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

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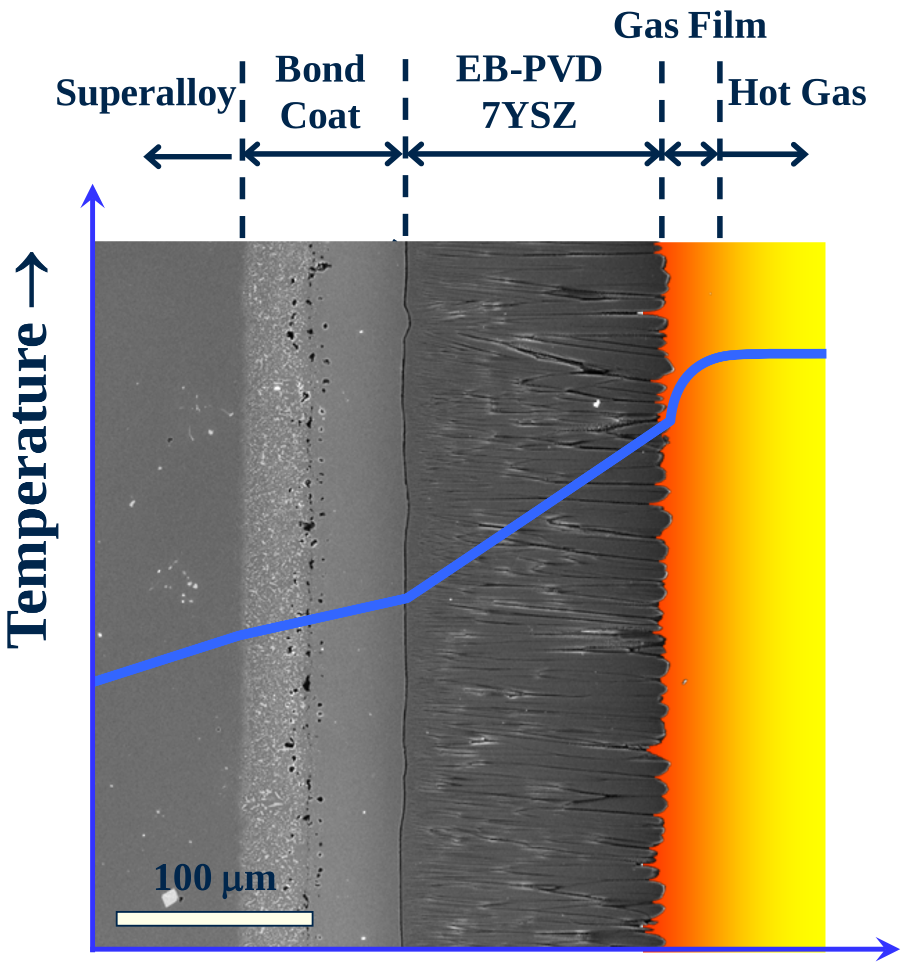
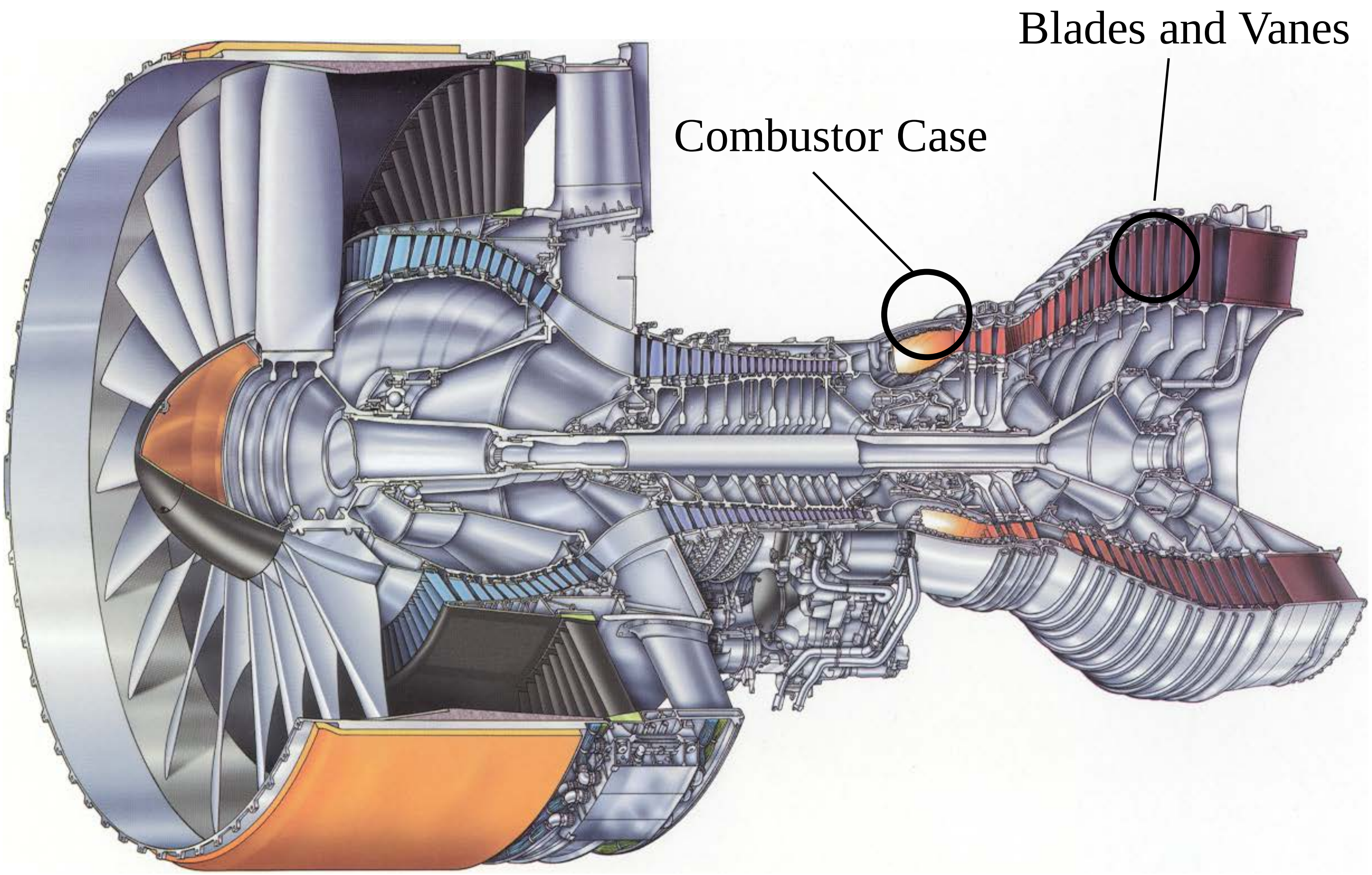
Microstructure & Requirements For TBCs



TBC Requirements

- Low Thermal Conductivity
- High Use Temperature
- High Durability
  - Toughness
  - Strain Tolerance

TBC Applications



Goals

- Reduce the thermal conductivity of TBCs to 0.5 watt/m-K 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 0.5 W/m-°K attained.**
- **SPPS YSZ TBCs can replace advanced low K TBCs with expensive rare earth content**
- **Under DOE STTR program high temperature low CTE YAG TBCs rendered durable by SPPS microstructure with vertical cracks.**

Presentation Outline I

- **Introduction to Solution precursor Plasma Spray (SPPS)**
- **Importance of vertical cracks in SPPS and our exciting new STTR program results.**
- **Development of process parameter-microstructure (IPB) relationship**
- **Failure of Image analysis to determine conductivity and introduction of laser flash methods**

Presentation Outline II

- Success in reducing thermal conductivity by a factor of 2.
- GdZr layer for higher temperature operation and contaminant (CMAS) resistance.
- Addition of aluminum to YSZ for improved CMAS resistance
- Addition of CaSO2 for CMAS resistance.
- Summary

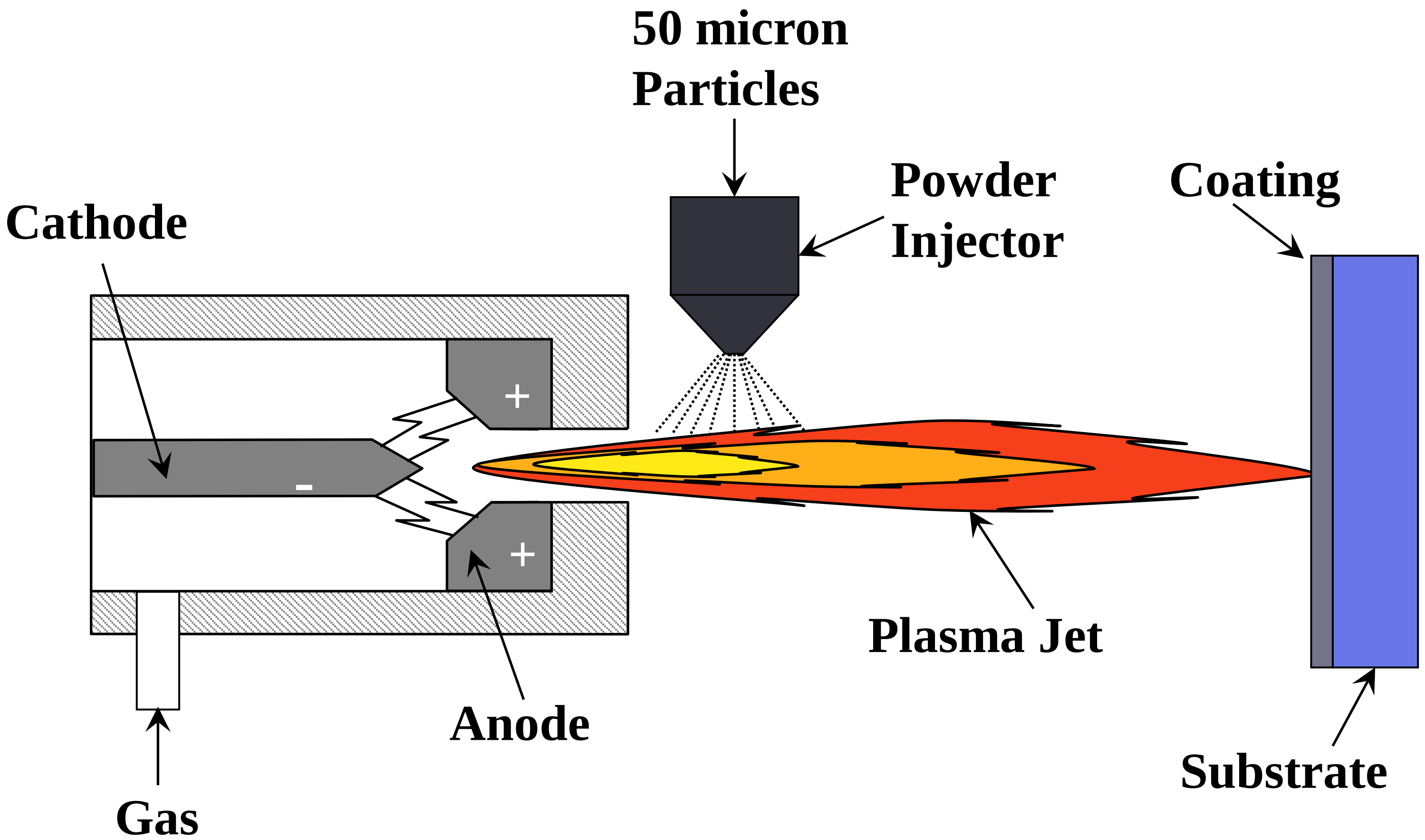
Goals will be accomplished by making and Testing TBC systems Using:

- Solution Precursor Thermal Spray in UConn thermal spray facility
- TBC Testing Facility
- Moist Environment Testing (being built for this program)

Program Plan

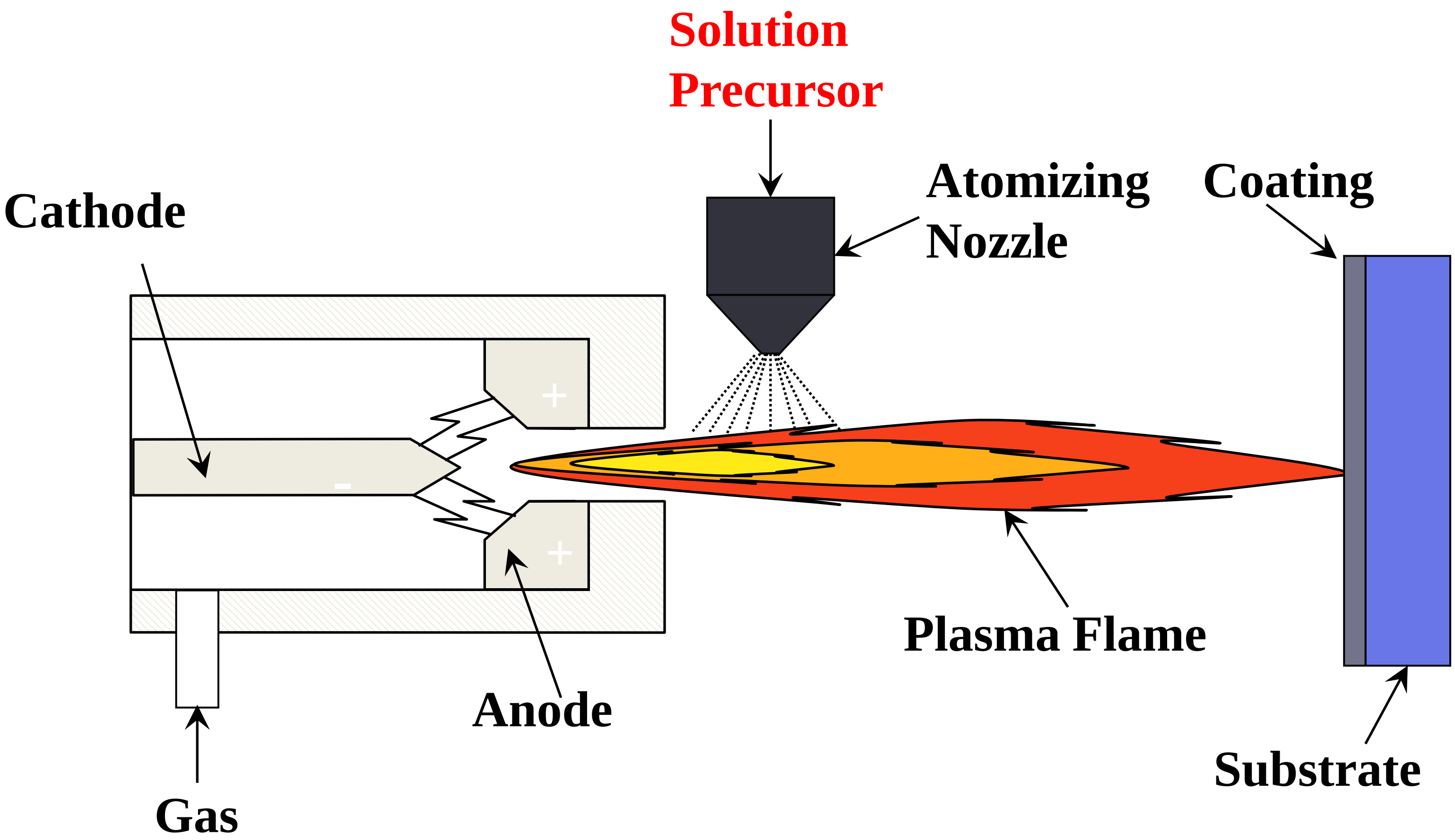
	YEAR 1				YEAR 2				YEAR 3			
TASK	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
1.Manage/Plan/Report												
2. SPPS of Low K TBC												
3. Test Low K TBC												
4. Fabricate Gd-Zr Layer												
5. Fab. Al-Ti Doped TBC												
6.Fab. $CaSo_4$ Additive												
7. CMAS Testing												
8. Moisture Testing												
9. Define Mechanisms												
10 Gradient Cyclic Testing												

