Low Thermal Conductivity, High Durability Thermal Barrier Coatings for IGCC Engines 10/1/11

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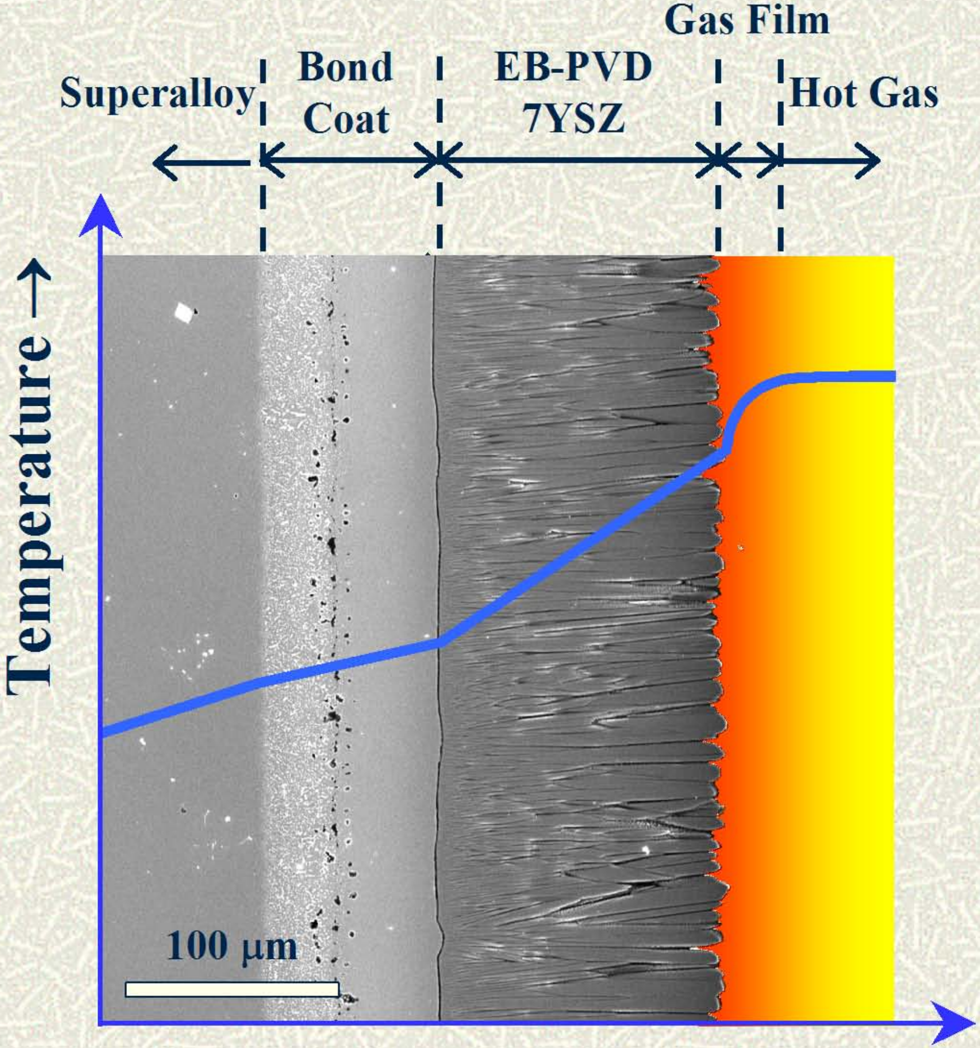
Critical Industrial Participation

- Pratt Whitney and Siemens will supply bond coated superalloy substrates.
- Pratt Whitney will make CMAS glass for use in CMAS exposure testing. (and advise on composition of the glass)
- Pratt Whitney is supplying on Ph D employee student to work on the project

Microstructure & Requirements For TBCs



TBC Requirements

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

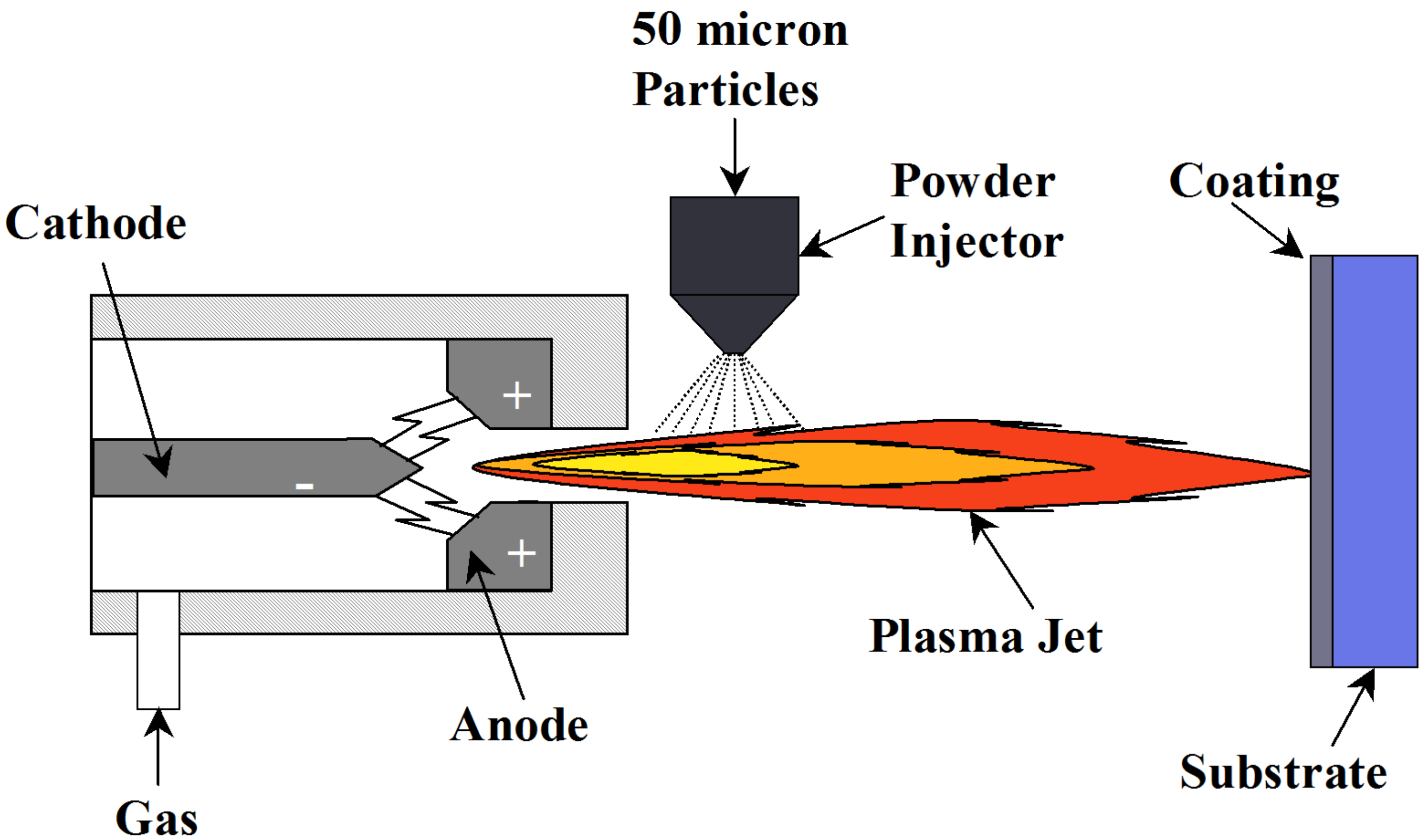
Goals

- Reduce thermal conductivity of YSZ TBCs to 0.5 watt/m^{o}K by use of inter-pass boundaries (IPBs).
- Increase the allowable surface temperature of the YSZ TBCs by 100^{o}C by use of thin, high temp. surface corrosion barriers layers (CBLs).
- Improve TBC durability in CMAS environment by use of CBLs + other methods.
- Reduce the use of rare earth elements compared to other low K TBCs

Key Program Processes/Tests

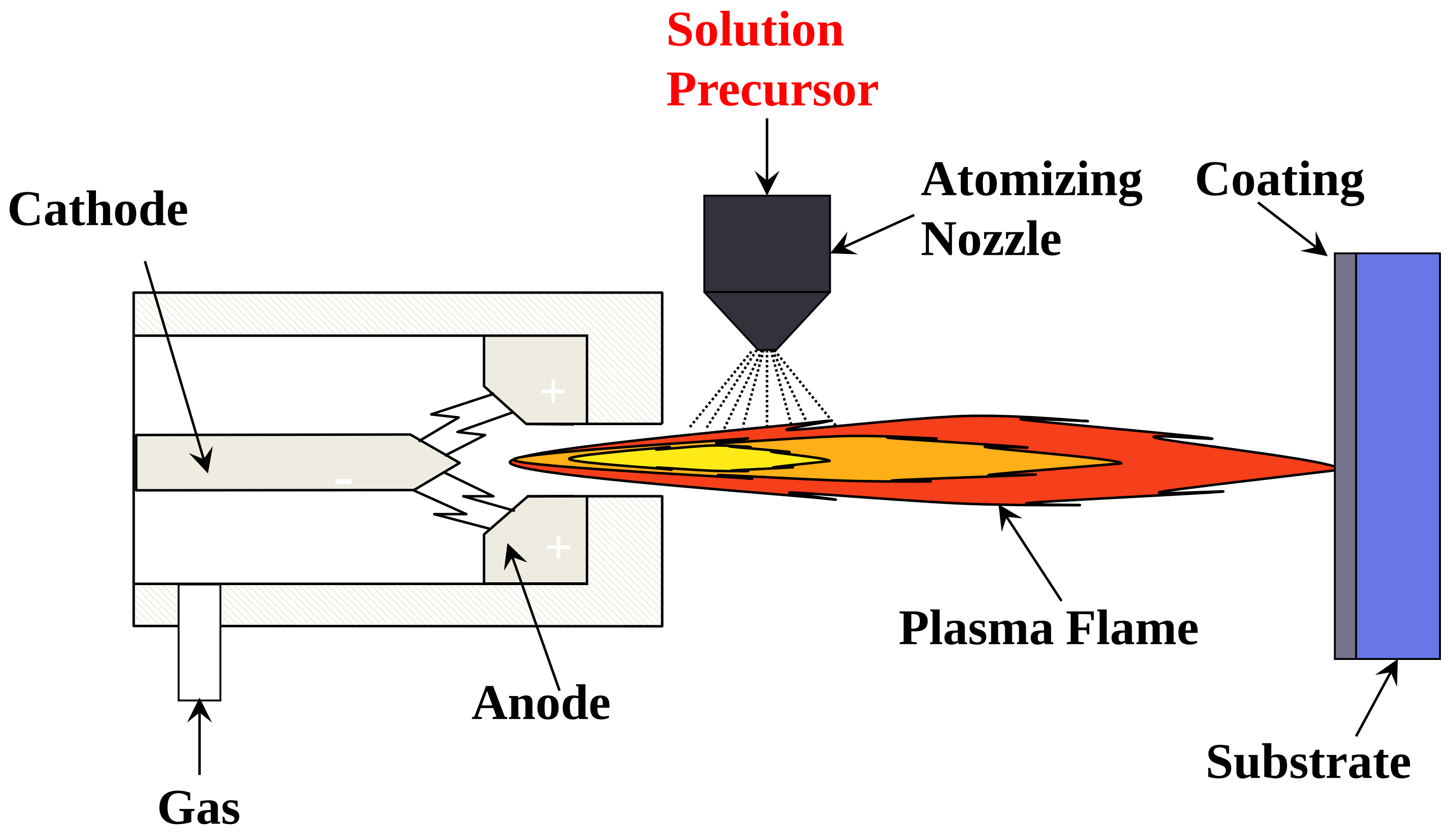
- UConn Thermal Spray Facility
- Solution Precursor Plasma Spray Process (SPPS)
- TBC Cyclic Furnace Testing Facility
- Moist Environment Testing (being build for this program)

