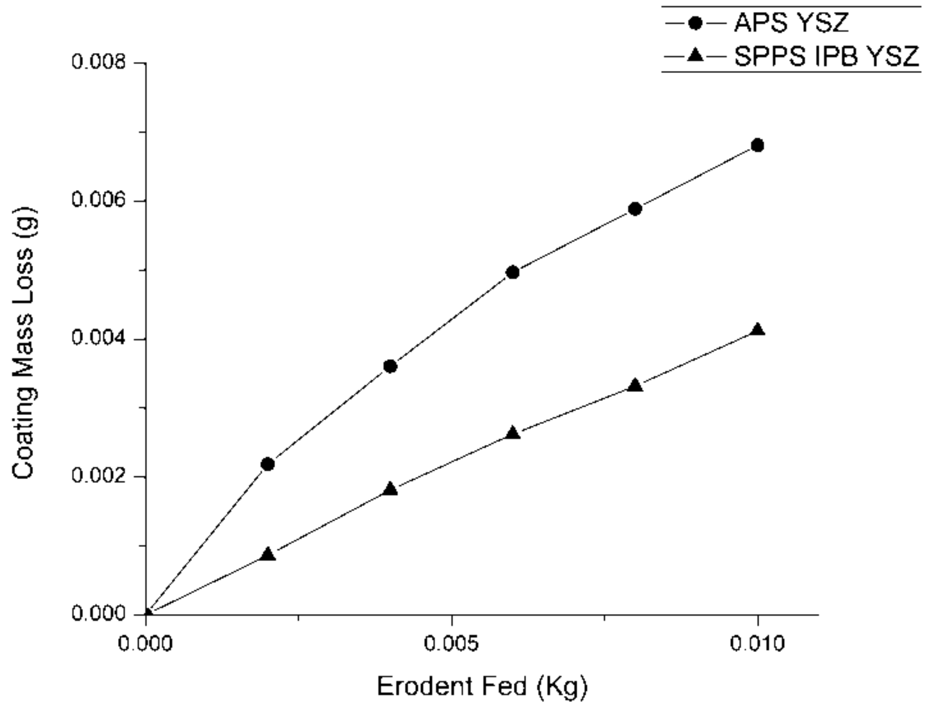


Padture NP, Gell M, Jordan EH, "Thermal barrier coatings for gas-turbine engine applications," *Science*, pp. 280-4, 2002

Performance of TBCs with IPBs
Erosion resistance comparable to APS



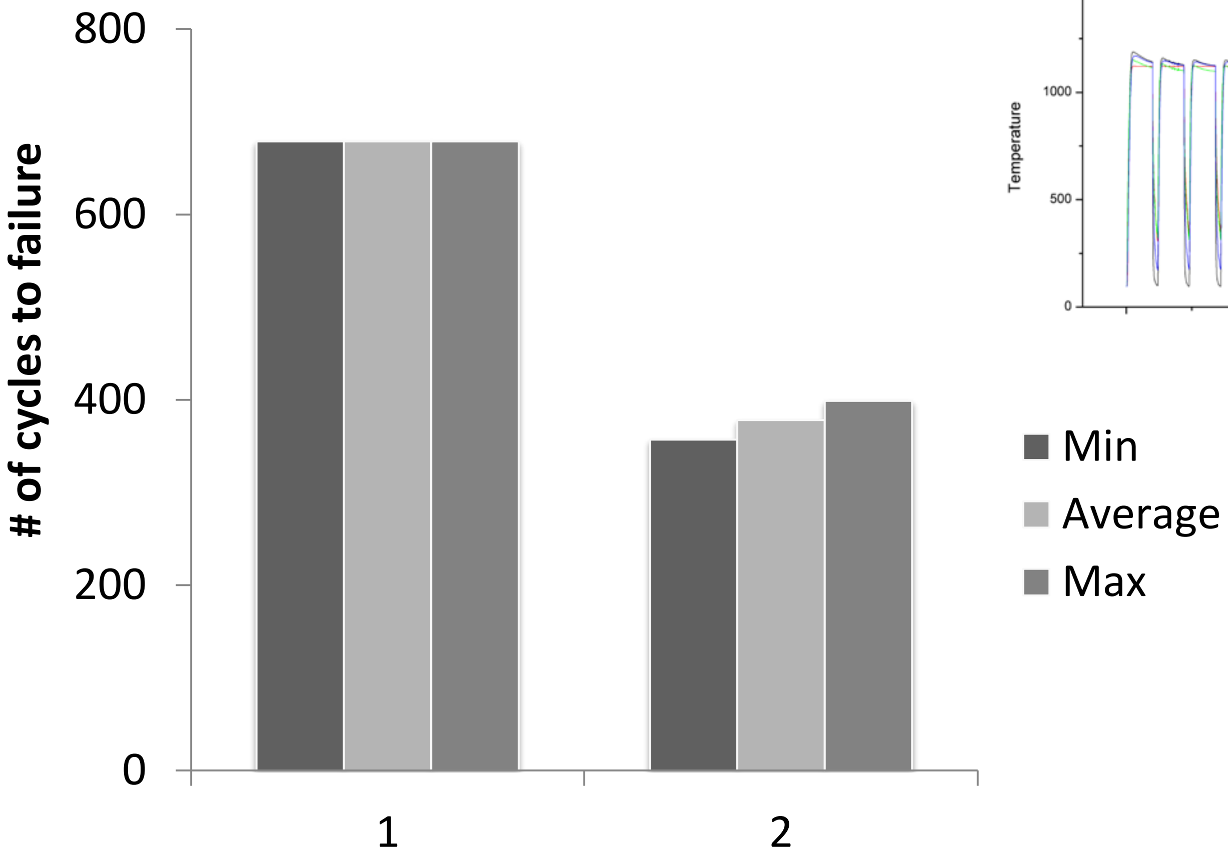
90º impingement

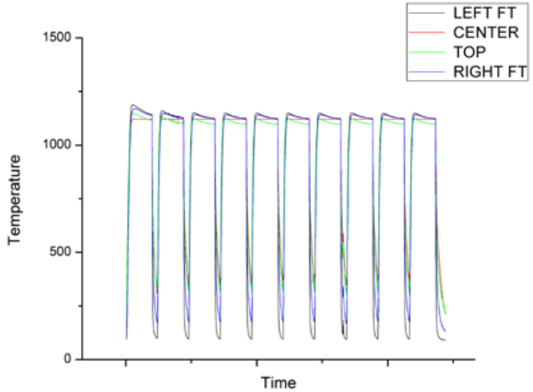


30º impingement

Performance of TBCs with IPBs

Better cyclic durability than APS

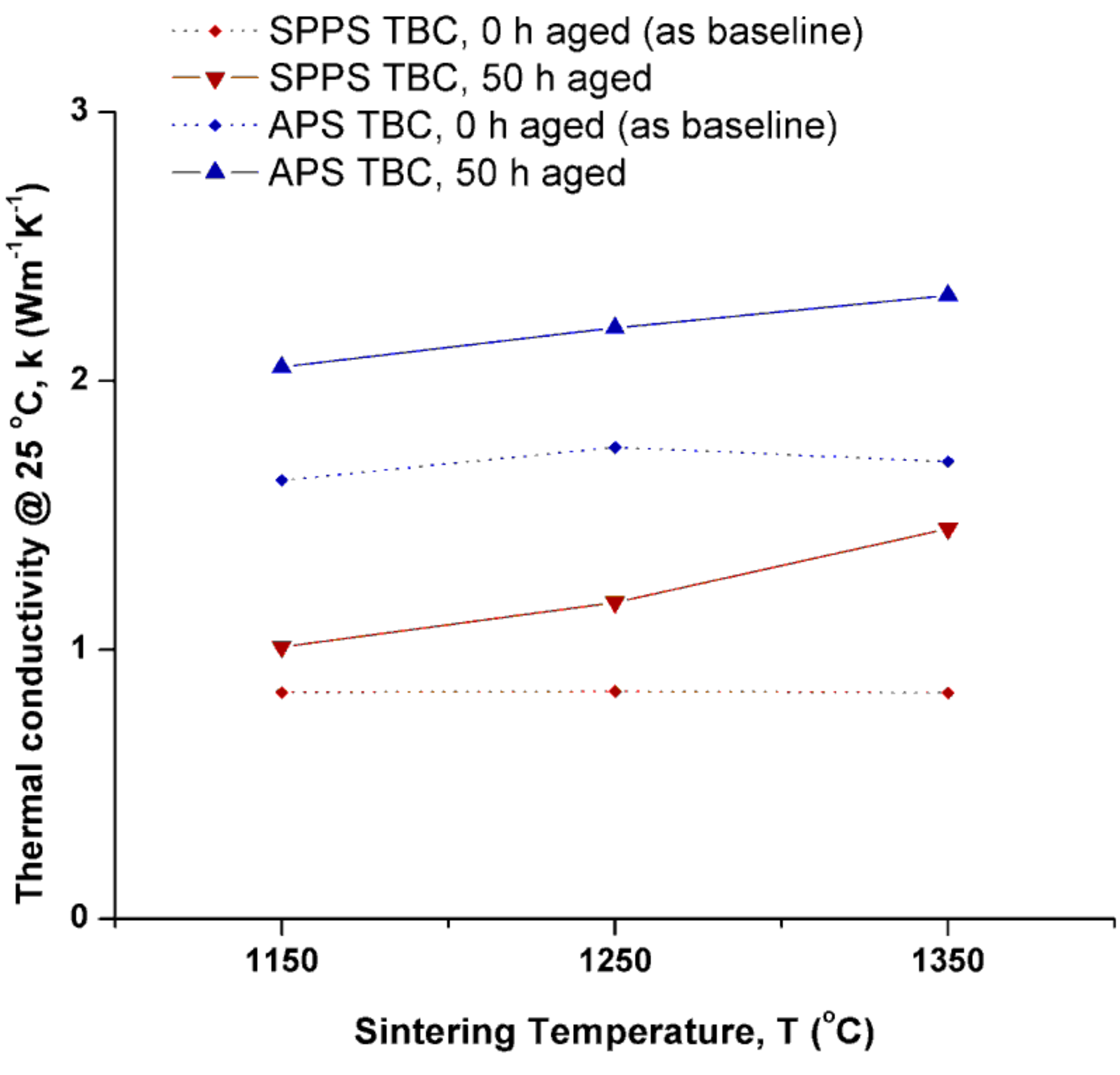


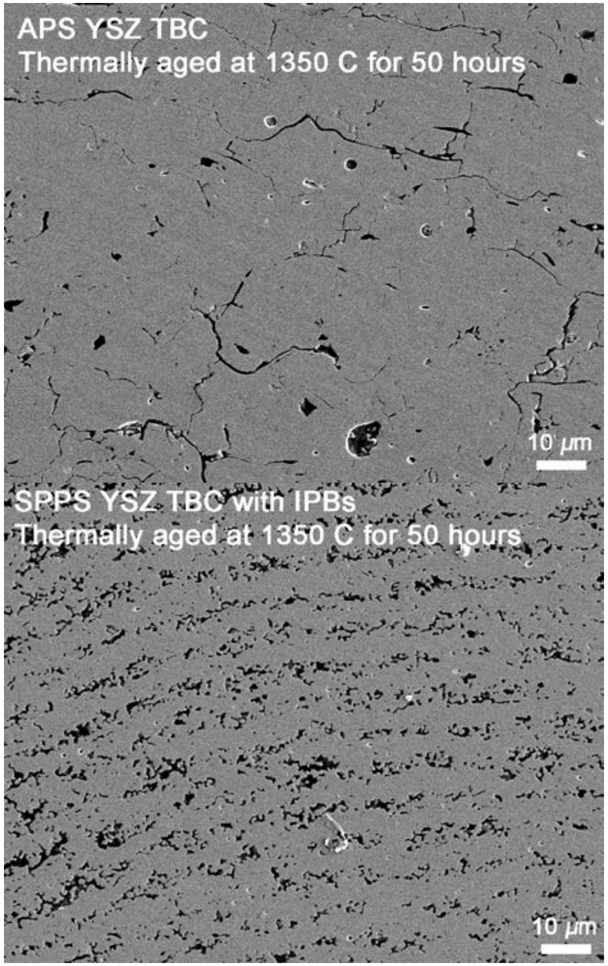


Cyclic furnace testing of: (1) 250 μm SPPS YSZ with IPBs, and (2) 250 μm APS YSZ.

