Advanced Thermal Barrier Coatings for Next Generation Gas-Turbine Engines Fueled by Coal-Derived Syngas

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Support
DoE NETL University Coal Research Program

DoE Project Officer
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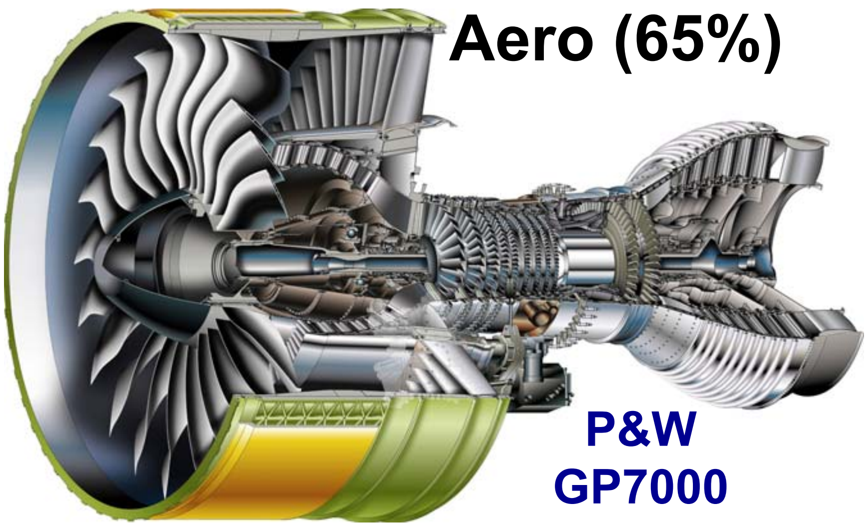
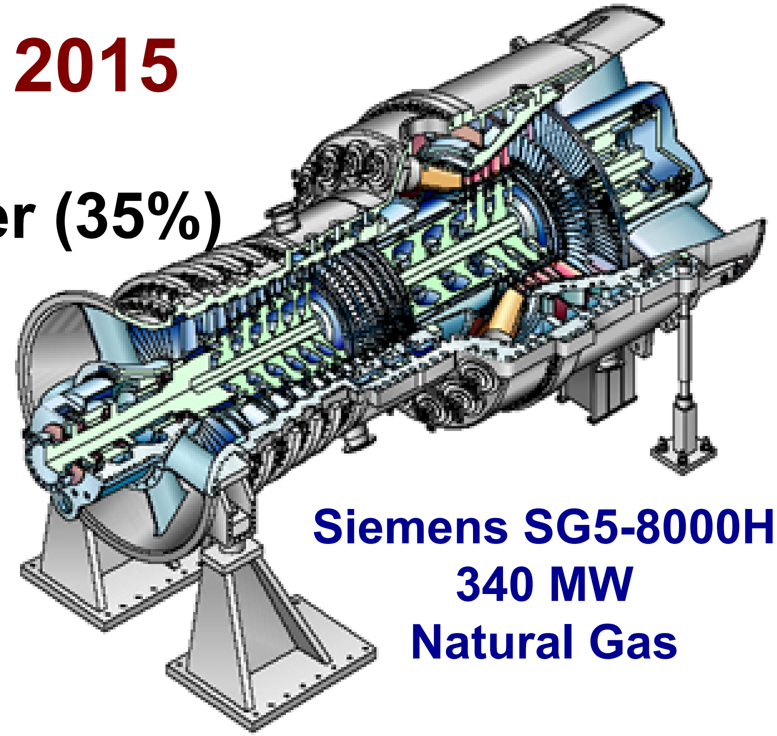
Gas-Turbine Engines: $55B by 2015

Aero (65%)



P&W
GP7000

Power (35%)



Siemens SG5-8000H
340 MW
Natural Gas

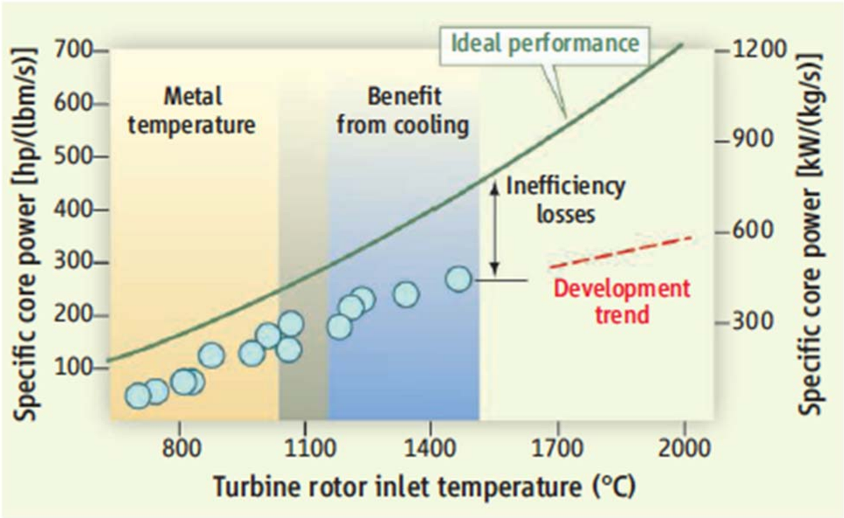
Langston, 2011

Motivation

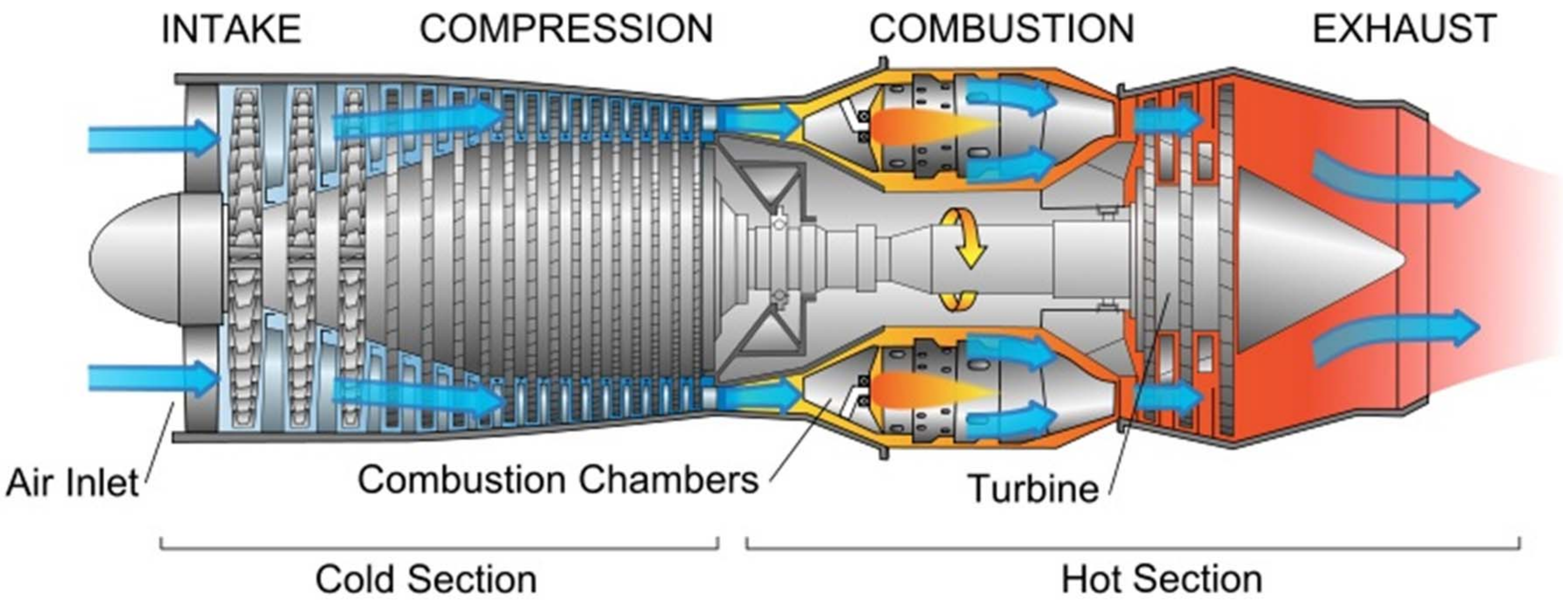
* **Need for Higher Power and Efficiency**
  - Aircraft Propulsion
  - Electricity Generation

* **Need for Higher Hot-Section Temps.**

* **Materials "Bottleneck":**
  - Improved Structural Alloys
  - Ceramic Matrix Composites
  - Ceramic Thermal Barrier Coatings (TBCs)



Perepezko, 2009



Ceramic Thermal Barrier Coatings (TBCs)

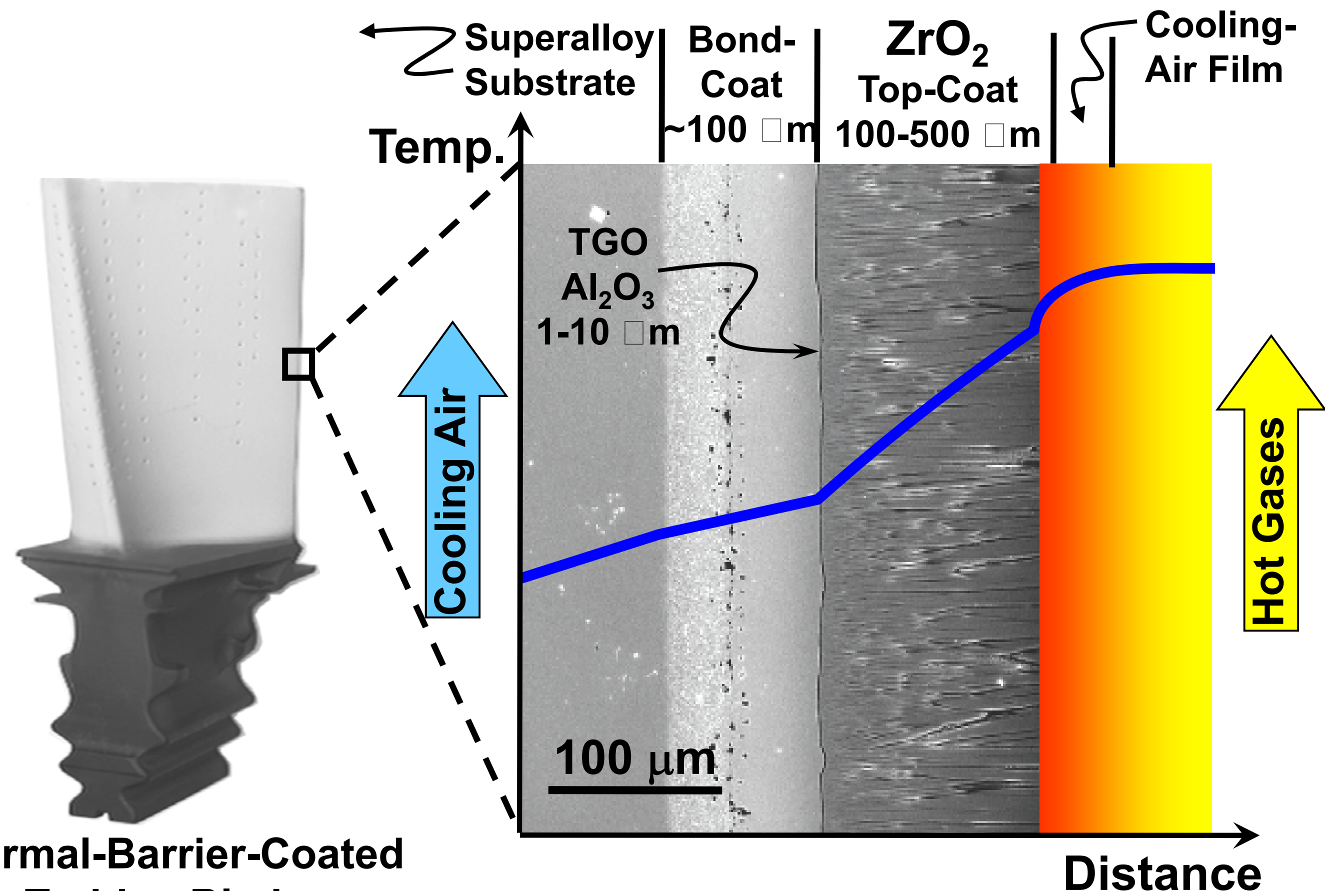
* Engines
  - Aero
  - Power

* Blades/Vanes, Combustors, Shrouds

* Strain-Tolerant, Low Th. Cond.

* Up to 300 ˚C Temp. Reduction

* Improved
  - Performance
  - Efficiency
  - Durability

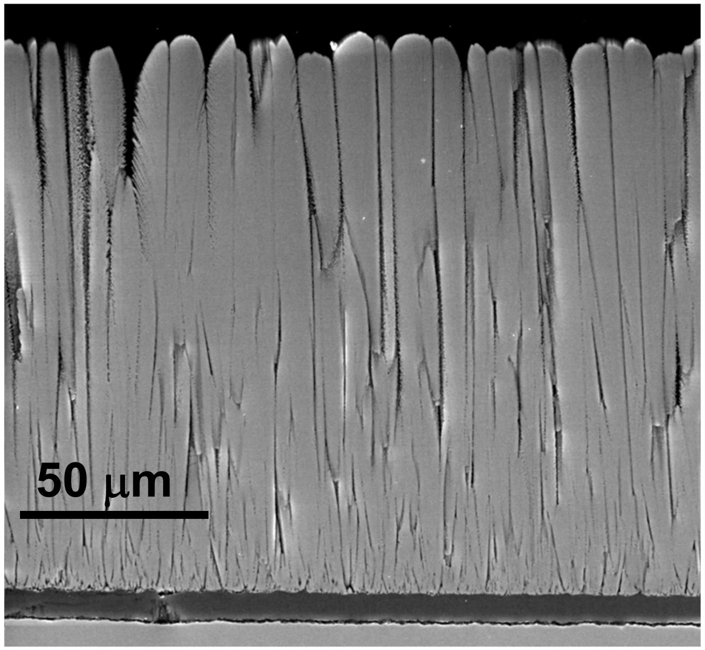


Thermal-Barrier-Coated Turbine Blade

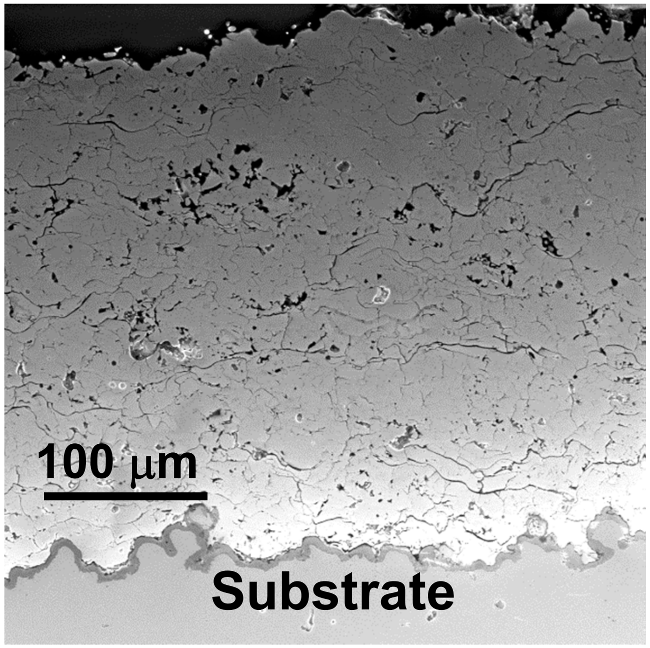
Science, 2002; *MRS Bull.*, 2012

Ceramic TBCs

Electron-Beam Physical Vapor Deposition



Air Plasma Spraying (APS)

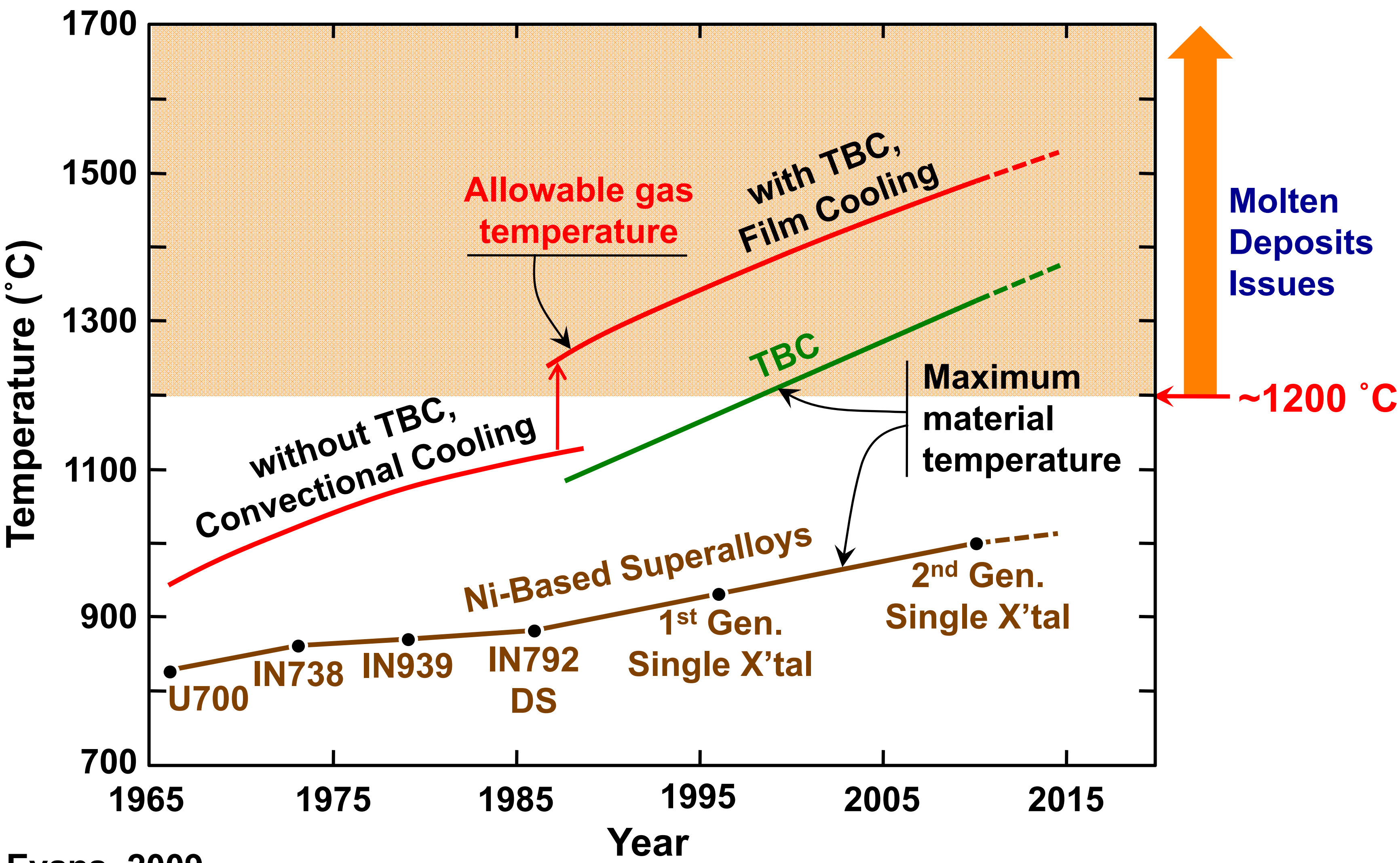


* Low Thermal Conductivity (ZrO_2 + 7 wt% Y_2O_3 Solid Soln.: 7YSZ)