Air Plasma Spray (APS)

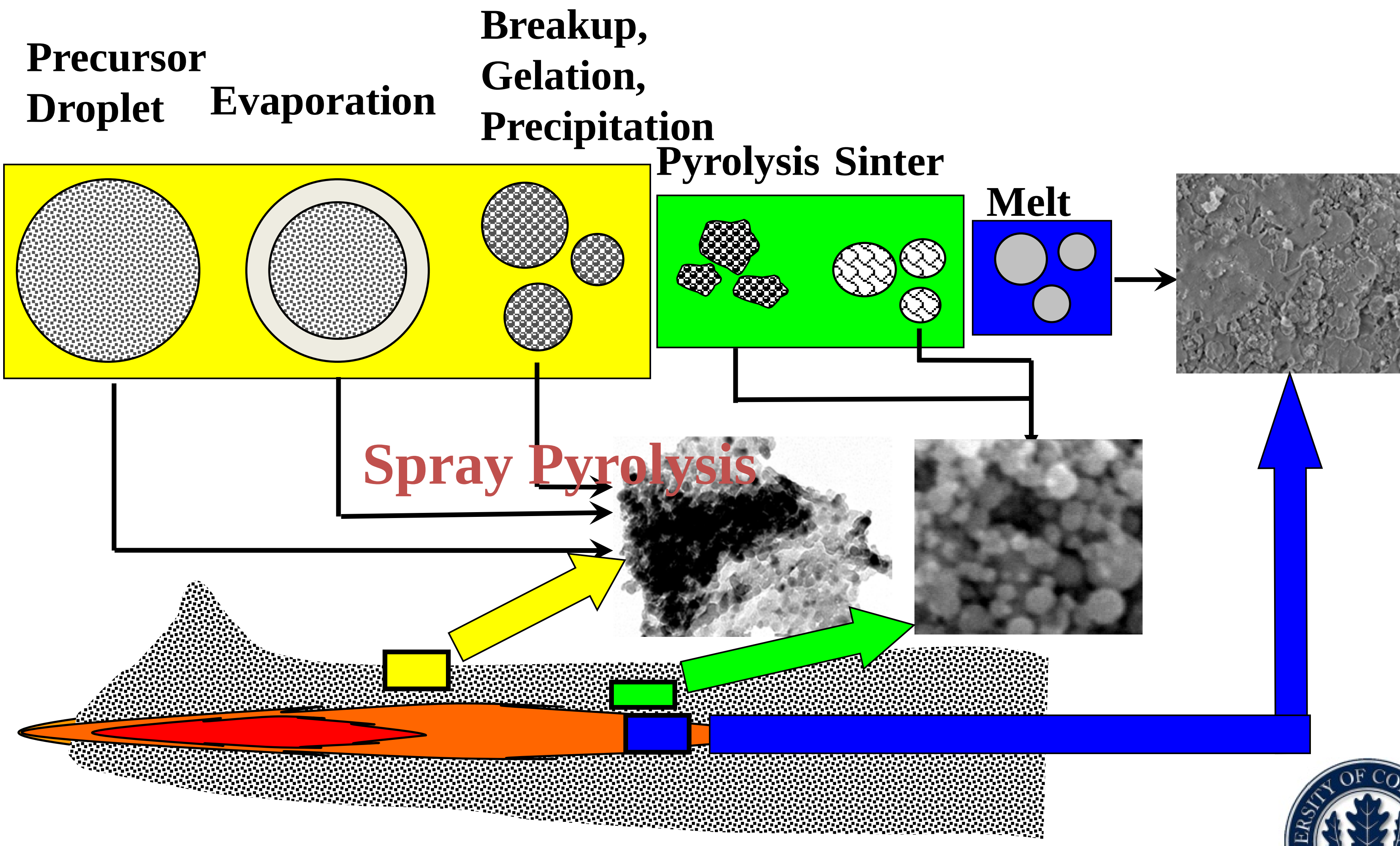


- Particles Melt and Build Splat Structure=> 7YSZ

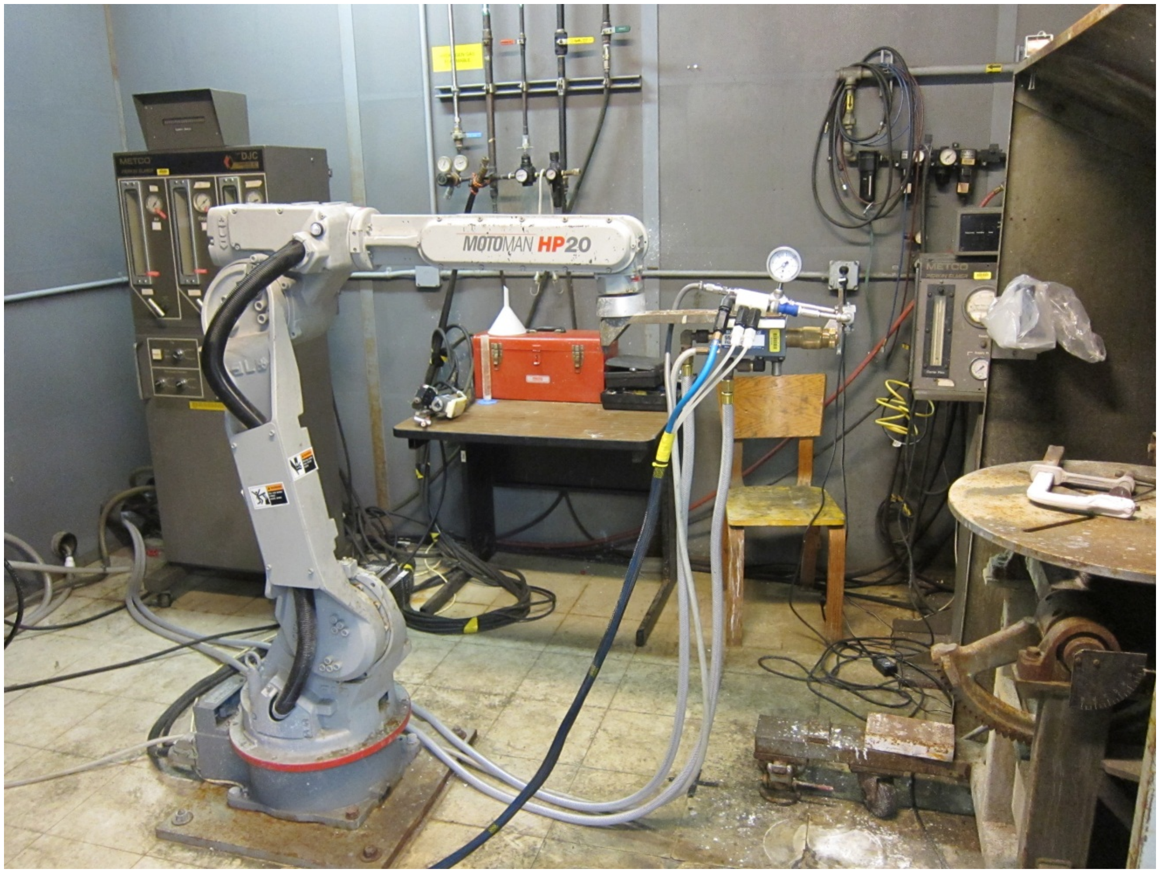
Solution Precursor Plasma Spray Process (SPPS)



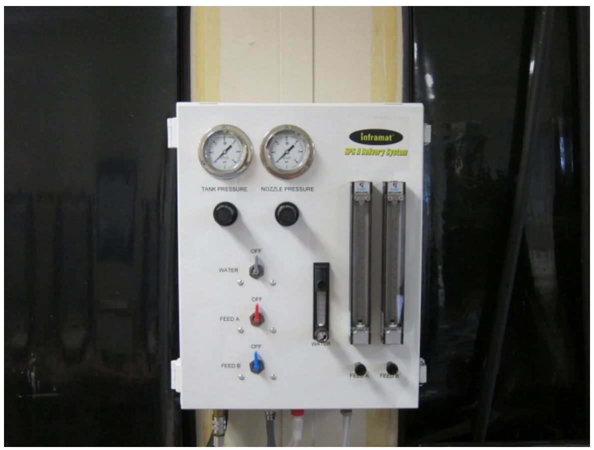
SPPS Deposition: Process Flexibility



UConn Thermal Spray Facility



Liquid Delivery Options



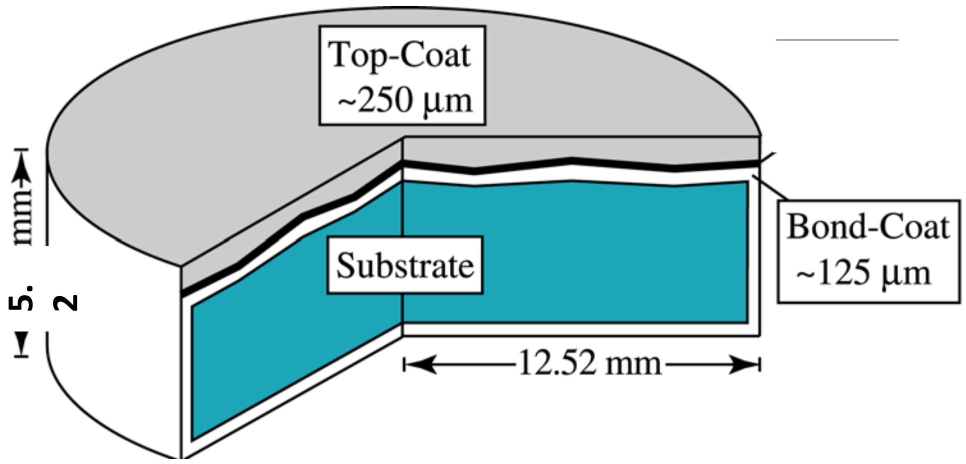
Standard Liquid Delivery System

Unique High Pressure System (33 atm)

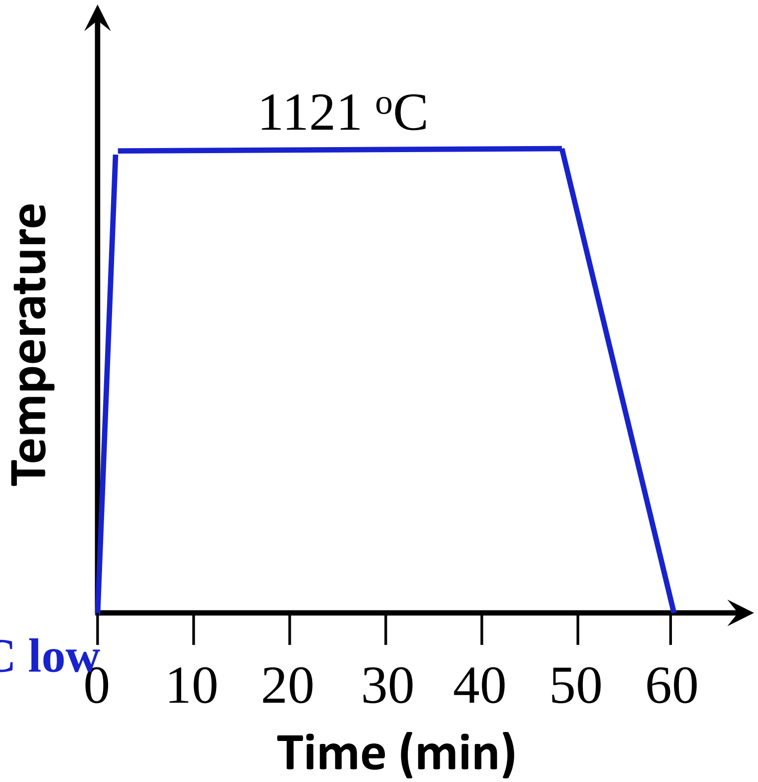
Cyclic Furnace Test Facility

Specimen Shape & Furnace Cycle

- **Disk-Shape Samples**



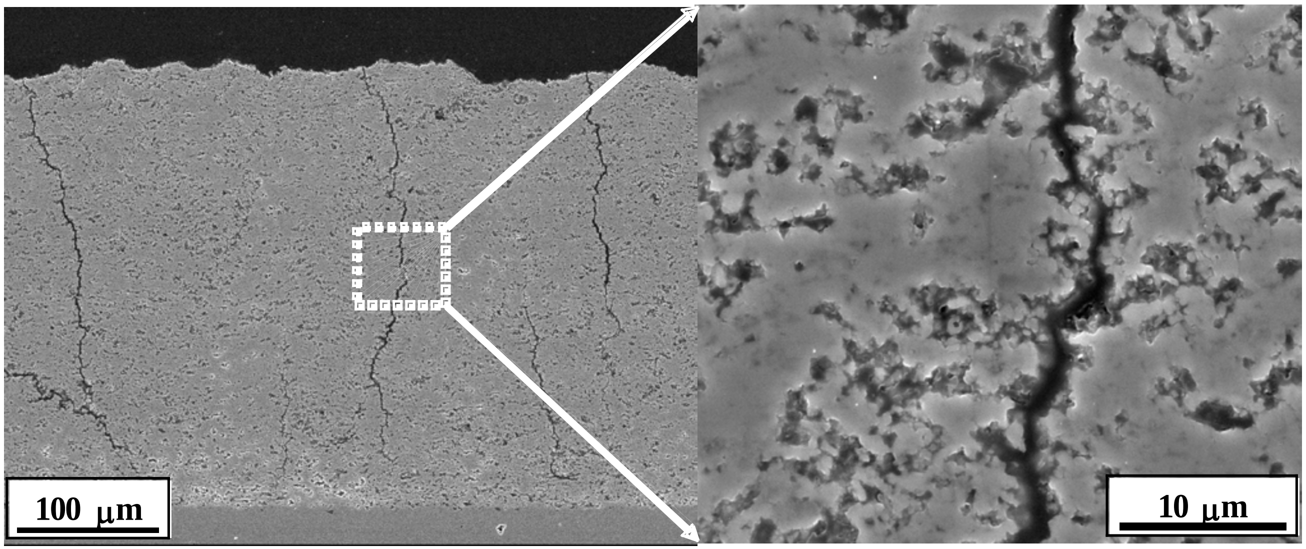
- **Thermal Cycling Life Test**



- **Put the TC on the sample, furnace TC is 20 °C low**
- **Rotate Sample to average hot spots**