Performance of TBCs with IPBs

Sintering behavior similar to APS





Contaminants Affect TBC Failure

CMAS:

Calcium magnesium aluminum silicate

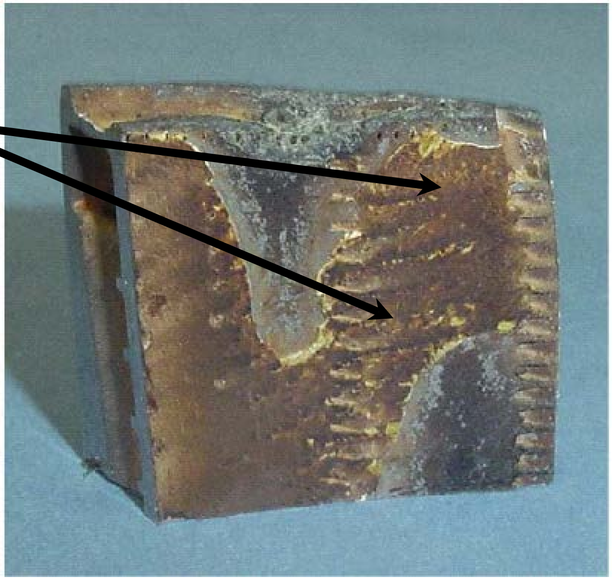
A 387 MW (H Machine) Engine Processes about $2X10^{10}$ Kg[1] of Air/Year

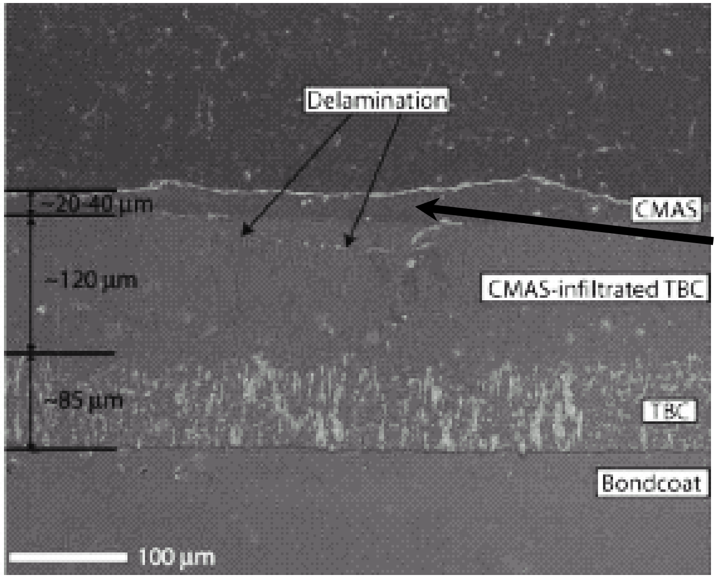
- **Jeffrey Bons gets fractional sticking of solids roughly 1%-10%**
- **1 PPM of solids would be 20,000 KG if it sticks even at 10%=2000 KG; it is still bad at 1%.**
- **To be a small problem you need about 1 PPB (20KG). CMAS is a PROBLEM.**
- [1]Chiesa, P. et al, Using Hydrogen as a Gas Turbine Fuel, J. of Engineering for Gas Turbine and Power 127, 73, 2005

CMAS Infiltration of 7YSZ Thermal Barrier Coating

Field Observation of CMAS Attack

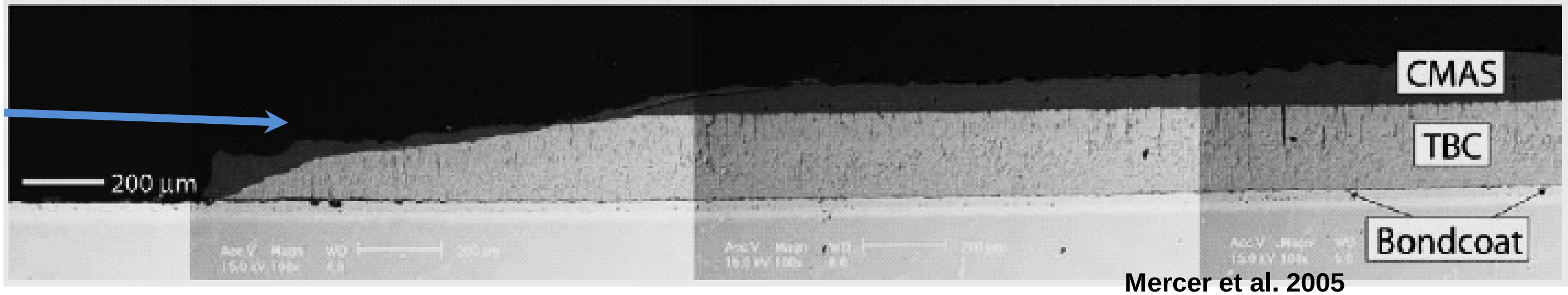
CMAS Deposits





Transverse Cracks that Lead to Shedding of Topcoat

Coating Loss Due to CMAS Infiltration



Mercer et al. 2005

Most Aggressive Attack Tends to Occur in Hottest Regions

1. Loss of Strain Tolerance-Mechanical Effect

A.G. Evans, J.W. Hutchinson / Surface & Coatings Technology 201 (2007) 7905–7916

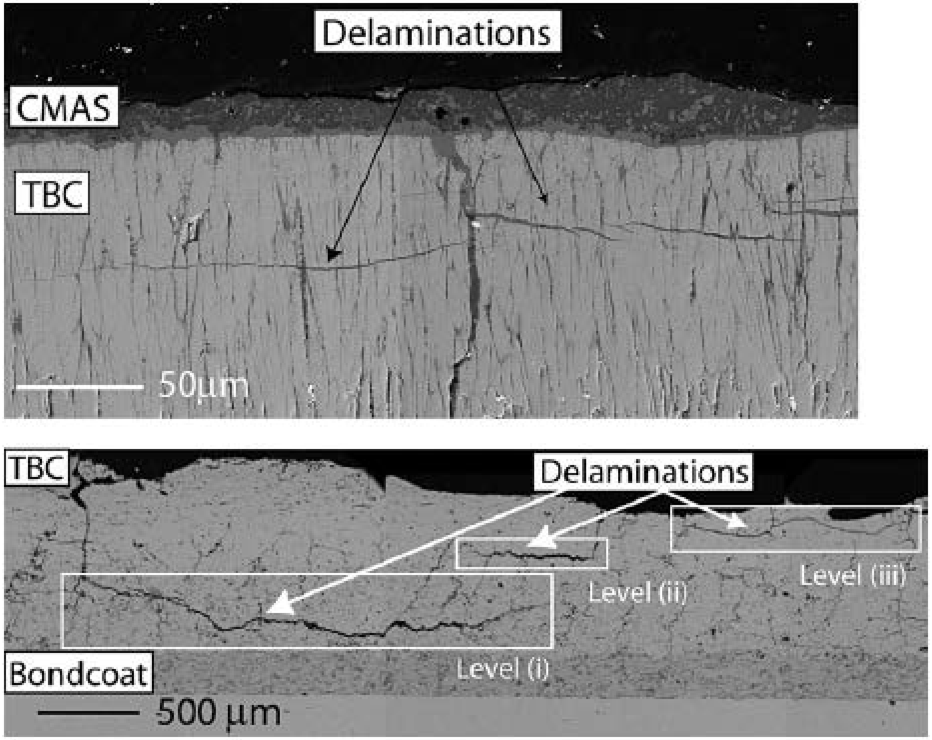


Fig. 1. Examples of delaminations in thermal barrier coatings obtained from components removed from engines subjected to CMAS penetration: (a) Sub-surface mode I delaminations in an airfoil with a TBC made by electron beam physical vapor deposition; the delaminations are within the penetrated zone [9]. (b) Delaminations at several locations within a shroud penetrated by CMAS; the TBC is 1 mm thick and deposited by air plasma spray (APS) [10].