* High Porosity (15 - 20%); Thickness 100 to 500 μm

* "Strain Tolerant" to Accomodate Th. Exp. Mismatch with Metal

Thermal Barrier Coatings (TBCs)



After Evans, 2009

Push for Higher Temperatures => New Materials Issues

Sources of Silicate Deposits in Aero Engines

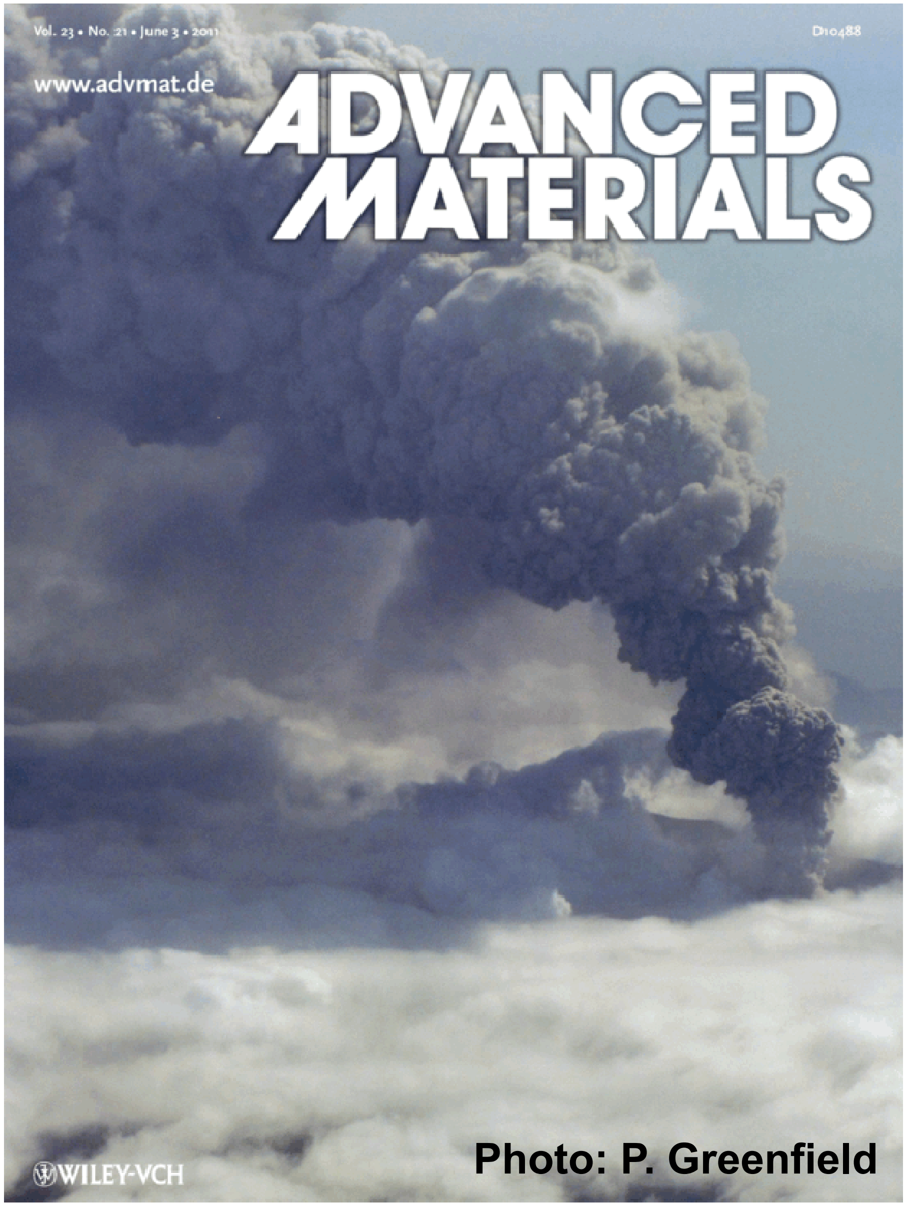
Calcium-Magnesium-Alumino-Silicate (CMAS) Sand

* **Sandstorms: ~0.1 mg/m^3**
  (Ansmann, *et al*. 2003)
* **Ambient: ~0.01 mg/m^3**
* **Runways: >1.0 mg/m^3 (?)**
* **Sand Ingested by Engines: 1 to 100 g/h**
  (Depends on Engine, Bypass Ratio...)

Damage to TBCs and Engines

Sources of Silicate Deposits in Aero Engines

Volcanic Ash CMAS



* Eyjafjallajökull Eruption in Iceland in 2010

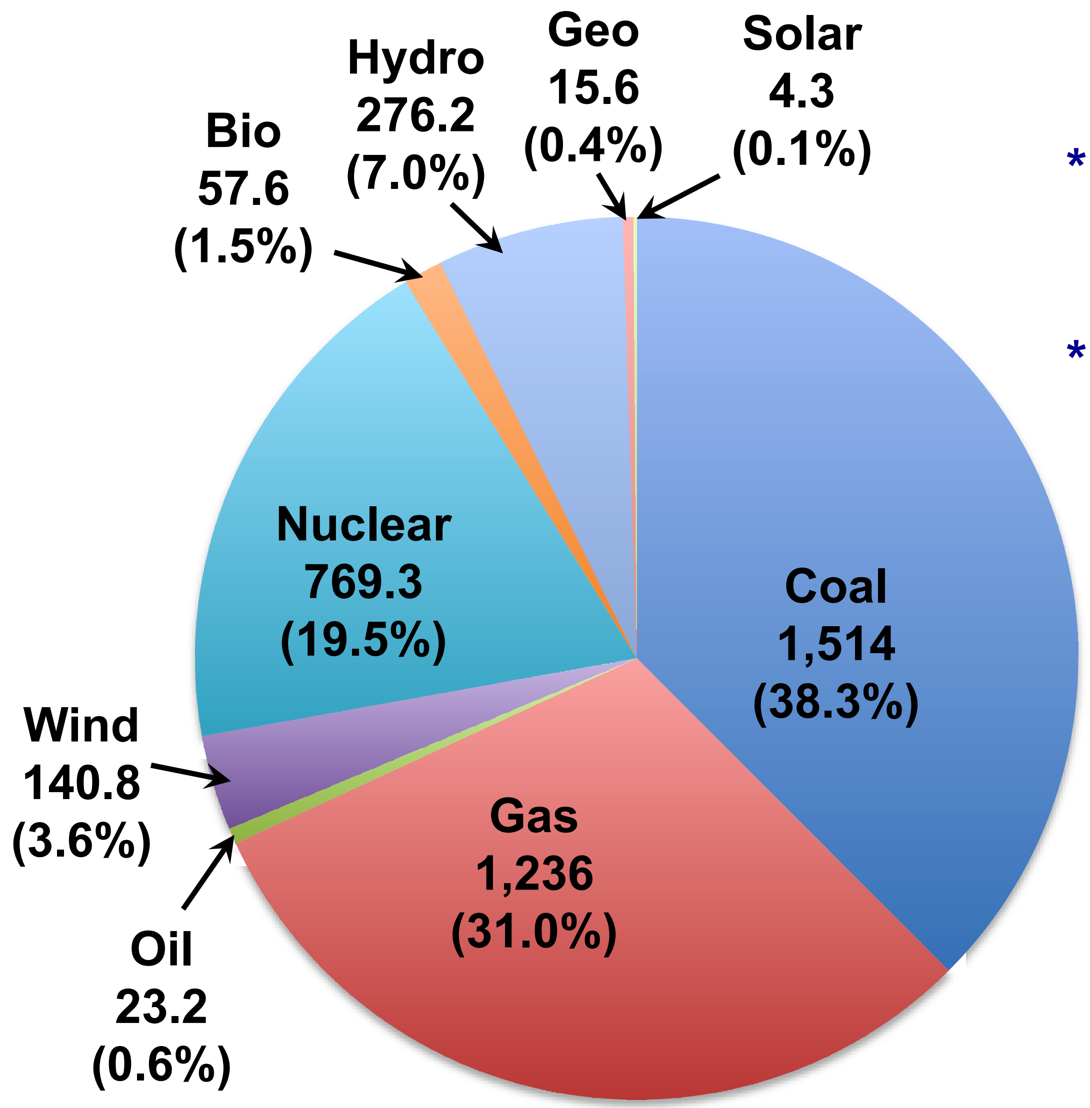
* Shut Down of Vast European Air Space for Several Days

* Economic Loss Approaching $2B

* Conc.: No-Fly Zone: >4.0 mg/m^3
Limited-Fly: 2.0-4.0 mg/m^3
Unrestricted: <2.0 mg/m^3
(Sultana, 2010)

Damage to TBCS and Engines

Sources of Silicate Deposits in Power Engines



* USA Electricity Generation by Source in 2012

* USA Total ~4,000 Billion KWh (World ~20,000 Billion KWh)

Need for Environmentally Responsible, Efficient Way of Using Available Coal

US Energy Info. Admin.
http://www.eia.doe.gov/fuelelectric.html

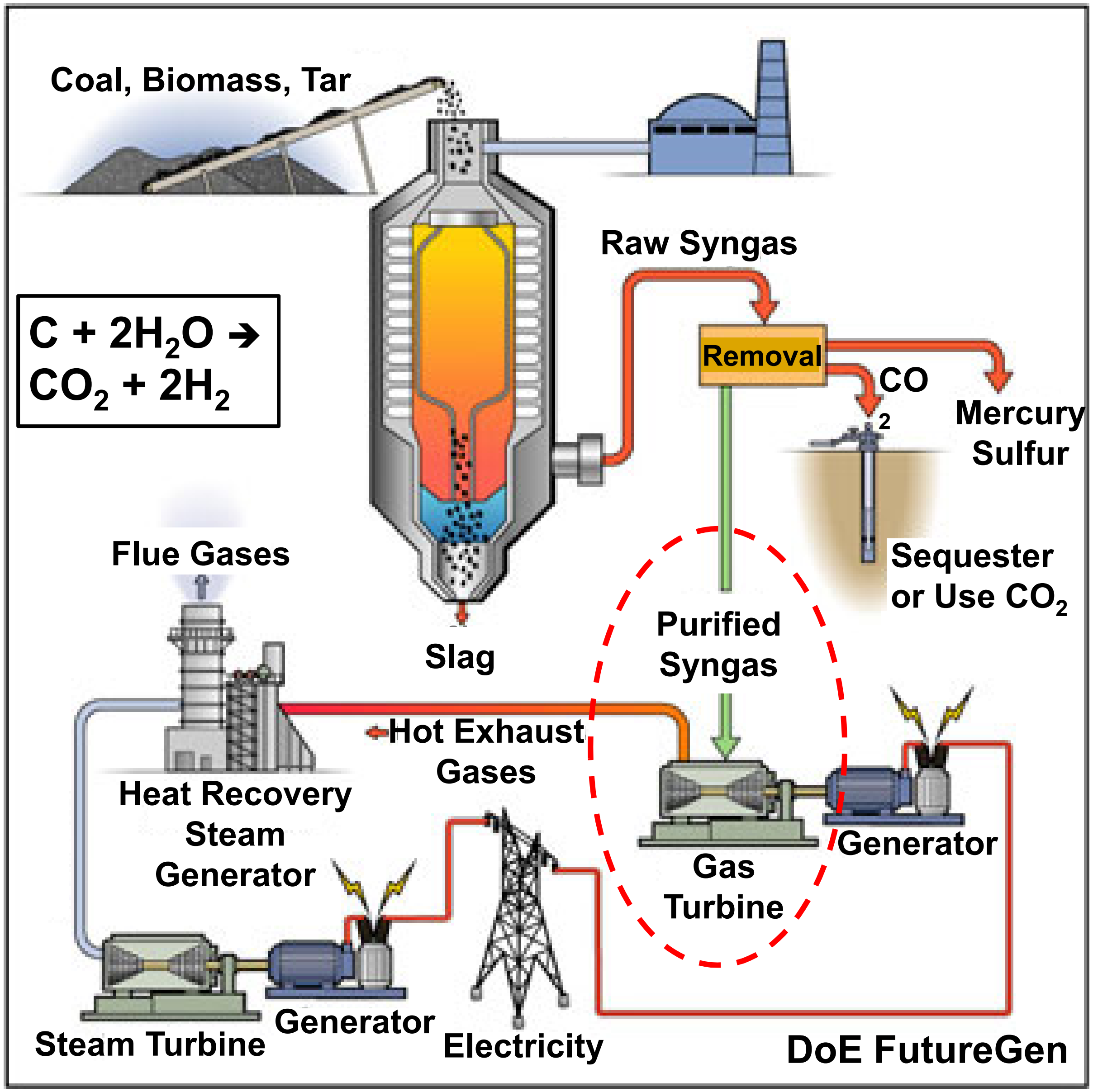
Sources of Silicate Deposits in Power Engines

Fly Ash CMAS

* Syngas Produced from Abundant Coal + H_2O
* CO_2 Capture/Sequester
* IGCC Plants Highly Efficient (~55%)
* H_2-Rich Syngas-Fired: Higher Temps., Water
    * F-Class: 1370 ˚C
    * H-Class: 1430 ˚C
    * J-Class: 1480 ˚C
    * X-Class: 1700 ˚C
* Syngas has Fly Ash (0.4 mg/m^3) (R. Wenglarz)
* Amb. Dust (0.01-0.1 mg/m^3)
* Kgs/day

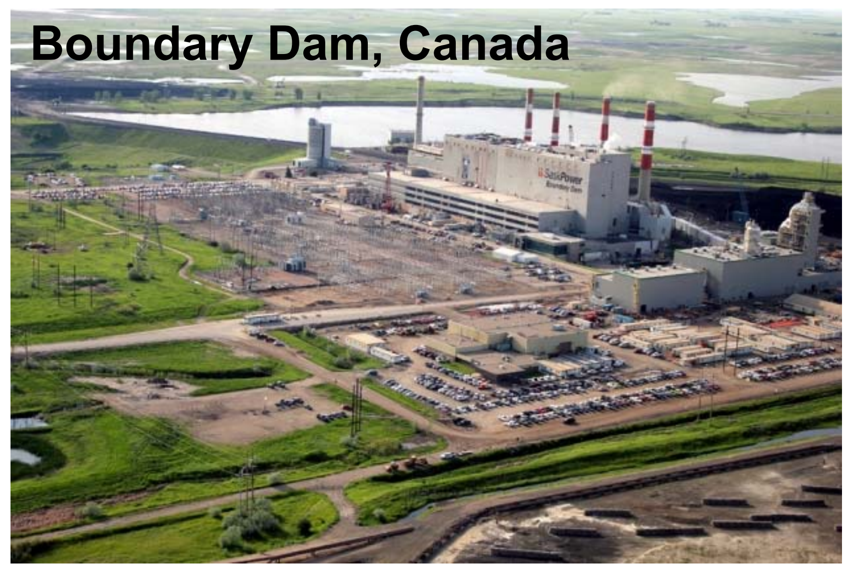
Damage to TBCs and Engines

Integrated Gasification Combined Cycle (IGCC)



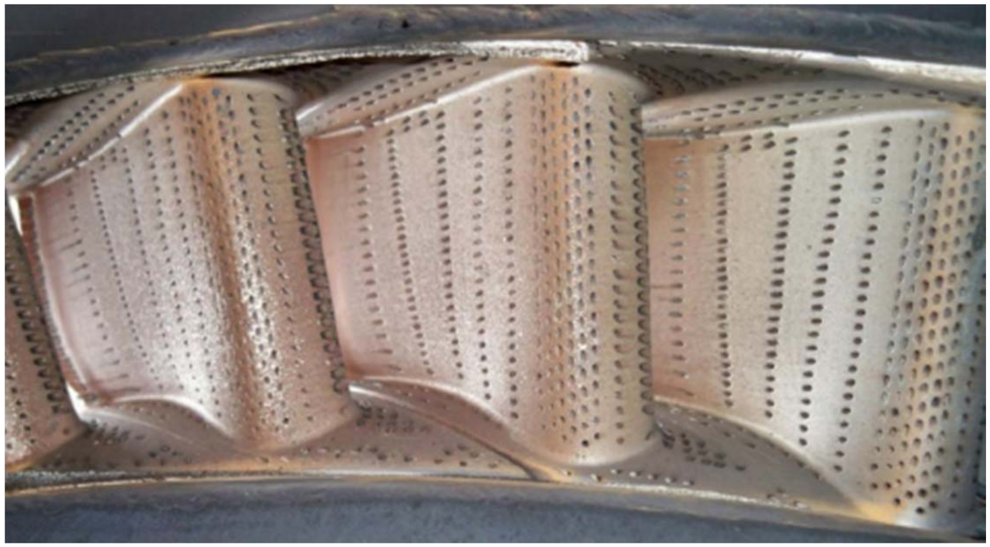
IGCC Power Plants

DoE

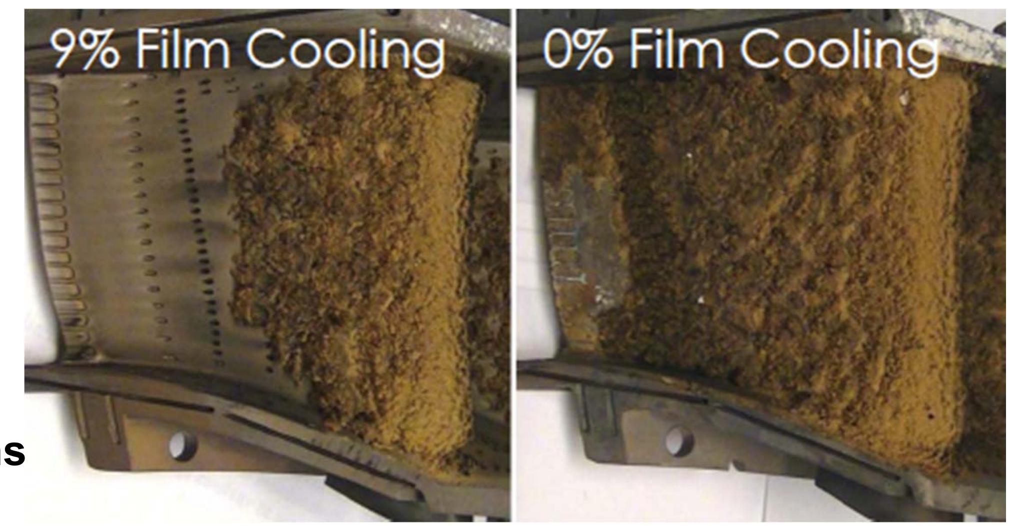


Sources of Silicate Deposits in Power Engines

Fly Ash (Lignite) Injection Tests on Hot Vanes (without TBC)