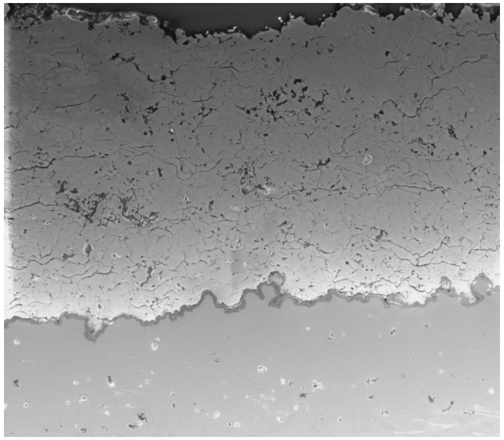
Air Plasma Spray (SPPS)



- Particles Melt and Build Splat Structure=> 7YSZ

Solution Precursor Plasma Spray Process



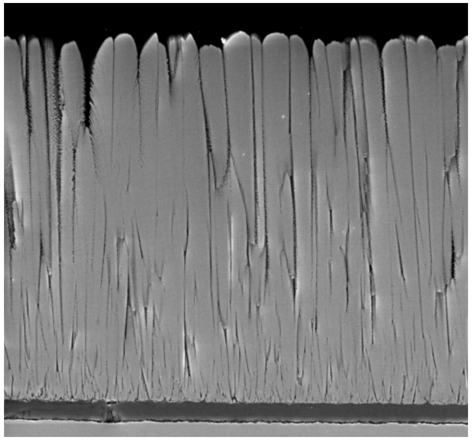


APS

Lower Thermal Cond. (√)

Shorter Spallation Life (✕)

Maxim thickness 1 mm (√)

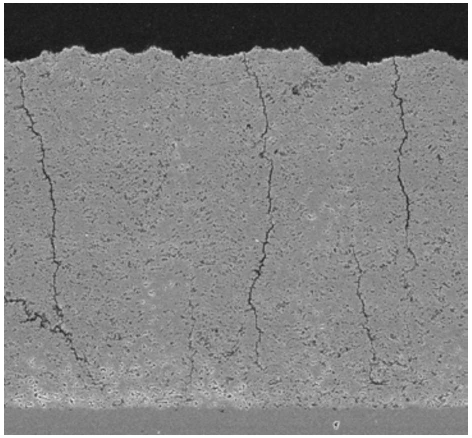


EB-PVD

Higher Thermal Cond. (✕)

Longer Spallation Life (√)

Maxim thickness 0.25 mm (X)



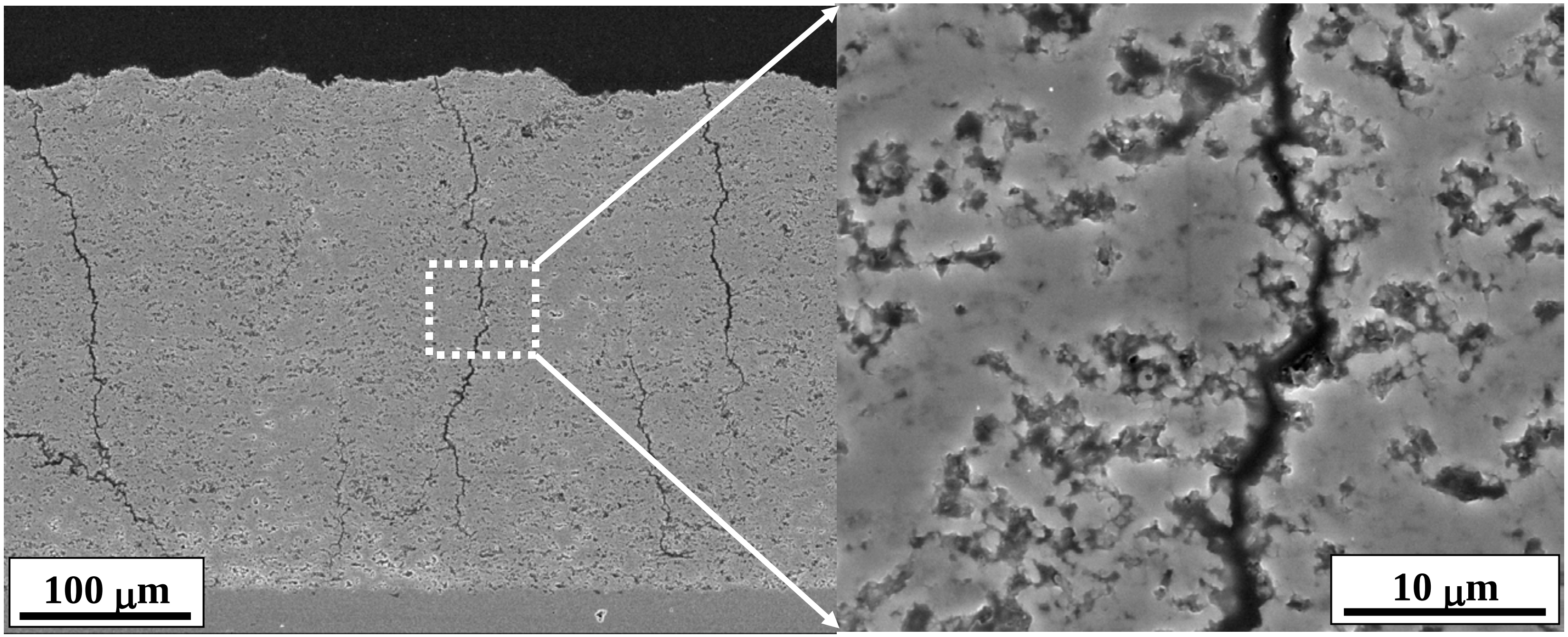
SPPS

Lower Thermal Cond. (√)

Longer Spallation Life (√)

Maxim thickness 2.5 mm (√)

Microstructure Of SPPS TBCs



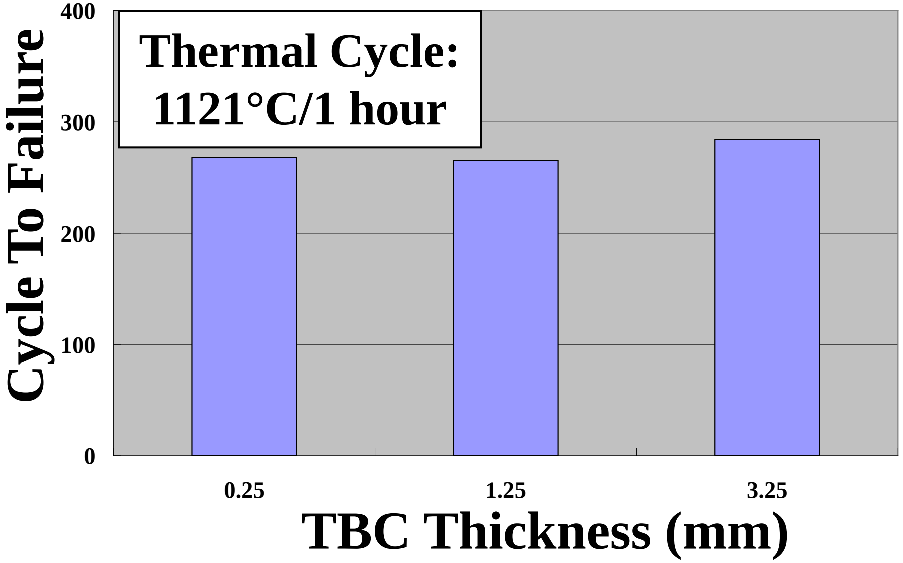
Unique Features

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

Advantages of Solution Spray

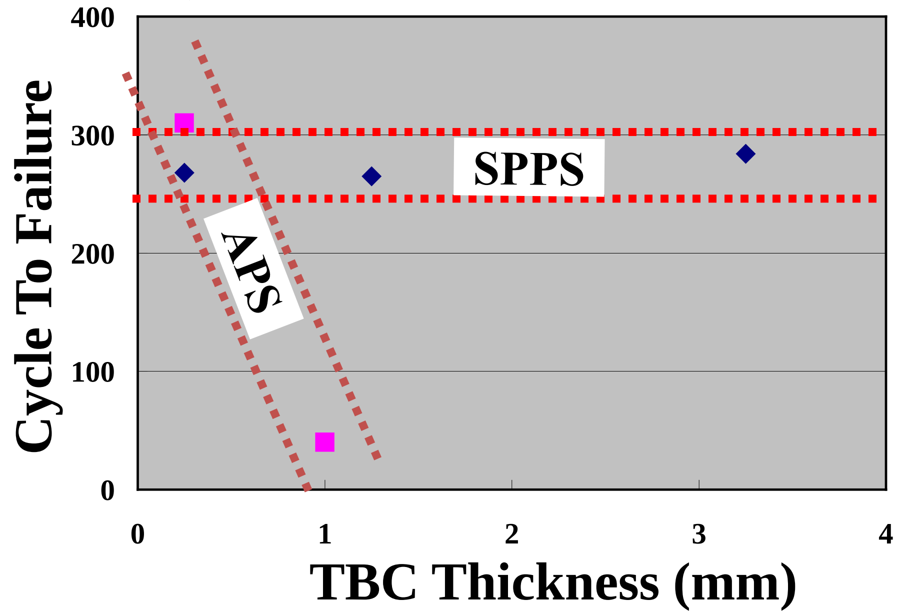
- Vertical stress relieving Cracks- Critical when thick
- Higher Fracture Toughness
- Rapid Composition Exploration (100X)
- Structured Porosity leading to low K coatings