Mechanics Modes for Loss of Strain Tolerance Developed by Hutchinson and Evans

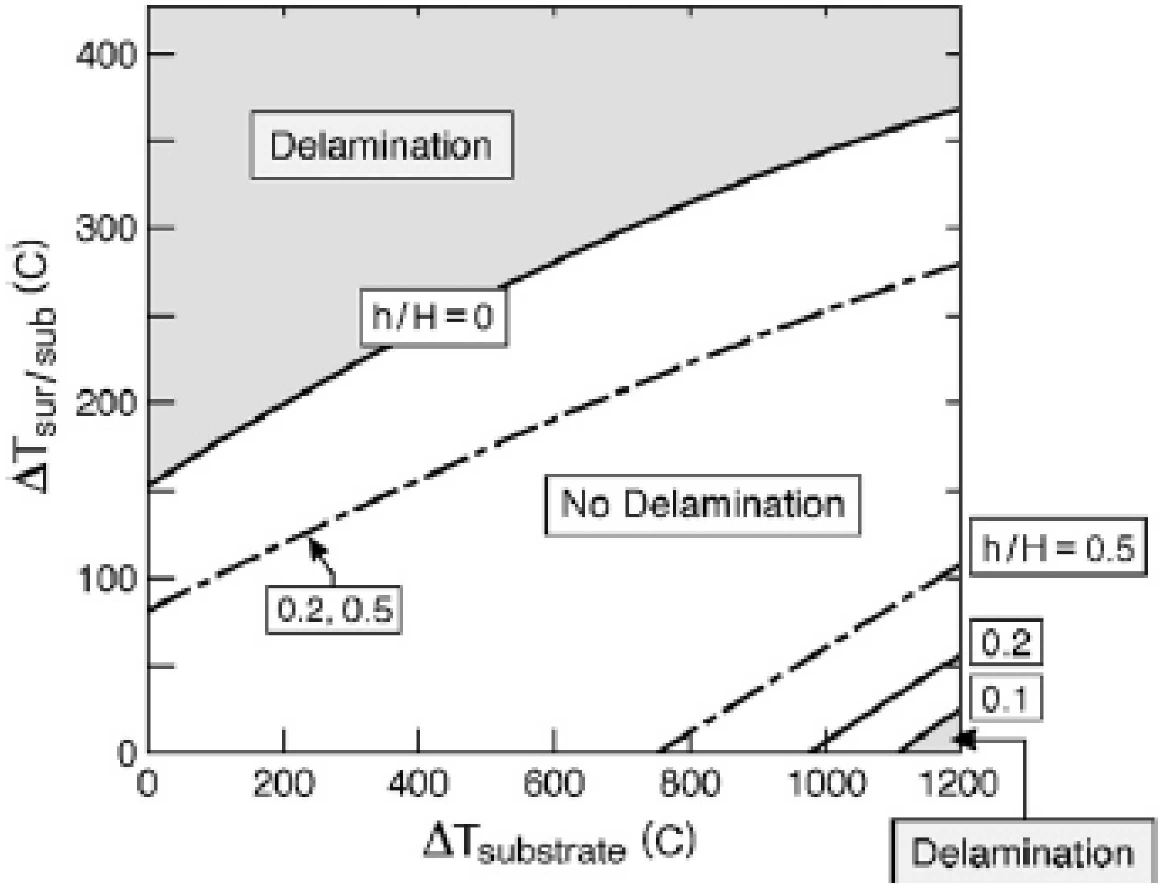


Fig. 10. A map for deep delamination in an APS–TBC on a superalloy substrate with CMAS infiltration to depth, h/H. The mixed mode toughness parameter is, $\lambda = 0.25$.

2. Many types of chemical and phase effects for example Y loss and destabilization of *t'*-ZrO_2 to monoclinic with a destructive volume change

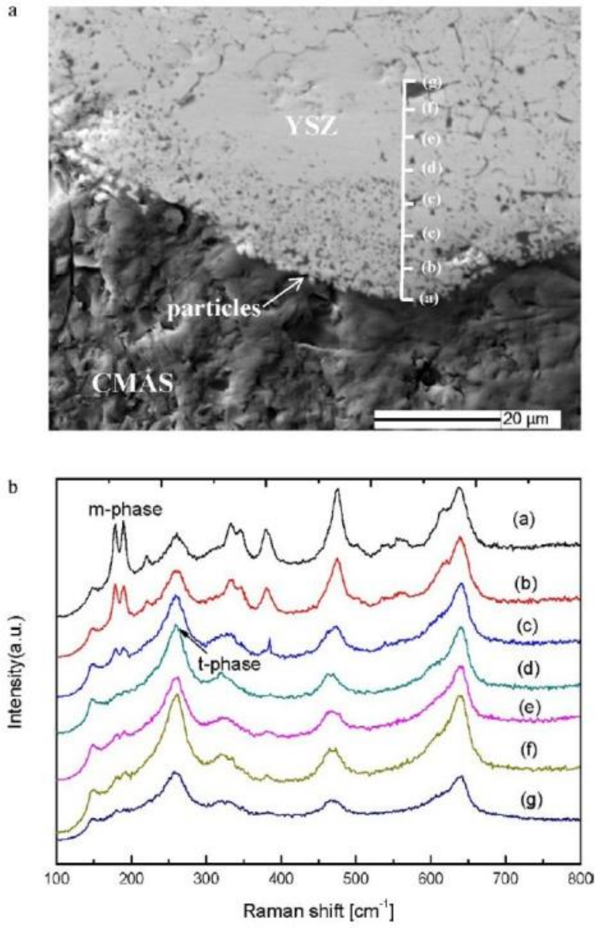
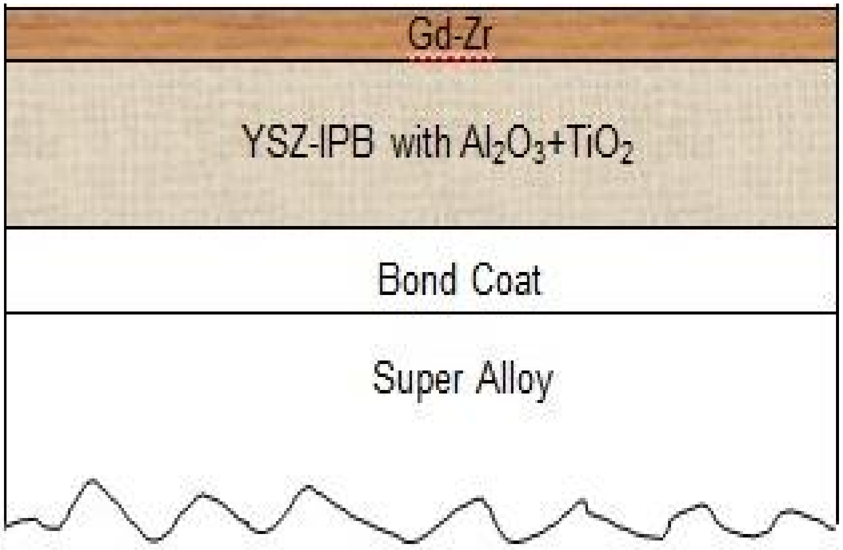


Fig. 4. (a) Micrograph of the interaction zone of CMAS deposit and YSZ coating after 4 h heat-treatment at 1250 °C, and (b) Raman spectra obtained from the positions marked in (a).

CMAS Damage Mitigation and Increased Temperature Capability to be Implemented

Three Approaches

1. Add GdZr to baseline system for higher temperature phase stability and CMAS resistance.

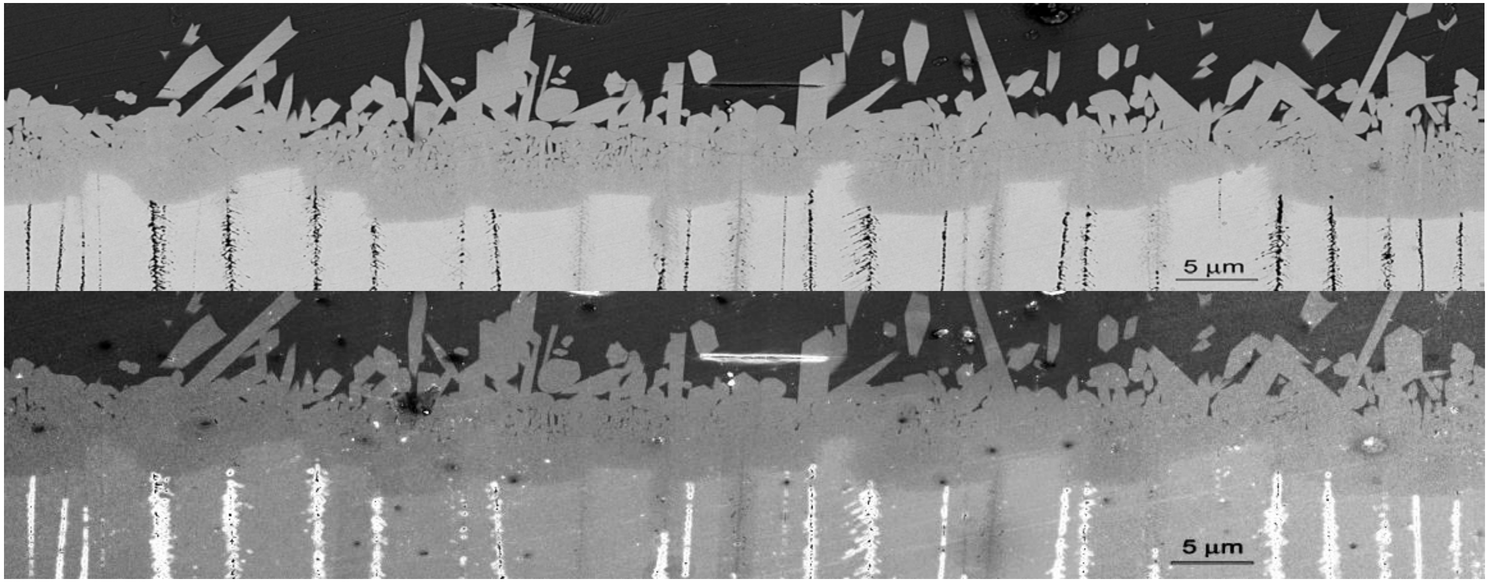


TBC system #2 with low conductivity solution plasma sprayed YSZ with IPBs and CMAS resistant high temperature tolerant GdZr protective surface layer (PSL).

Why $Gd_2Zr_2O_7$?

- **Higher temperature phase stability limit than 1150 ^{o}C (YSZ) vs. 1550 ^{o}C (GdZr)**
- **Half the conductivity of YSZ**
- **Inhibit CMAS infiltration by precipitating out apatite phases from the glassy CMAS**