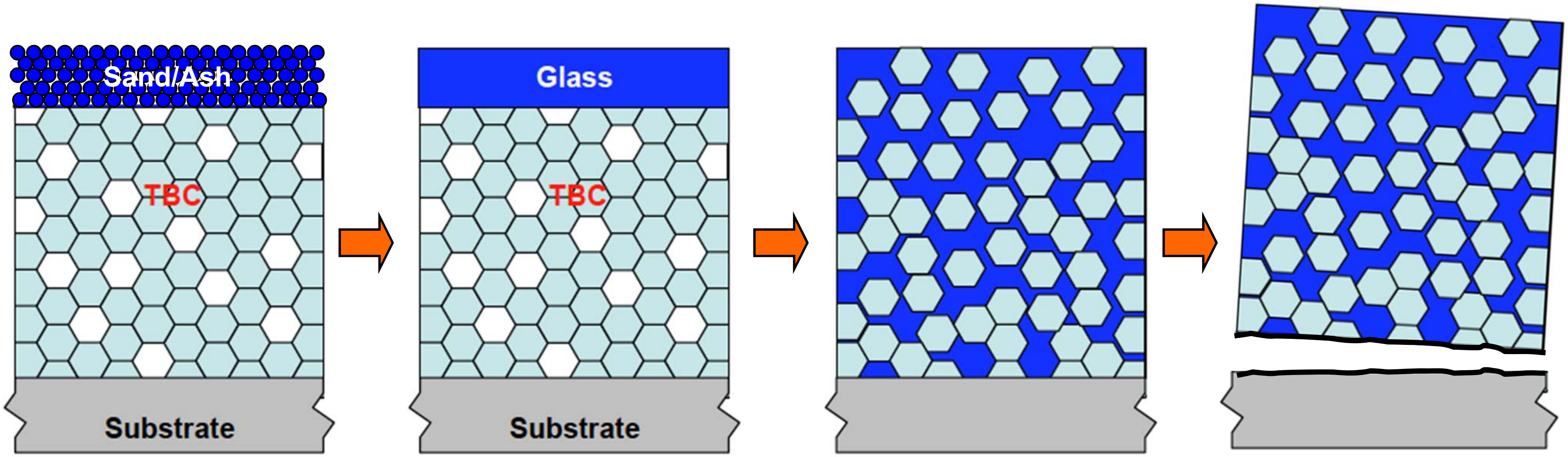
1010 ˚C
1 h Fly Ash Injection



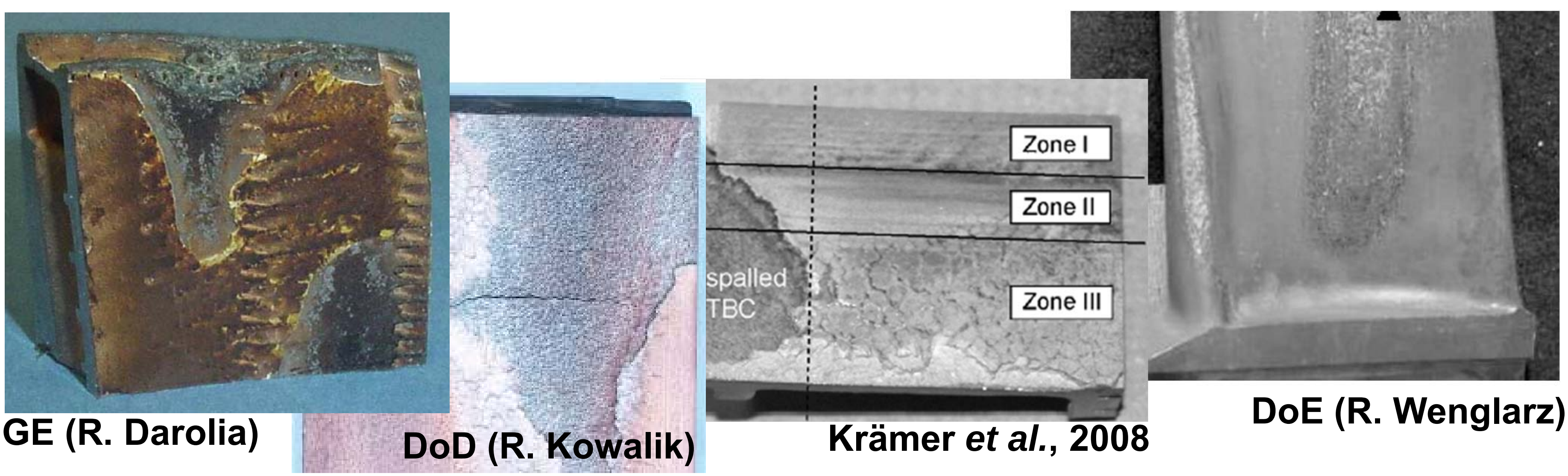
1066 ˚C
0.5 h Fly Ash Injection

J. Bons

Thermo-Chemo-Mechanical Damage of TBCs



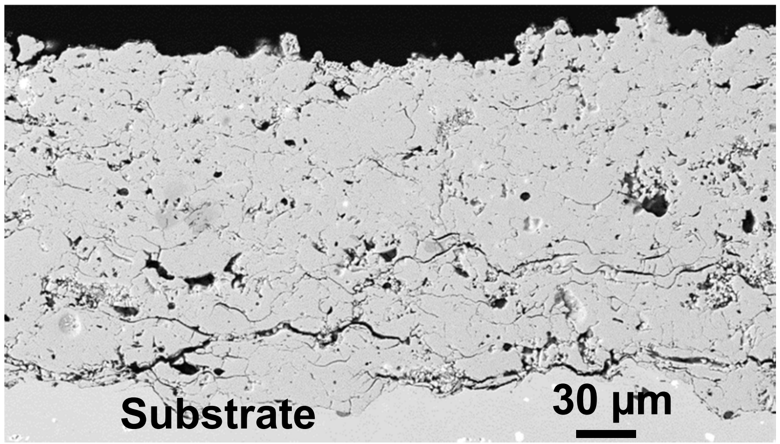
Accumulation → Melting → Penetration, Exfoliation → Loss of Strain Tolerance

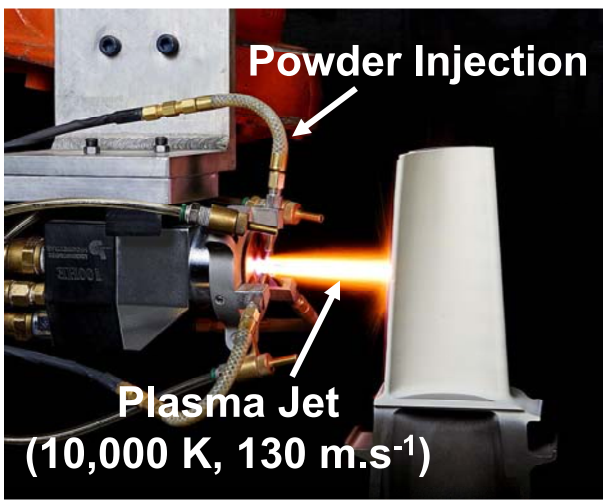


GE (R. Darolia) DoD (R. Kowalik) Krämer *et al.*, 2008 DoE (R. Wenglarz)

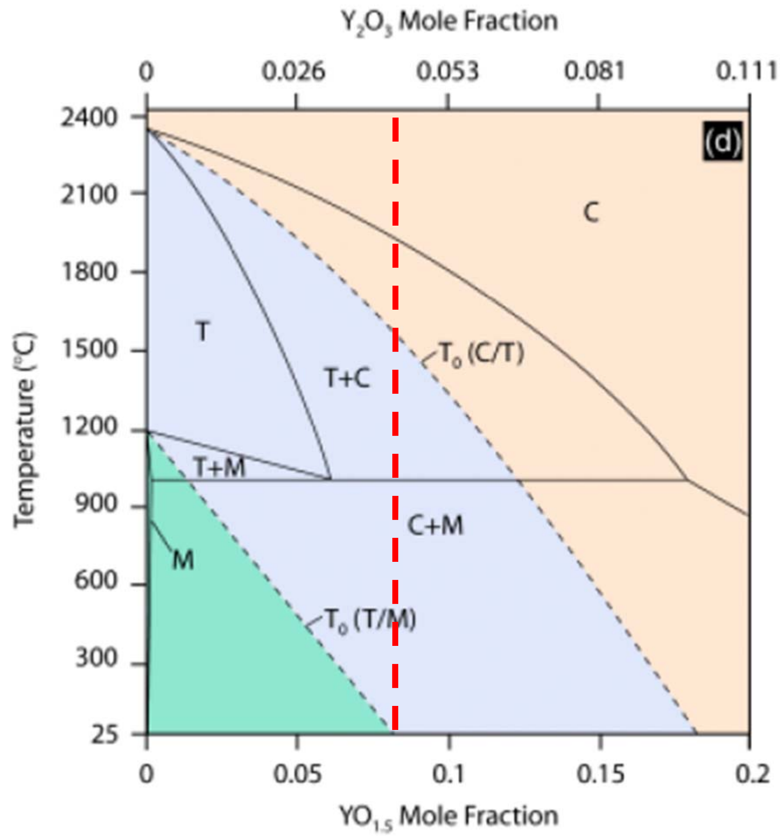
Molten Silicates Damage to APS 7YSZ TBCs

Air Plasma Spray (APS)
7 wt% Y_2O_3 Stabilized ZrO_2 (7YSZ) TBC





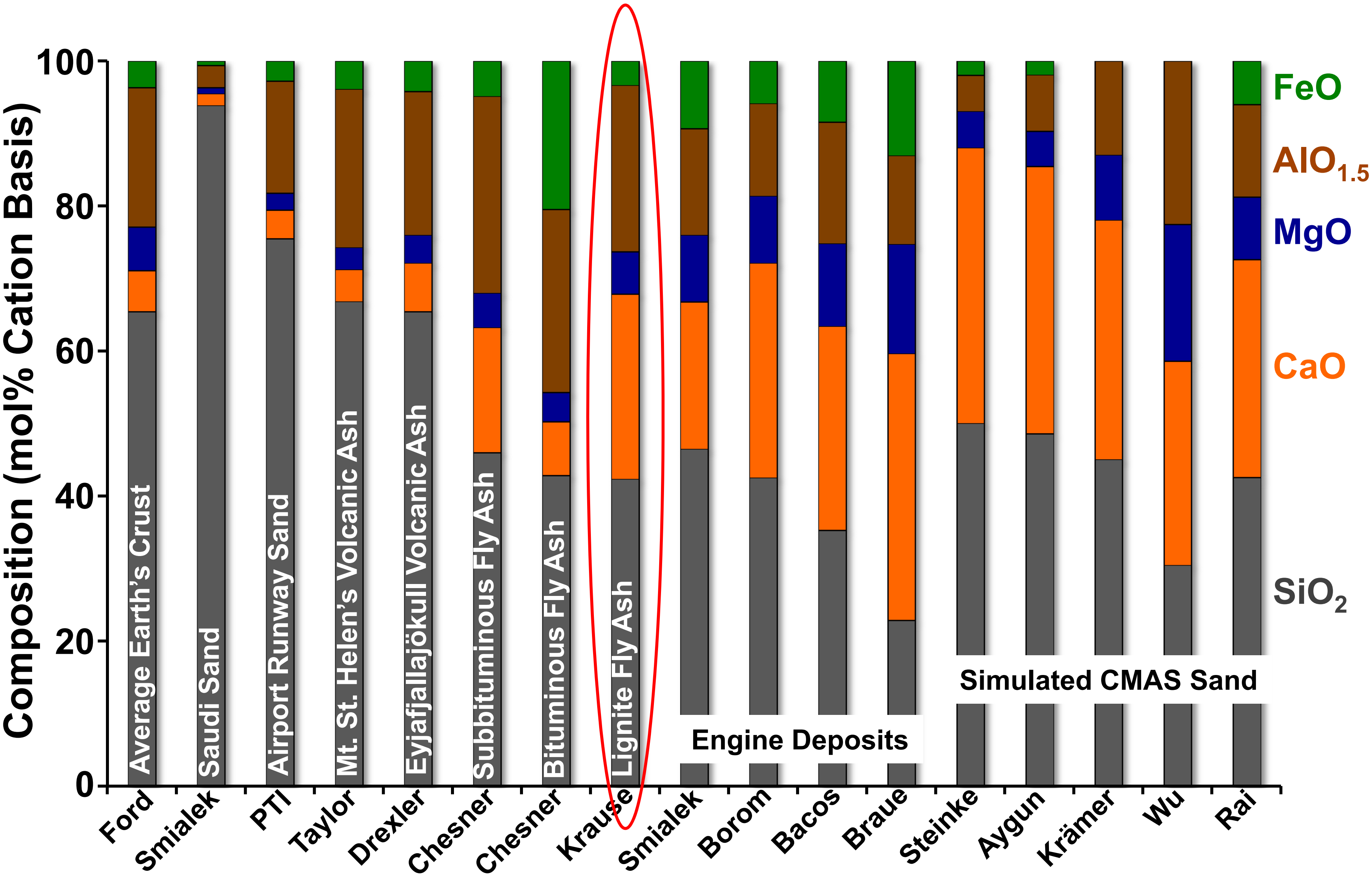
S. Sampath



Chevalier *et al.* 2009

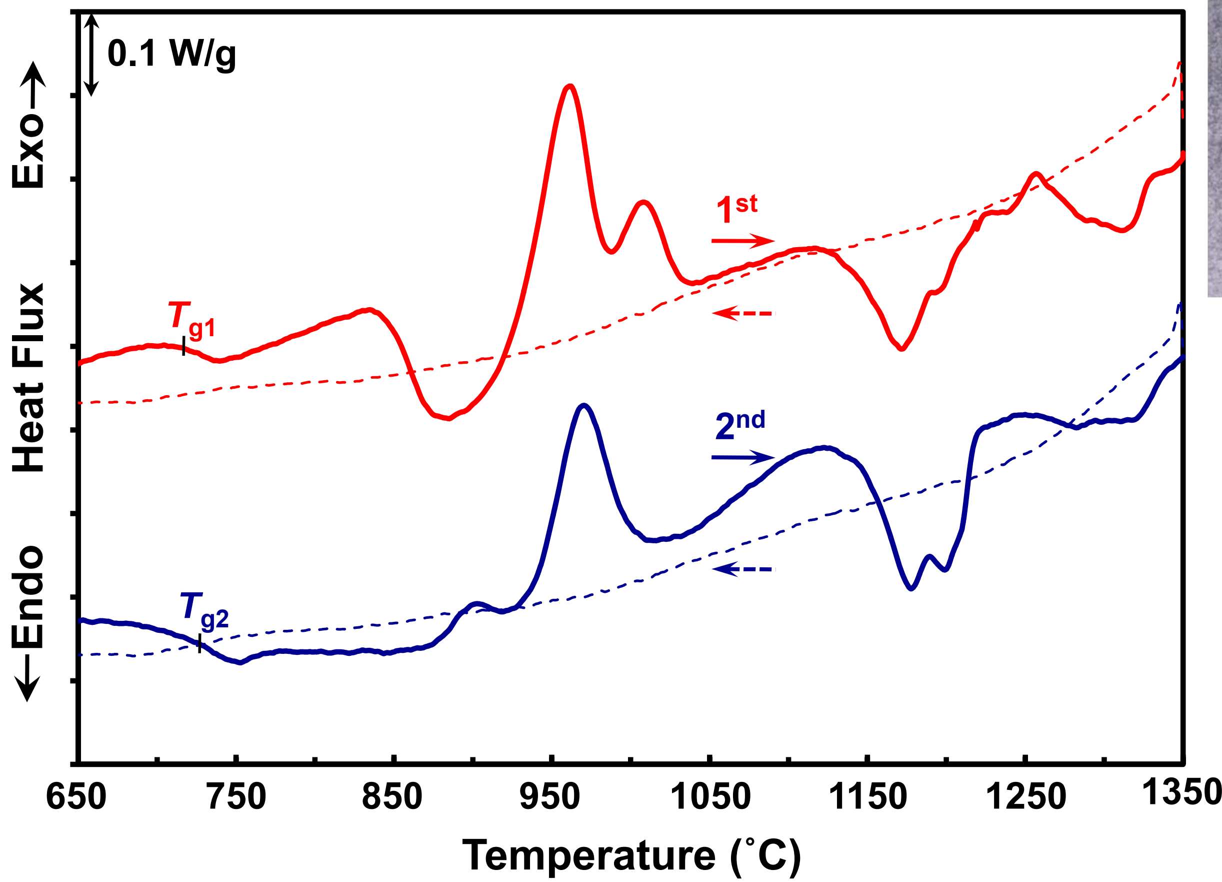
7YSZ *t'* phase has high toughness due to reversible ferroelastic toughening.