Effect of SPPS TBC Thickness On Durability



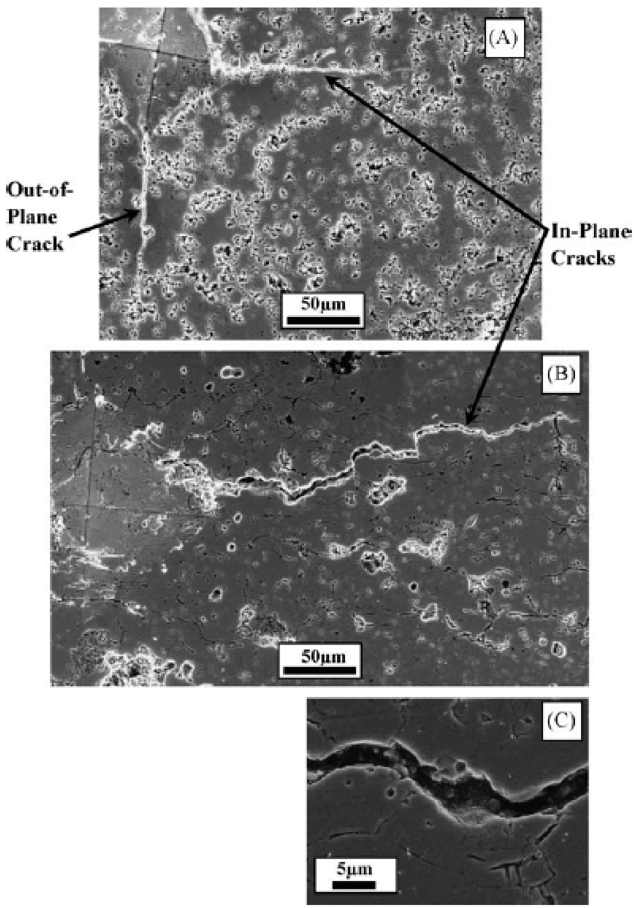
Substrate: CMSX-4

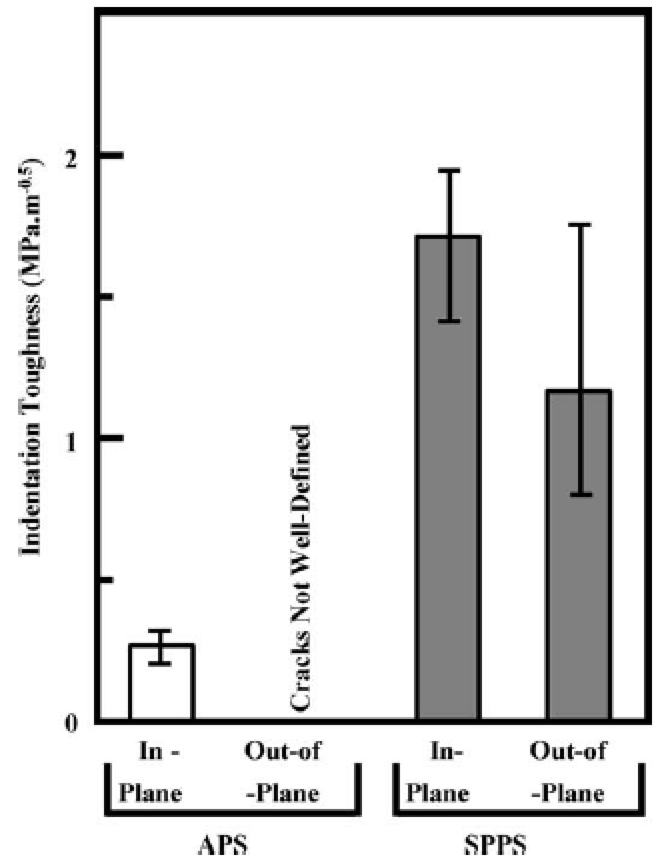
Bond Coat: Co210



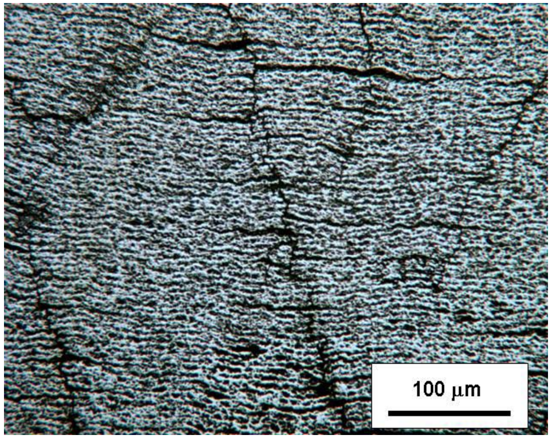
SPPS Coating have 5X higher In Plane Toughness

Fig. 4. SEM micrographs of Vickers indentation (49 N load) sites in: (A) SPPS coating and (B) APS coating. Arrows indicate in-plane and out-of-plane cracks. (C) High-magnification SEM micrograph showing the in-plane indentation crack following a "splat" boundary in the APS coating.





Structured Porosity Lead to Lower Thermal Conductivity



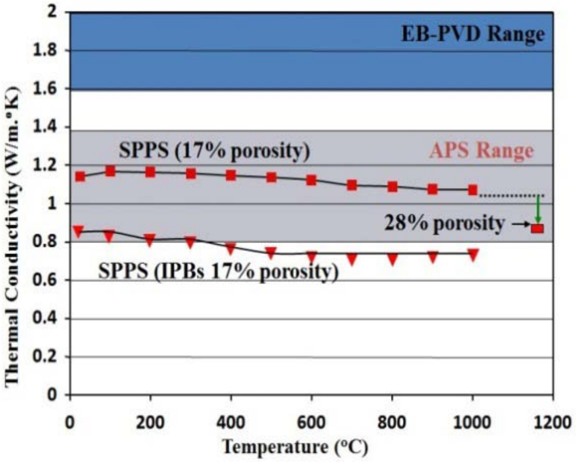
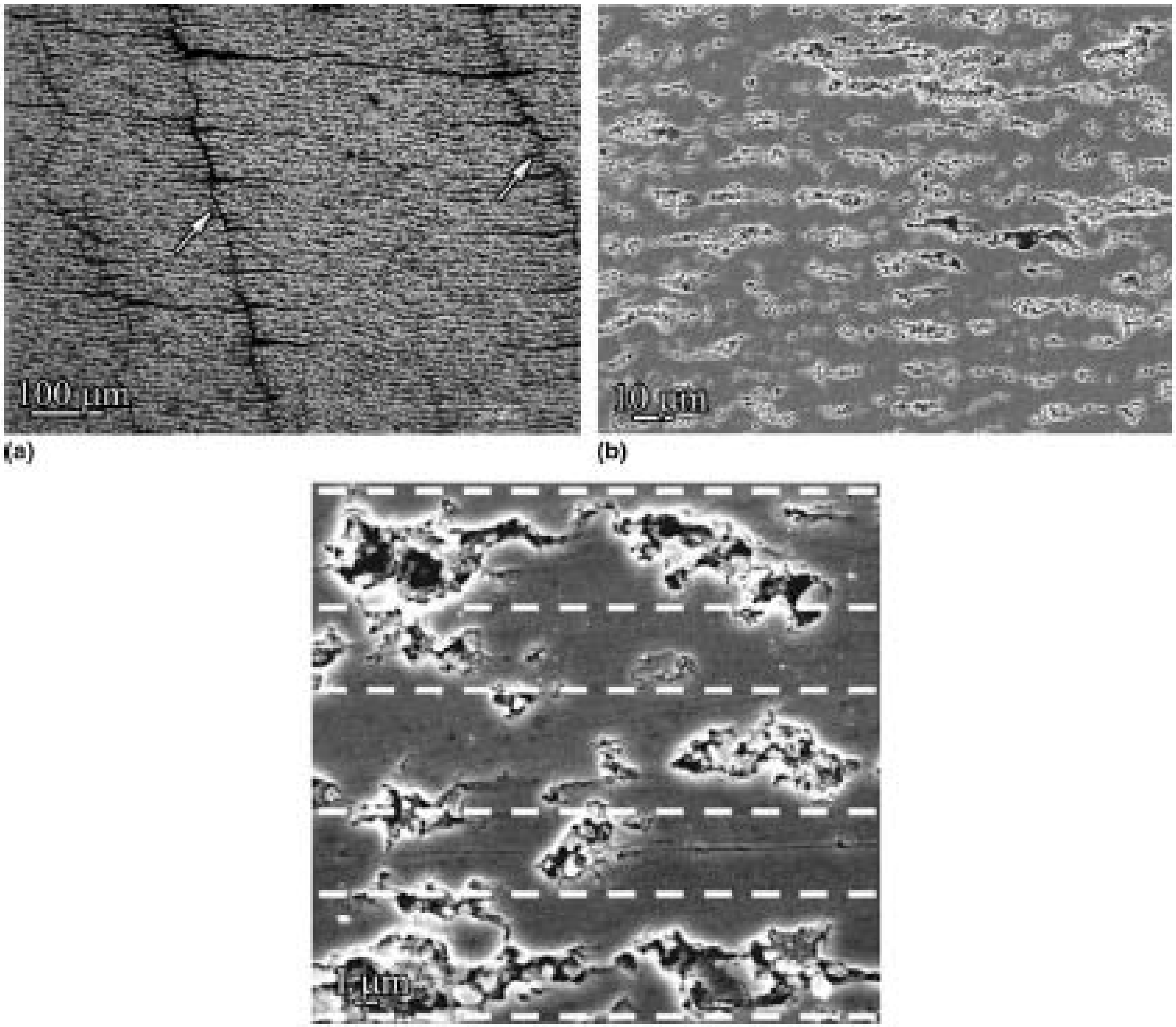


Figure 3. (a) SPPS YSZ TBC with IPBs (a) and resultant, reduced thermal conductivity

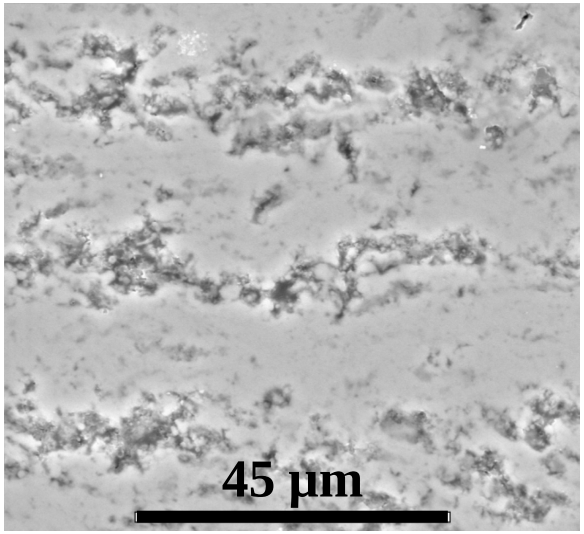
IPB Microstructure

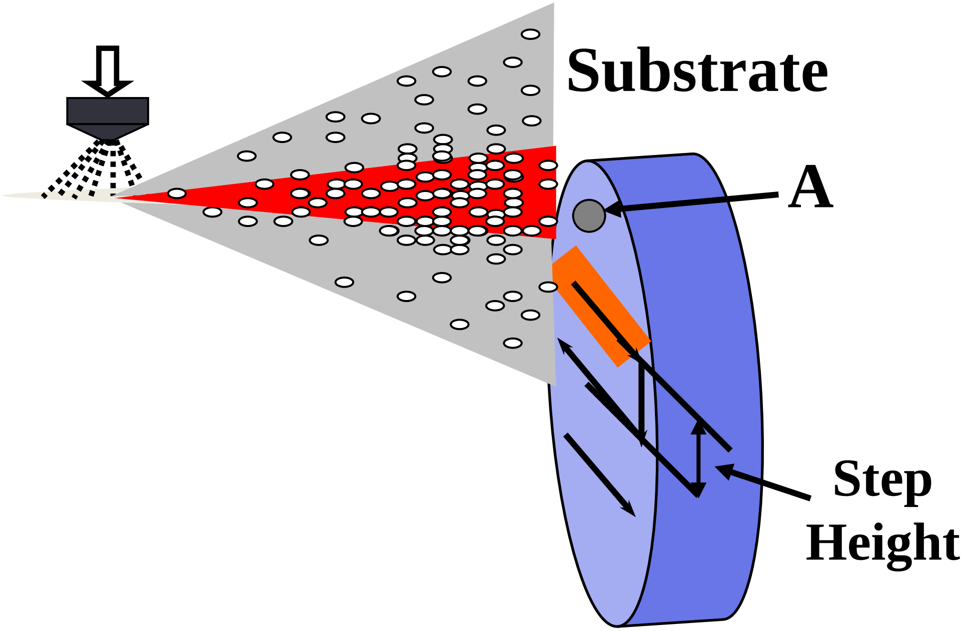
A.D. Jadhav et al. / Acta Materialia 54 (2006) 3343–3349



(a) (b) (c)

Formation of Inter-Pass Boundaries





UConn Thermal Spray Facility

Metco 9MB Plasma Spray System

Metco 9MC Control

4MP Dual Powder Feeder

9MB Plasma Gun

Liquid Delivery Options

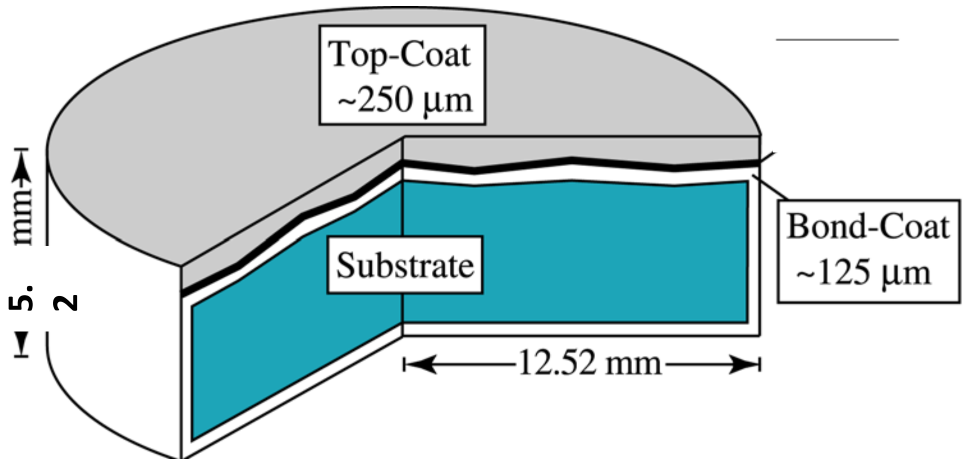
Standard Inframat System

Unique High Pressure System (33 atm)