SPPS TBCs Have Unique Features

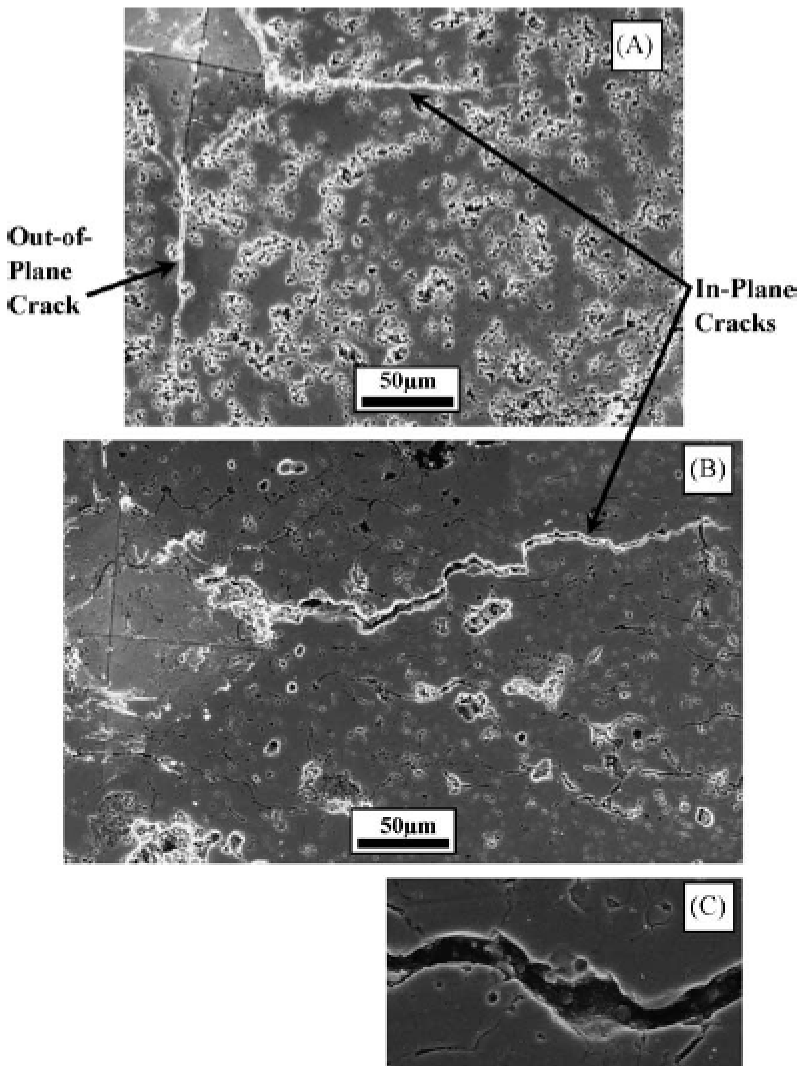
Microstructure Of SPPS TBCs

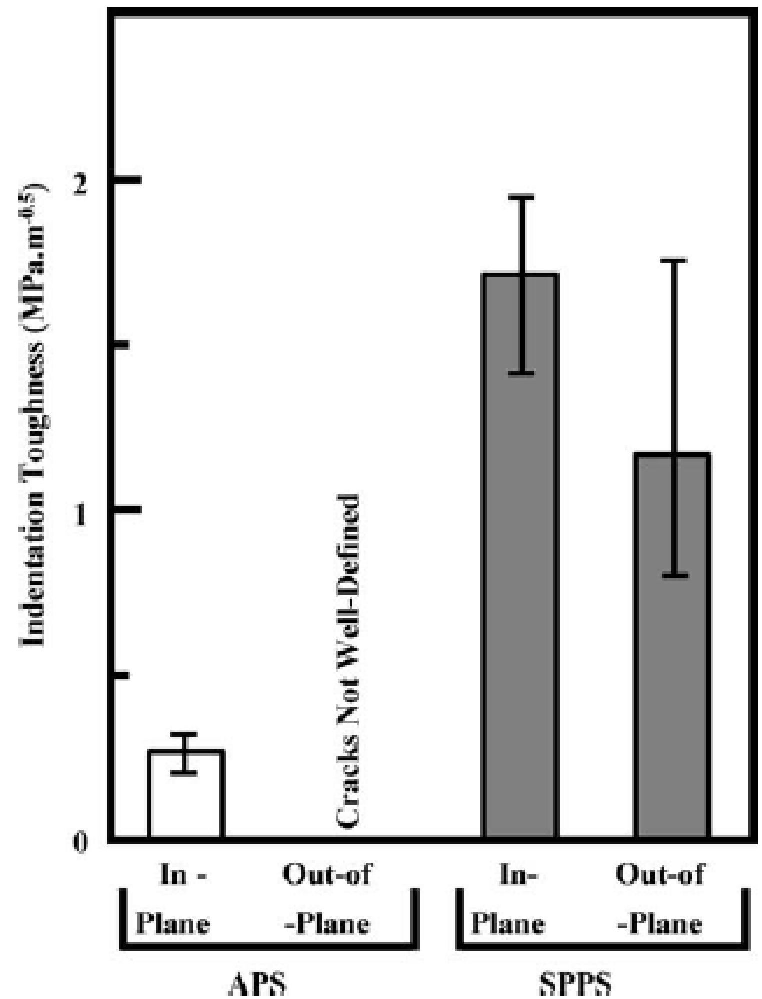


Unique Features

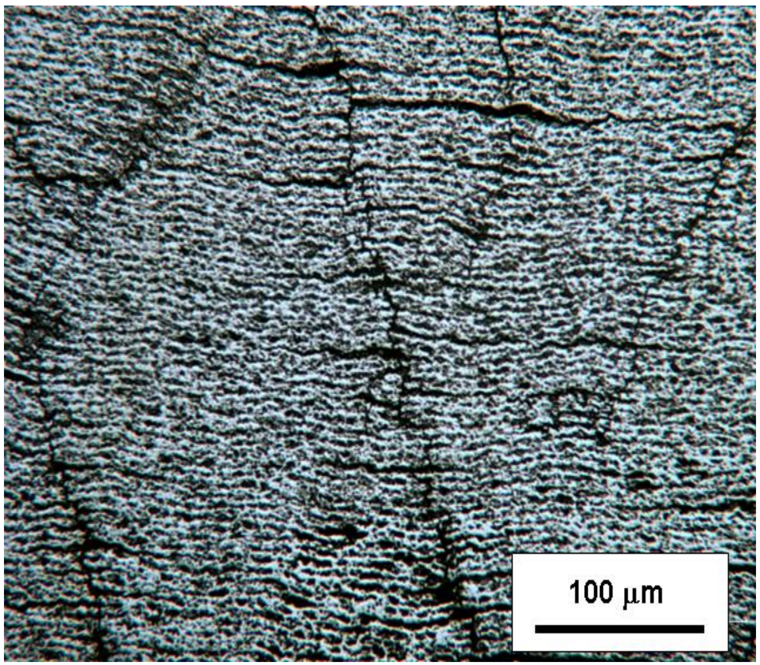
- **3D Nano & Micrometer Pororsity**
- **Through-Thickness Cracks**
- **Ultra-Fine Splats**

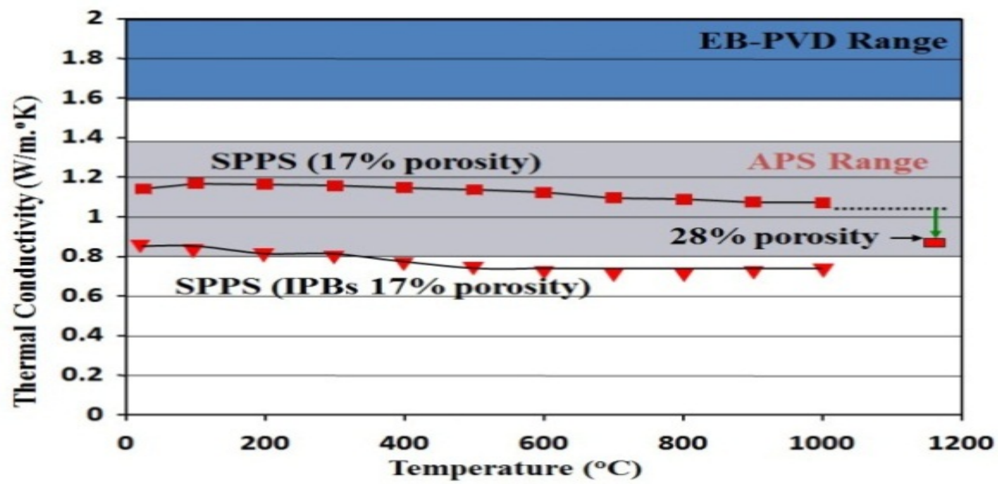
SPPS Coating have 7X higher In Plane Toughness





Structured Planar Porosity (IPBs) Leads to Lower Thermal Conductivity





Advantages of Solution Precursor Plasma Spray

- Vertical stress relieving cracks
- Higher Fracture Toughness
- Rapid Composition Exploration (100X)
- Structured Porosity (IPBs) leading to low K coatings

Work Done under HiFunda/UConn STTR DOE Program

Patcharin Burke Program Manager

Thermal Expansion Mismatch Drive Cyclic Stresses

- TBC Stress=$E_{tbc}(\alpha_{tbc}-\alpha_{metal})(T-T_{stress\ free})/(1-\nu)$
- The lower the coefficient of expansion α_{tbc} higher the stress
- Many Ceramics ruled out because of low CTE that otherwise have desirable properties. Vertical cracks can lift this restriction.
- Example: Yttrium Aluminum Garnet (YAG)

Properties of YSZ and YAG

Material Property	YSZ	YAG
Melting Point (^oC)	2680	1950
Maximum Operating Temperature (^oC)	1200-1300	**1800**
Thermal Conductivity at 1350 ^oC (W/mol-K)	2.0-3.0 (measured)	2.5 (extrapolated)
Thermal Expansion Coefficient (ppm/K)	9.5×10^{-6}	** 7.5×10^{-6}
Density (g/cc)	6.10	**4.55**
Vickers Hardness	1200	1700

HiFunda LLC
Innovations - Ideas - Solutions

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Thermal Cycling Test Results
(1180^{o}C/12 hrs)
--Failure Lives To 50% Spallation--

APS YSZ Baseline**	SPPS YAG TBCs Type I	SPPS YAG TBCs Type II
1. 72 hrs	1. 300 hrs*	1. 300 hrs*
2. 120 hrs	2. 300 hrs*	2. 300 hrs*
	3. 300 hrs*	3. 300 hrs*

*Intact, still running

**Baseline: IN939, NiCoCrAlY Bond Coat, YSZ Top Coat

Prior Test Experience With Variety of Advanced TBCs: 60-200 hrs

Returning to SPPS YSZ

Initial SPPS Trials/Thermal Conductivity Measurements

- **Taguchi DOE Spray Trials to optimize IPBs for minimum thermal conductivity (0.5 watt/m-^{o}K).**
- **Access Outcome Using Image Based Finite Element (OOF) Calculated Thermal Conductivity.**
- **Image Based Thermal Conductivity Determination (OOF) was not Reliable**

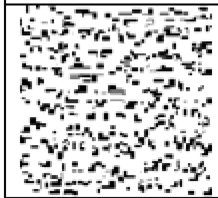
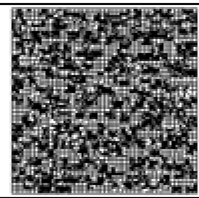
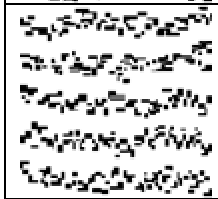
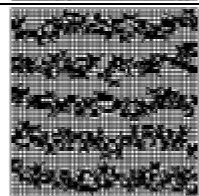
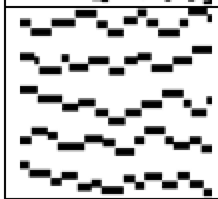
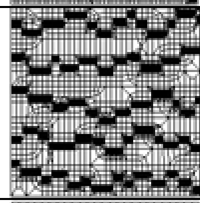
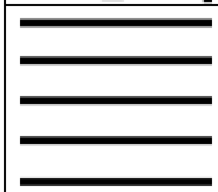
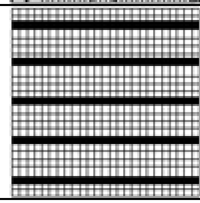
Modified Plan

- **Use a Lesser Number of Laser Flash Measured Thermal Conductivity and Heuristically Understanding to Reach the Thermal Conductivity Goal of cutting in half the conductivity to 0.5 watt/meter- ^{o}K**

Development of Heuristics Needed to Make Optimal IPBs

By Modeling and Testing

Artificial Microstructures for Insight Analyzed by OOF

Image	Porosity	Mesh	Homogeneity in Mesh	Ave. Heat Flux [y]	Ave. Temp Gradient [y]	Thermal Conductivity
	0.198		0.963	0.05653	0.04	1.413
	0.198		0.974	0.04689	0.04	1.172
	0.20		0.984	0.04016	0.04	1.004
	0.20		1.0	0.004126	0.04	0.103

1. **Circuitous Path with as narrow as possible bridge points**

Over 100 Different Spray Conducted

- **25 have had thermal conductivity measured**
- **10 have been measured in LFA prior to selecting ideal substrate**
- **15 have been measured with ideal substrate thickness.**

Base Line Systems

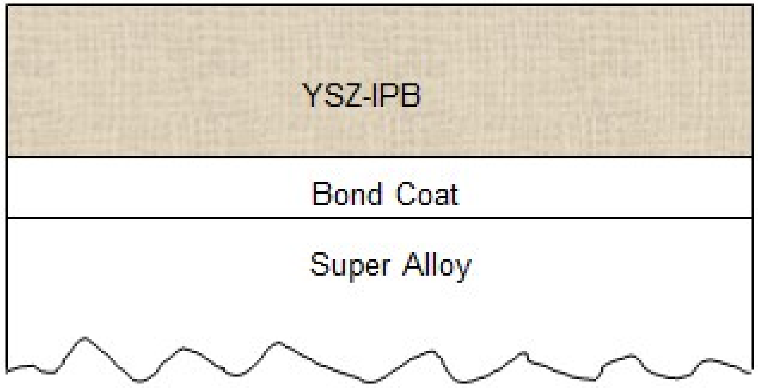
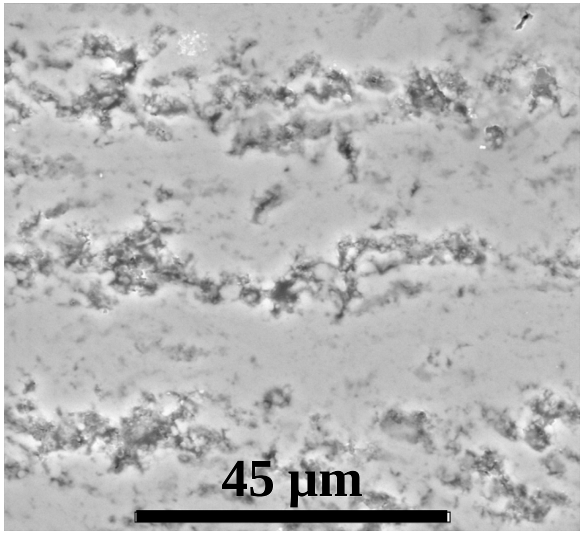