Major CMAS Compositions



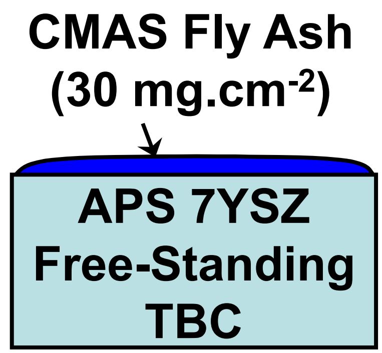
After Levi *et al.*, 2012

Remelted Lignite Fly Ash (CMAS)

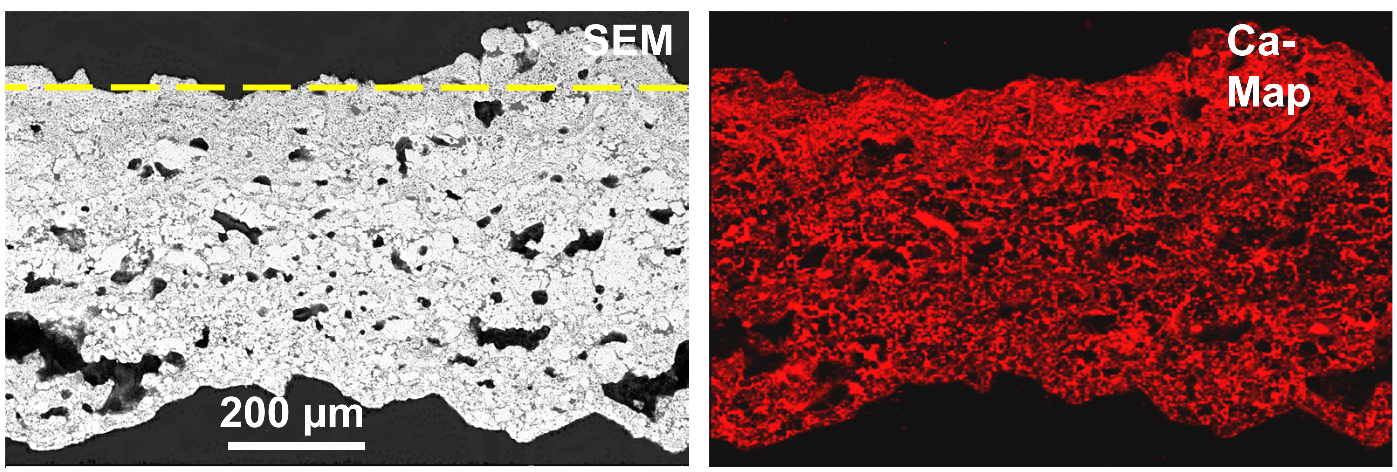


* Remelted (1500 ˚C) Lignite Fly Ash (Ball-Milled): Glass Powder
* Glass Transition -> Surface Crystallization -> Crystallization -> Melting
* Fully Molten at 1350 ˚C; Refreezes as Bulk Glass
* TBC/CMAS Experiments at ~1350 ˚C to Ensure Molten Glassy CMAS

APS 7YSZ TBCs Interactions with Fly Ash CMAS

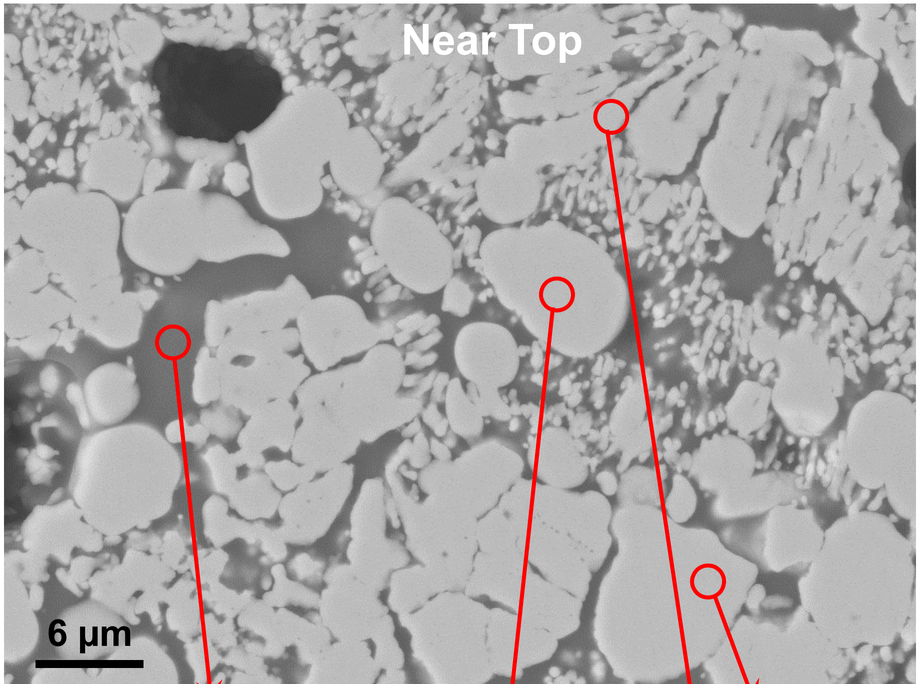


Heat-Treatment 1340 ˚C, 24 h



TBC Fully Penetrated

APS 7YSZ TBCs Interactions with Fly Ash CMAS

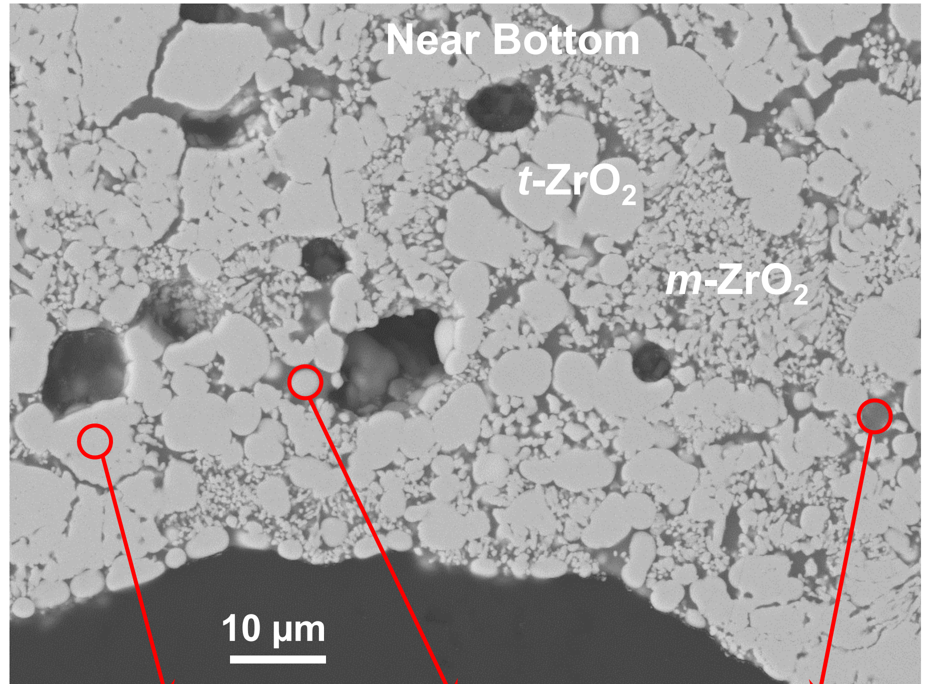


Na	2
Mg	4
Al	17
Si	38
Ca	24
Ti	1
Fe	2
Y	3
Zr	9

Ca	3
Fe	1
Y	12
Zr	84

Si	2
Ca	3
Y	6
Zr	89

Y	9
Zr	91



Si	2
Ca	2
Y	8
Zr	88

Mg	2
Al	8
Si	18
Ca	12
Fe	2
Y	9
Zr	49

Na	2
Mg	4
Al	14
Si	29
Ca	18
Fe	2
Y	4
Zr	27

EDS Composition Atom % Cation Basis

CMAS Damage Mechanisms in 7YSZ

* CMAS Melts into a Glass

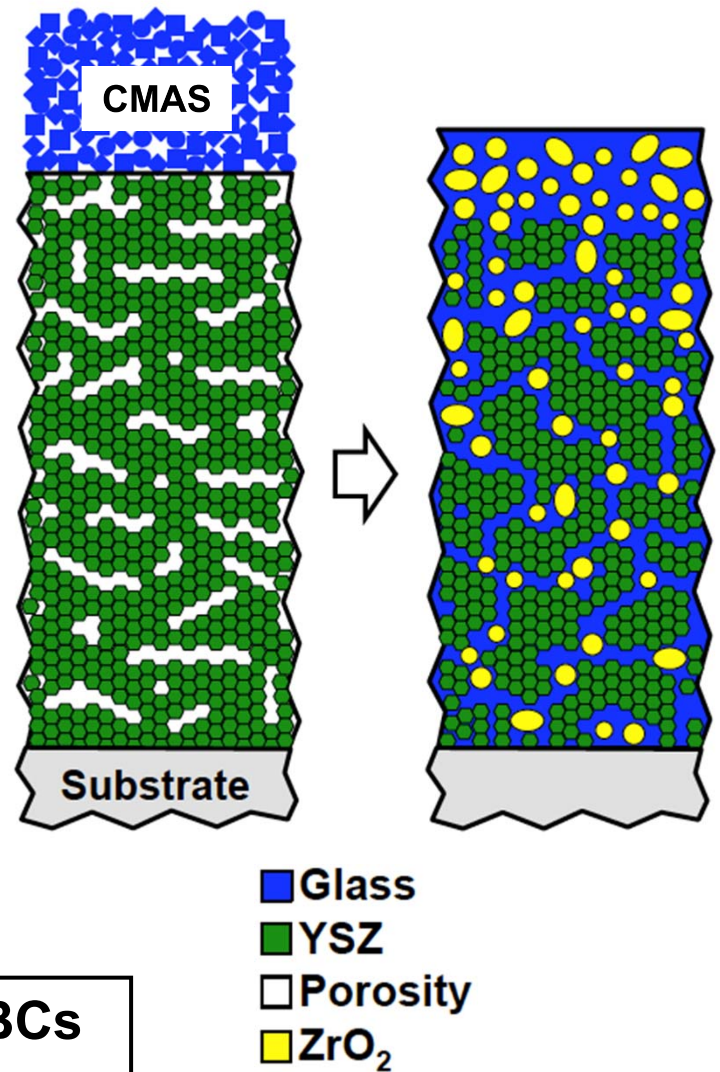
* Infiltrates Pores/Cracks

* Penetrates 7YSZ Grain Boundaries

* Dilatation and Exfoliation

* Reaction Between CMAS and 7YSZ: Dissolution of Some *t'*-7YSZ, Reprecipitation as Y-Depleted *m*-ZrO_2 and *t*-ZrO_2, Glass Y-Enriched

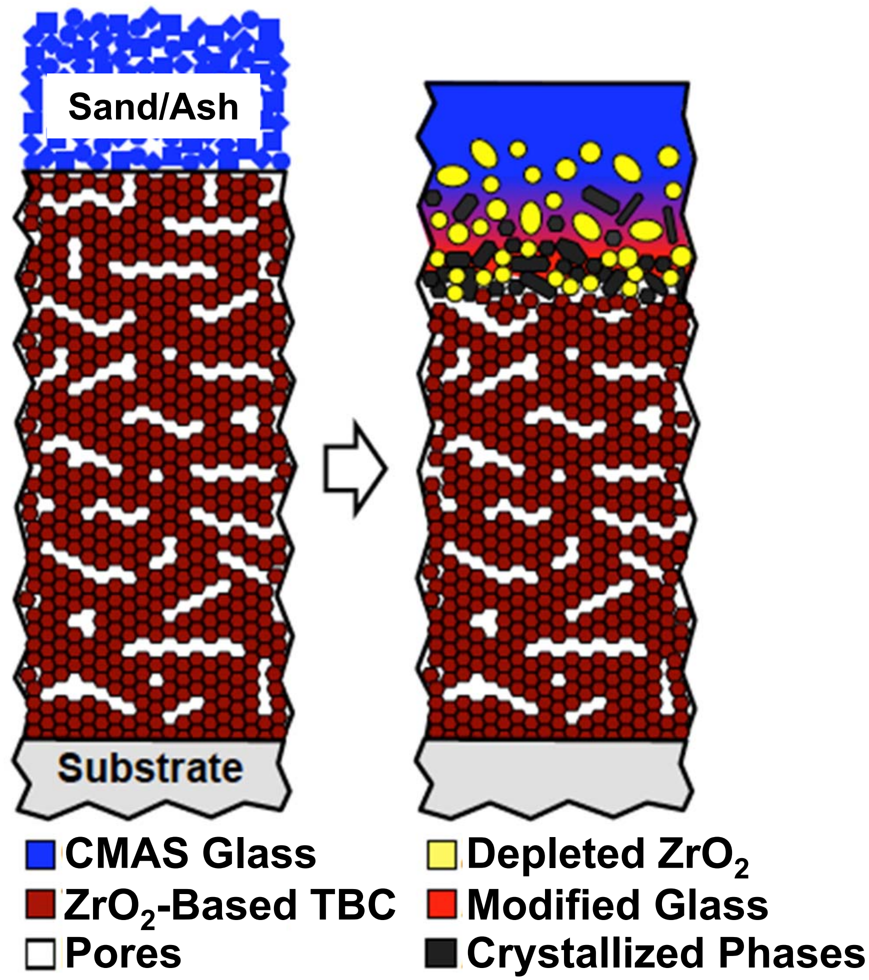
* Little Effect on Glass Composition with Small Amount of Solute (Y_2O_3) in TBC: Y:Zr :: 0.083:1



Optimized 7YSZ TBCs Not Suitable for Repelling CMAS Attack

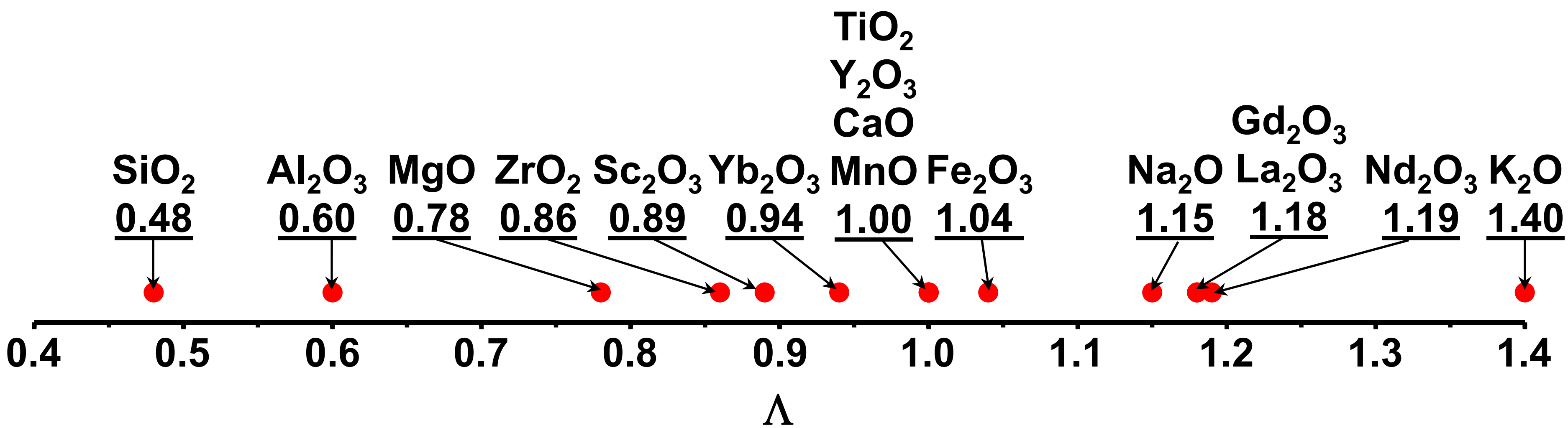
CMAS Damage Mitigation Approach

* Vigorous Reaction Between TBC and CMAS
* Large Amount of Solute in ZrO_2-Based TBC: Solute:Zr :: 1:1 (cf. Y:Zr :: 0.083:1 in 7YSZ)
* Rapid Accumulation of Solute in CMAS Glass Over Short Penetration Depth
* Crystallization of Modified CMAS
* Refractory Crystallized Phases Seal TBC
* Arrest of CMAS Front



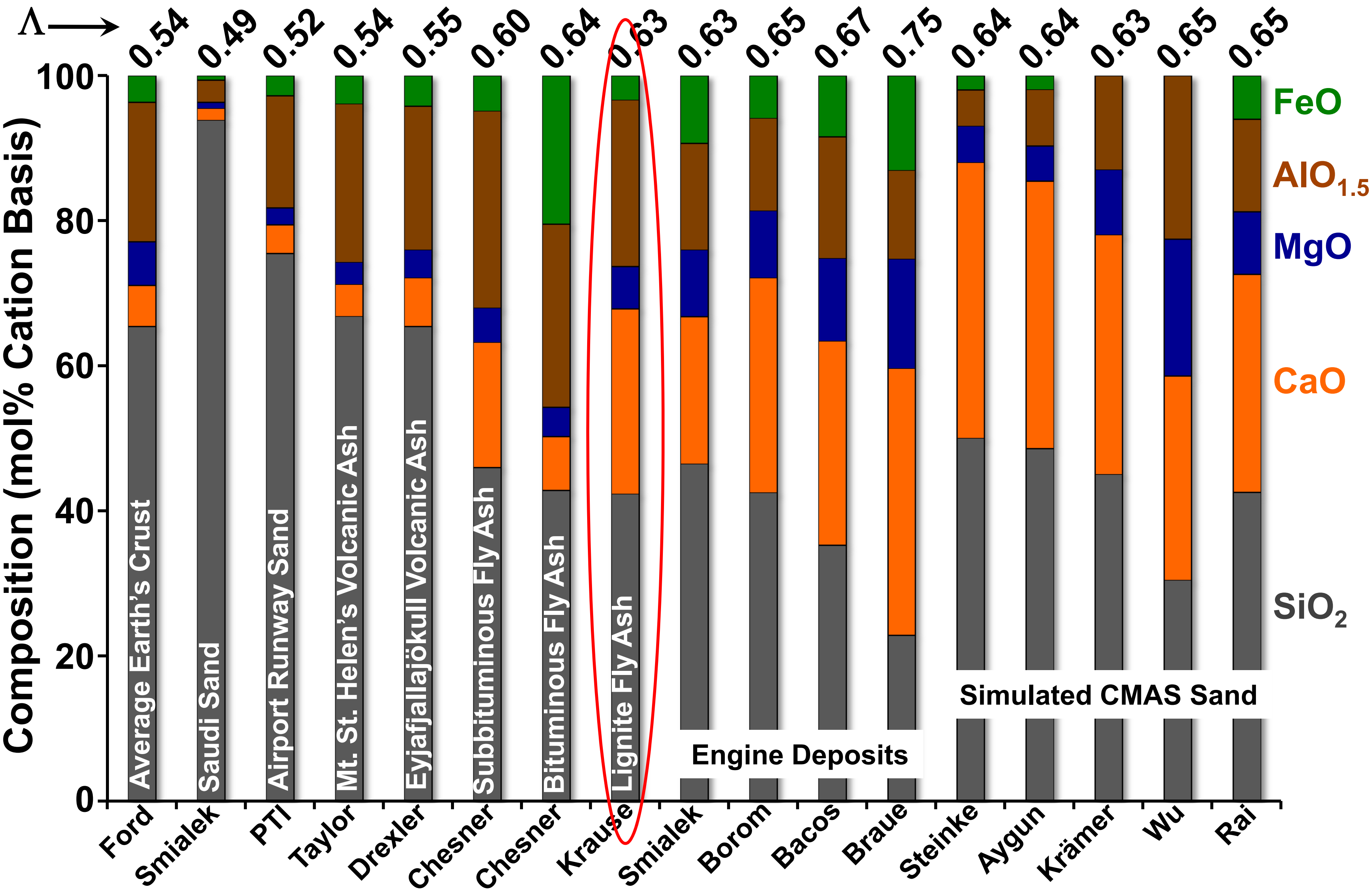
TBC/CMAS Reactivity: Optical Basicity (Λ) Concept