Cyclic Furnace Test Facility

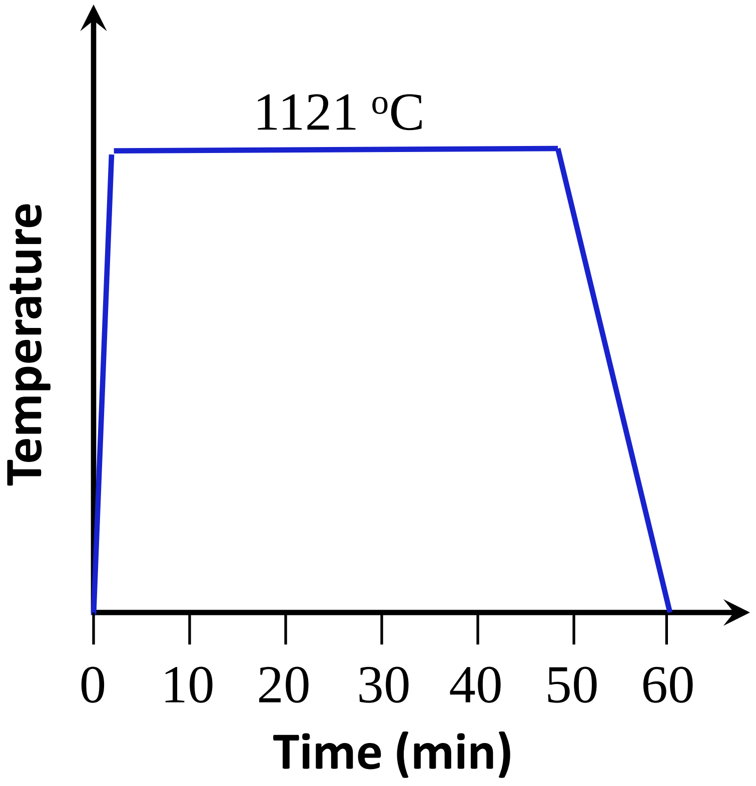
Specimen Shape & Furnace Cycle

- **Disk-Shape Samples**



- **Substrate: SC superalloy**
- **Bond-Coat: APS NiCoCrAlY**
- **Top-Coat: SPPS Layered**

- **Thermal Cycling Life Test**



Vast Reference Data Base

- GTD 111- GE DV
- HY 230 with Ni Co Cr Al Y and SPPS
- Rene N-5 Pt-Al BC with EB-PVD
- CMSX-4, Pt Al with EB-PVD
- CMSX-4 , MCrAlY+Si,Hf-EB-PVD
- PWA 1484- APS Ni Cr Al Y -APS

10 More Types Tested

#	S1	S2	S3	S4	S5	S6	S7	S8	A1	E1
Top Coat Process	SPPS	SPPS	SPPS	SPPS	SPPS	SPPS	SPPS	SPPS	DVC/APS	EB-PVD
Bond Coat Category	MCrAlY	MCrAlY	MCrAlY	MCrAlY	MCrAlY	MCrAlY	MCrAlY	MCrAlY	MCrAlY	Pt-Al
Bond Coat Process	APS	APS	APS	HVOF	HVOF	LPPS	LPPS	LPPS	APS	CVD
Substrate	H230	H230	NA	H230	CMSX-4	CMSX-4	MARM509	NA	GTD-111	CMSX-4

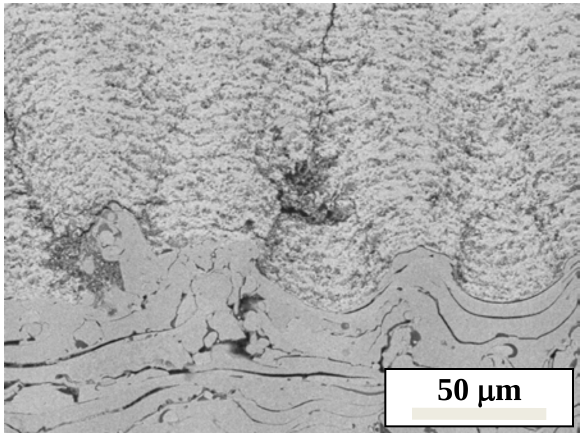
Bond Coat Composition

	Co	Ni	Cr	Al	Y	Si	Hf
S1, S2		bal	20	10	1		
S4	23-26	Bal.	15-19	9-11	0.2-0.4		
S5, S6	Bal	32	21	8	0.5		
S7	20	Bal	18	12.5	0.6	0.4	0.25
?S8	Bal	32	21	8	0.5		

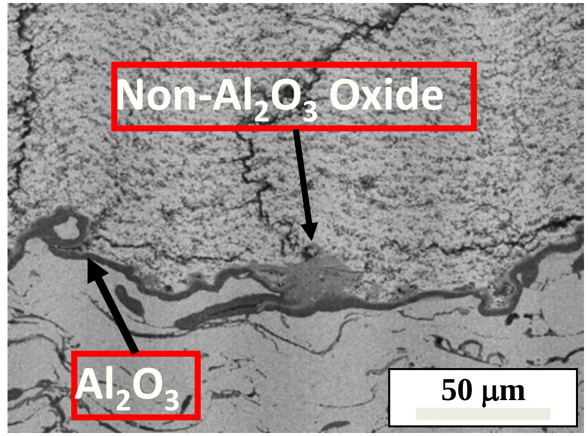
Test Results at 1121 C 1 Hour Cycles

#	S1	S2	S3	S5	S6	S7	S8	A1	E2
Cycle Life	1140 1140* 1230 1230	573, 595* 785* 1049* 1206	697*	300* 350	245, 270* 290	220, 245*	125 140*	Ave. 300	Ave. 458
Failure % in ceramic	70%	60-75%	50%	60%	25%	50%	30%	-	-

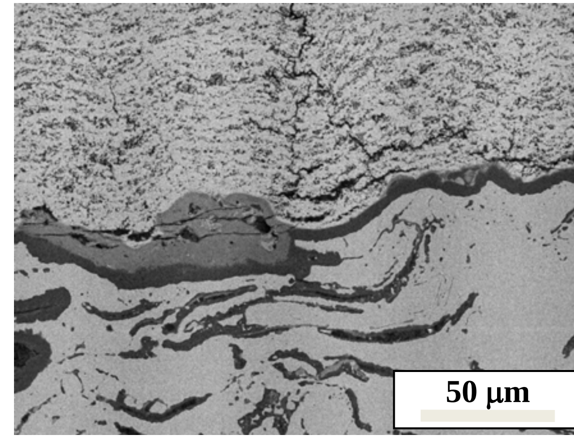
Change of Microstructure with Thermal Cycling