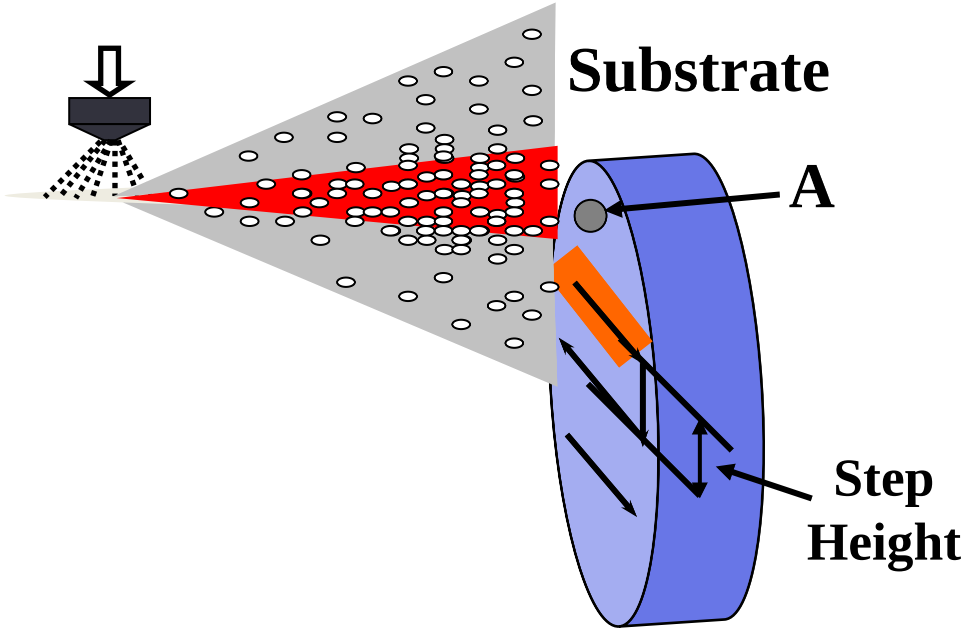
Figure 6. TBC #1, a Low K SPPS YSZ TBC using IPBs and porosity

Effects of Processing Variables On IPB Formation

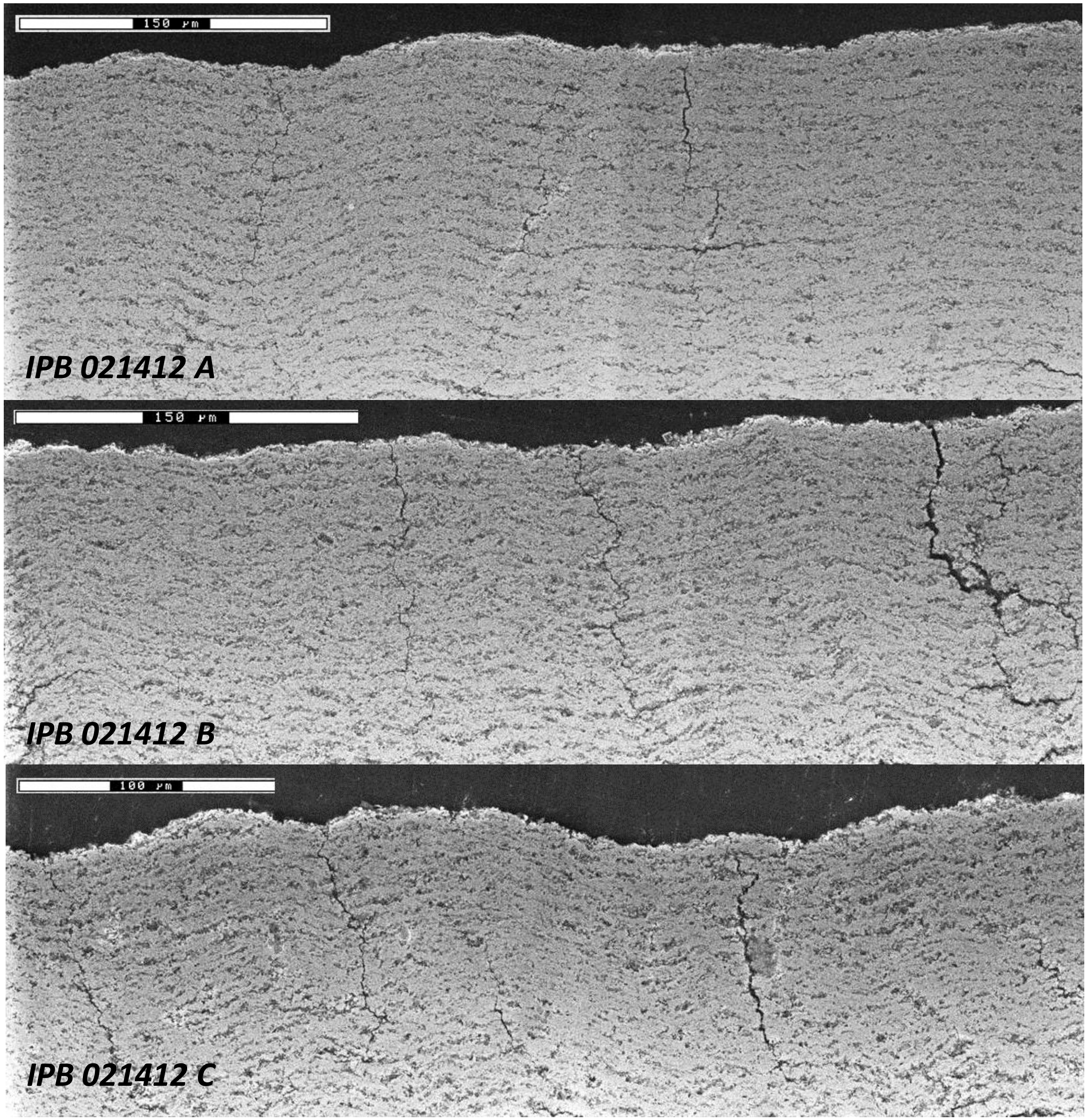
- Spray Distance
- Precursor Injection Method
- Precursor Feed Rate
- Raster Scan Step Height

Formation of Inter-Pass Boundaries





Effect of Spray Distance on IPBs



Atomizing Bete with 2 mm index.
1 min cooling/15 passes. Stainless steel substrate.

4.13 cm SD

IPB 021412 A

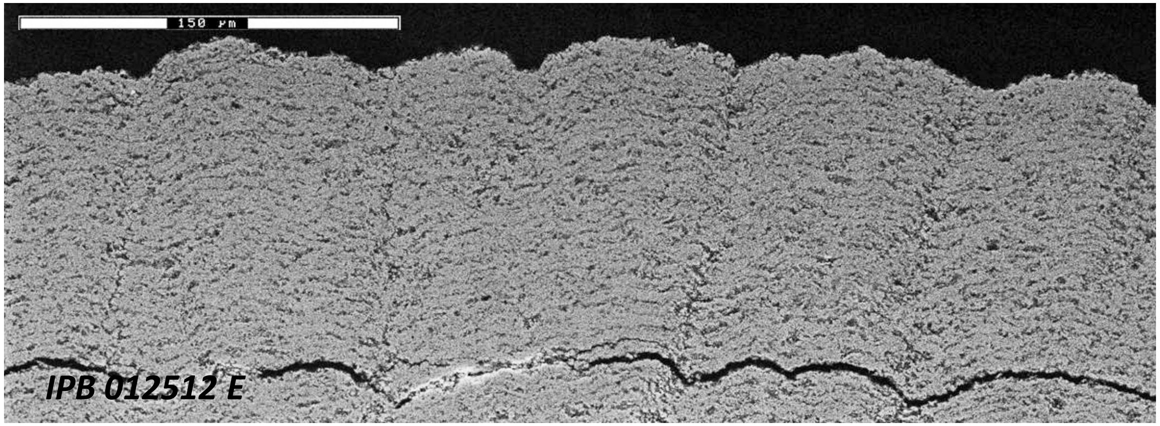
4.44 cm SD

IPB 021412 B

4.76 cm SD

IPB 021412 C

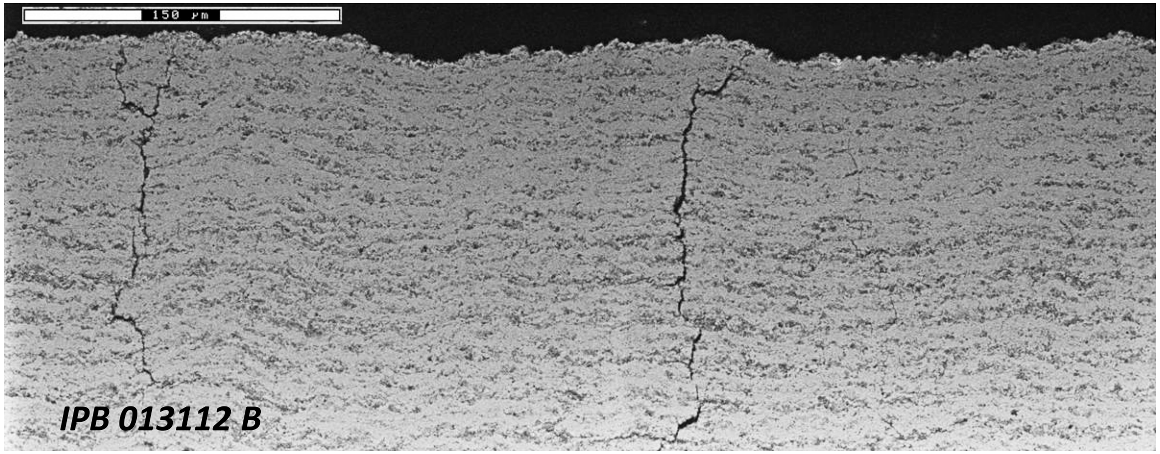
Precursor Injection Method & IPBs



Standard 7YSZ precursor solution. 2 mm index. 4.44 cm SD 40 s cooling/5 passes. Stainless steel substrate.

Bete Atomizing

IPB 012512 E



Stream Injection

IPB 013112 B

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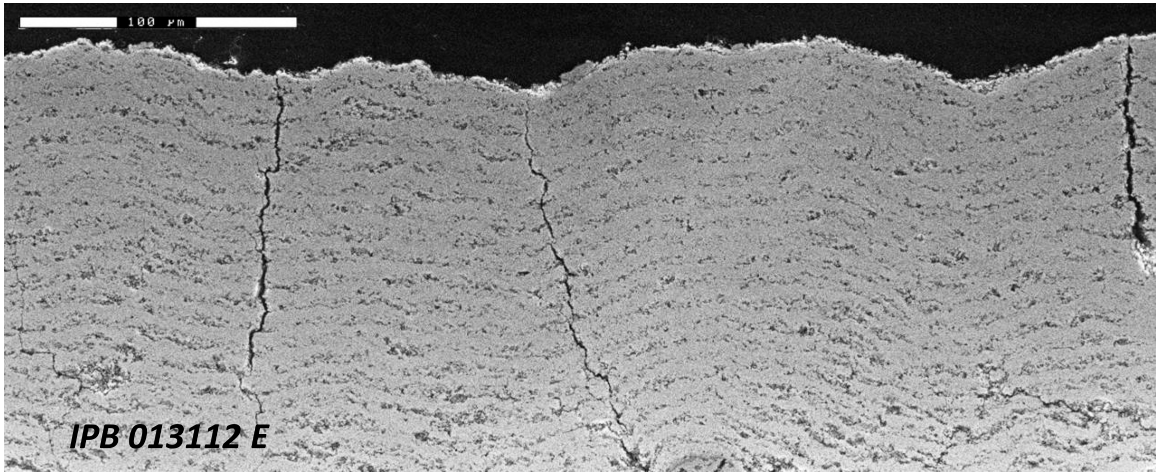
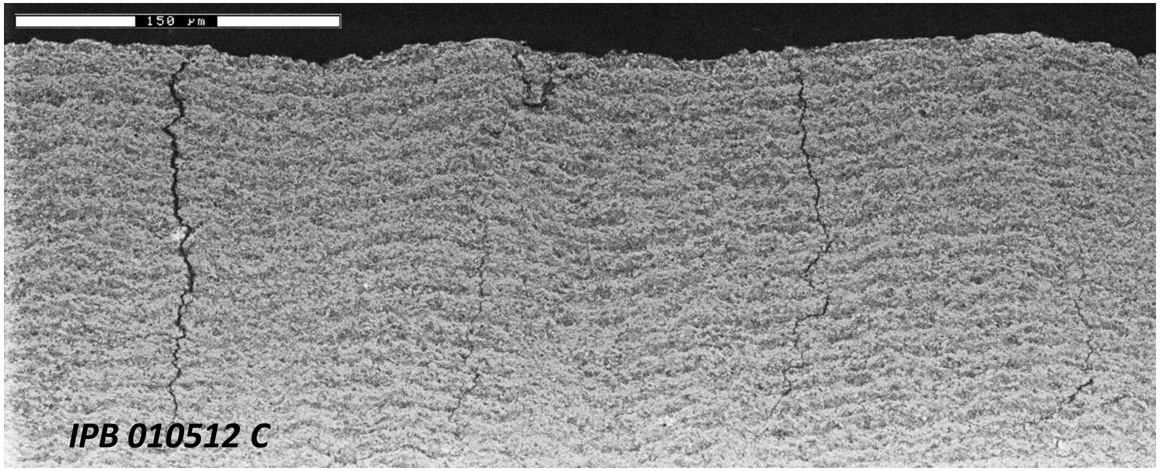
Precursor Feed Rate & IPBs



Standard 7YSZ Precursor Solution. Stream Injection. 4.44 cm SD. Stainless steel substrate.