* Used in Glass Science to Determine Chemical Reactivity (Duffy *et al.*)
* Based on Lewis Acid-Base Theory
* Ability of O^{2-} to Donate Electrons
* Depends on the Polarizability of the Cation(s)
* Measured Using UV-Spectroscopy, XPS, Refractivity, Electronegativity
* $\Lambda = X_A \times \Lambda_A + X_B \times \Lambda_B + X_C \times \Lambda_C + \ldots$
* Reactivity Between Oxides Proportional to $\Delta\Lambda$: Large $\Delta\Lambda$ TBC/CMAS



Duffy; Dimitrov and Sakka

Major CMAS Compositions: Optical Basicities



After Levi *et al.*, 2012

CMAS Damage Mitigation Approach: Optical Basicity and "Model" Study

* Effects of "Solute" Type and Concentration in TBC Ceramics
  - Ionic Radii: $Gd^{3+} > Y^{3+} > Yb^{3+}$
  - Concentration: Low and High

TBC Compositions	Solute:Zr Ratio	Λ	$\Delta\Lambda$ (Fly Ash Λ 0.63)
7YSZ	0.083:1	0.87	0.24
6.8GdSZ	0.083:1	0.88	0.25
$Y_2O_3.2ZrO_2$	1:1	0.92	0.29
$Gd_2Zr_2O_7$	1:1	1.00	0.37
$Yb_2Zr_2O_7$	1:1	0.89	0.26

High Reactivity Between TBCs and Fly Ash CMAS Expected

TBC Ceramics/CMAS Interactions: “Model” Study

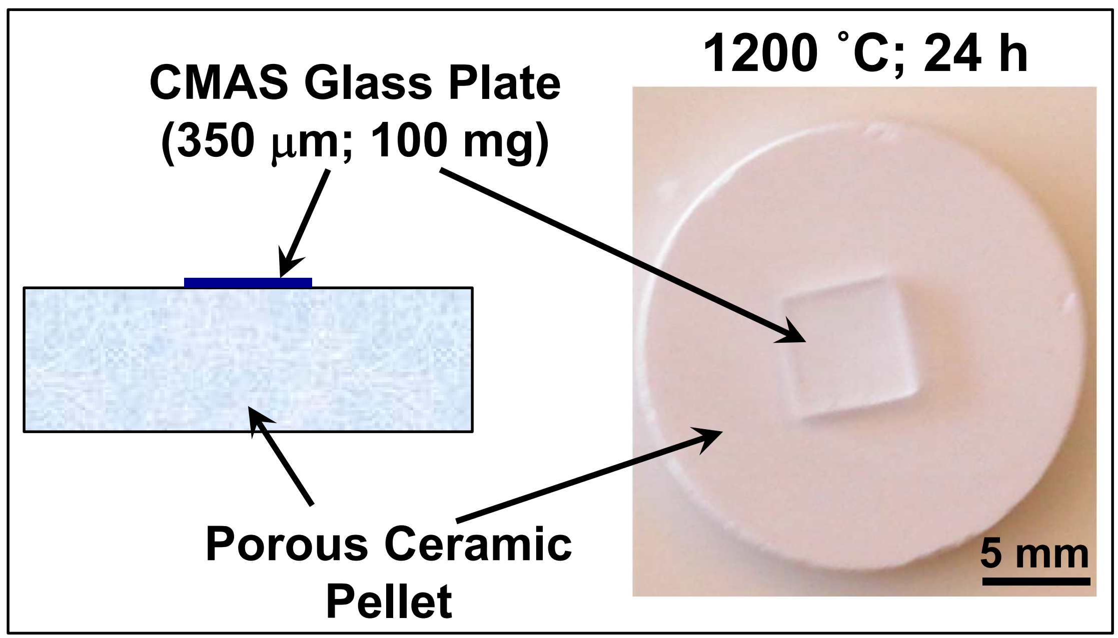
* Effects of “Solute” Type and Concentration in TBC Ceramics

TBC Compositions	Solute:Zr Ratio
7YSZ	0.083:1
6.8GdSZ	0.083:1
$Y_2O_3.2ZrO_2$	1:1
$Gd_2Zr_2O_7$	1:1
$Yb_2Zr_2O_7$	1:1

* Partially Sintered Ceramic Pellets (~15% Porosity)

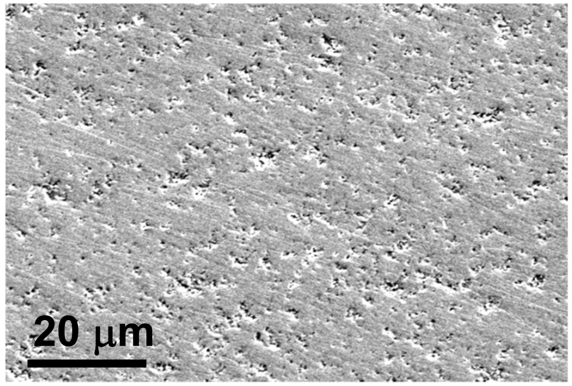
* Sand CMAS Glass: Λ = 0.63

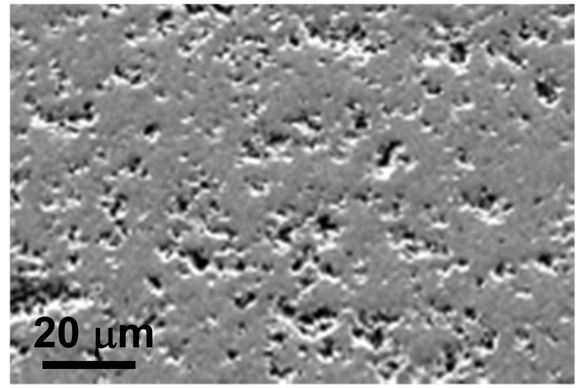
Acta Mat. 2012



TBC Ceramics/CMAS Glass Interactions

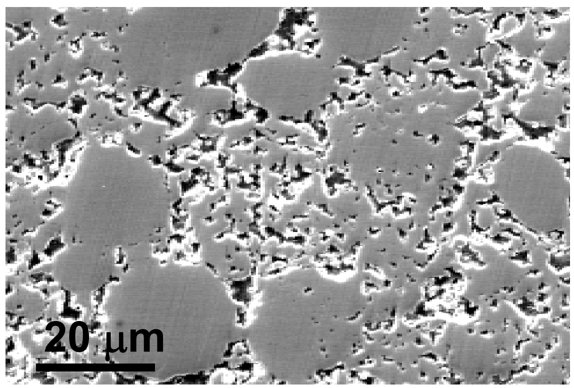
7YSZ
3.9 m% Y_2O_3
Y:Zr::0.08:1

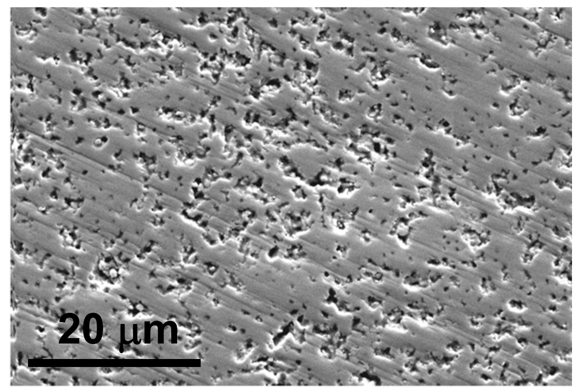




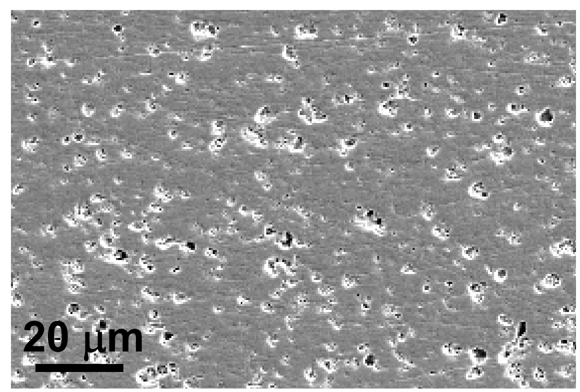
$Y_2O_3.2ZrO_2$
33.3 m% Y_2O_3
Y:Zr::1:1

6.8GdSZ
3.9 m% Gd_2O_3
Gd:Zr::0.08:1





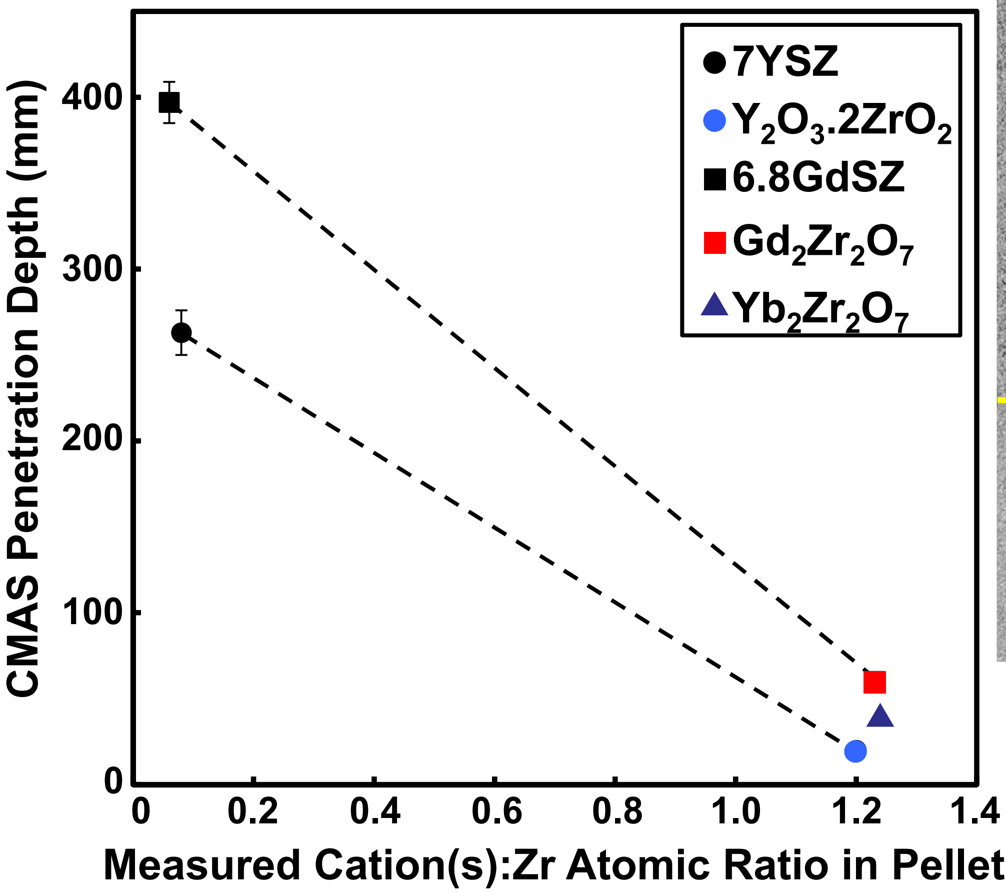
$Gd_2Zr_2O_7$
33.3 m% Gd_2O_3
Gd:Zr::1:1

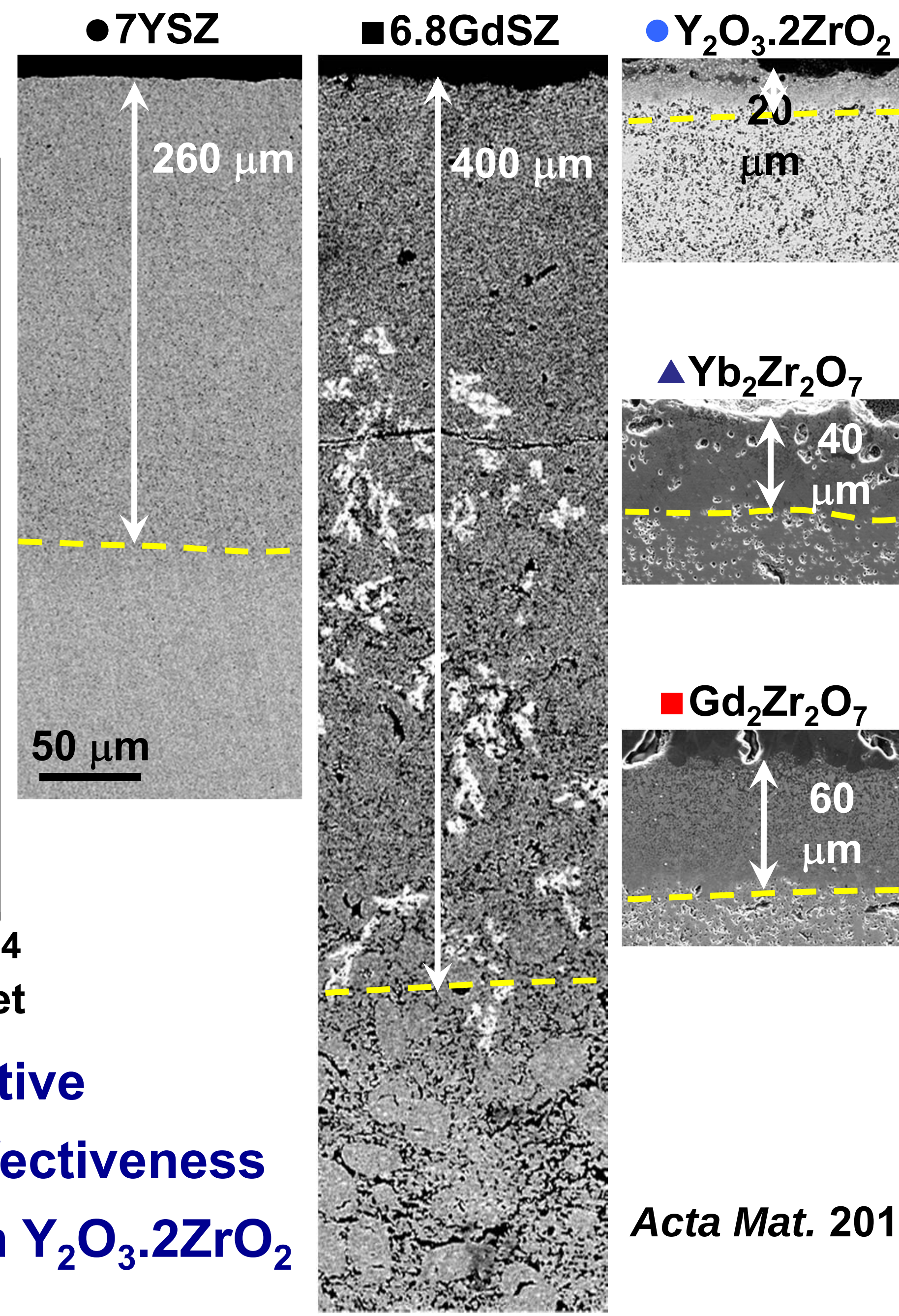


$Yb_2Zr_2O_7$
33.3 m% Yb_2O_3
Yb:Zr::1:1

TBC Ceramics/CMAS Interactions

1200 ˚C; 24 h

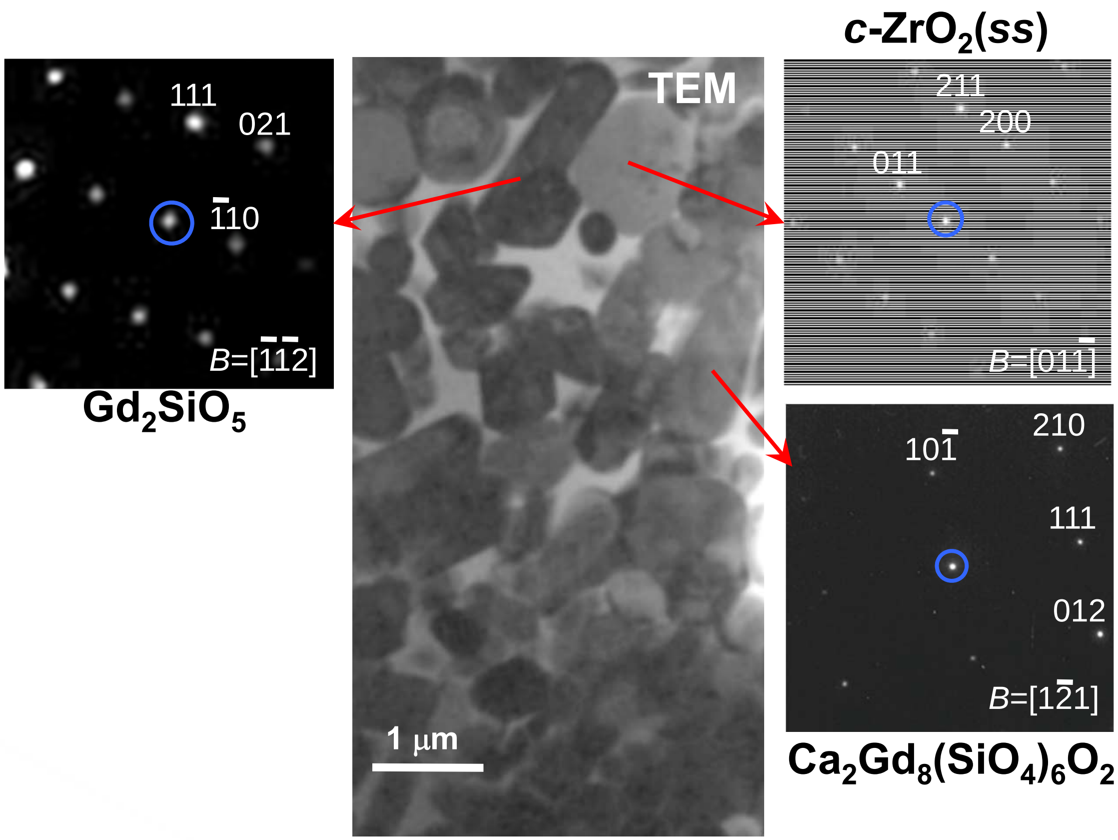


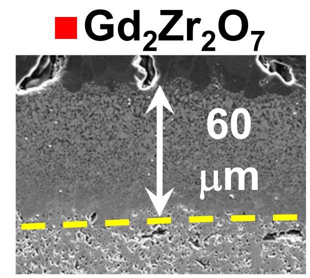


* Solute Concentration Most Effective
* At High Conc.: Gd < Yb < Y in Effectiveness
* Almost Complete Suppression in $Y_2O_3.2ZrO_2$