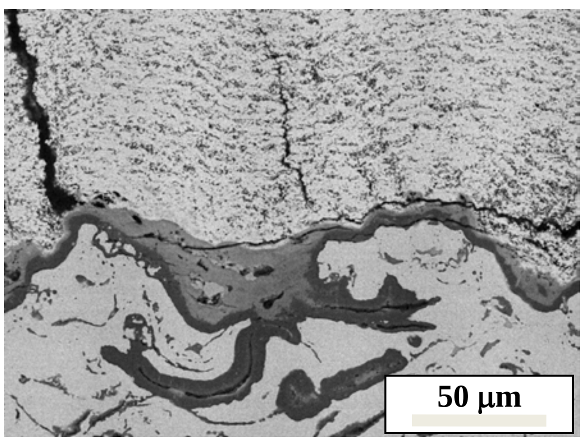
As-Sprayed



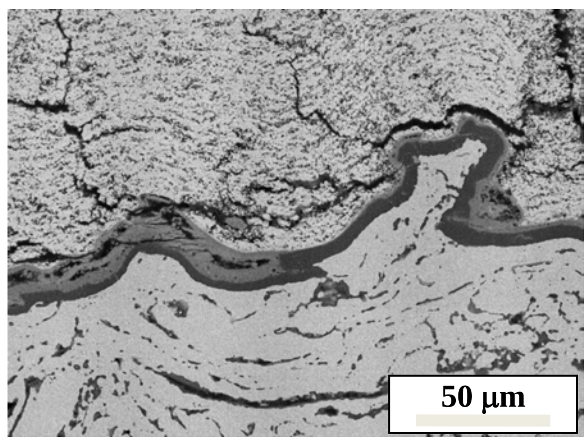
40 Cycles



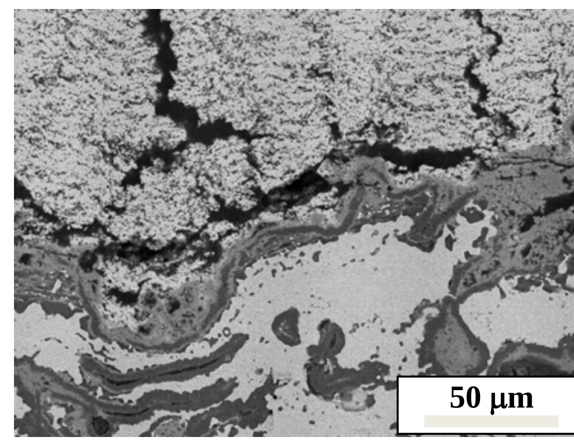
200 Cycles



400 Cycles

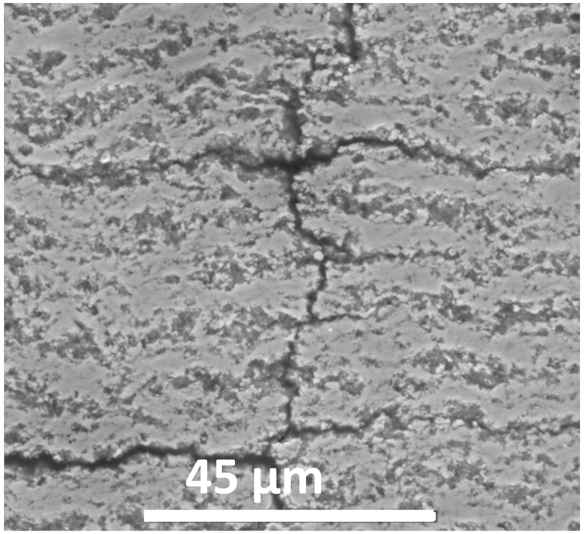


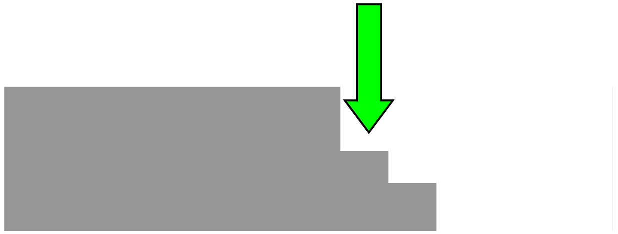
600 Cycles

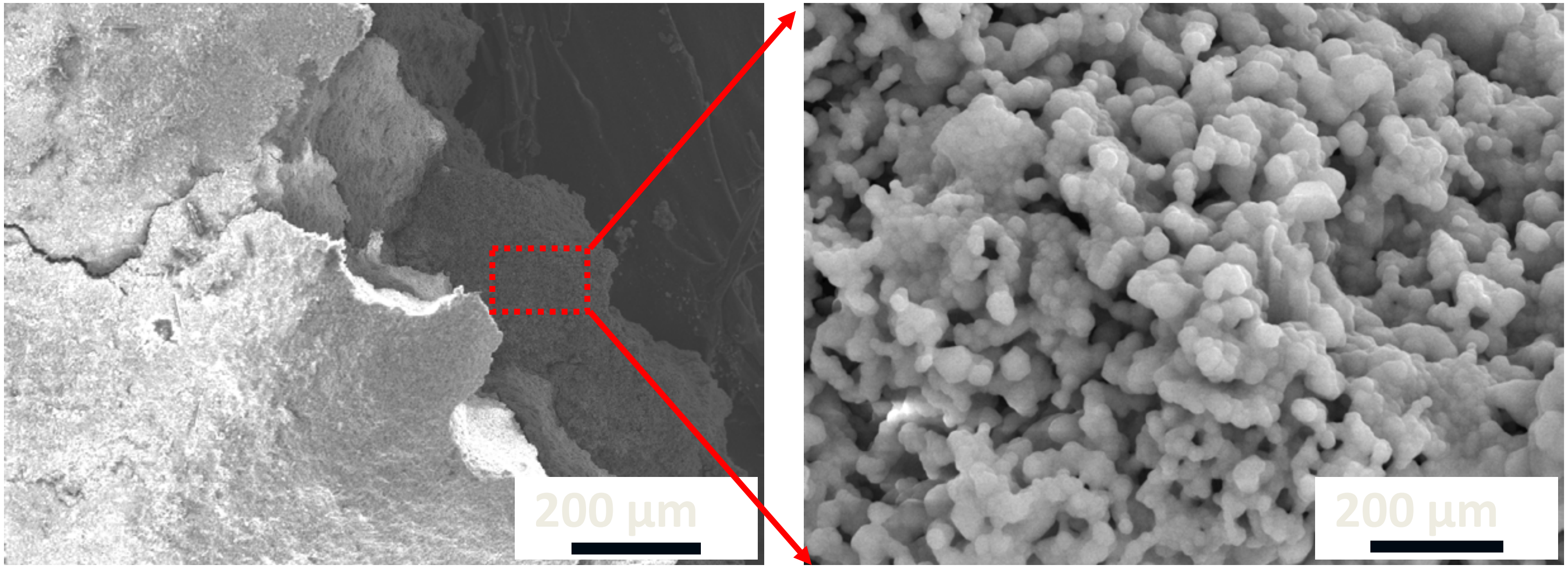


800 Cycles

Morphology of Inter-Pass Boundary

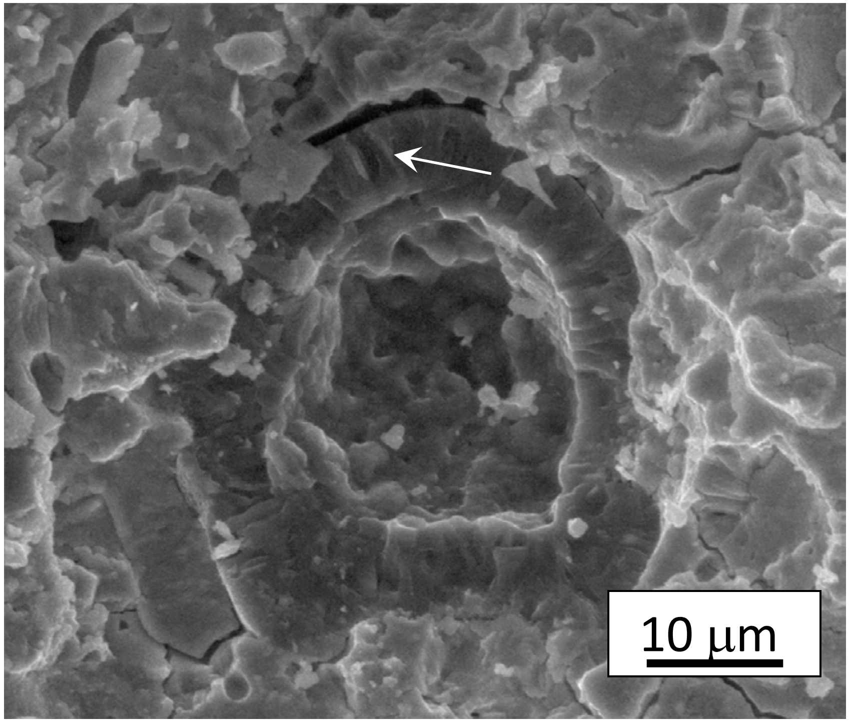




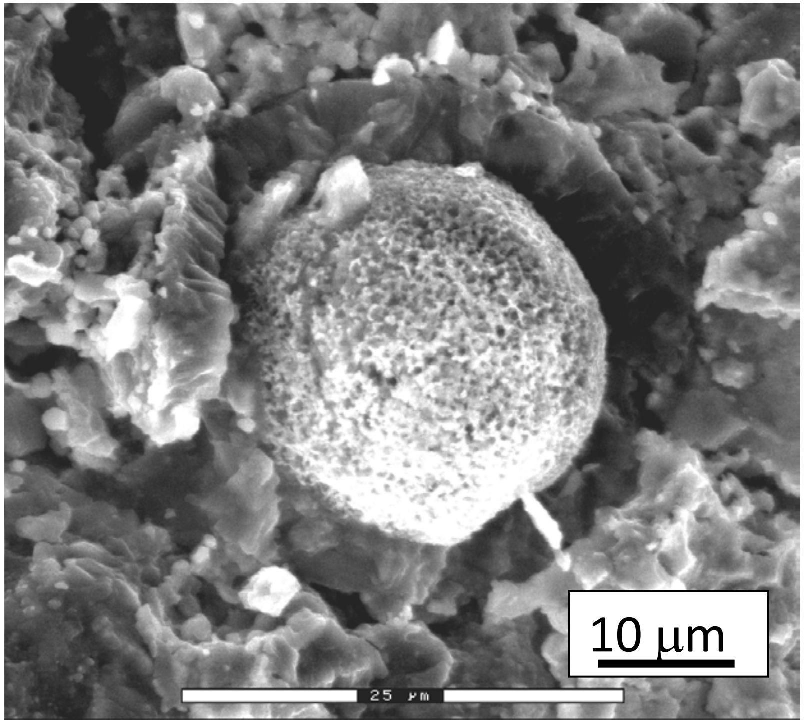


Spallation Surface Features

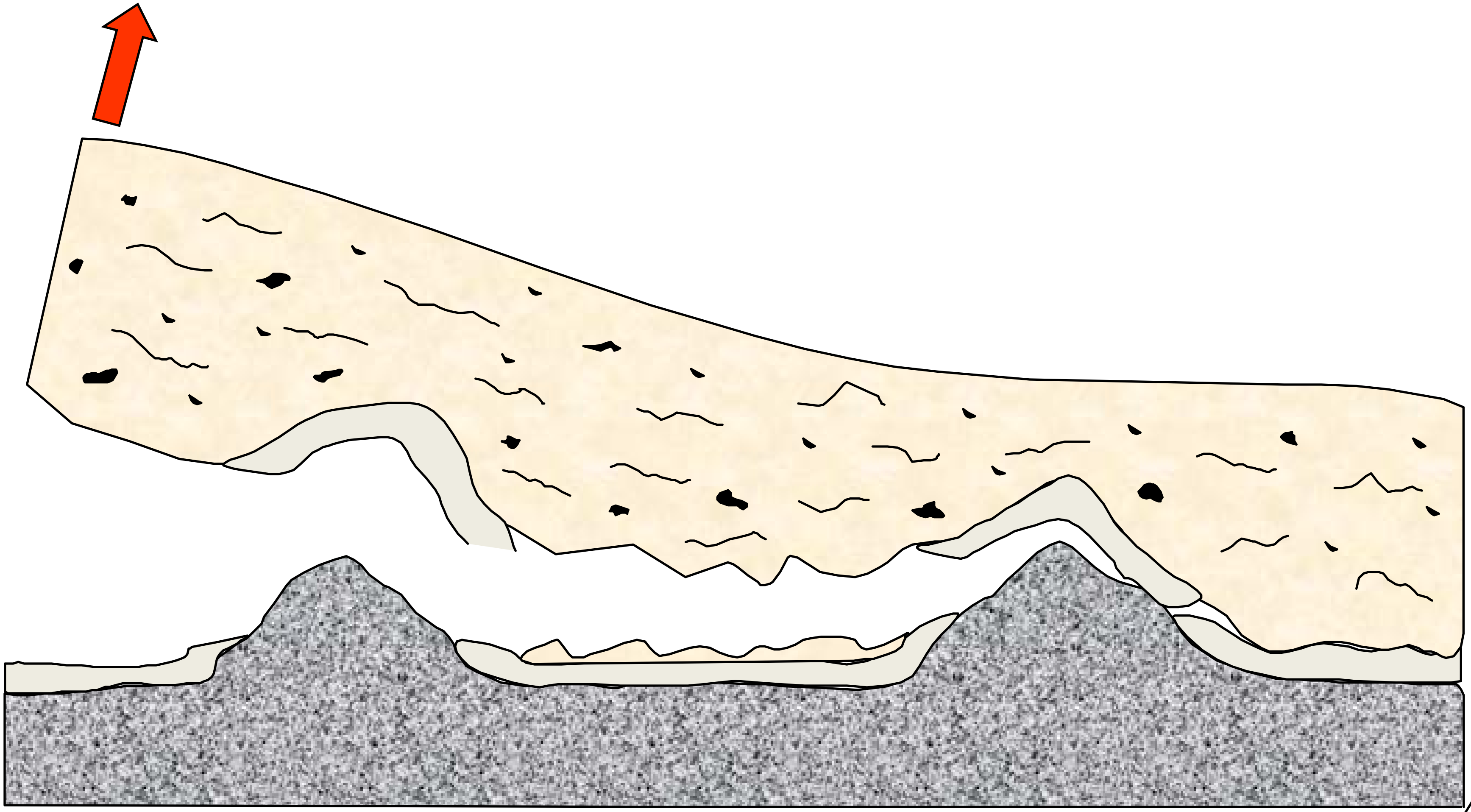
- Ceramic "Bottom" Side



- Metal "Top" Side



Failure Mode of Plasma Sprayed TBCs



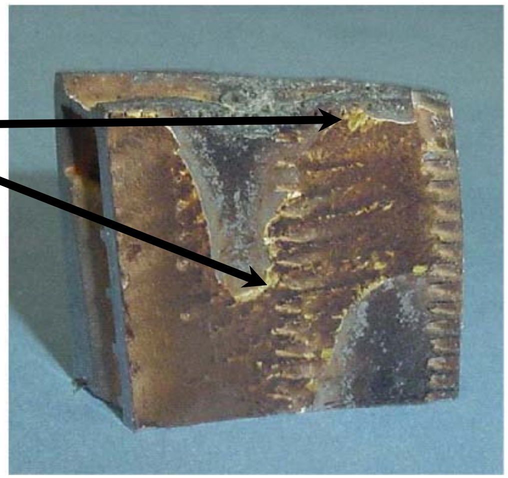
Contaminants Affect Failure

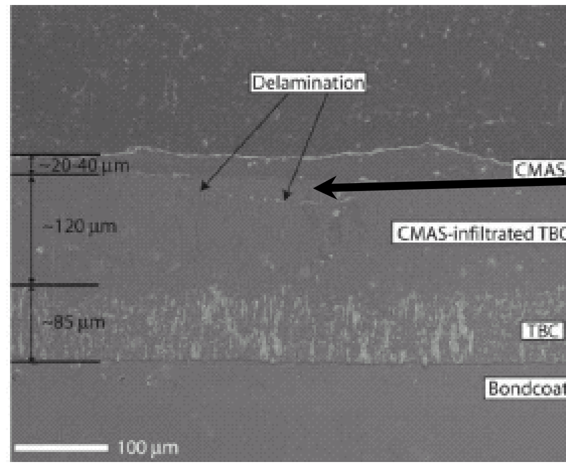
Calcium, Magnesium, Aluminum
Silicon= CMAS