#6: 38 mL/min

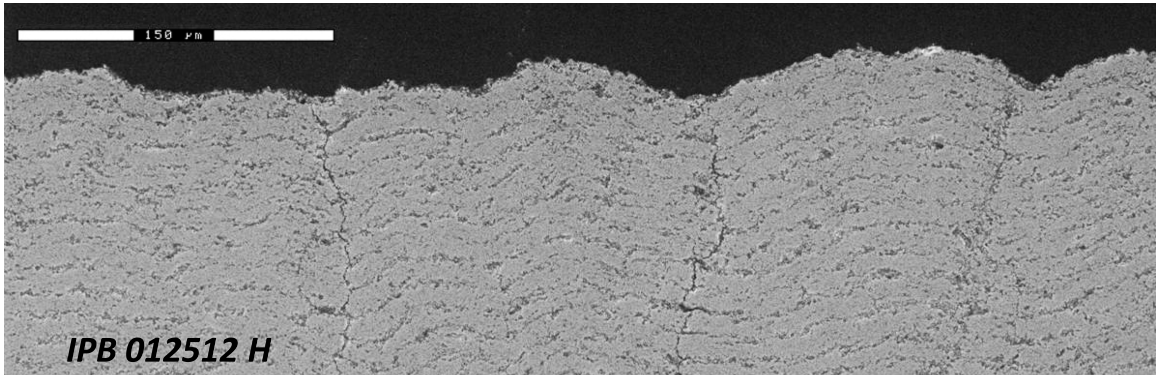
IPB 013112 E

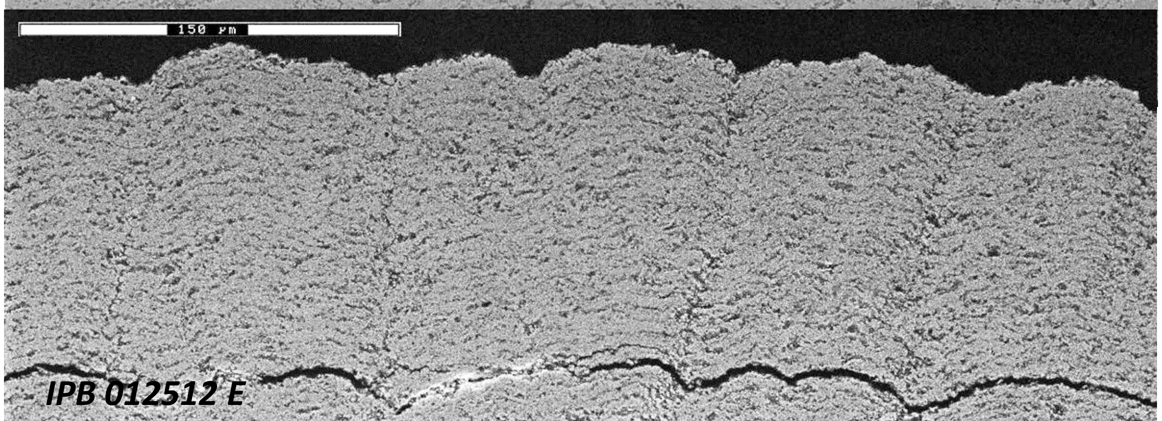


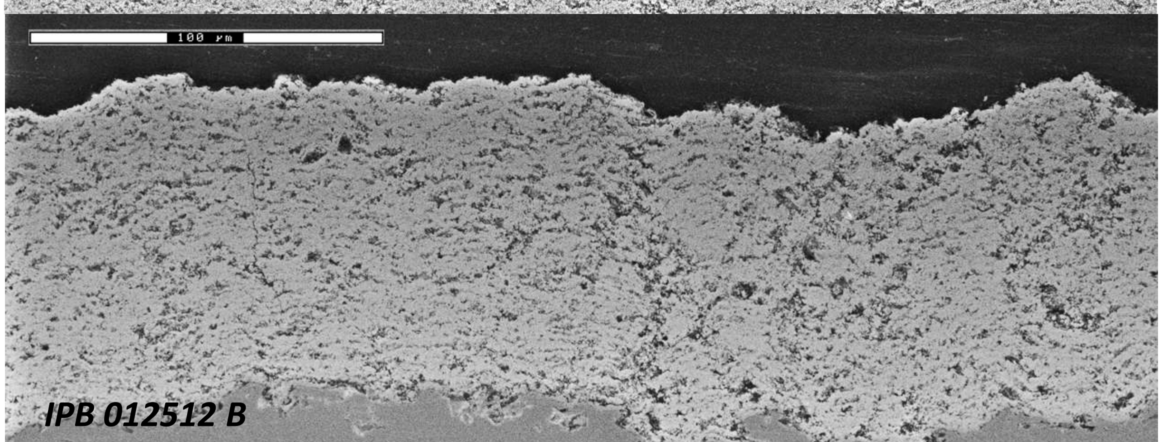
#8: 106 mL/min

IPB 010512 C

Raster Scan Height & IPBs-I







Standard 7YSZ Precursor Solution. **Bete Atomzing**. 4.44 cm SD. 40 s cooling/5 passes. Stainless steel substrate.

1 mm index

IPB 012512 H

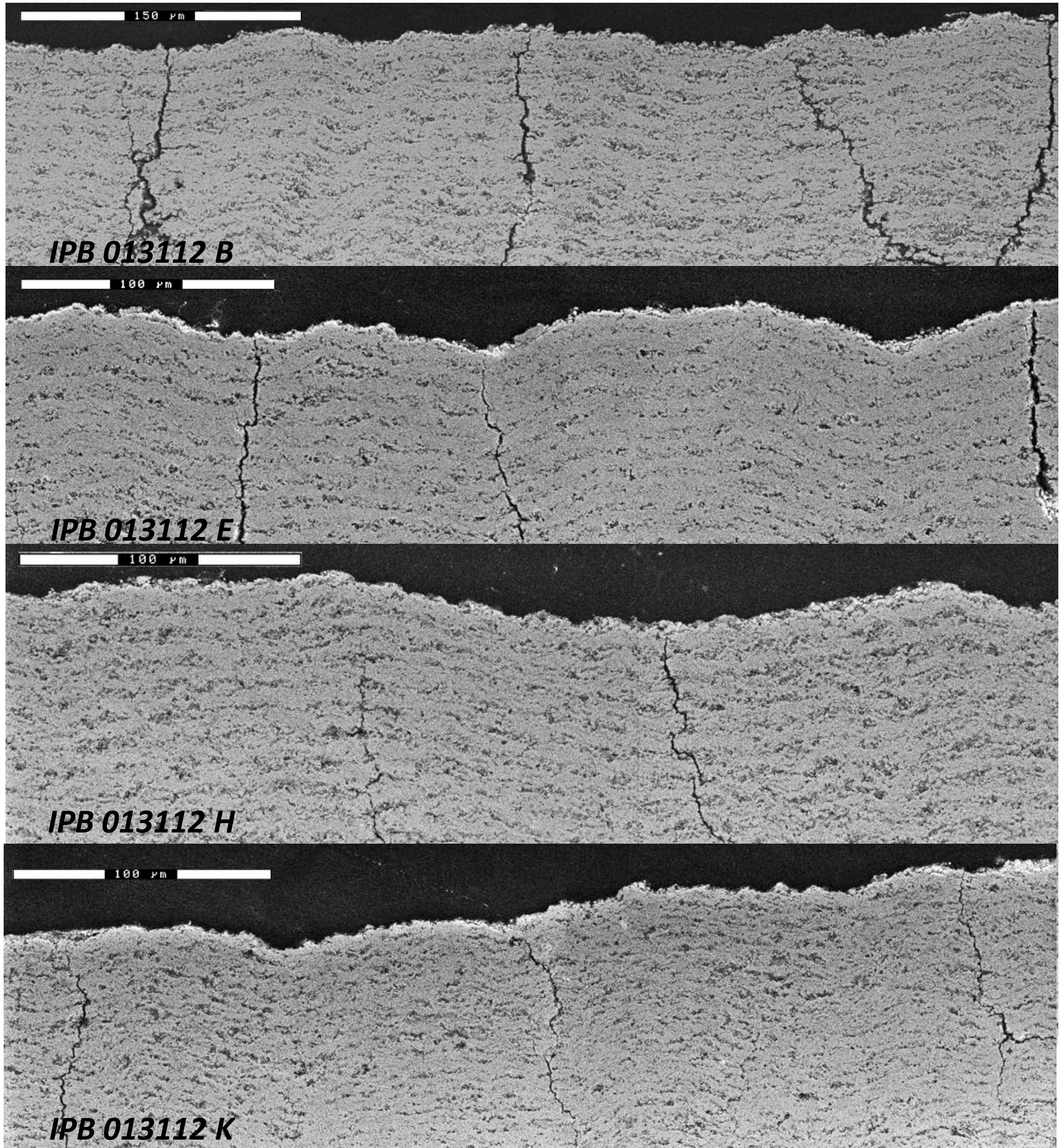
2 mm index

IPB 012512 E

3 mm index

IPB 012512 B

Effect of Raster Scan On IPBs-II



Standard 7YSZ Precursor Solution. **Stream Injection**. 4.44 cm SD. 40 s cooling/5 passes. Stainless steel substrate.

2 mm index

IPB 013112 B

3 mm index

IPB 013112 E

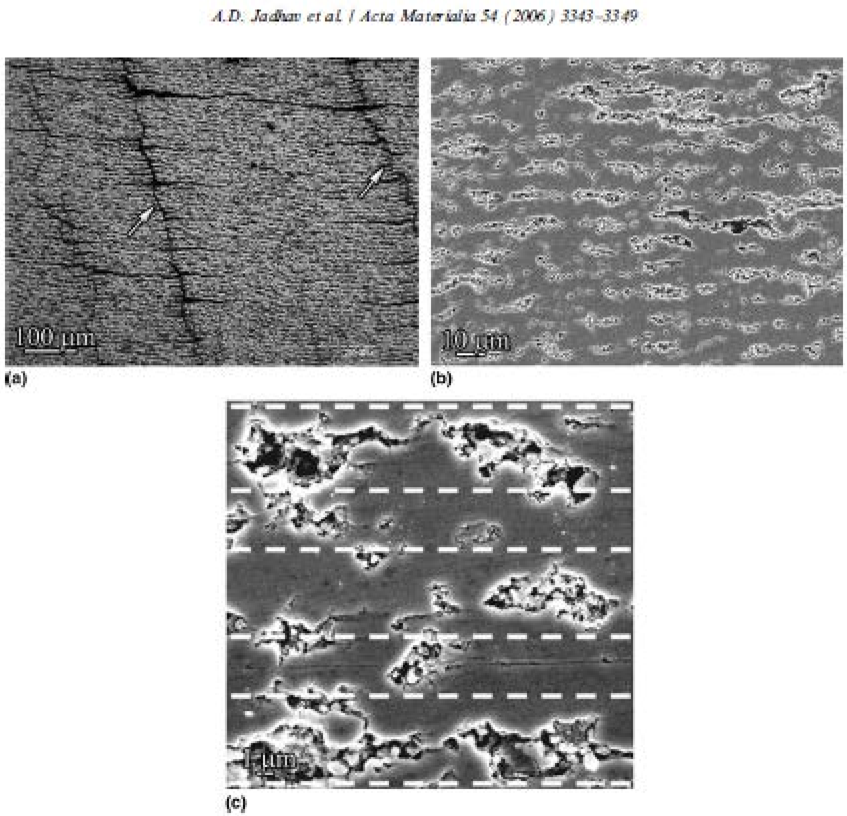
4 mm index

IPB 013112 H

6 mm index

IPB 013112 K

Calculating Thermal Conductivity



Finite Element Mesh Generated from Micrograph Using OOF Program

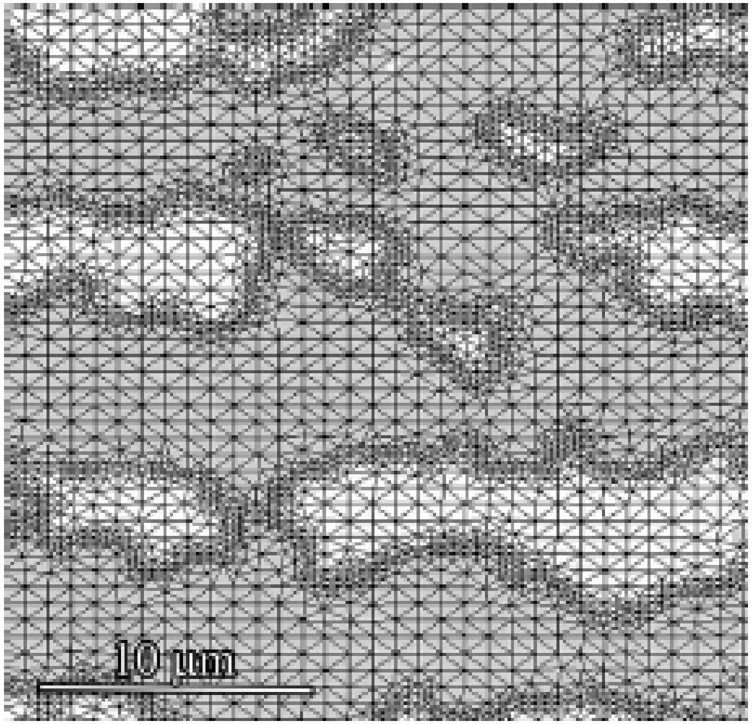


Image Based (OOF) Conductivity NOT Reliable

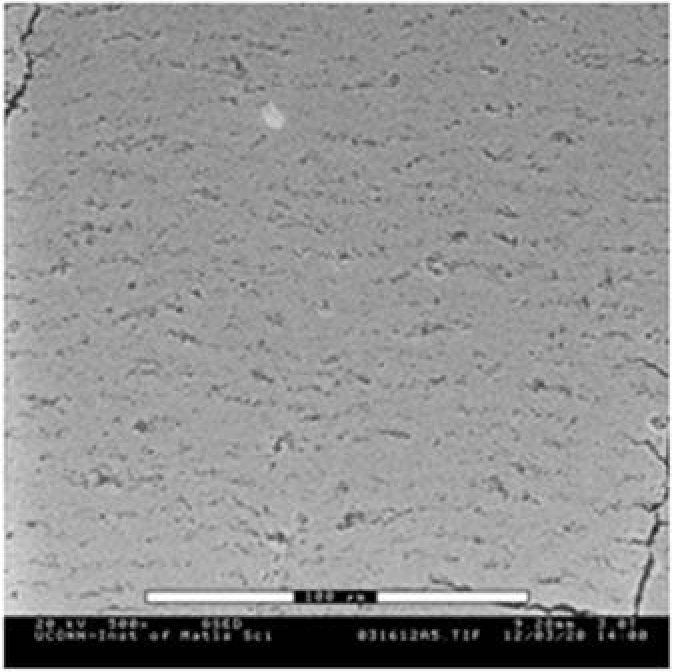
Sample	LFA		OOF		Note
	Temp	Thermal Conductivity	Temp	Thermal Conductivity	
Stainless steel substrate	100 C	16.5			Single-layer model, 3mm substrate, 6mm piece
IPB#042412-C	150 C	0.72	150 C	0.919	Two-layer model, 3mm substrate, 6mm piece
IPB#042412-D	150 C	0.99	150 C	1.13	Two-layer model, 3mm substrate, 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.