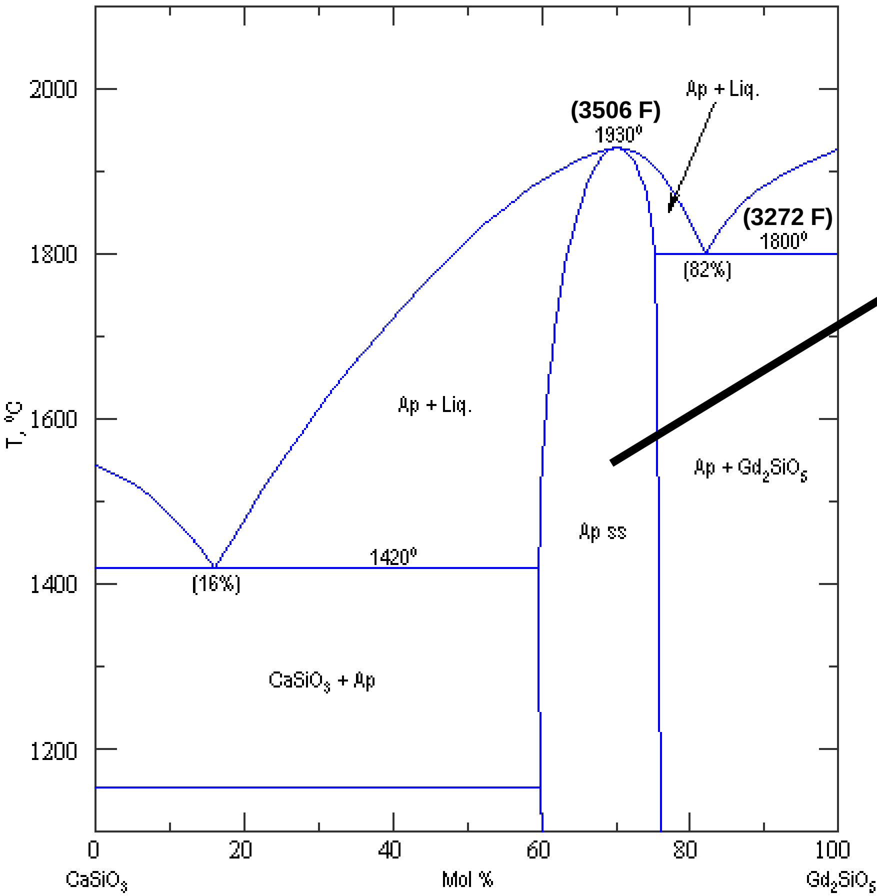
CMAS Resistance of GdZr

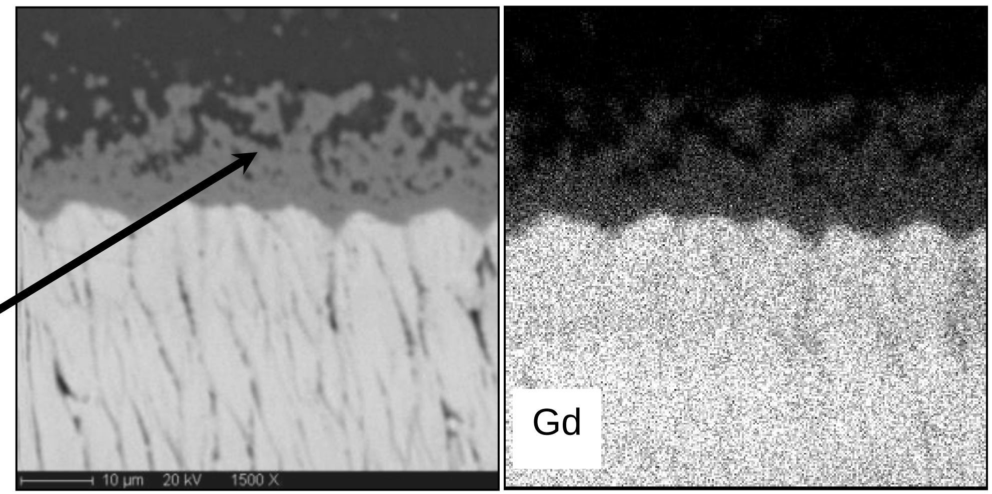


From Carlos Levi, UCSB

Analysis of $Gd_2Zr_2O_7$/CMAS Reaction Product

Sealant Layer Identified as Hexagonal Apatite Phase, $CaGd_4(SiO_4)_3O$



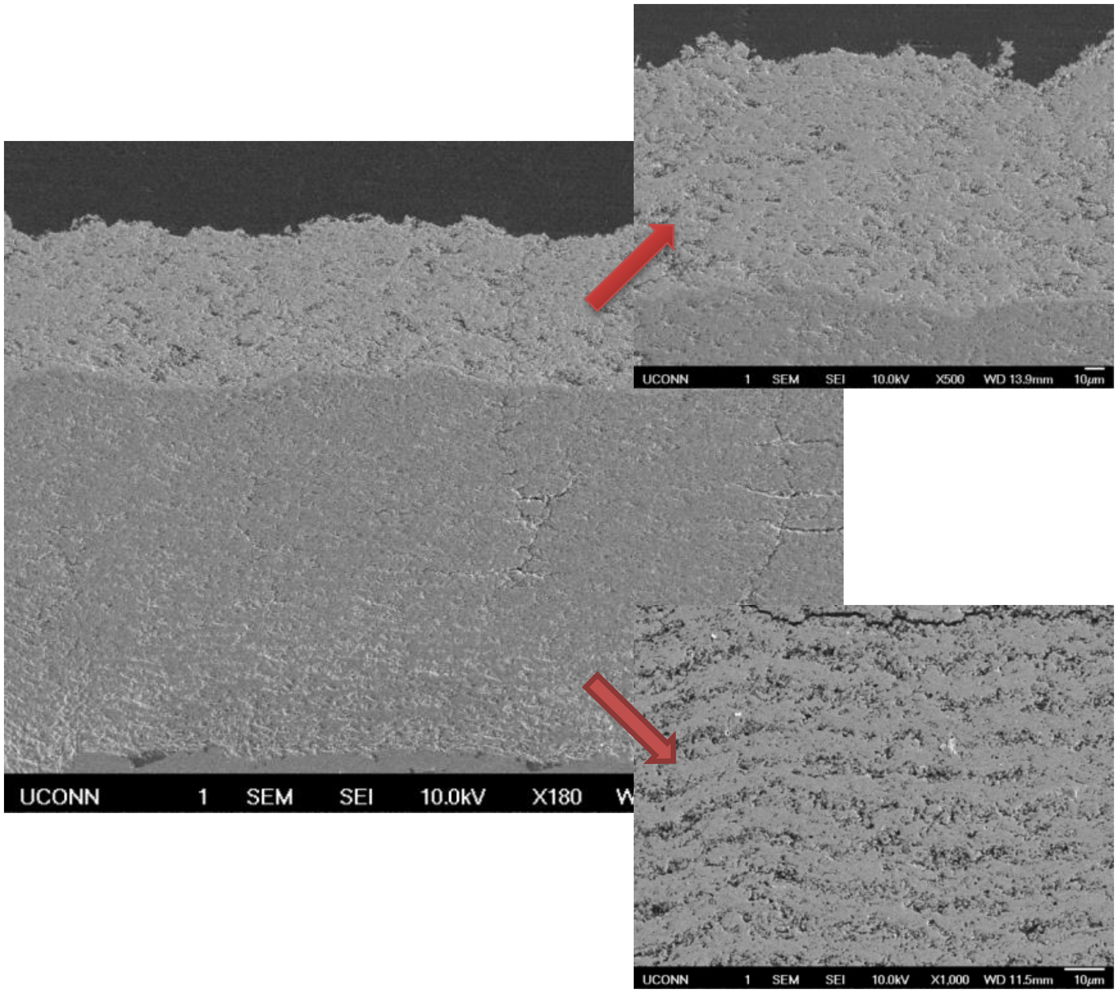


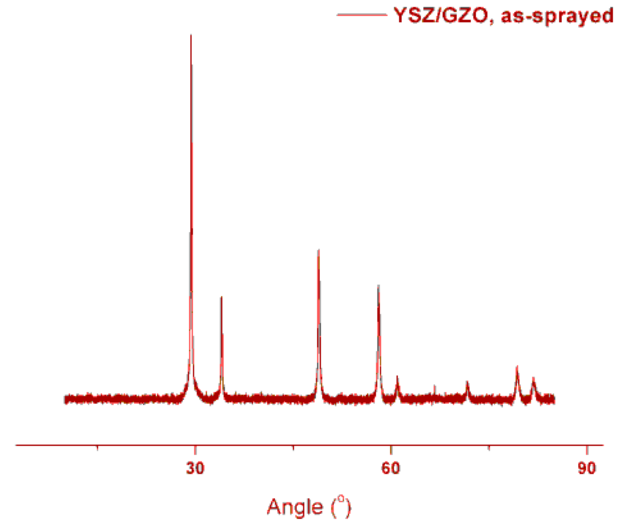
Gd Base TBC

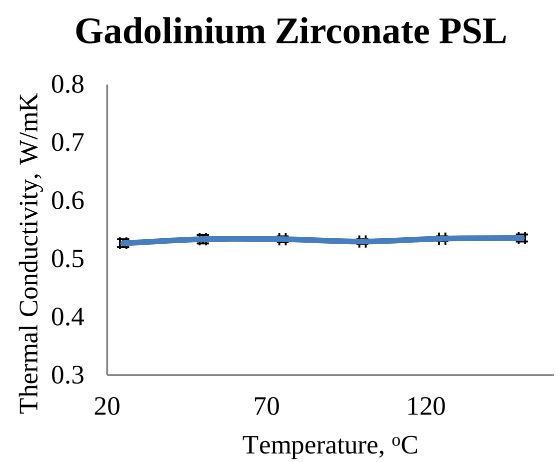
Coating system needs to be designed such that coating/CMAS constituents form stable refractory compound

From Levi, UCSB

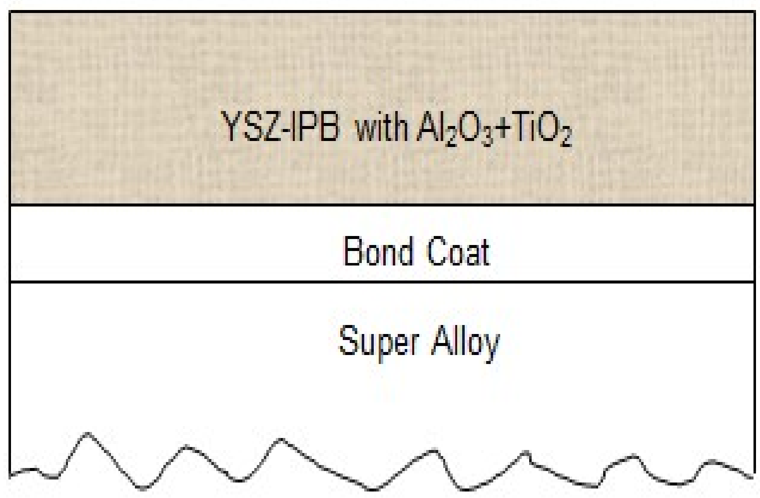
GdZr PSL Deposited on YSZ TBCs using SPPS Process, fluorite