CMAS Infiltration of 7YSZ Thermal Barrier Coating

Field Observation of CMAS Attack

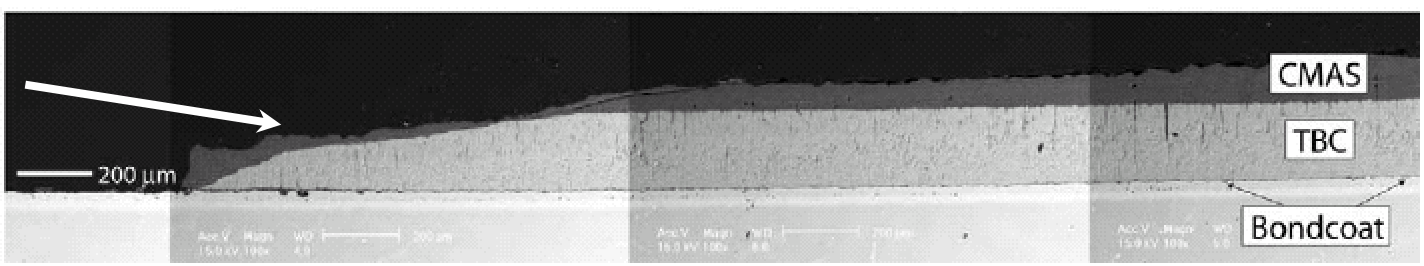
CMAS Deposits





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

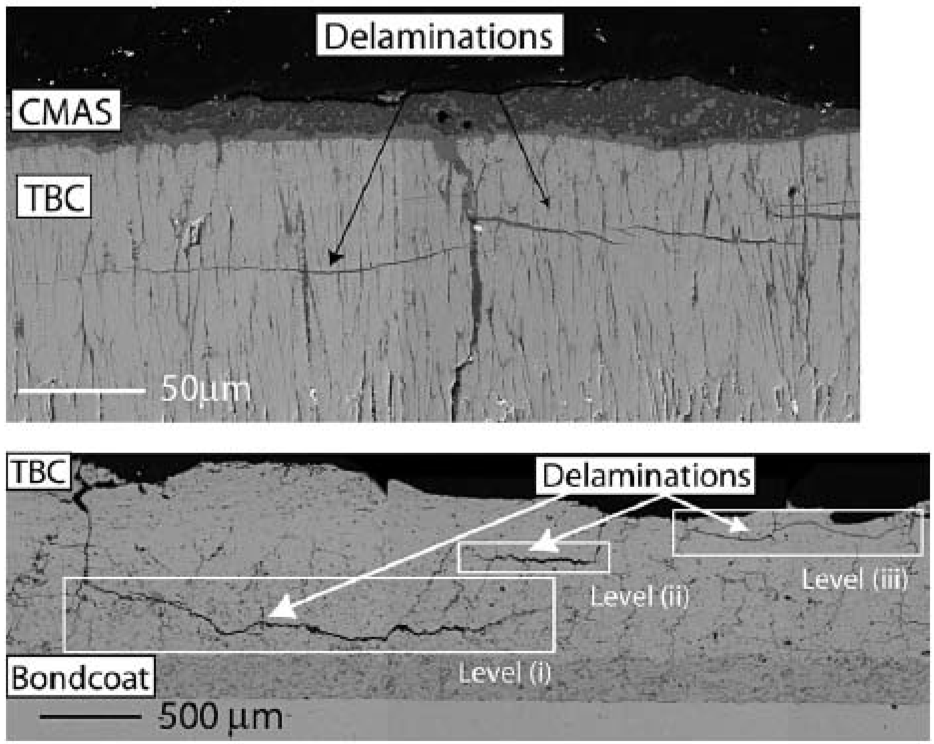


Fig. 1. Examples of delaminations in thermal barrier coatings obtained from components removed from engines subjected to CMAS penetration: (a) Sub-surface mode I delaminations in an airfoil with a TBC made by electron beam physical vapor deposition; the delaminations are within the penetrated zone [9].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

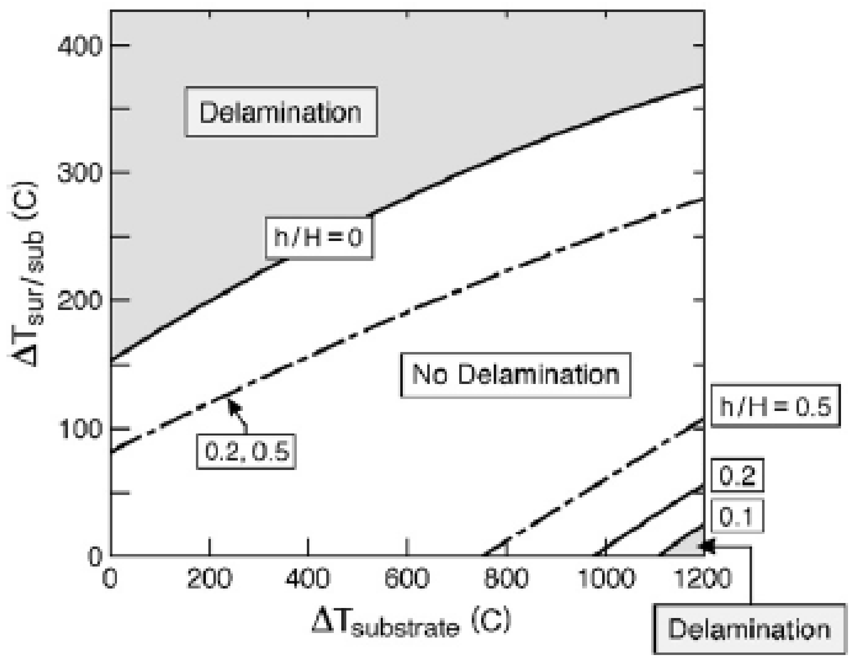


Fig. 10. A map for deep delamination in an APS–TBC on a superalloy substrate with CMAS infiltration to depth, h/H. The mixed mode toughness parameter is, $\lambda = 0.25$.

2. Many types of chemical and Phase Effects for example Y loss and destabilization of t phase Zr 0_2 to Monoclinic with a destructive volume change

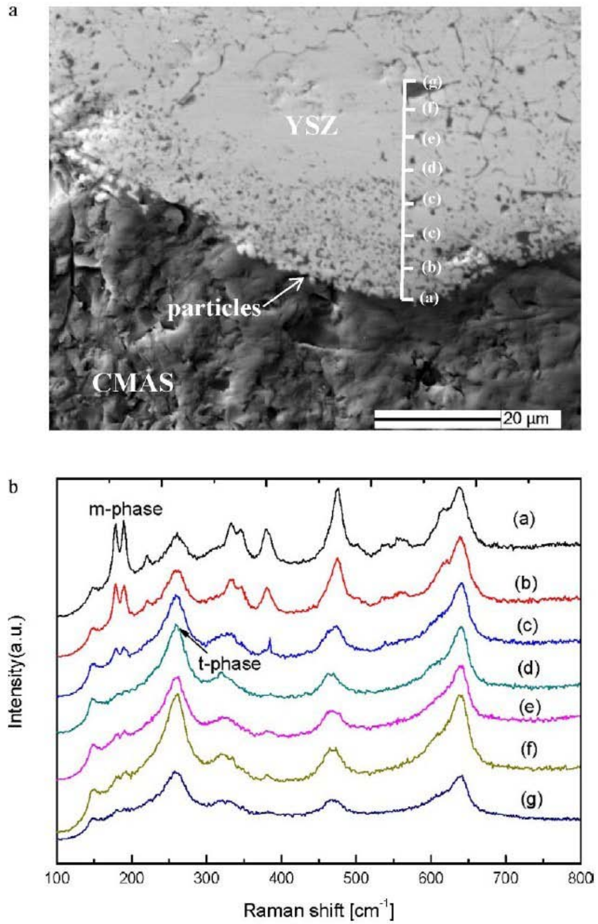


Fig. 4. (a) Micrograph of the interaction zone of CMAS deposit and YSZ coating after 4 h heat-treatment at 1250 °C, and (b) Raman spectra obtained from the positions marked in (a).

Proposed Work Plan

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											■	■

Minimization of Thermal Conductivity Using IPBs

- Experimental Design of spray trials
- Outcome assessment by thermal conductivity calculation verified by measurement

Base Line System

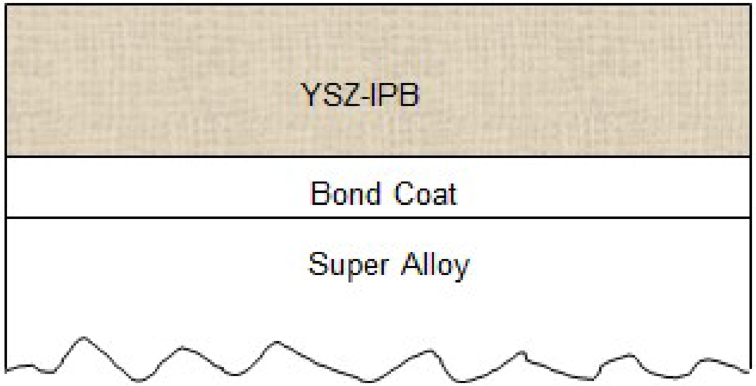
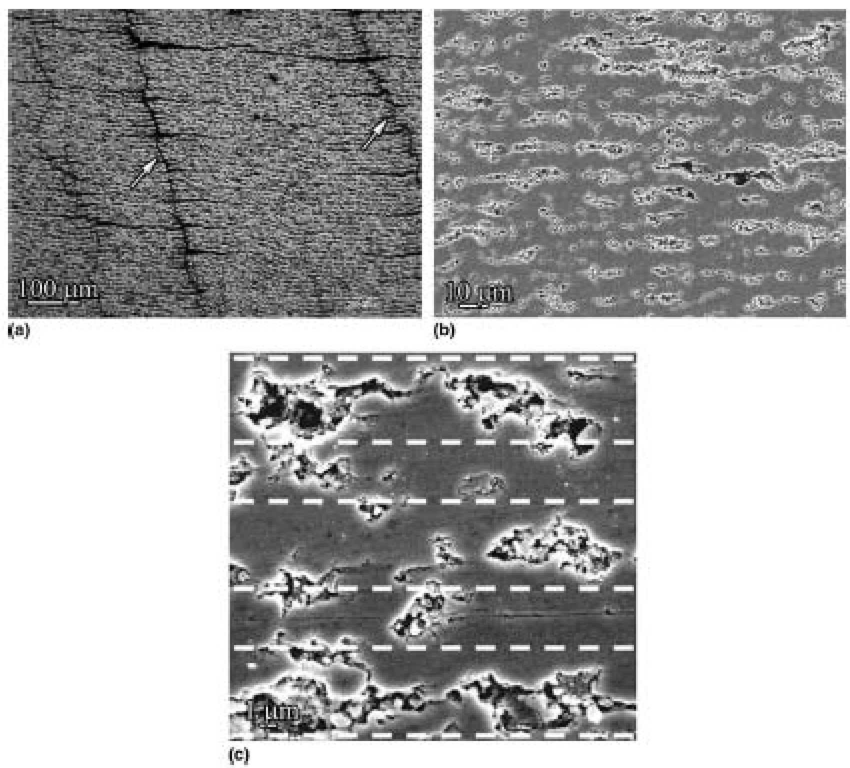


Figure 6. TBC #1, a Low K SPPS YSZ TBC using IPBs and porosity

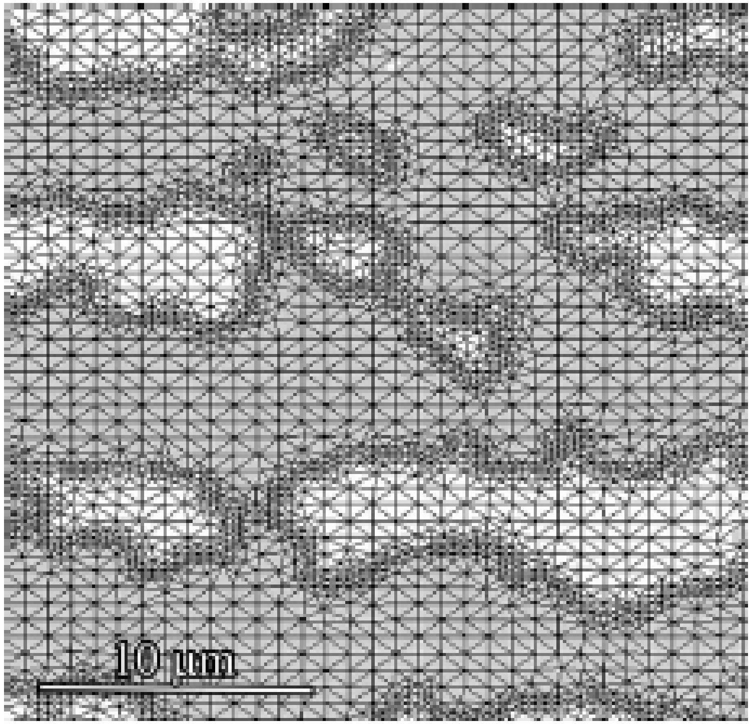
Rapid Measurement of Thermal Conductivity