1. **Porosity not Easily Distinguished from Other Regions**
2. **Is only 2-D**

A, 1.625" SD

500X



Laser Flash Apparatus

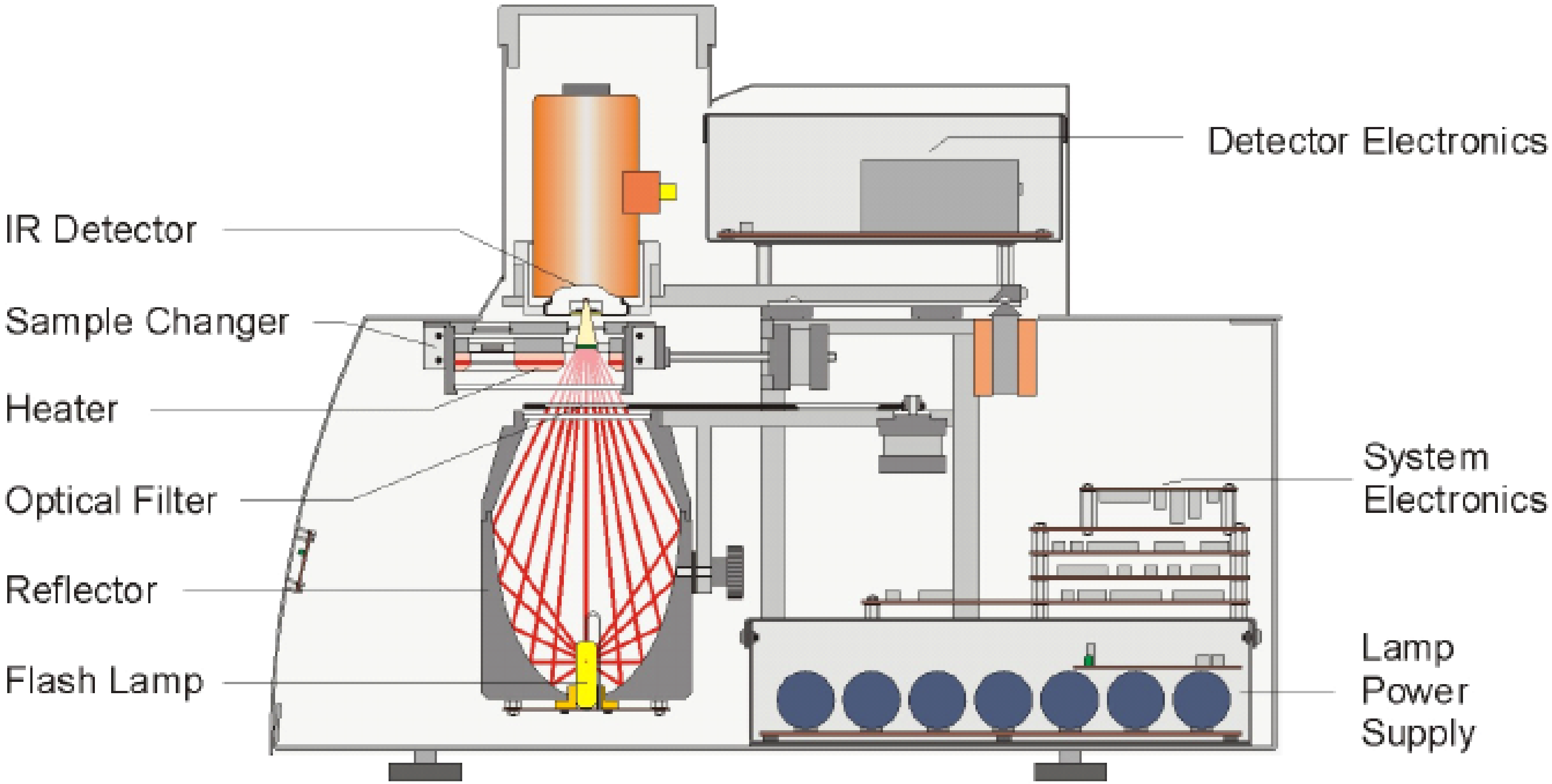


Figure 2: Schematic of the NETZSCH LFA 447

Laser Flash Schematic

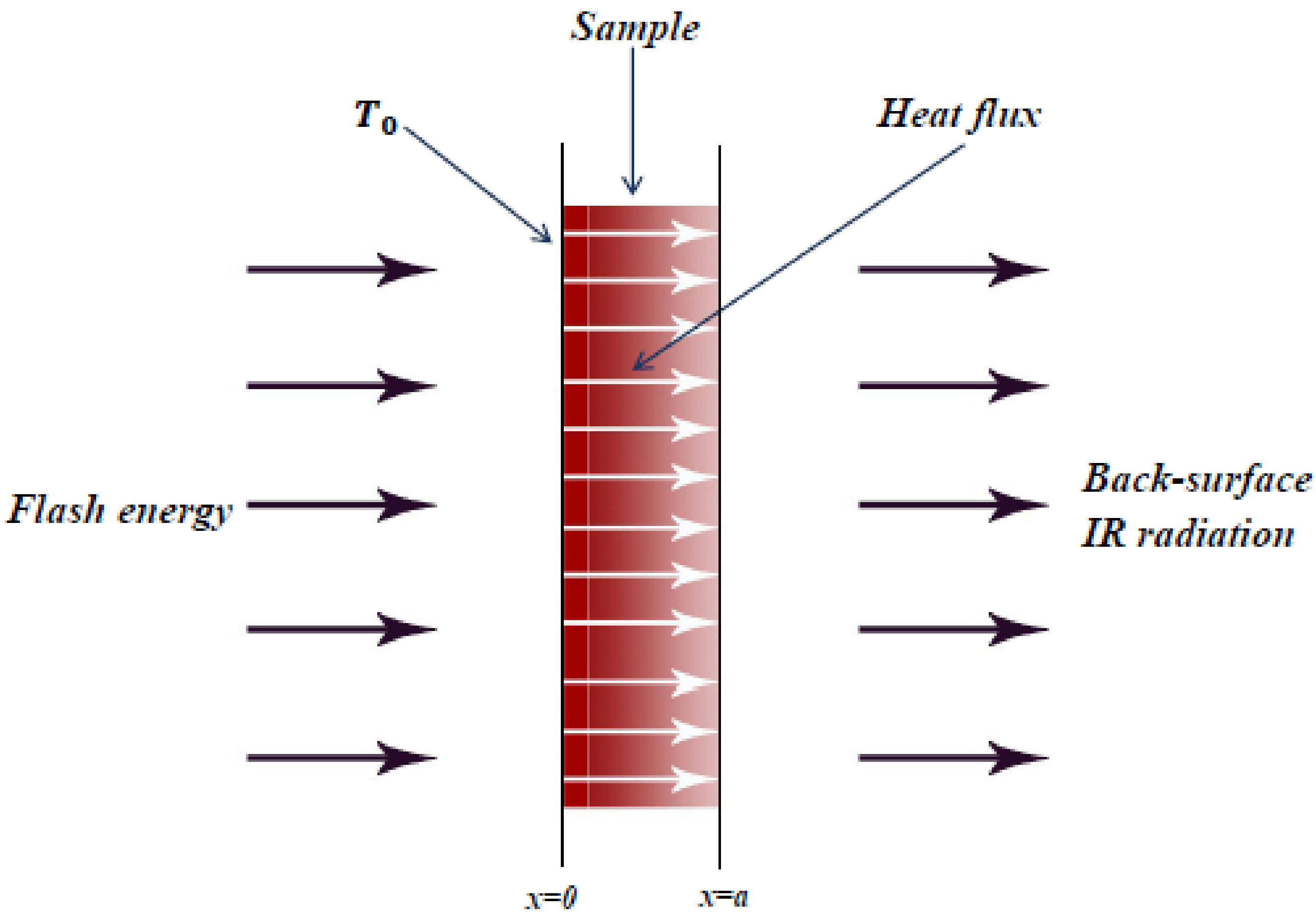


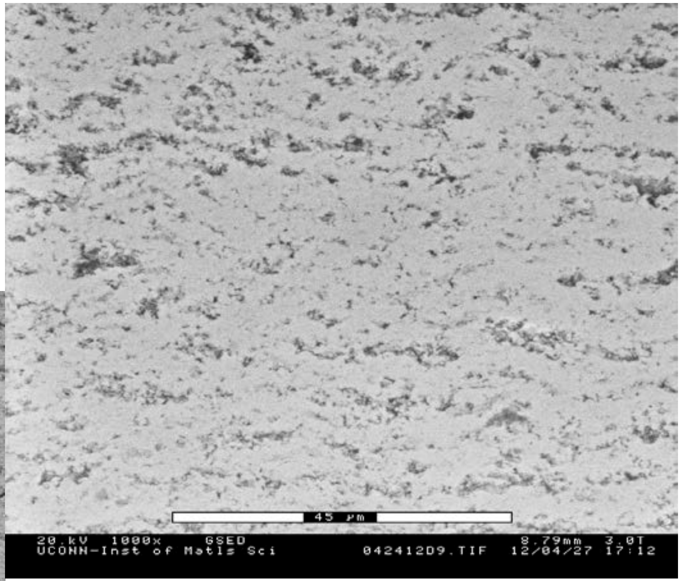
Figure: Diagram of the flash method for measuring thermal diffusivity.

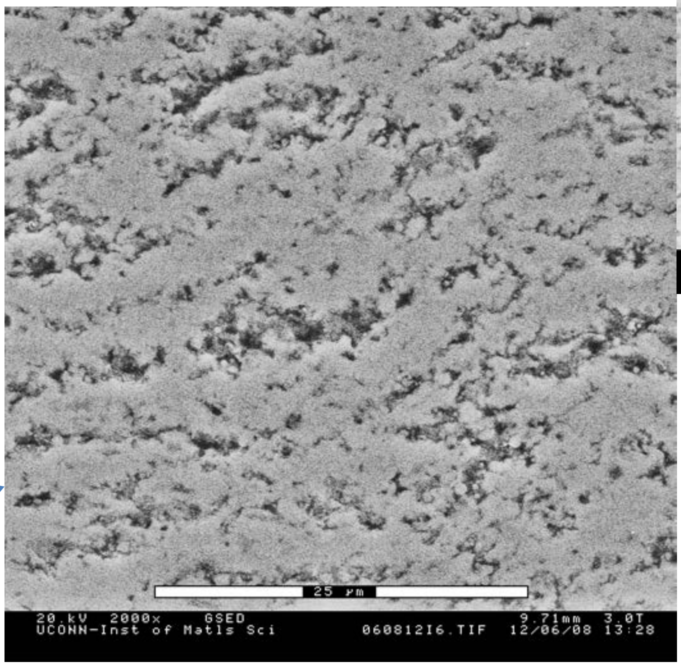
Creating Low Thermal Conductivity

By Structuring the Porosity via Inter-pass boundaries (IPBs)

Thermal Conductivity of SPPS YSZ TBCs With IPBs
Laser Flash- Twelve Specimens

1.47
1.31
1.12
1.09
1.08
0.97
0.90
0.83
0.82
0.67
0.66
0.65
0.53





Significant Program Achievement

- Reduced YSZ TBC Thermal Conductivity
  by >50% to 0.53 watt/m-oK
- Further Reduction Likely With IPB Optimization
- Low Thermal Conductivity Now Possible Without Scarce, Expensive Rare Earth Oxides

Contaminants Affect TBC Failure

Calcium, Magnesium, Aluminum
Silicon= CMAS

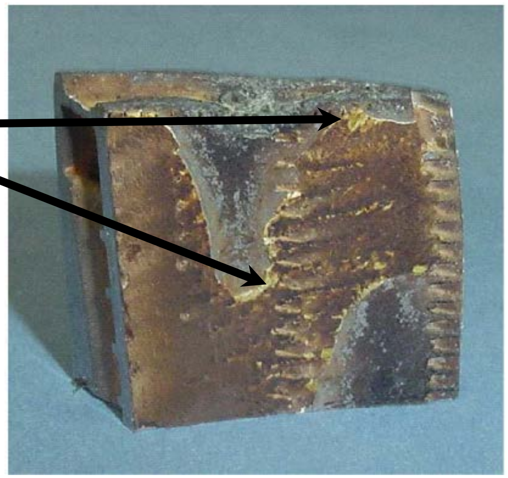
A 387 MW (H Machine) Engine processes about $2X10^{10}$ Kg[1] of Air/ year

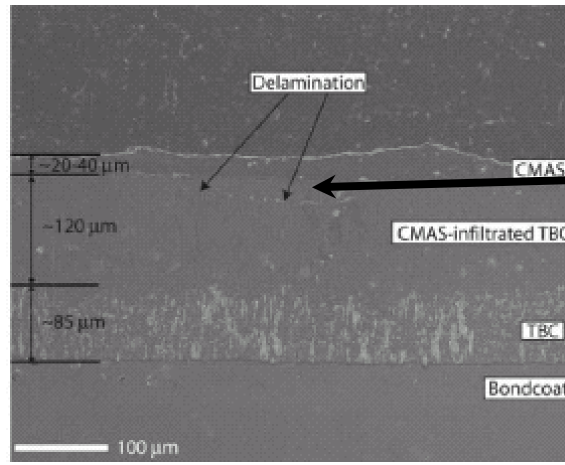
- Jeffrey Bons gets fractional sticking of solids roughly 1%-10%
- 1 PPM of solids would be 20,000 Kg if it sticks even at 10%=2000 Kg it is very bad at 1% bad.
- To be a small problem you need about 1 PPB (20Kg) clean up. **CMAS will be a Problem.**
- [1]Chiesa, P. et al, Using Hydrogen as a Gas Turbine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

CMAS Infiltration of 7YSZ Thermal Barrier Coating

Field Observation of CMAS Attack

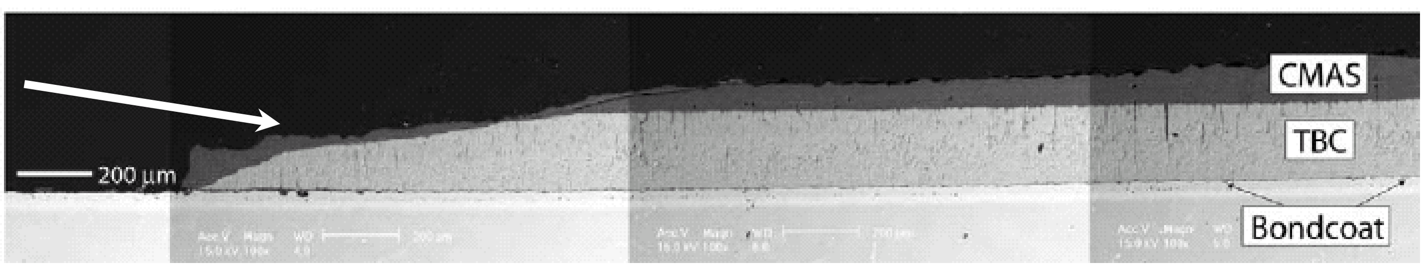
CMAS Deposits





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

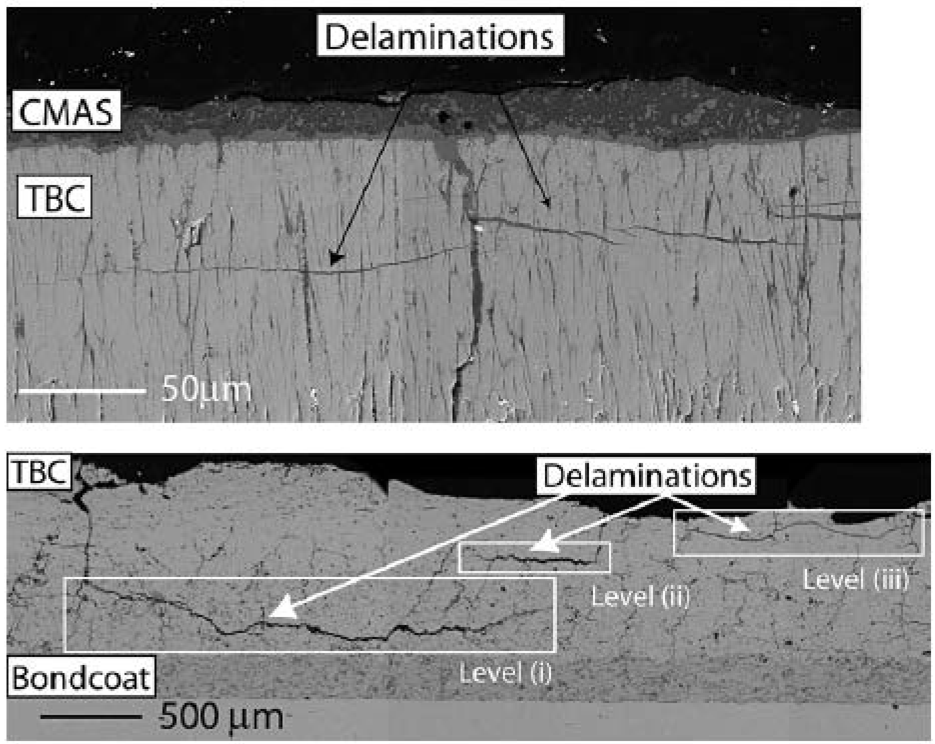


Fig. 1. Examples of delaminations in thermal barrier coatings obtained from components removed from engines subjected to CMAS penetration: (a) Sub-surface mode I delaminations in an airfoil with a TBC made by electron beam physical vapor deposition; the delaminations are within the penetrated zone [9]. (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