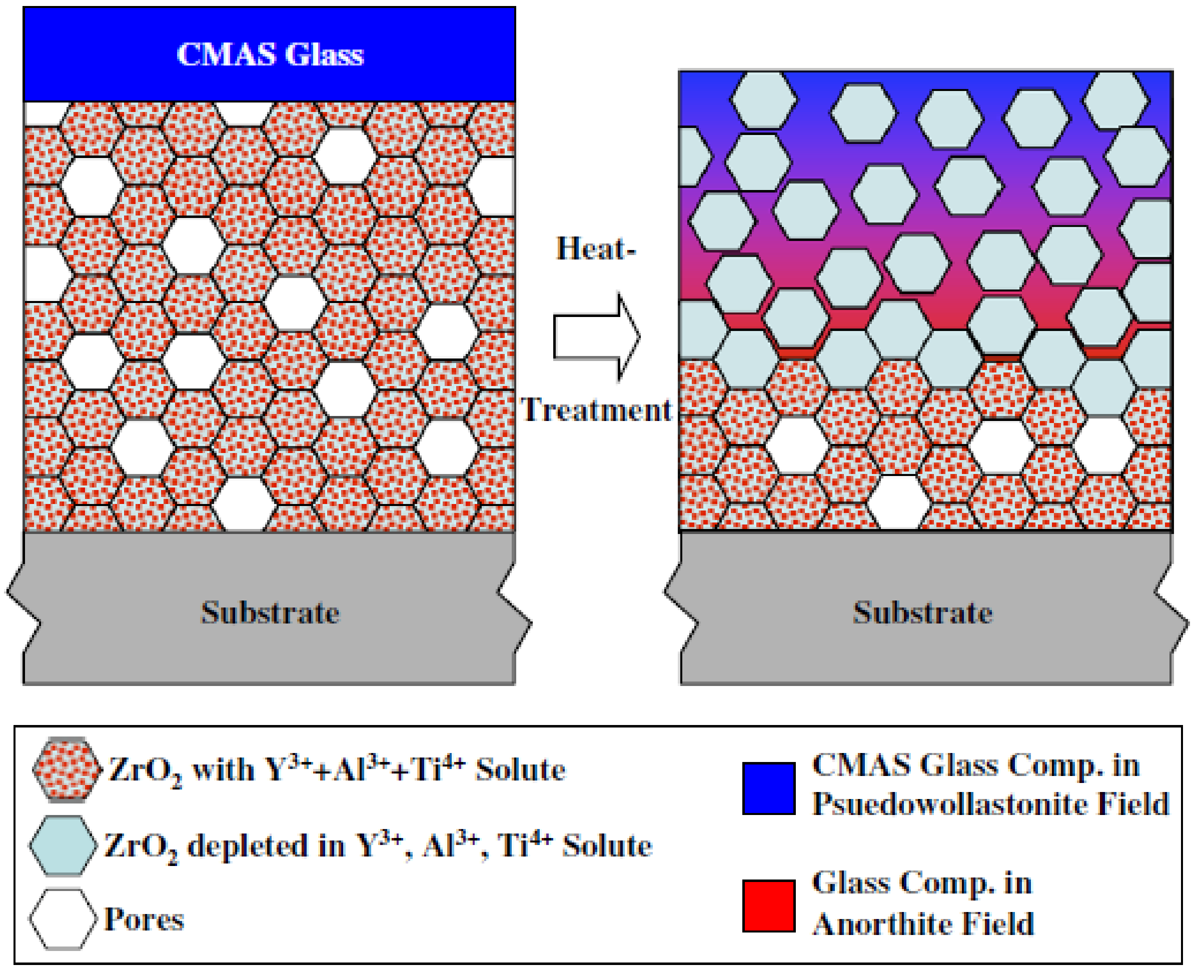
2. Add Metastable Al_2O_3/TiO_2 to Block CMAS in the YSZ Layer



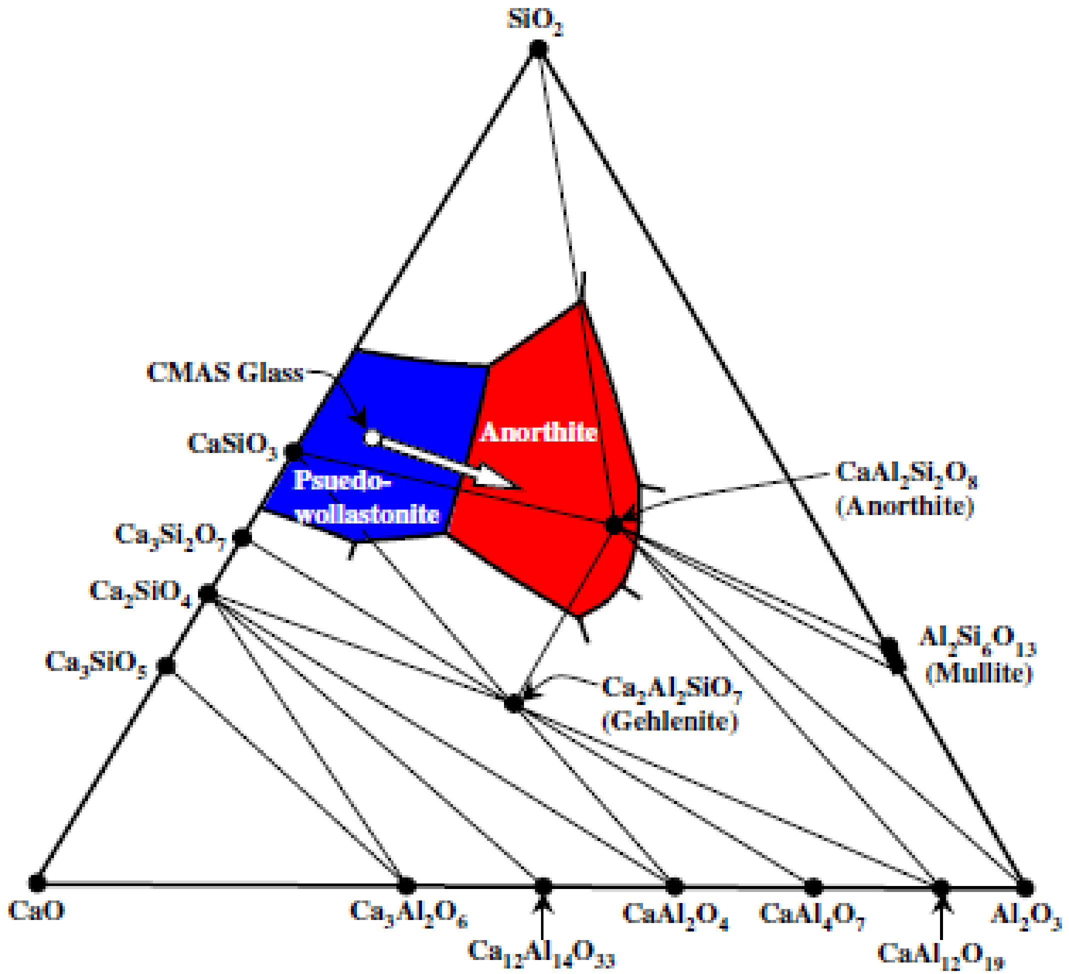
TBC system #3 Al_2O_3/TiO_2-doped SPPS YSZ TBCs with thermal-conductivity-reducing IPBs

How It Works

A. Aygun et al. / Acta Materialia 55 (2007) 6734–6745

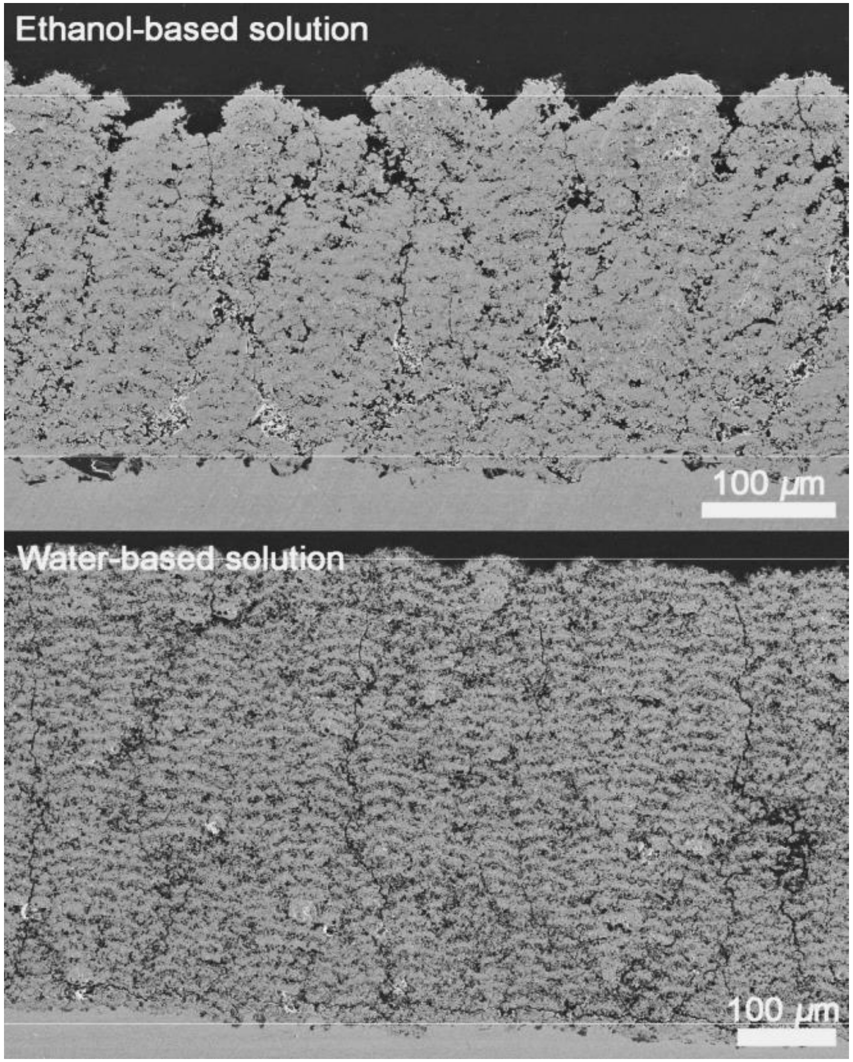


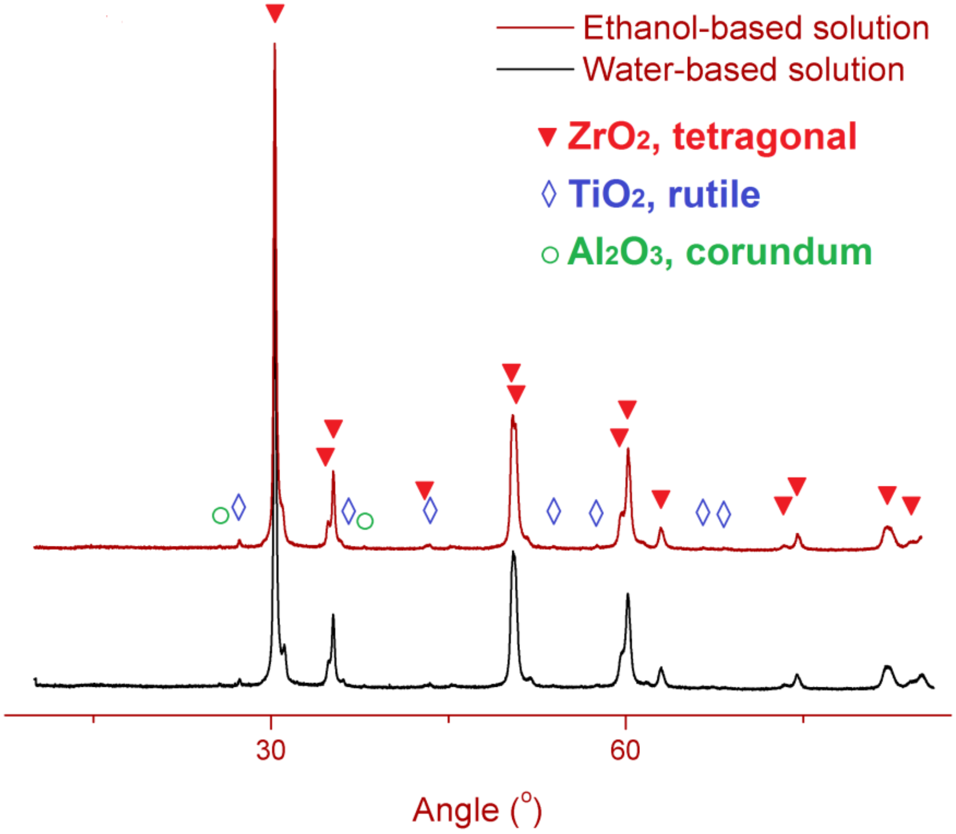
Microscopy Showing Anorthite Phase is Blocking the Infiltration