Acta Mat. 2012

$Gd_2Zr_2O_7$

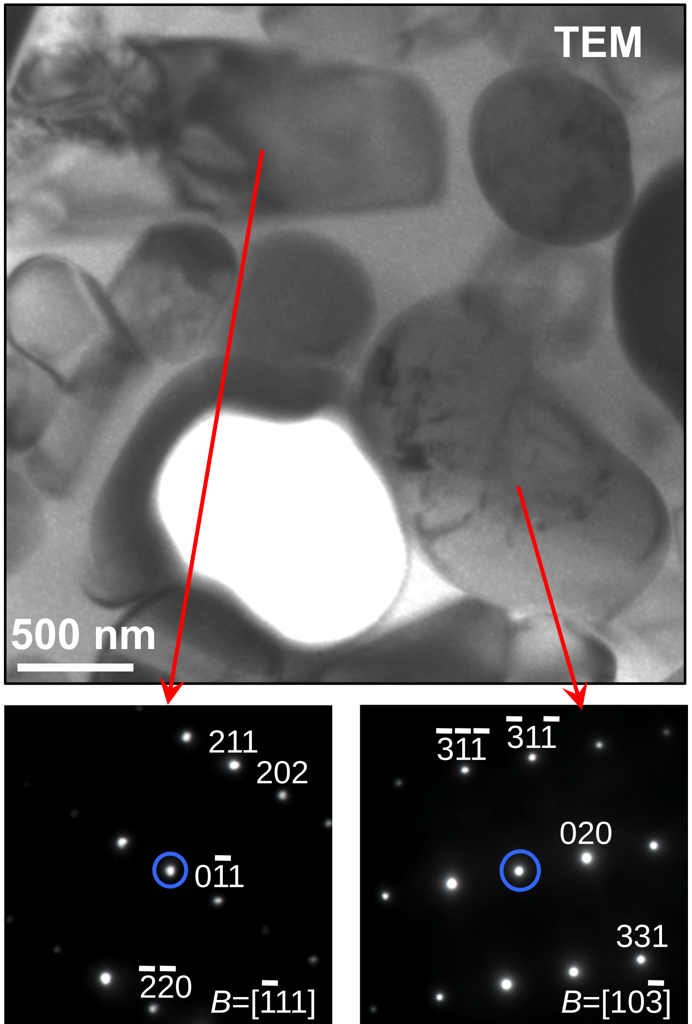




Primary Crystallized Phase in Arrest Region: $Ca_2Gd_8(SiO_4)_6O_2$

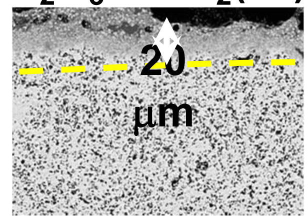
***Acta Mat.* 2012**

$Y_2O_3.2ZrO_2(ss)$



$Ca_4Y_6(SiO_4)_6O$ c-$ZrO_2(ss)$

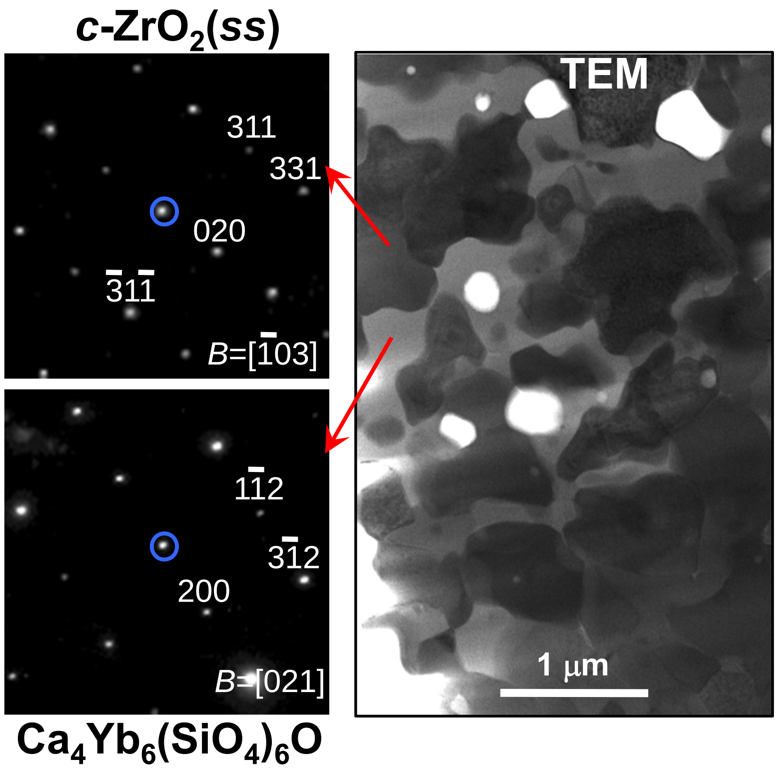
$Y_2O_3.2ZrO_2(ss)$

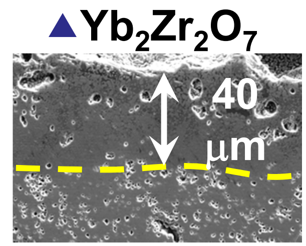


Primary Crystallized Phase in Arrest Region: $Ca_4Y_6(SiO_4)_6O$

***Acta Mat.* 2012**

$Yb_2Zr_2O_7$

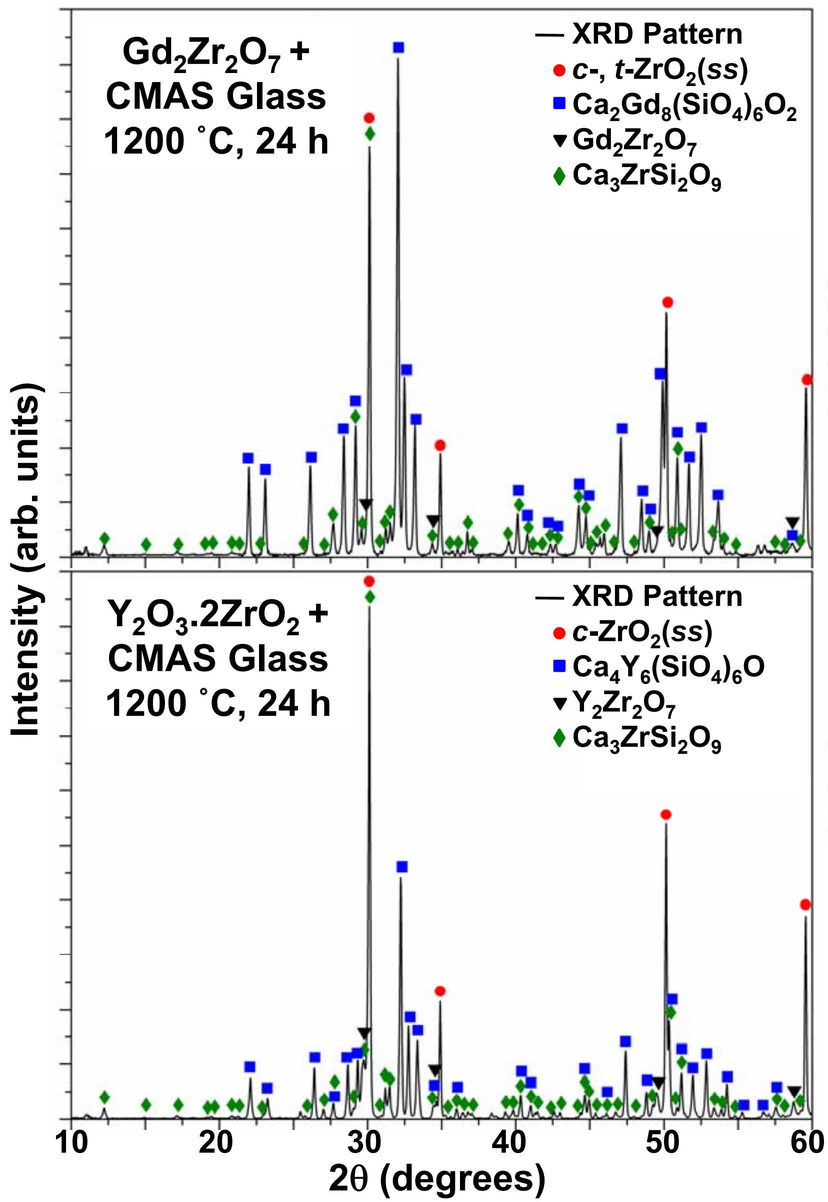




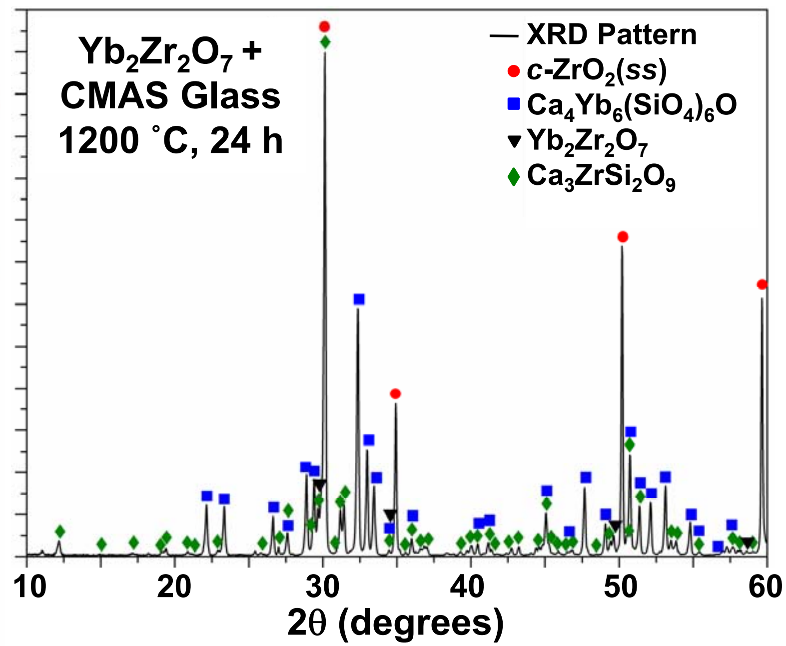
Primary Crystallized Phase in Arrest Region: $Ca_4Yb_6(SiO_4)_6O$

***Acta Mat.* 2012**

TBC Ceramics/CMAS Interactions



XRD of Powder Mixtures (50:50) Heat-Treated at 1200 ˚C, 24 h



Acta Mat. 2012

Silicate Apatites

* $Gd_2Zr_2O_7$
  - Forms $Ca_2Gd_8(SiO_4)_6O_2$
  - A^I: All (2) Ca^{2+} + 2 Gd^{3+}
  - A^{II}: 6 Gd^{3+}
  - $(Ca_2Gd_2)Gd_6(SiO_4)_6O_2$
  - Need 8 Gd Atoms
* $Y_2O_3.2ZrO_2$(*ss*)
  - Forms $Ca_4Y_6(SiO_4)_6O$
  - A^I: All (4) Ca^{2+}
  - A^{II}: All (6) Y^{3+}
  - Need 6 Y Atoms
* $Yb_2Zr_2O_7$
  - Forms $Ca_4Yb_6(SiO_4)_6O$
  - A^I: All (4) Ca^{2+}
  - A^{II}: All (6) Yb^{3+}
  - Need 6 Yb Atoms, But Apatite Crystallization Propensity Decreases with RE Size

(Quintas *et al.*, 2008)

Acta Mat. 2012

CN=9 CN=7

$$A^{I}_{4}A^{II}_{6}(SiO_4)_6O_x$$

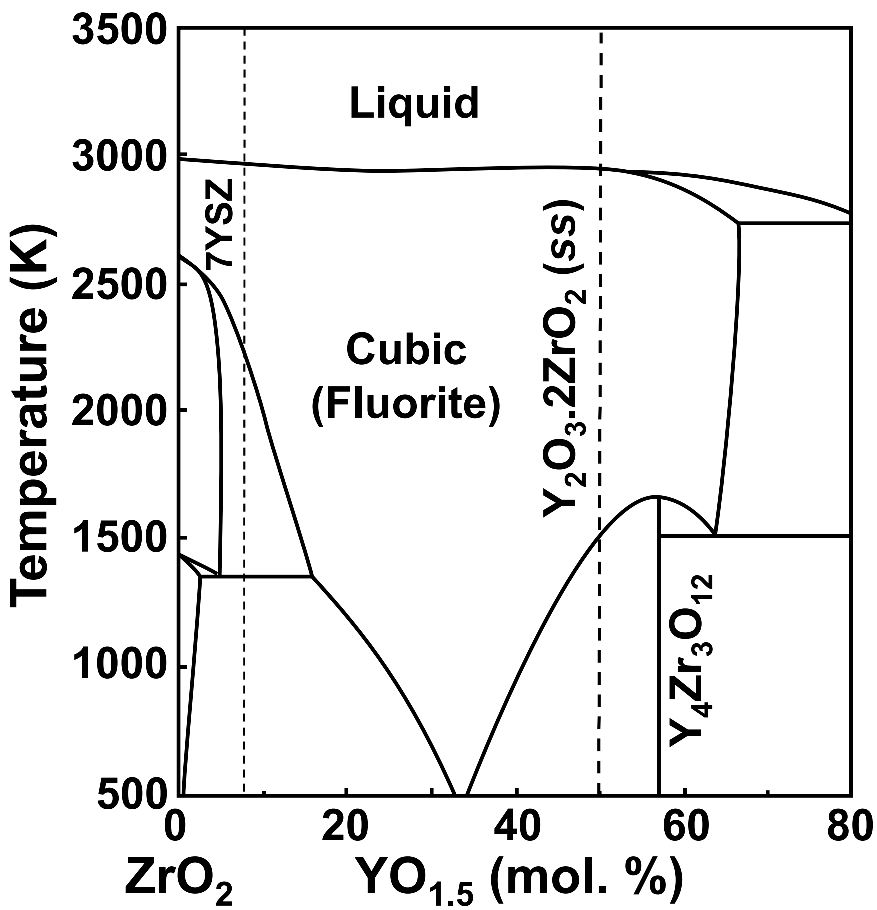
Cation "A"	A^I Site (pm)	A^{II} Site (pm)
Lu^{3+}	103	-
Yb^{3+}	104	93
Er^{3+}	106	95
Y^{3+}	108	96
Gd^{3+}	111	100
Sm^{3+}	113	102
Nd^{3+}	116	-
Ca^{2+}	118	106
Ce^{3+}	120	107
La^{3+}	122	110

Harder to Crystallize Apatite ↑

↓ Need More RE^{3+} to Form Apatite

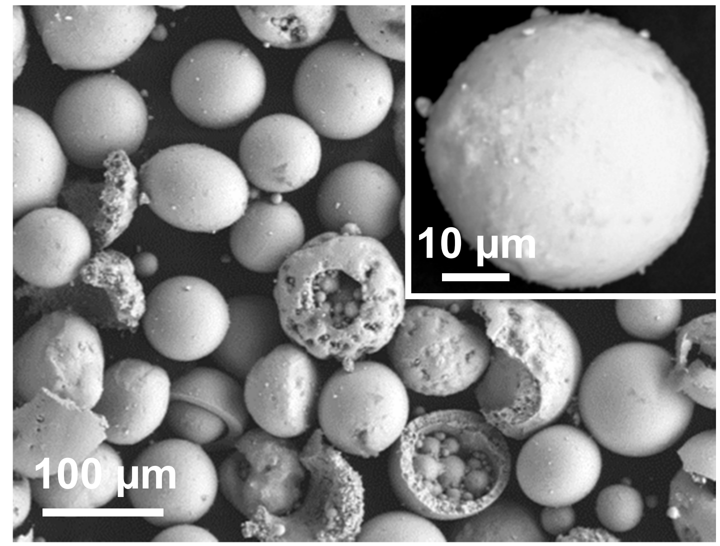
Shannon, 1976

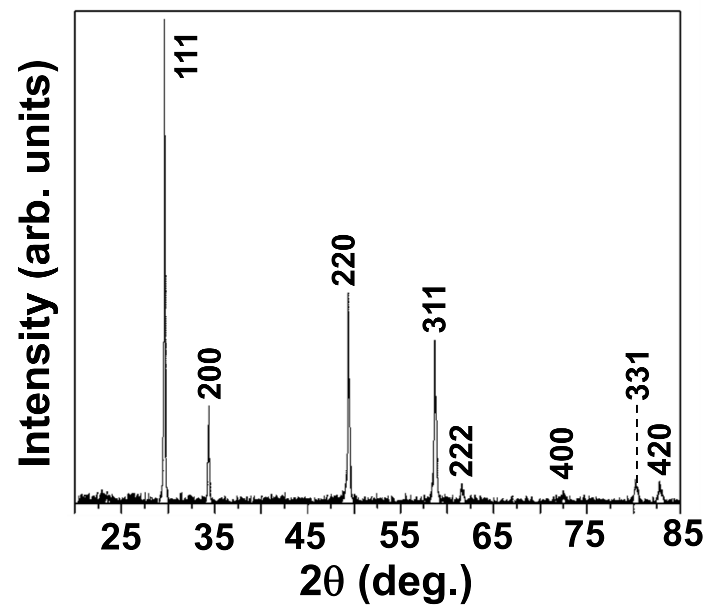
$Y_2O_3.2ZrO_2$(*ss*) APS TBCs



Jacobson *et al.*, 2004

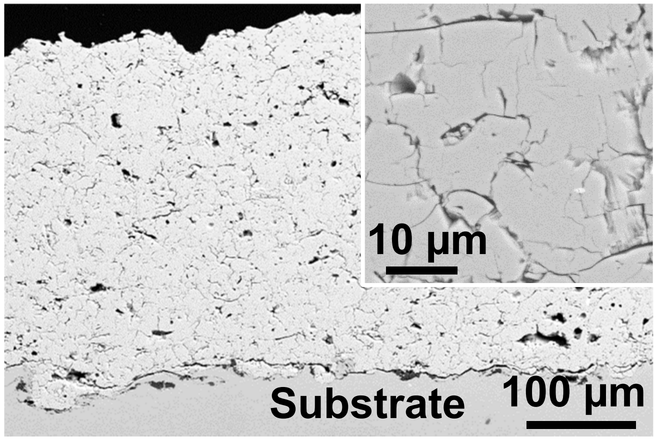
APS Custom Powders (in collaboration with Sulzer)