Calculating Thermal Conductivity

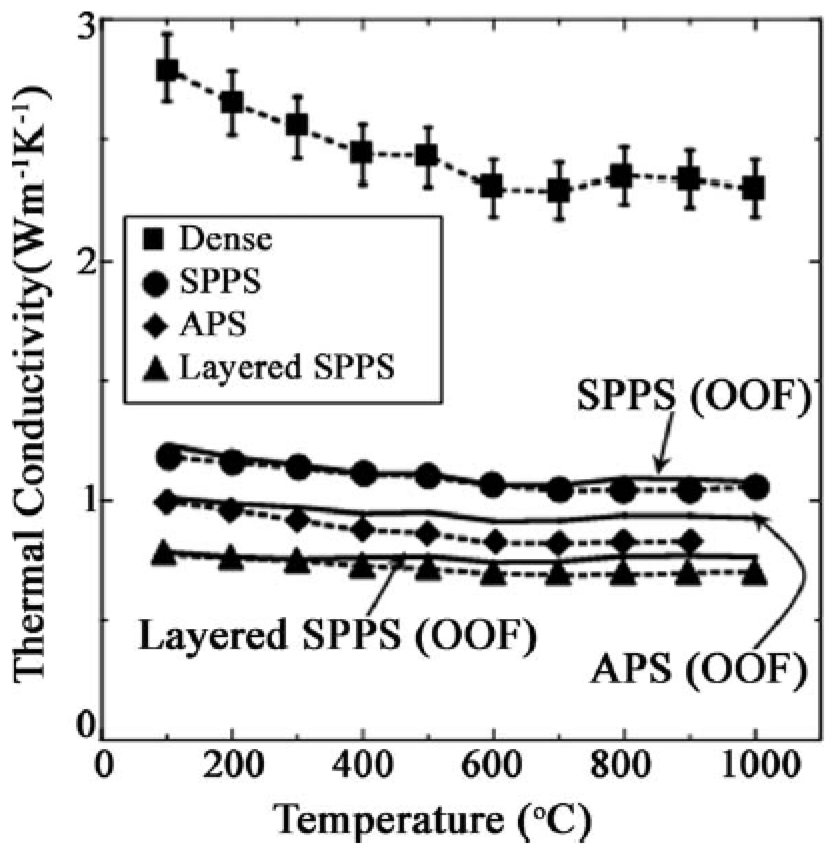
A.D. Jadhav et al. / Acta Materialia 54 (2006) 3343–3349



Finite Element Mesh Generated from Micrograph Using OOF Program



Calculated Conductivity Agrees Well with Experiments



CMAS Damage Mitigation to be Implemented

Three Approaches

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

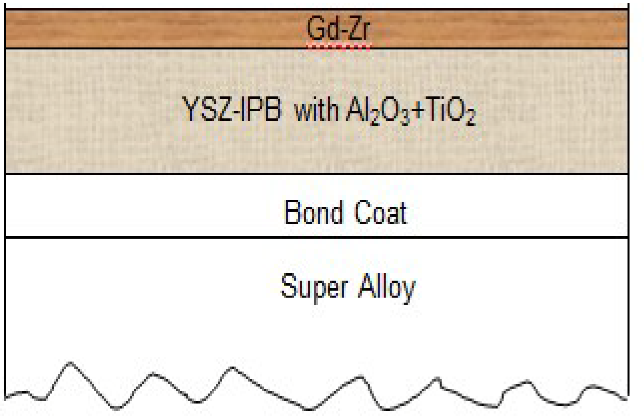
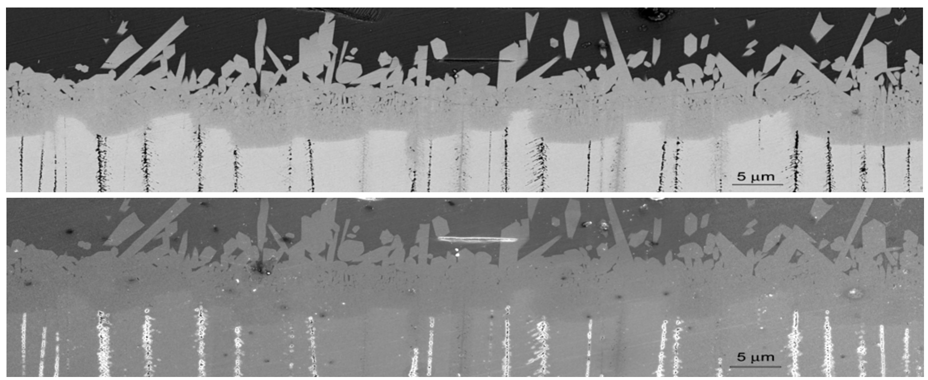


Figure 7. TBC system #2 with low conductivity solution plasma sprayed YSZ with IPBS and CMAS resistant high temperature tolerant Gc-Zr protective surface layer (PSL).

CMAS Resistance of GdZr



Add Metastable Al_2O_3 + to block CMAS in the YSZ layer

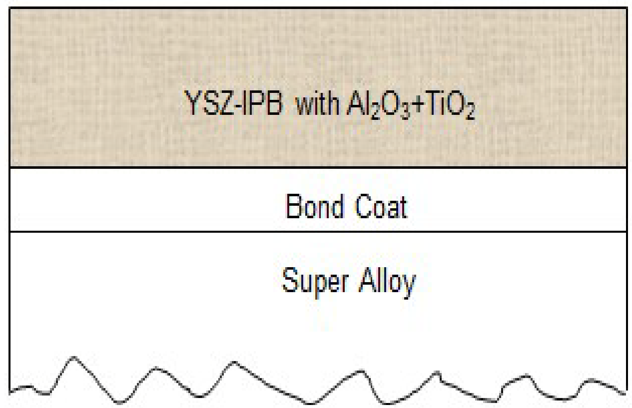
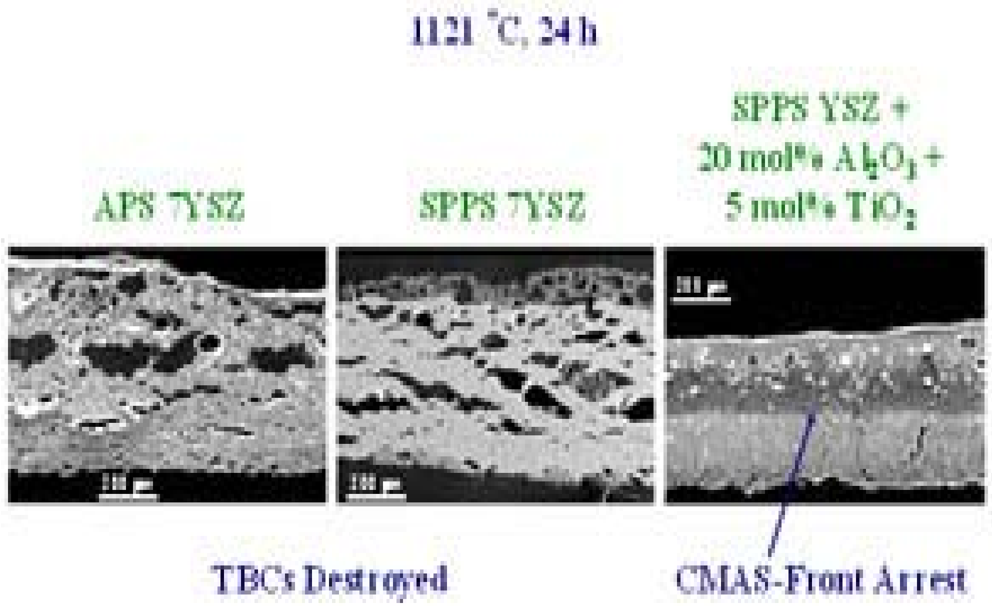


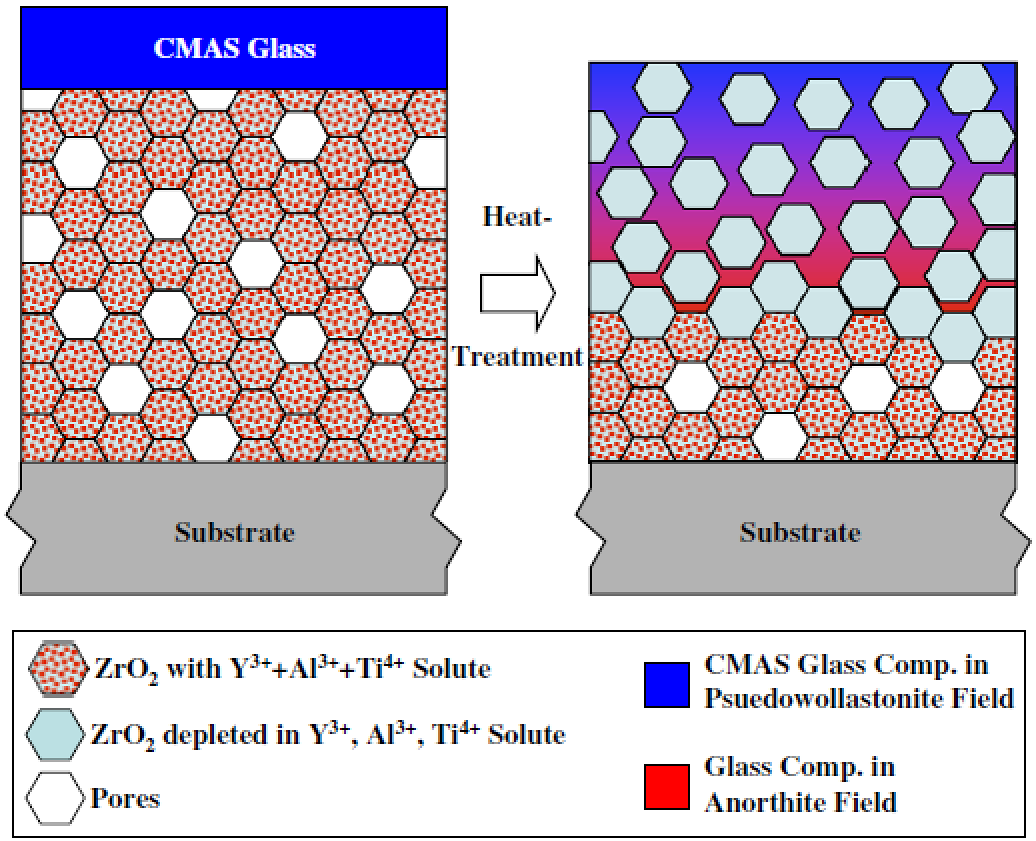
Figure 9. TBC system #4 has features of TBC #1-3 with calcium sulfate infiltration.