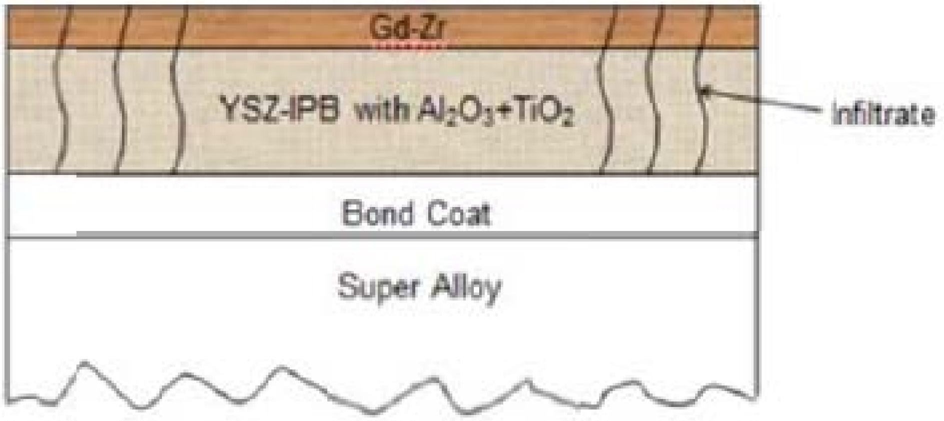
Enhancing Corrosion Resistance

Al_2O_3/TiO_2-doped SPPS YSZ with IPBs

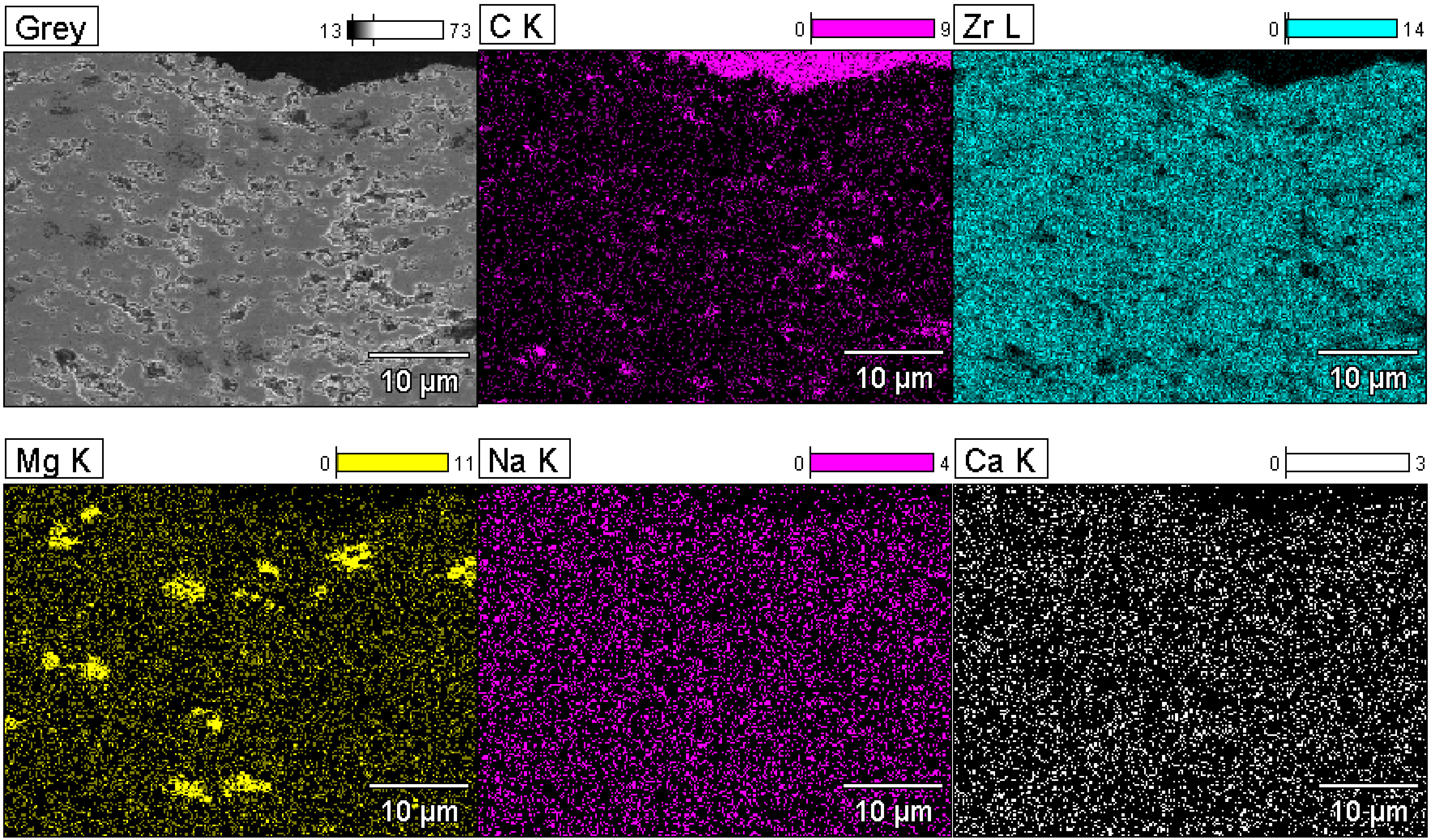




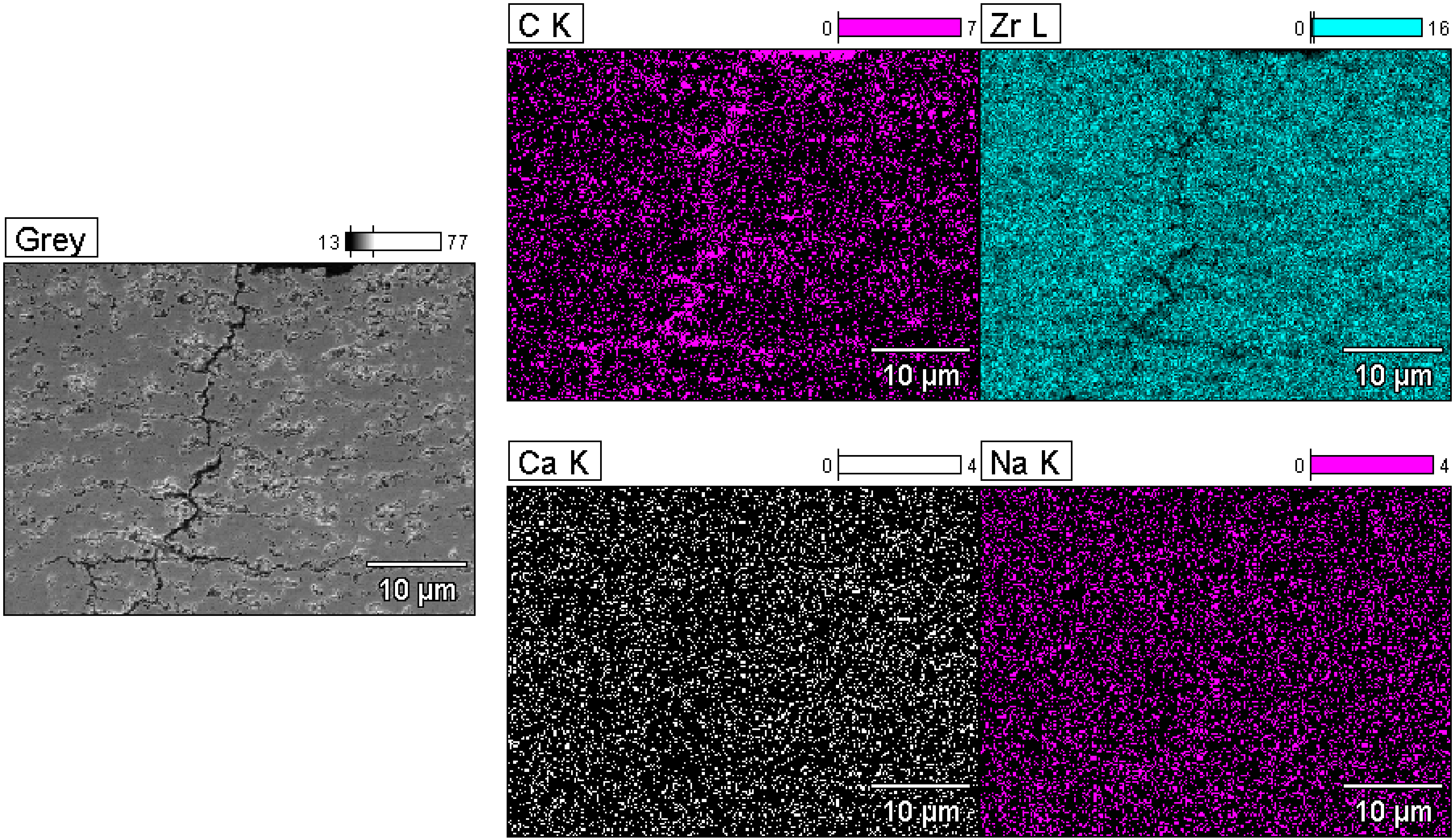
3. Infiltration of $CaSO_4$ via a Low Melting Eutectic of $NaSO_4$-$CaSO_4$-$MgSO_4$