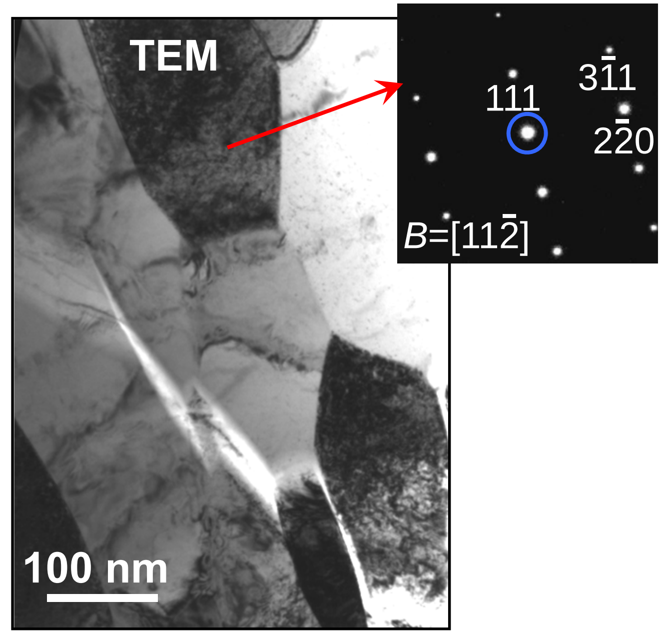
$Y_2O_3.2ZrO_2$(*ss*) APS TBCs

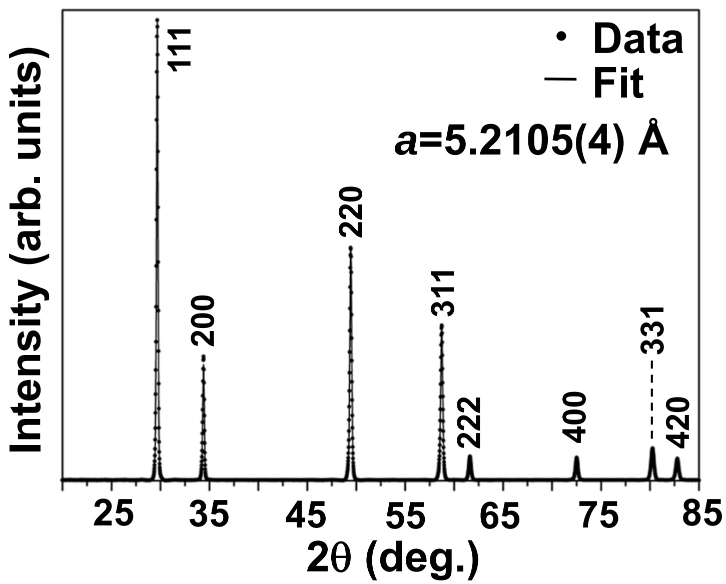
Single-Phase Cubic (Fluorite)