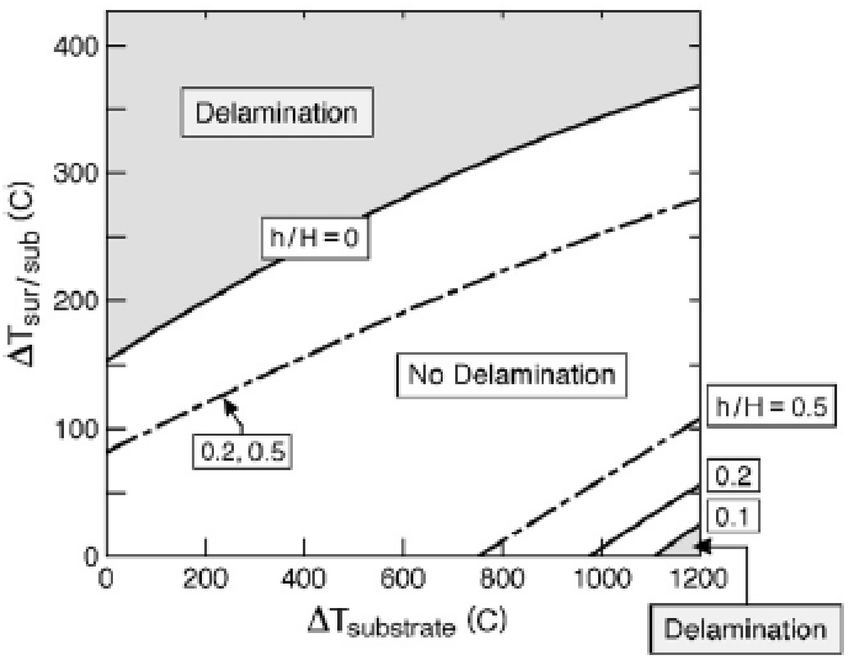


Fig. 10. A map for deep delamination in an APS–TBC on a superalloy substrate with CMAS infiltration to depth, h/H. The mixed mode toughness parameter is, $\lambda = 0.25$.

2. Many types of chemical and Phase Effects for example Y loss and destabilization of t phase Zr 02 to Monoclinic with a destructive volume change

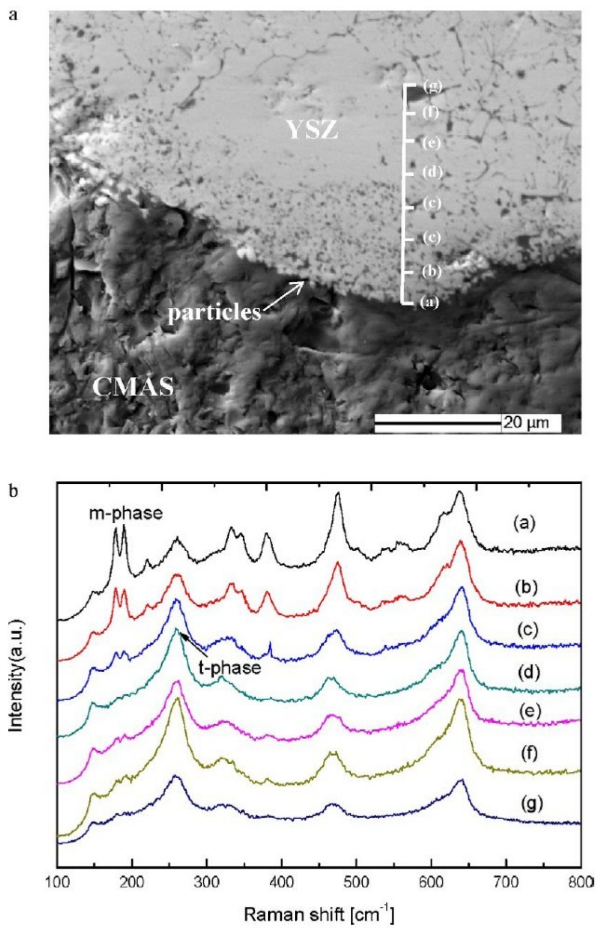


Fig. 4. (a) Micrograph of the interaction zone of CMAS deposit and YSZ coating after 4 h heat-treatment at 1250 °C, and (b) Raman spectra obtained from the positions marked in (a).

CMAS Damage Mitigation and Increased Temperature Capability to be Implemented

Three Approaches

1. Add Gd-Zr to baseline system for higher temperature phase stability and CMAS

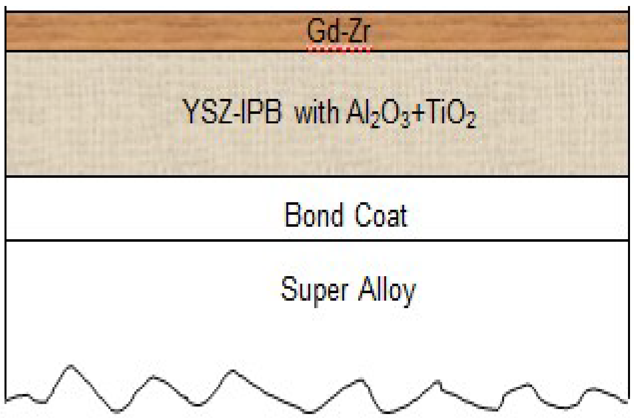
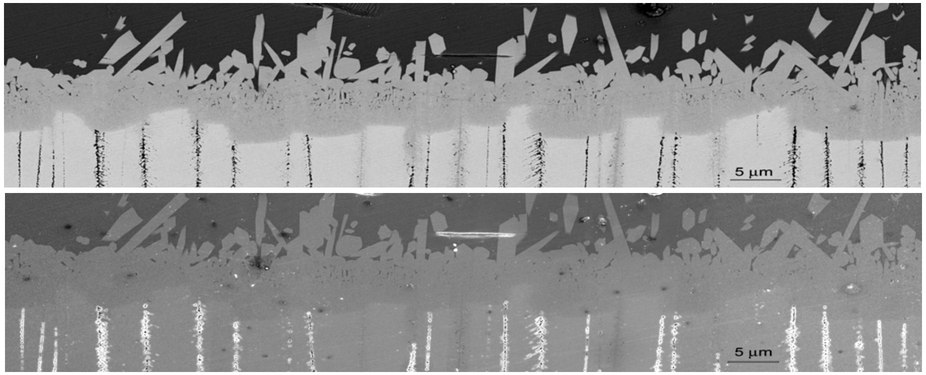


Figure 7. TBC system #2 with low conductivity solution plasma sprayed YSZ with IPBS and CMAS resistant high temperature tolerant Gc-Zr protective surface layer (PSL).

Why $Gd_2\ Zr_2O_7$?

- **Higher Temperature Phase Stability limit YSZ 1150 ^{o}C vs. 1550 ^{o}C For GdZr
- Half the Conductivity of YSZ
- Better CMAS Resistance

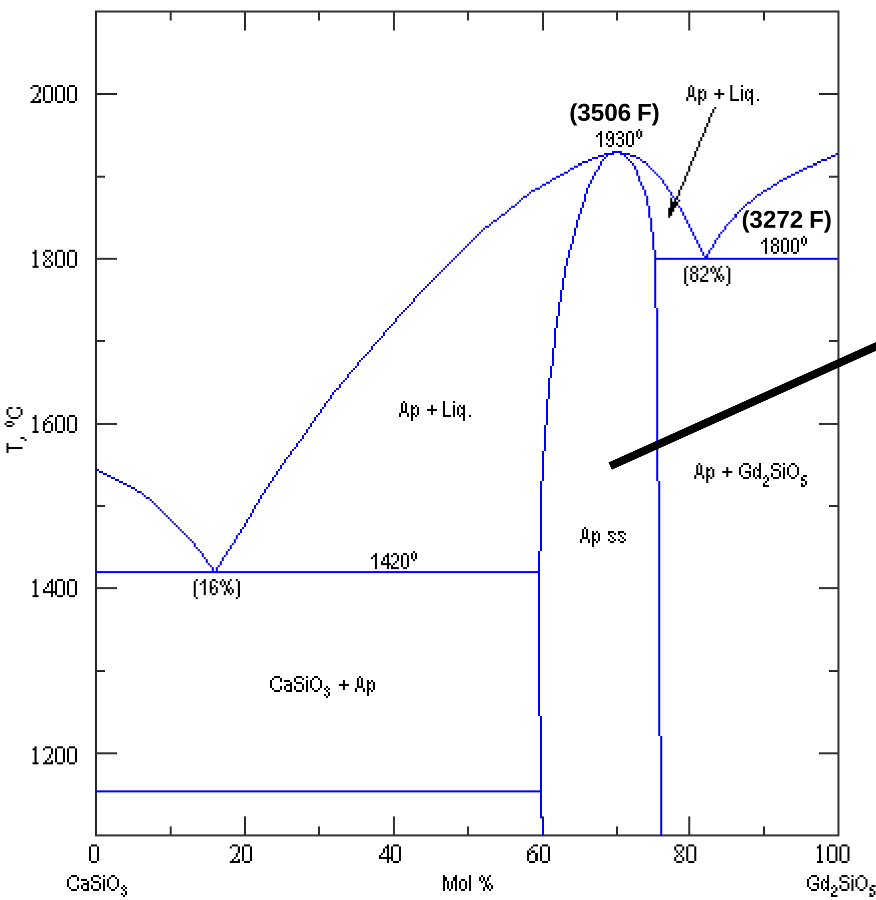
CMAS Resistance of GdZr

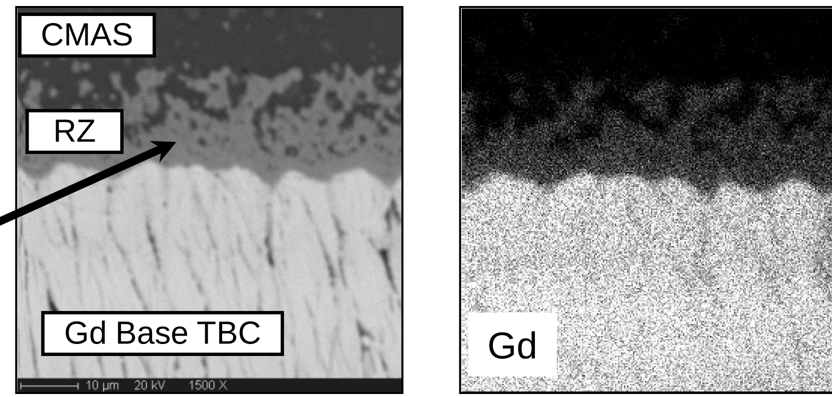


From Carlos Levi, UCSB

Analysis of $Gd_2Zr_2O_7$/CMAS Reaction Product

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

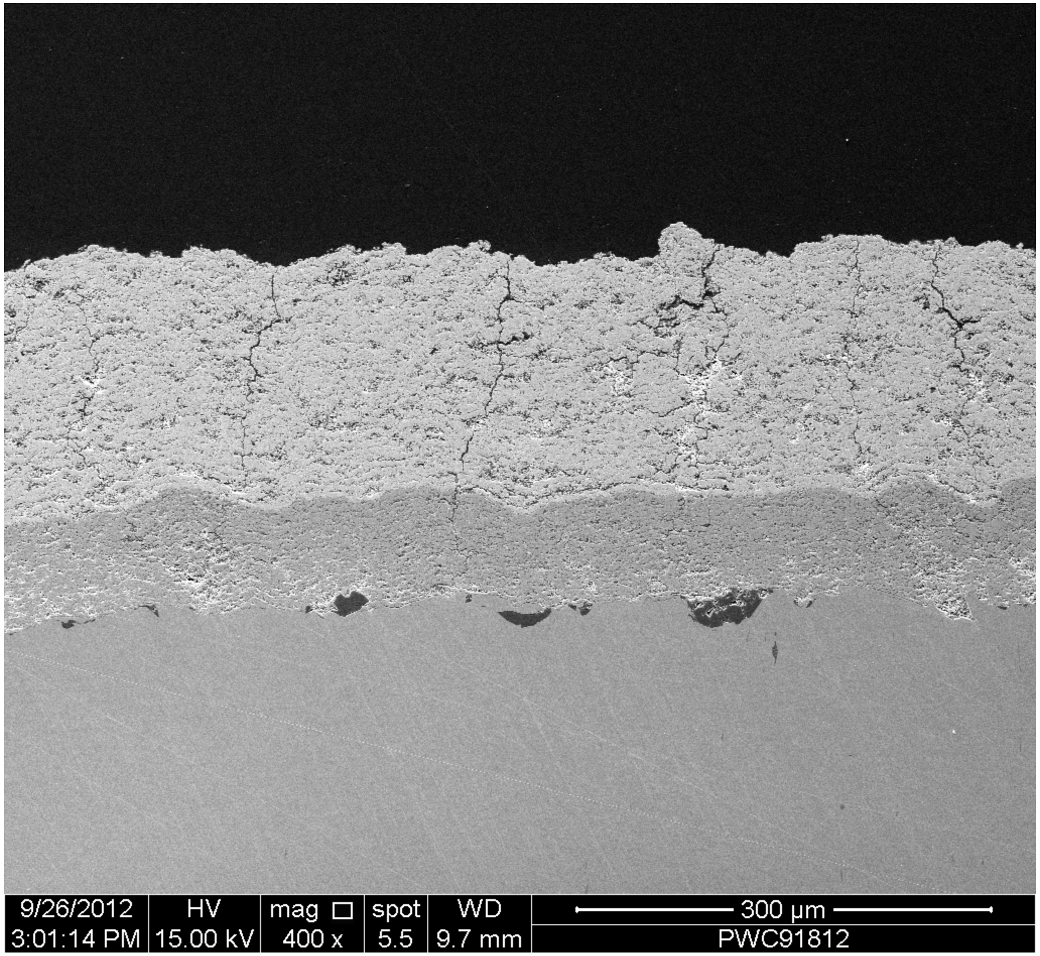




Coating System Needs to be Designed Such That Coating/CMAS Constituents Form Stable Refractory Compound