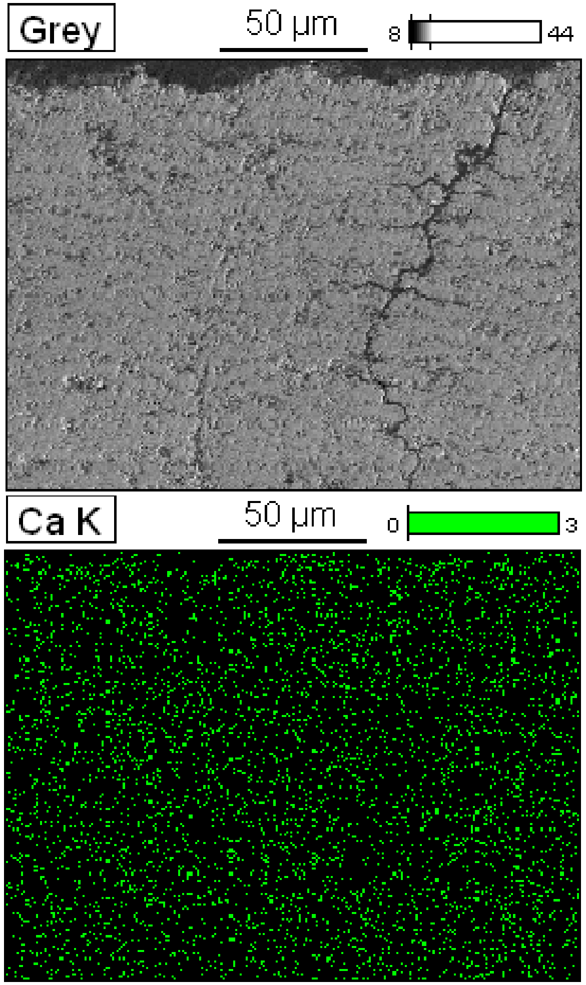
Infiltration of $CaSO_4$ via a Low (700 ºC) Melting Eutectic of $NaSO_4$-$CaSO_4$-$MgSO_4$

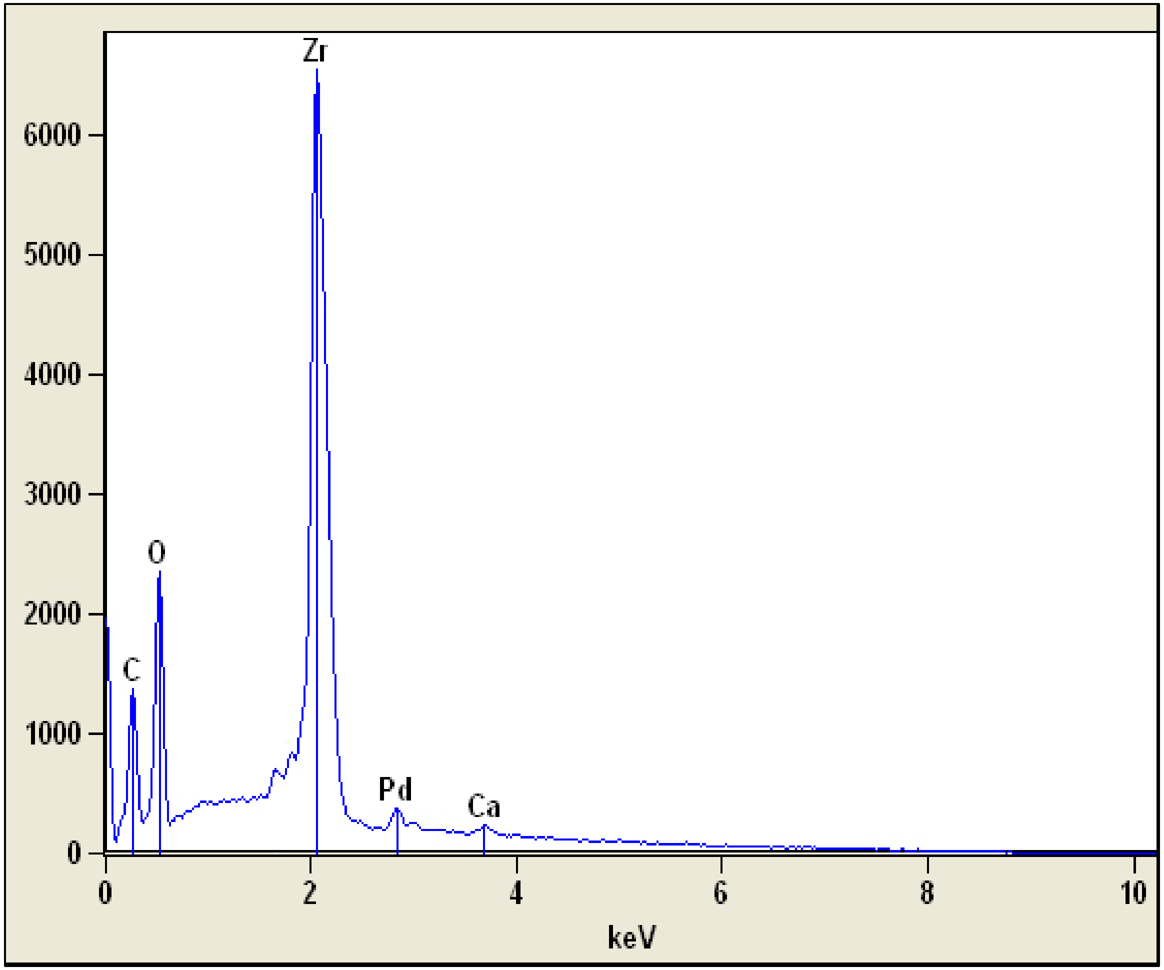


3’. Infiltration of $CaSO_4$ via a Mixture (950 ºC) of $NaSO_4$-$CaSO_4$



3”. Infiltration of $CaSO_4$ via a Solution

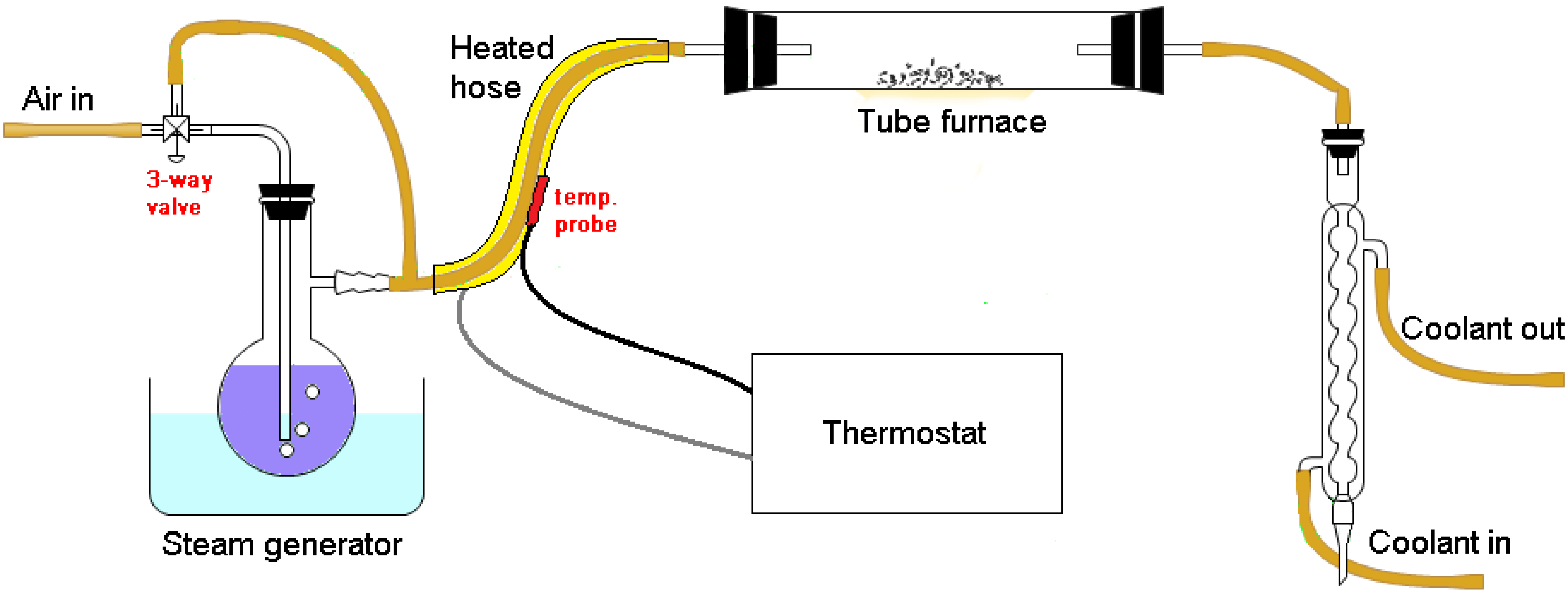




High-Temperature Environmental Test

High Temp Environmental Test

Experimental apparatus



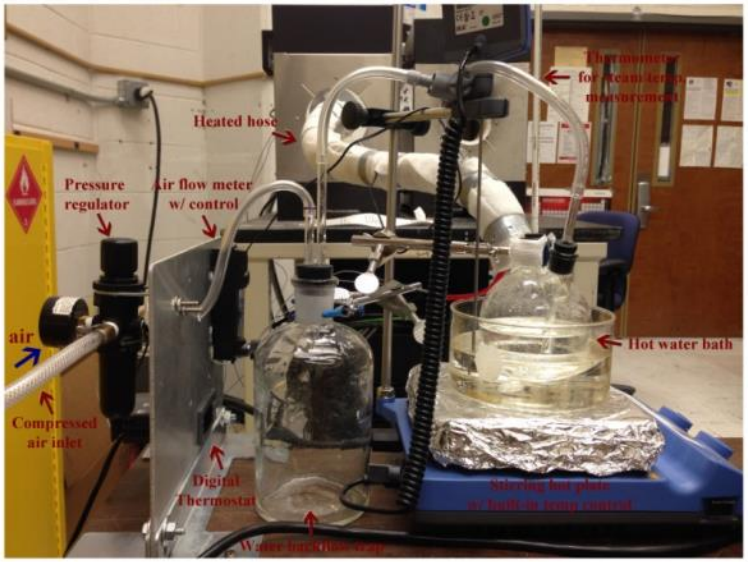
Air flow rate: 5 cm/min (0.41 SCFH)

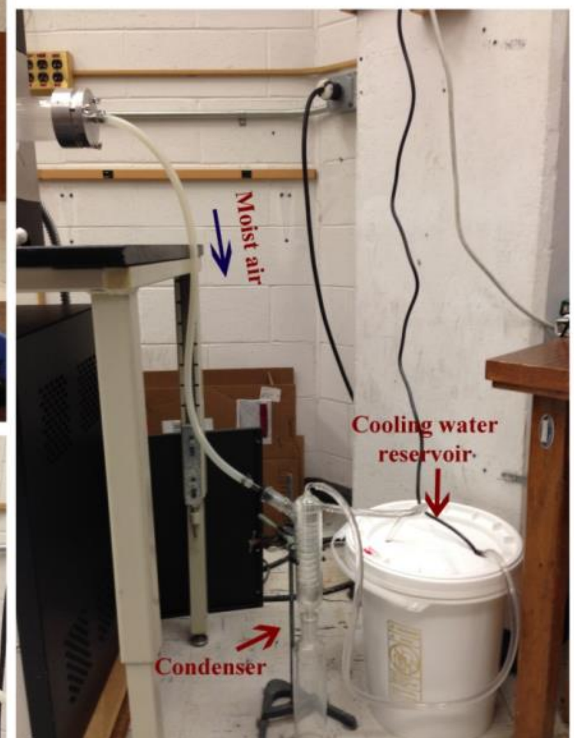
Humidity: 30% H_2O (74 ^oC steam in flask, 69~71 ^oC in the heated hose)