2. Addition of metastable Al + more

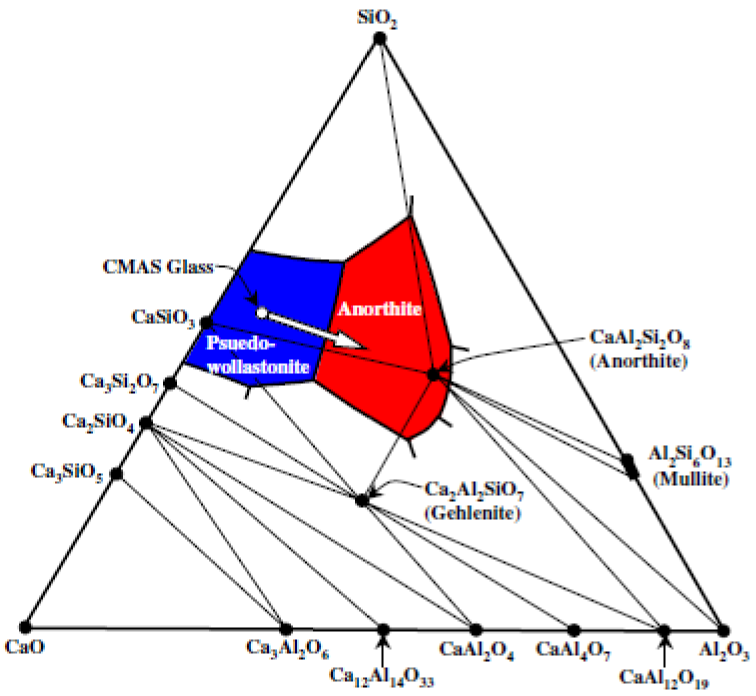


CMAS composition is altered to Anorthite Filed

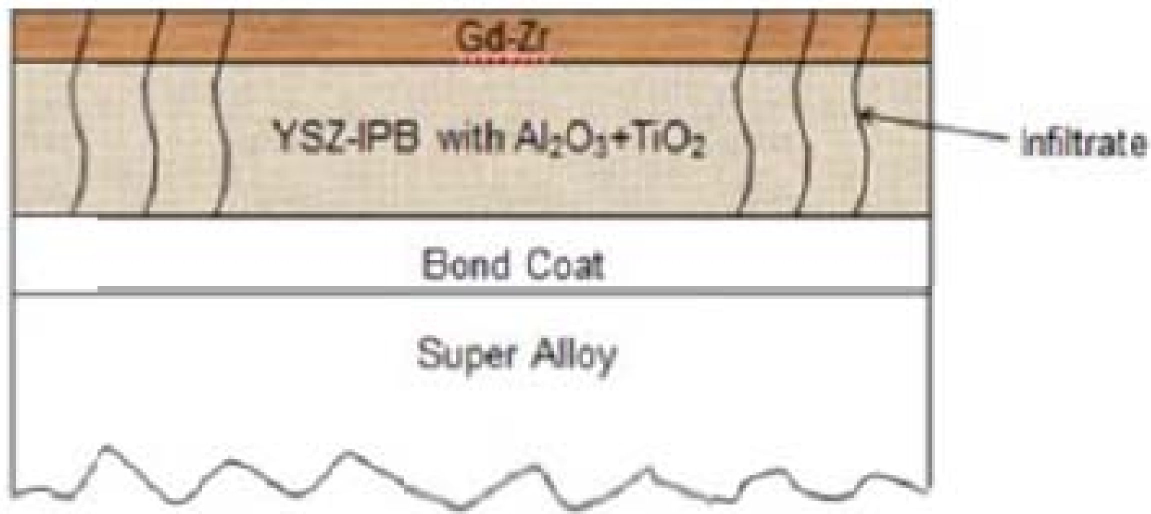
A. Aygun et al. / Acta Materialia 55 (2007) 6734–6745



Microscopy Shows Anorthite phase is blocking

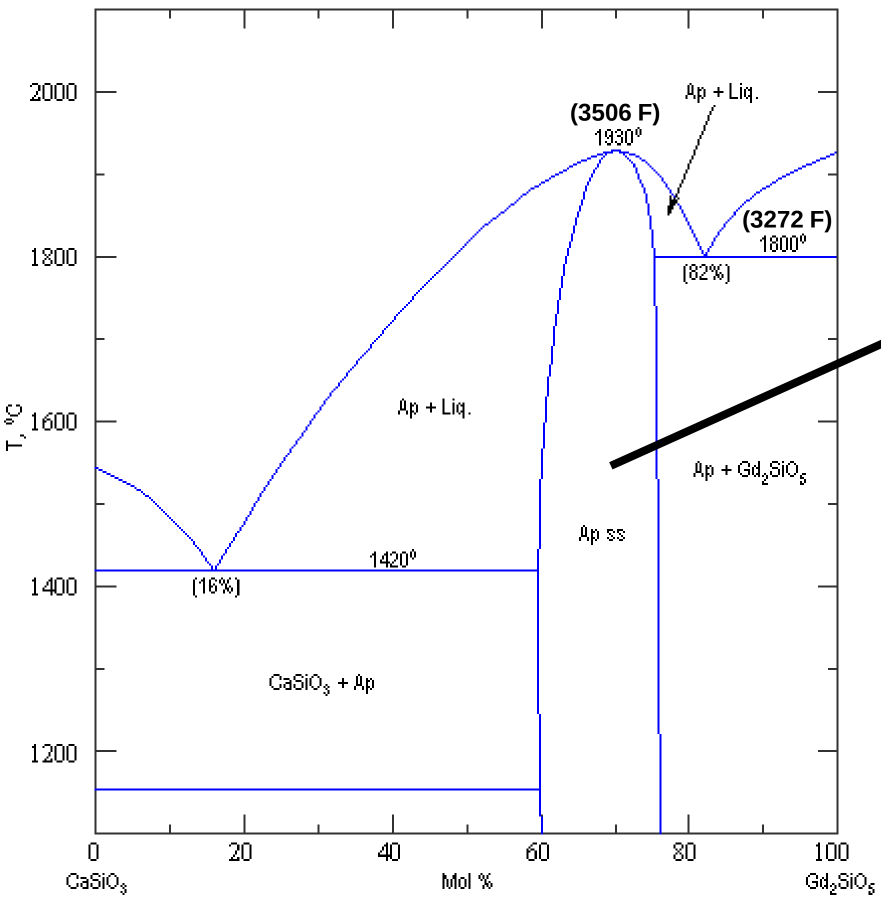


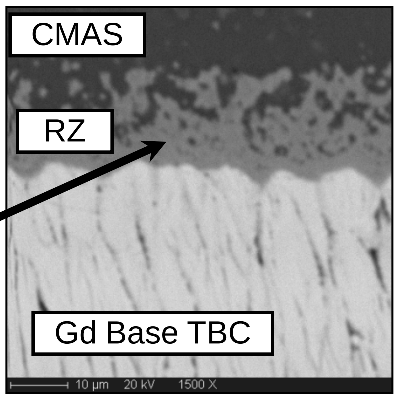
3. Infiltration of CaSO4 via a low melting eutectic of NaSo4-CaSo4-MgSo4

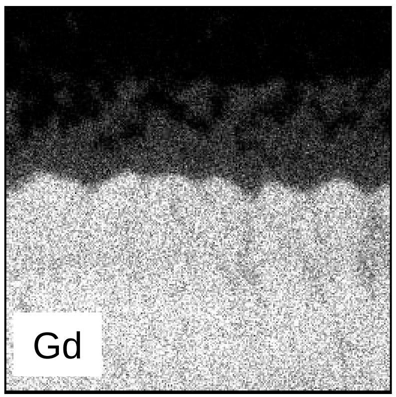


Analysis of $Gd_2Zr_2O_7$/CMAS Reaction Product

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

Courtesy of Carlos Levi, UCSB

3. Infiltration with CaSO4 found in the field by Breau

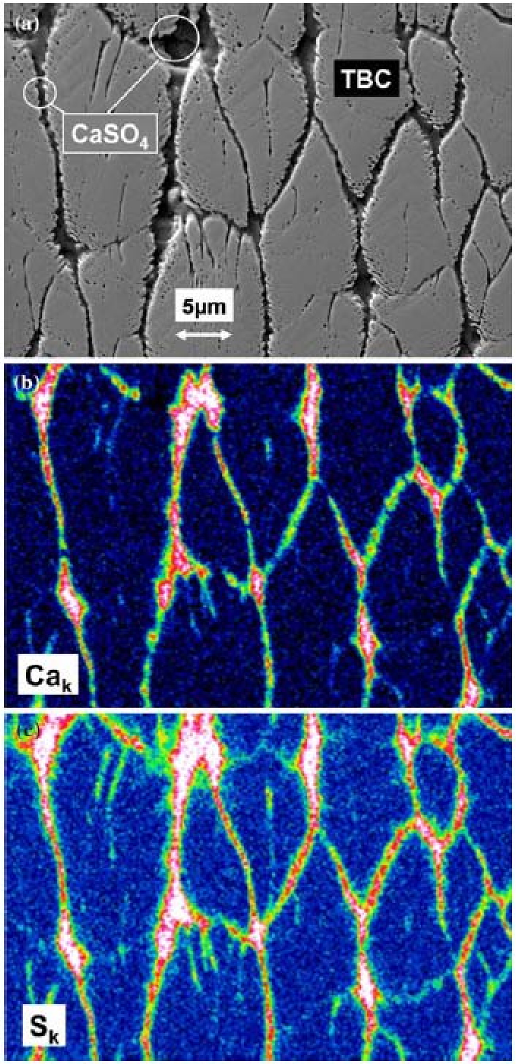


Fig. 3 a middle section of the YSZ top coat displaying $CaSO_4$ infiltration of open porosity (suction-surface/region B, SEM, secondary electron image), b and c elementary mapping (Ca_k, S_k) proving that $CaSO_4$ is continuous within the intercolumnar pore network of the coating

Composition of the CMAS blocking Ca-Mg-Si materials found

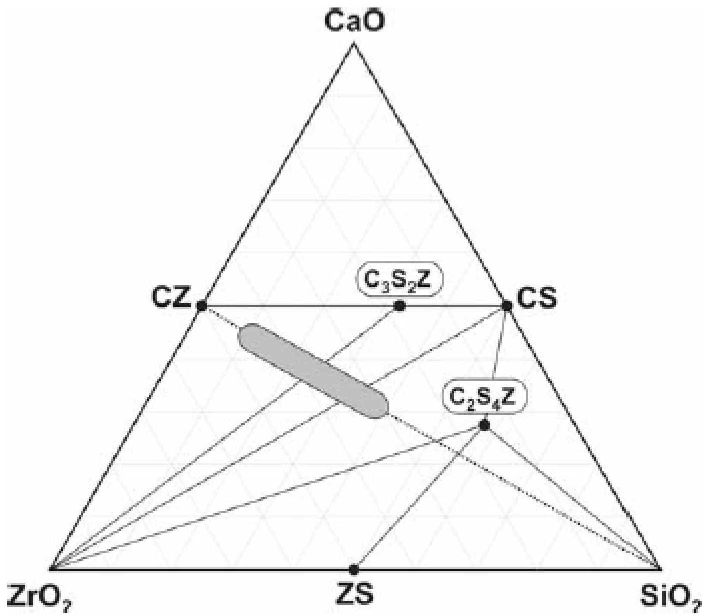


Fig. 13 Compatibility triangles in the ternary $CaO–ZrO_2–SiO_2$ (mol%) at 1,300 °C (modified after [39, 40]) serving as a first approximation for pertinent phase assemblages at the CMAS/YSZ interface. Shaded area represents the compositional variation of the Ca–Zr–Fe-silicate which plots close to the join $CZ-SiO_2$ (given by dotted line). Abbreviations: C = CaO, S = SiO_2, Z = ZrO_2, CZ = $CaZrO_3$, C_3S_2Z = $Ca_3ZrSi_2O_9$, C_2S_4Z = $Ca_2ZrSi_4O_{12}$, CS = $CaSiO_3$, ZS = $ZrSiO_4$. Compatibility triangles in the subsystem CaO–CZ–CS are omitted

Summary

- Project Goals are;
  - Reduce thermal conductivity 0.5 watt/m^{o}K
  - Increase surface temperature allowable by 100C
  - Significantly improve CMAS resistance
- Inter-Pass Boundaries will be used and optimized to lower thermal conductivity
- A top layer of GdZr will be used to:
  - Allow +100°C surface temperature + high purity SPPS
  - Reduce CMAS attack
- Al-Ti Metasable solutes+ will be added to the YSZ to reduce CMAS infiltration.
- CaSO4 will be used for the first time to arrest CMAS infiltration.

Summary

- Results will be validated with CMAS testing in cyclic furnace tests and high moisture tests
- Detailed mechanism of failure will be evaluated for the test run and Modification of the TBC will be made as mechanisms suggest.
- Substrates are to be supplied by Siemens and Pratt and Whitney

Questions ?