From Levi, UCSB

Gadolinium Zirconate Sample Spray Conditions Developed at UConn



Add Metastable Al2O3 to block CMAS in the YSZ layer

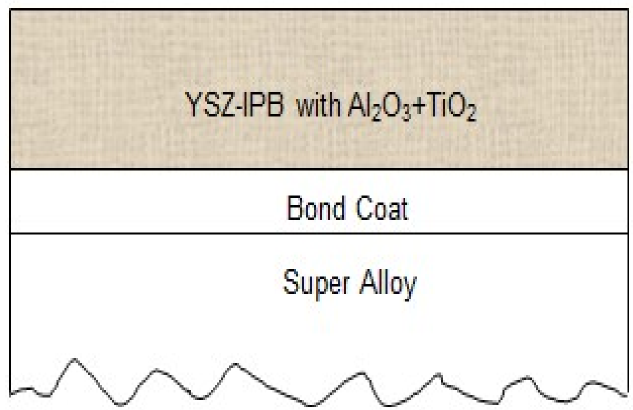
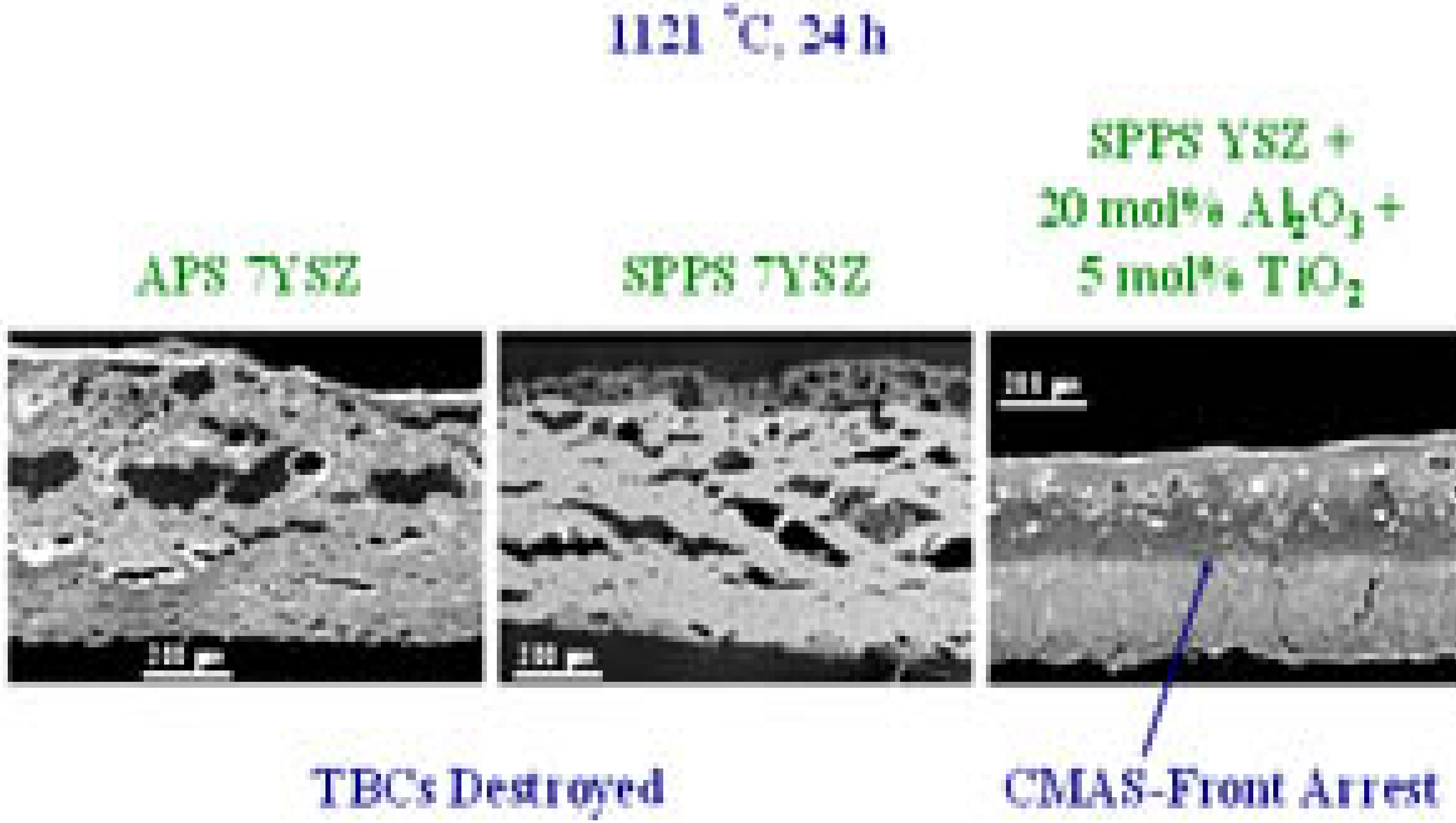


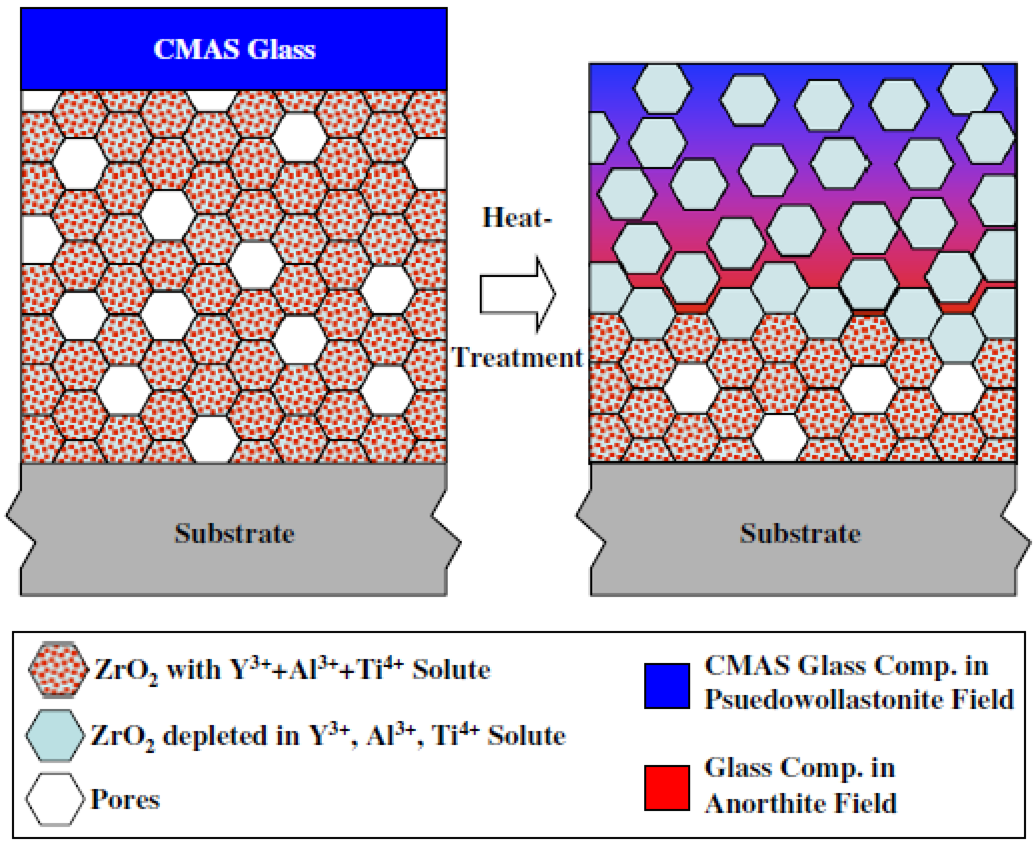
Figure 9. TBC system #4 has features of TBC #1-3 with calcium sulfate infiltration.

2. Addition of metastable Al

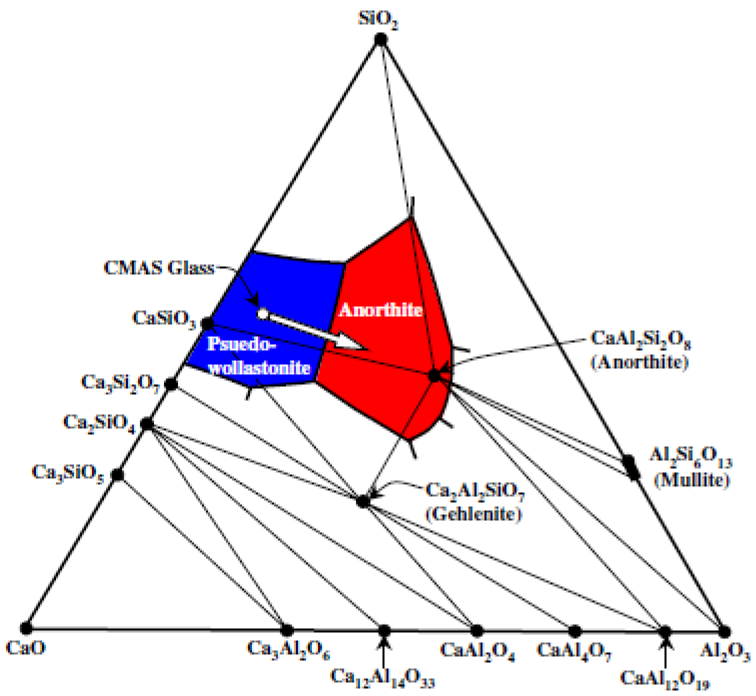


How it Works

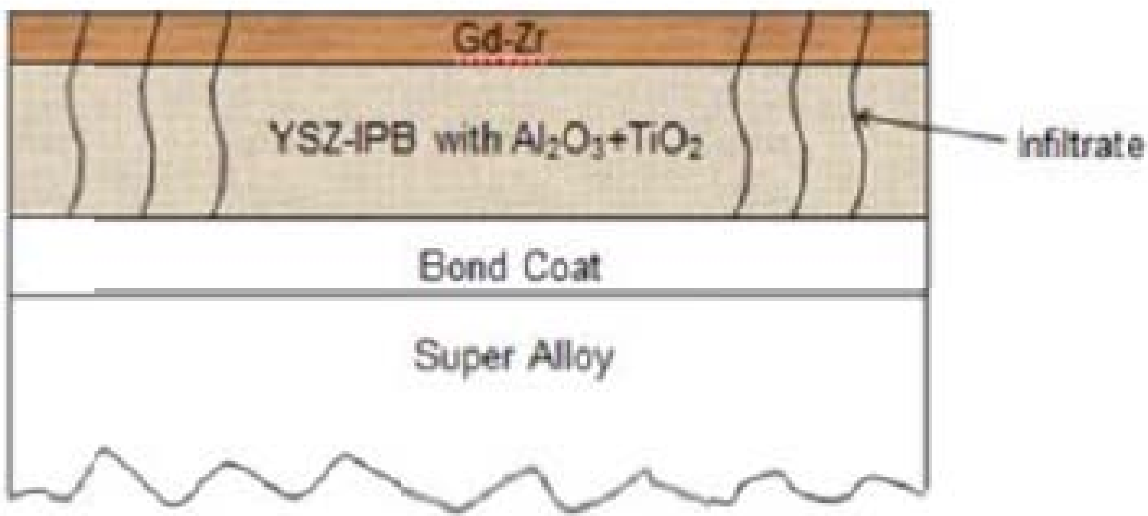
A. Aygun et al. / Acta Materialia 55 (2007) 6734–6745



Microscopy Shows Anorthite phase is blocking



3. Infiltration of CaSO4 via a low melting eutectic of NaSo4-CaSo4-MgSo4



3. Infiltration with CaSO4 found in the field by Braue

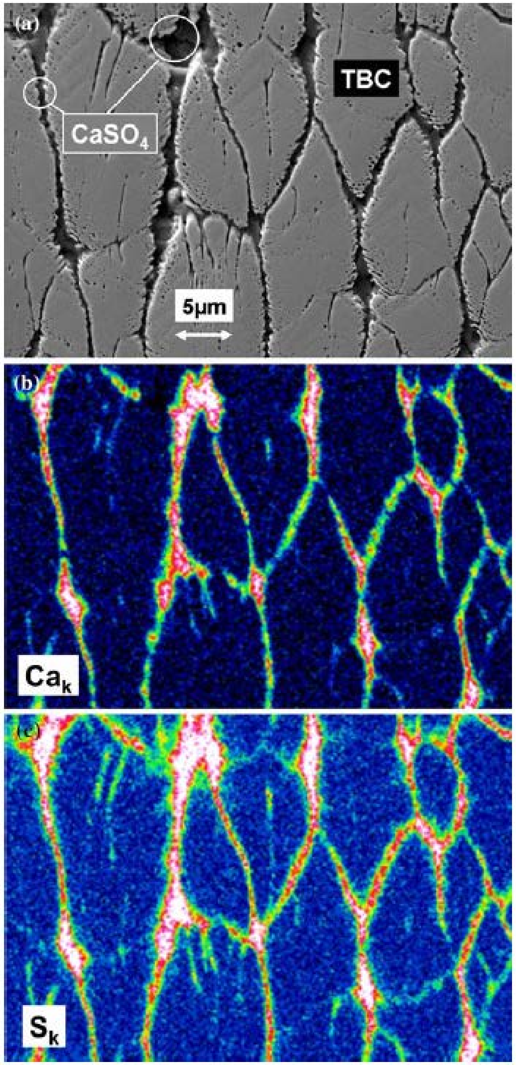


Fig. 3 **a** middle section of the YSZ top coat displaying $CaSO_4$ infiltration of open porosity (suction-surface/region B, SEM, secondary electron image), **b** and **c** elementary mapping (Ca_k, S_k) proving that $CaSO_4$ is continuous within the intercolumnar pore network of the coating

Summary & Plans

- **Project Goals:**
  - Reduce conductivity to 0.5 Watt/M-°K
  - Increase surface temperature allowable to 1300 ^{o}C
  - Significantly improve CMAS resistance
- **Structured Porosity (IPBs) will be used and optimized to lower thermal conductivity to < 0.5 Watt/M-°K**
- **A top layer of GdZr will be used to:**
  - Allow 1300 C surface temperature
  - Reduce CMAS attack
- **Al-Ti Metasable solutes will be added to the YSZ to reduce CMAS infiltration**
- **$CaSO_4$ will be used for the first time to arrest CMAS infiltration.**

Questions ?