Tube furnace: 1121 ^oC

Zhao W and Gleeson B, "Steam effects on the oxidation behavior of Al_2O_3-scale forming Ni-based alloys", Oxid. Met. (2013) 79: 613-625

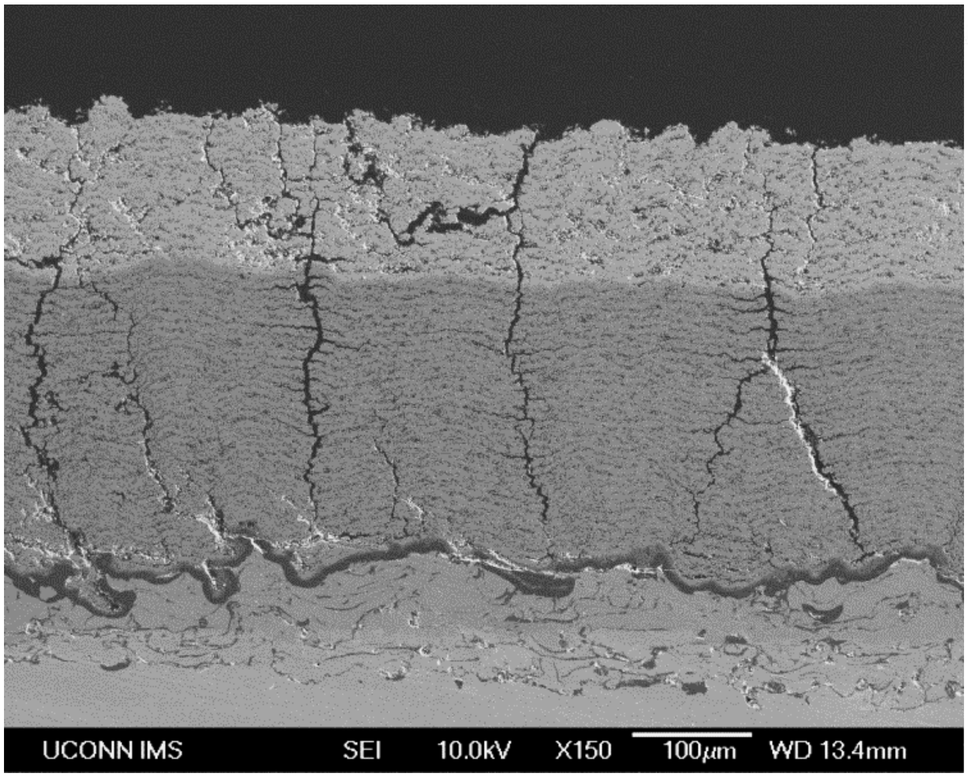
High Temp Environmental Test
Experimental apparatus

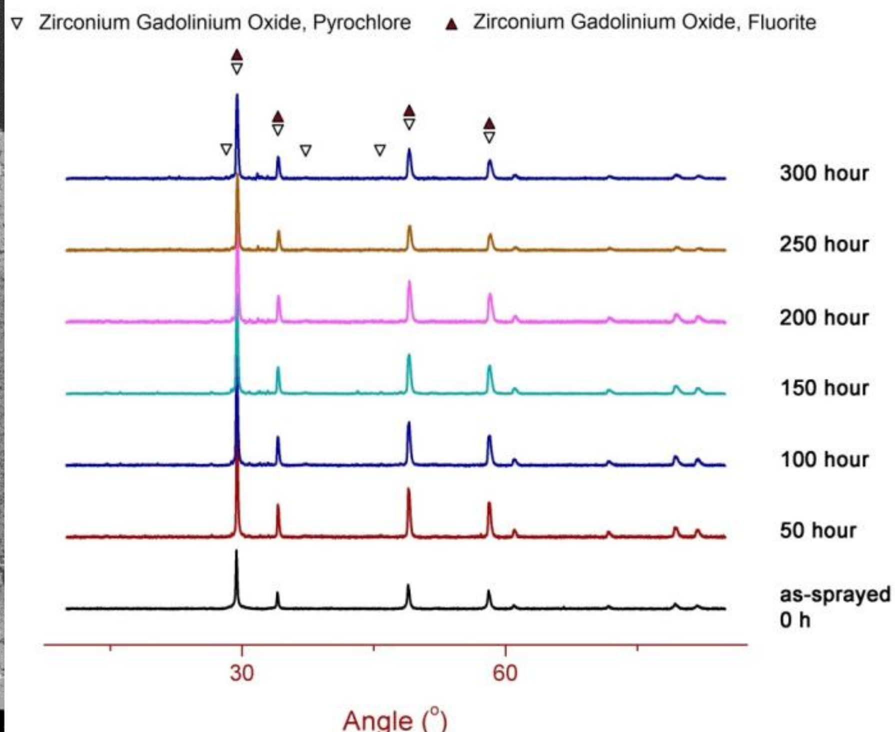




High Temp Environmental Test

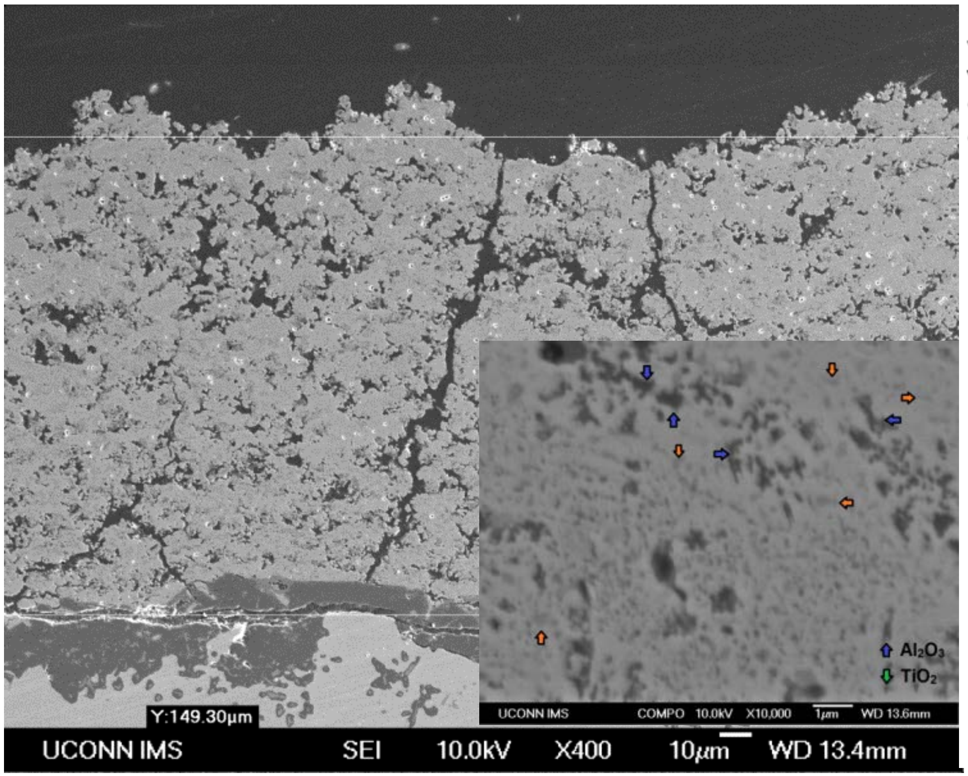
SPPS IPB YSZ/GZO tested up to 300 hours

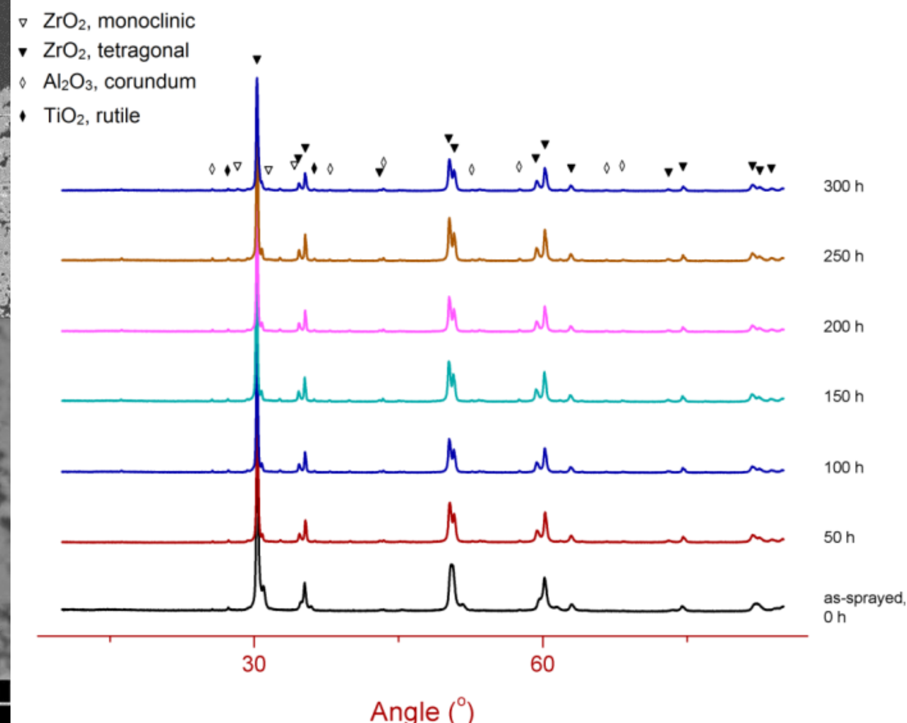




High Temp Environmental Test

Al_2O_3/TiO_2-doped SPPS YSZ tested up to 300 hours





Summary

- **Project Goals:**
  - Structured porosity optimized to reduce conductivity to 0.6 $Wm^{-1}K^{-1}$
  - Increase surface temperature allowable to 1300 ^{o}C
  - Significantly improve CMAS resistance
- **A top layer of GdZr will be used to:**
  - Allow 1300 ^{o}C surface temperature
  - Improved CMAS resistance
- **Al_2O_3/TiO_2 metastable solutes added to the YSZ to reduce CMAS infiltration, while the IPB feature is maintained**
- **$CaSO_4$ used for the first time to try to arrest CMAS infiltration.**

Future Work

- **Cyclic CMAS testing in “ spritz” test.**
- **Furnace ageing without moisture for comparison.**
- **Increasing the viscosity of the Ca SO_4 precursor and re use vacuum infiltration to preferentially deposit in vertical cracks.**

Questions?