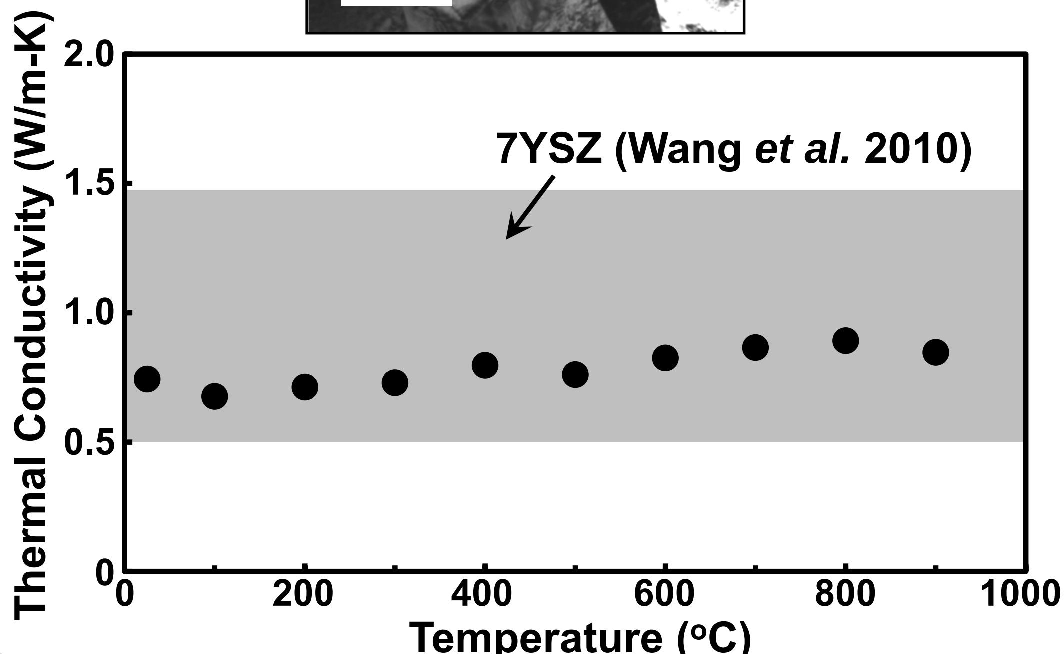


11.4% Porosity

~300 μm Thickness

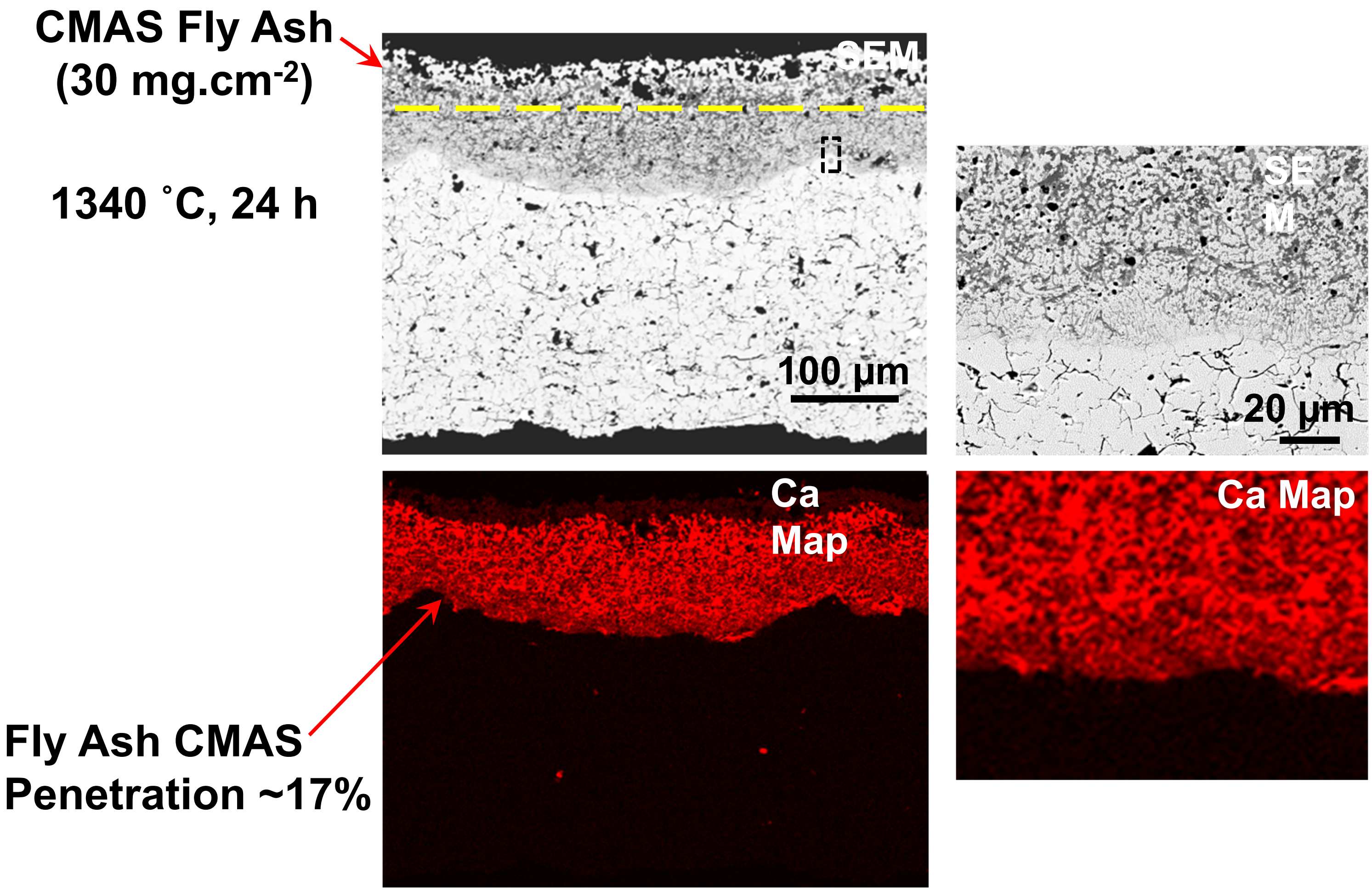






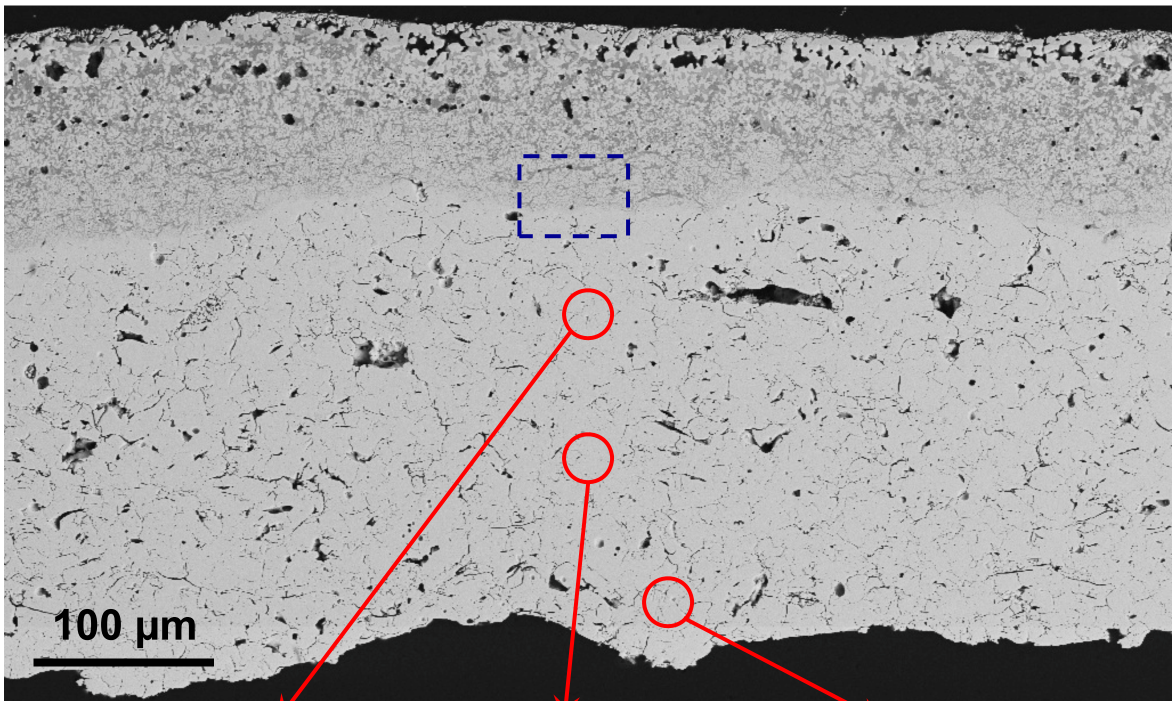
In Collaboration with Prof. S. Sampath

$Y_2O_3.2ZrO_2$(*ss*) APS TBCs: Fly Ash CMAS



$Y_2O_3.2ZrO_2$(*ss*) APS TBCs:
Fly Ash CMAS

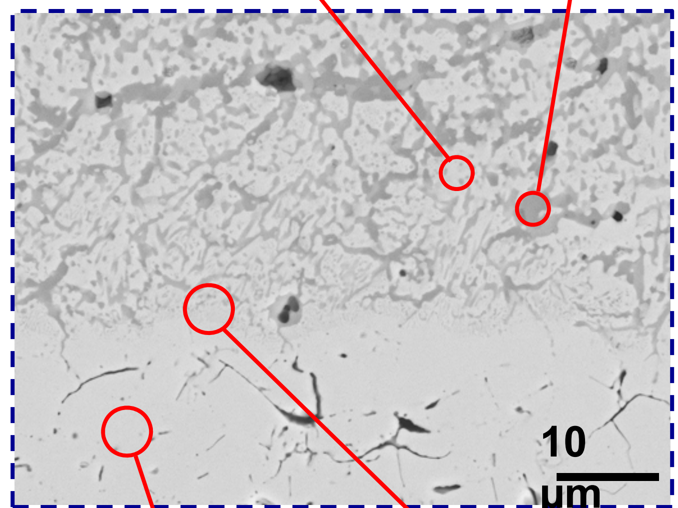
EDS Composition
Atom % Cation Basis



Y	54
Zr	46

Y	53
Zr	47

Y	53
Zr	47



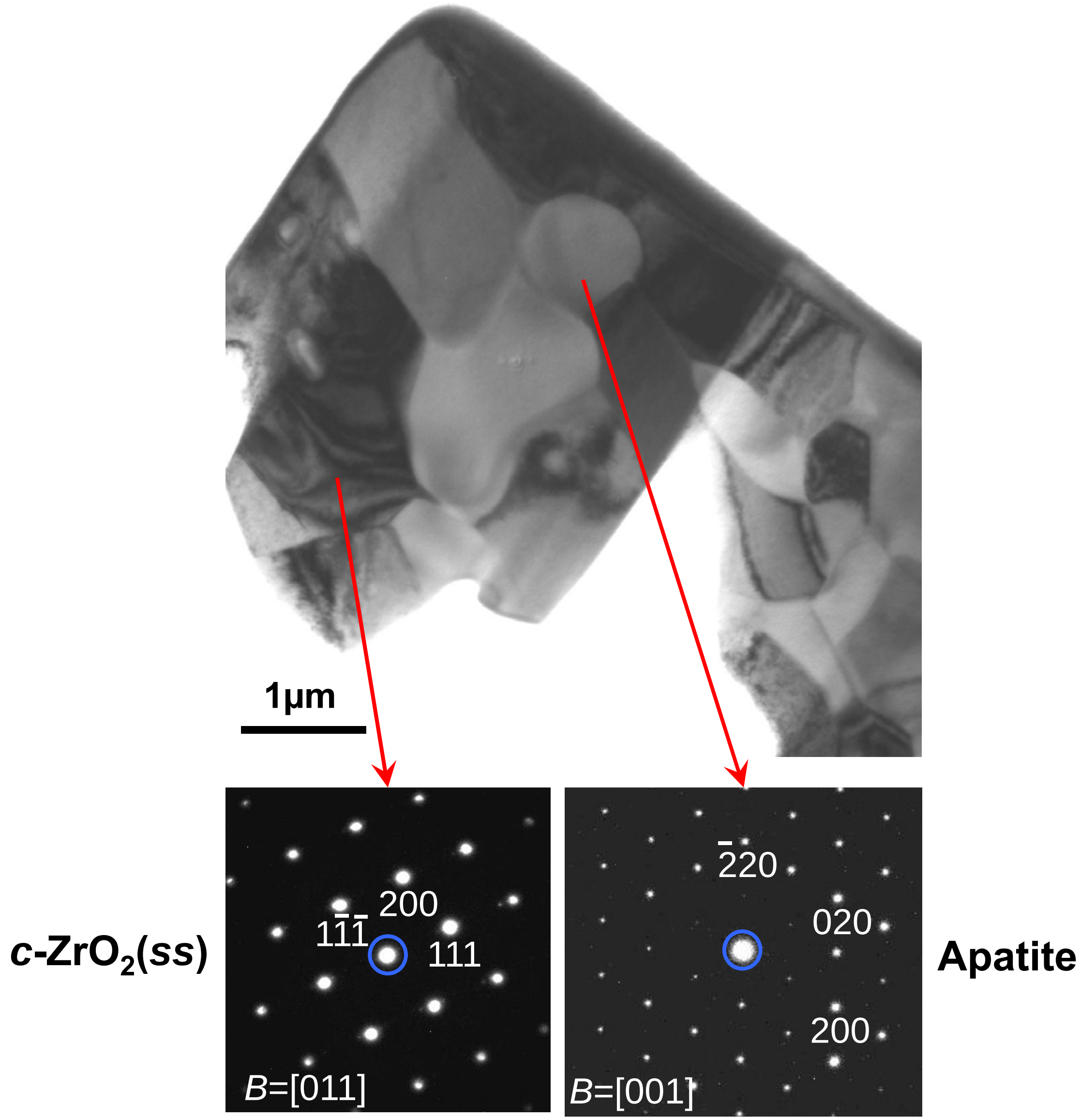
Al	2.5
Si	13.5
Ca	7
Y	40
Zr	37

Mg	4
Al	14
Si	23.5
Ca	13.5
Fe	1.5
Y	35
Zr	8.5

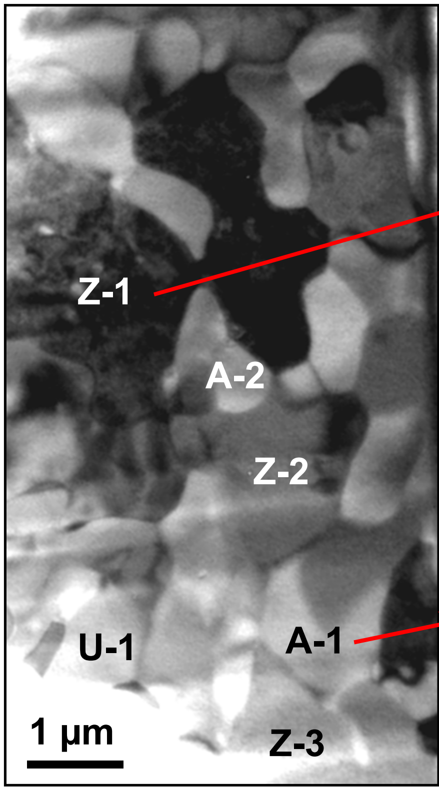
Y	56
Zr	44

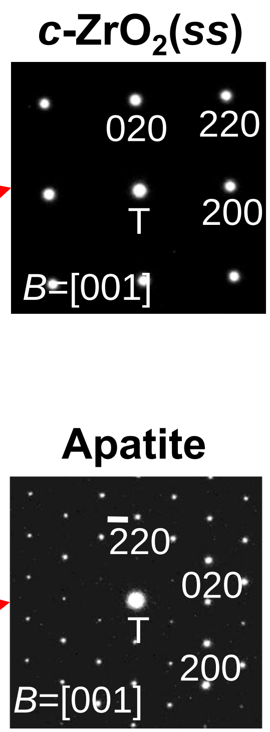
Si	6.5
Ca	4.5
Y	47
Zr	42

$Y_2O_3.2ZrO_2$(*ss*) APS TBCs: Fly Ash CMAS



$Y_2O_3.2ZrO_2(ss)$ APS TBCs: Fly Ash CMAS



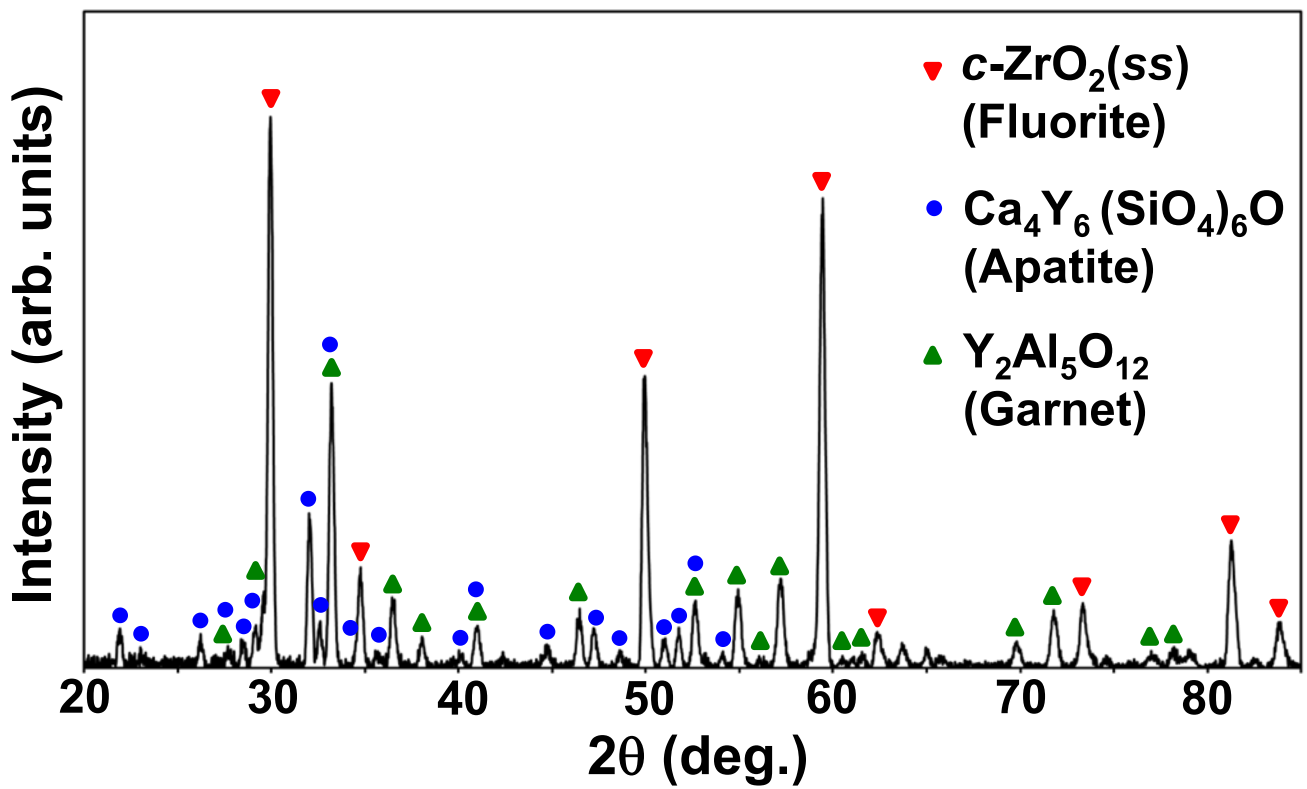


At.% (Λ)	Ca	Si	Y	Zr	Al
YZO (0.92)	-	-	50	50	-
Apatite (0.72	25	37.5	37.5	-	-
Z-1 (0.90)	-	-	37	63	-
Z-2 (0.91)	-	-	44	57	-
Z-3 (0.90)	3	-	35	62	-
A-1 (0.72)	14	45	41	-	-
A-2 (0.71)	14	47	39	-	-
U-1 (0.74)	30	34	24	5	7

Primary Phases in Arrest Region:
Apatite + *c*-ZrO_2(*ss*)

$Y_2O_3.2ZrO_2(ss)$: Fly Ash CMAS

XRD of Powder Mixture (50:50)
Heat-Treated at 1340 ˚C, 24 h



Fly Ash CMAS Damage Mitigation Approach

* Vigorous Reaction Between TBC and Fly Ash CMAS

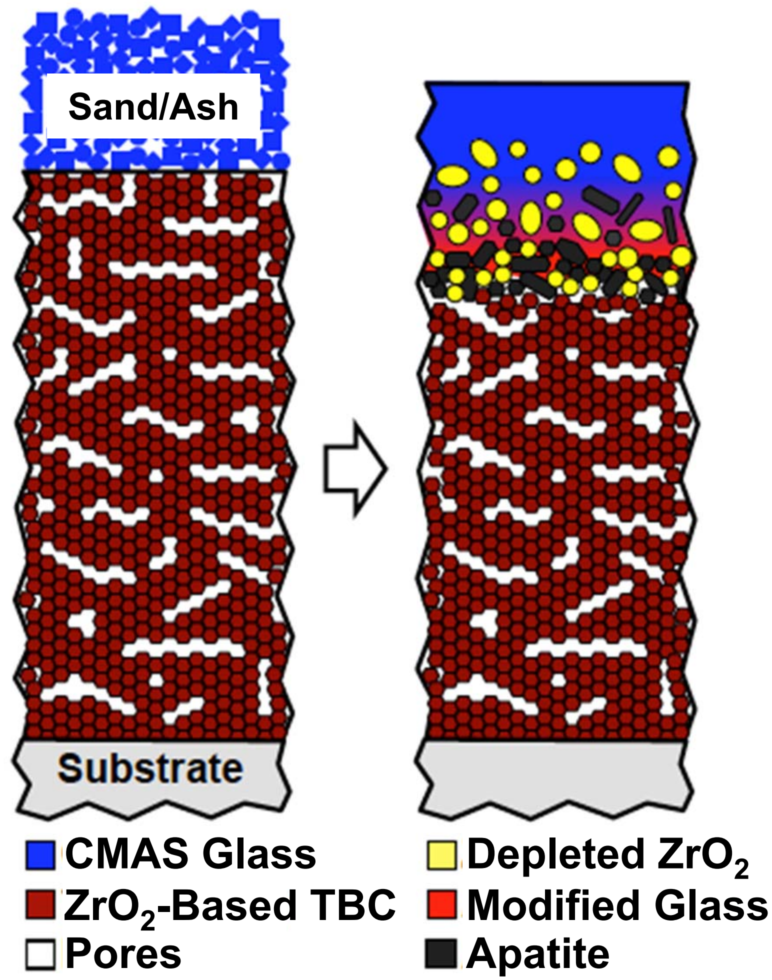
* Large Amount of Solute in $Y_2O_3.2ZrO_2$(*ss*): Y:Zr :: 1:1 (cf. Y:Zr :: 0.083:1 in 7YSZ)

* Rapid Accumulation of Solute in CMAS Glass Over Short Penetration Depth

* Crystallization of Modified CMAS

* Refractory Crystallized Phases (*e.g.* Apatite) Seal TBC

* Arrest of CMAS Front



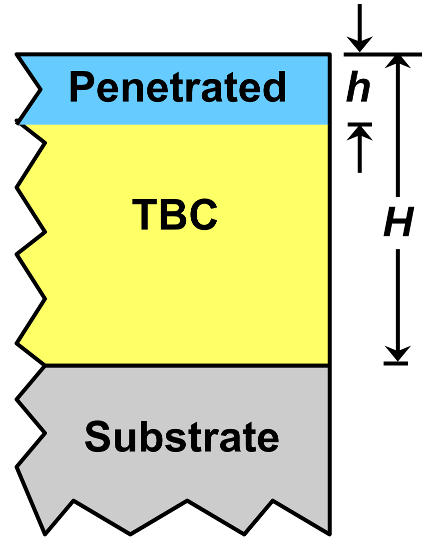
Thermo-Chemo-Mechanical Testing

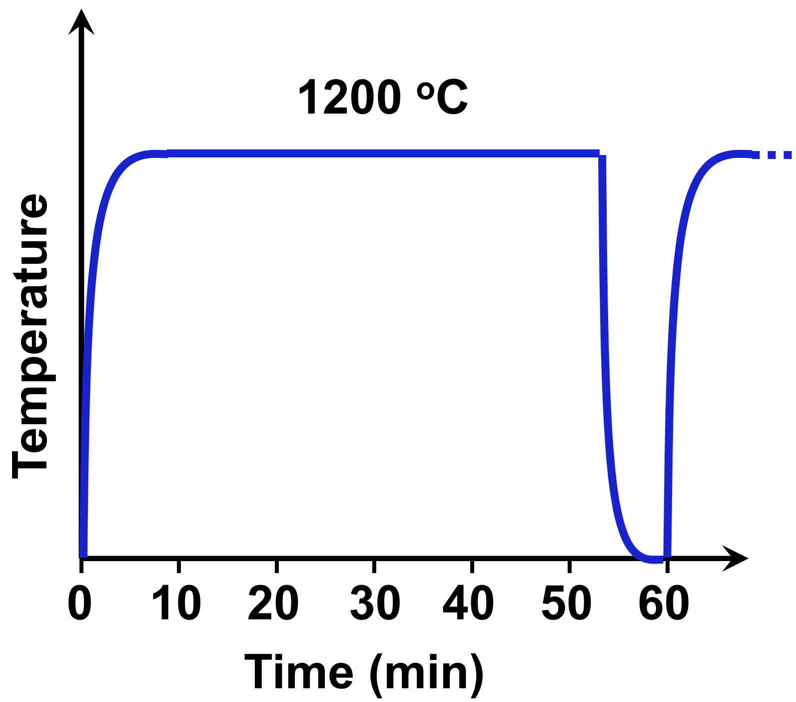
* Arrest of Penetrating Front

* Still ~17% TBC Thickness Penetrated:
  Stiffer Glaze

* Partial Loss of Strain Tolerance:
  TBC Spallation

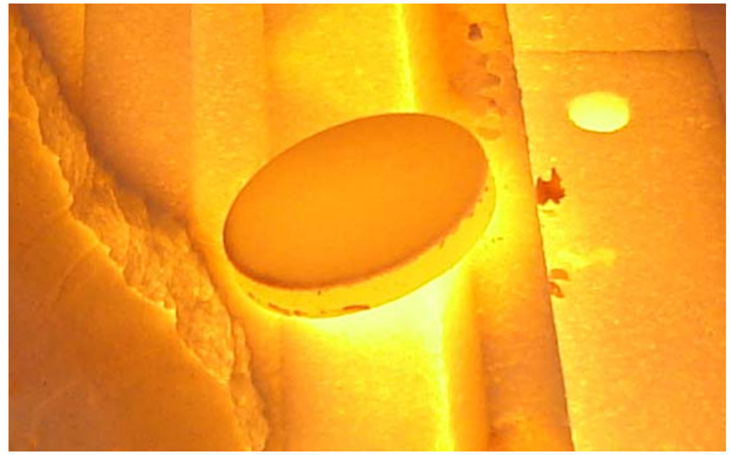
* Conventional Furnace Cyclic Testing

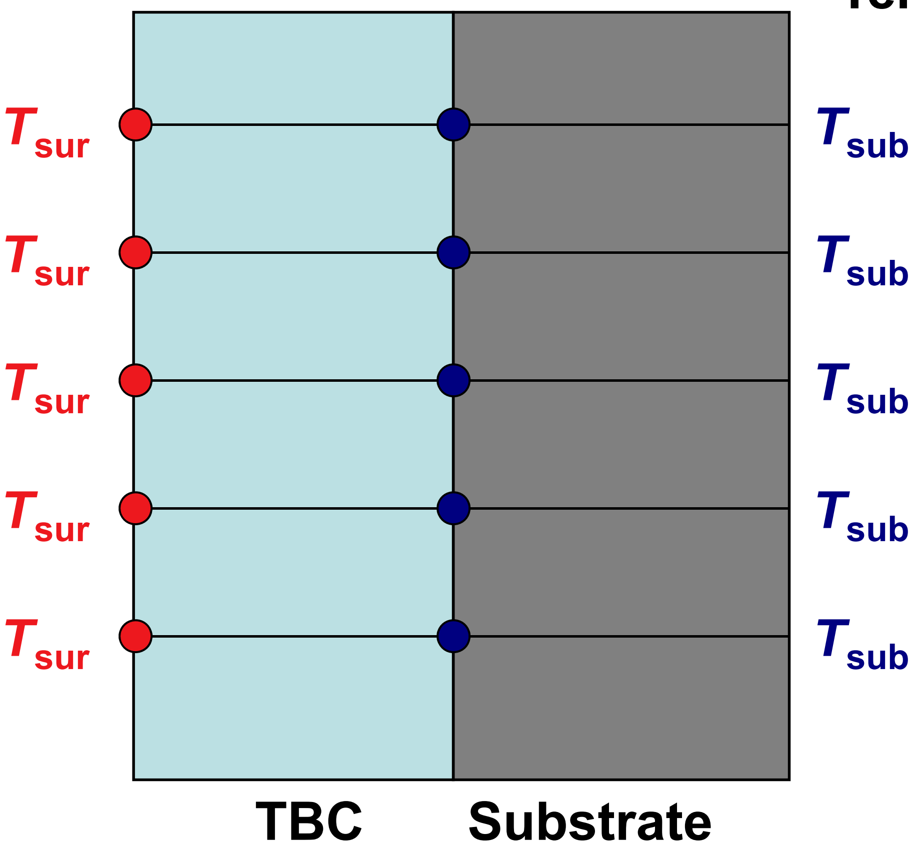


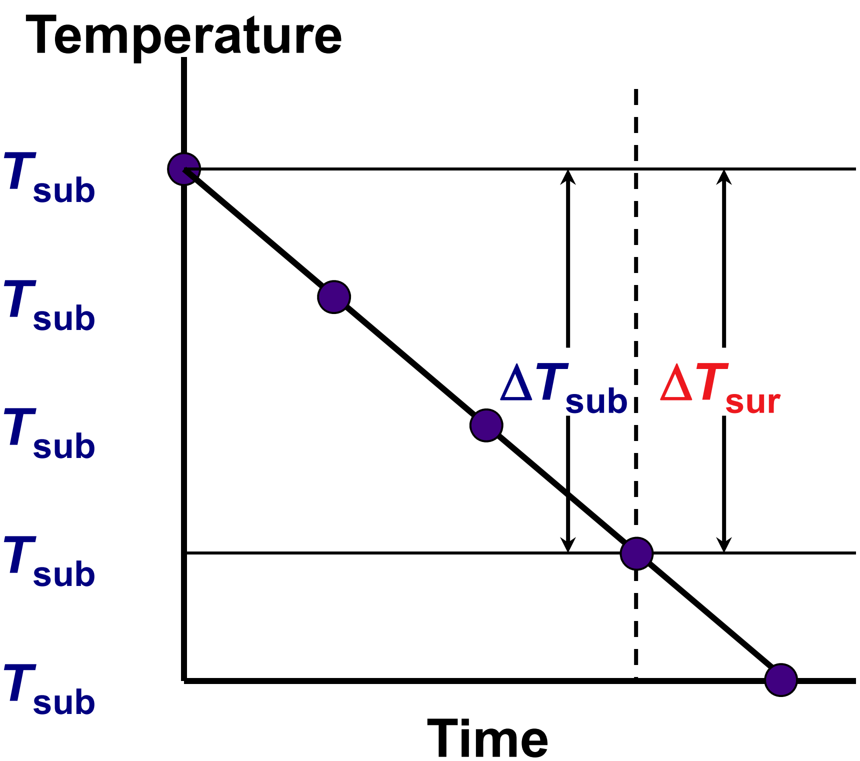


Conventional Furnace Cyclic Testing

* Maximum Temperature Limited by Substrate



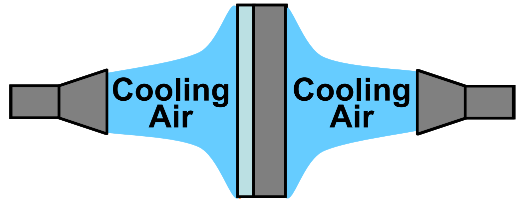


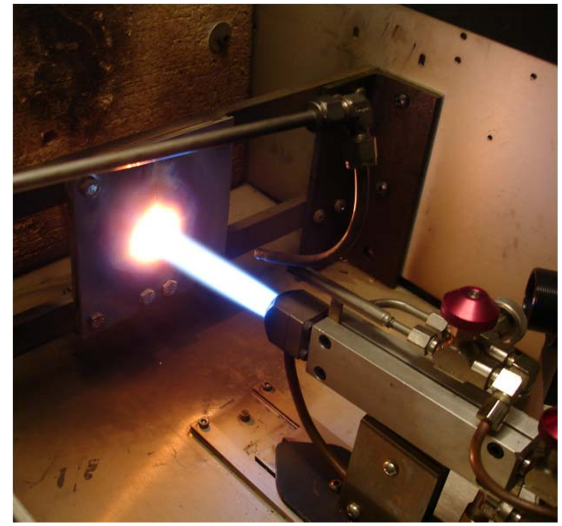


$$\Delta T_{sur} - \Delta T_{sub} = 0$$

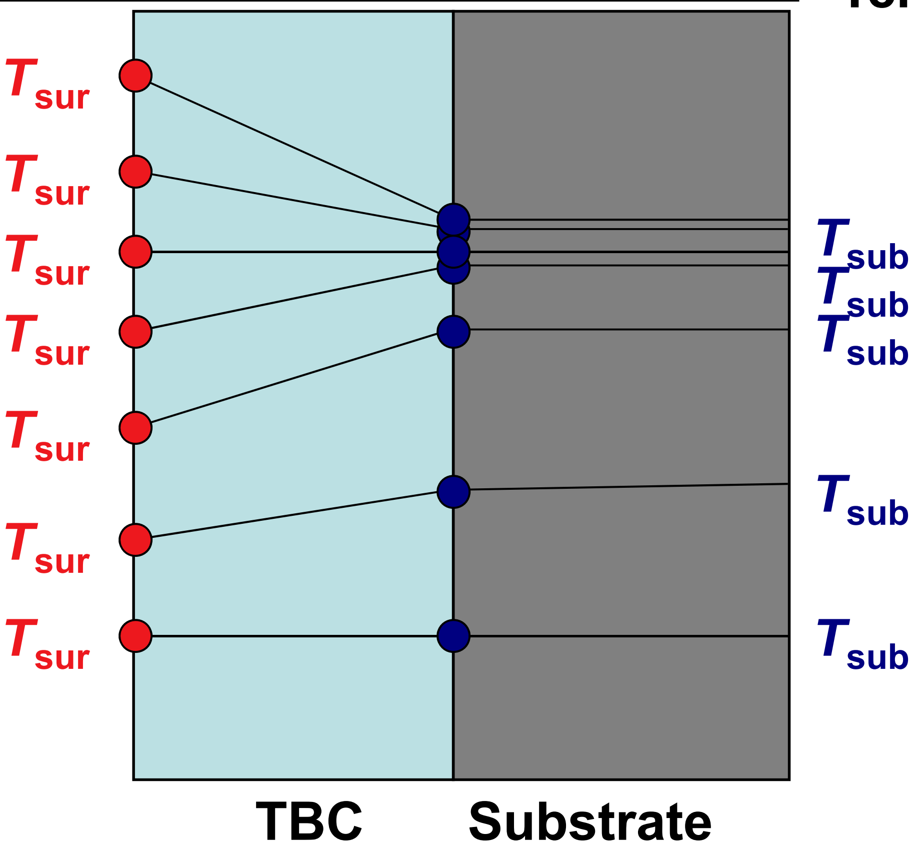
Thermal-Gradient Cyclic Testing

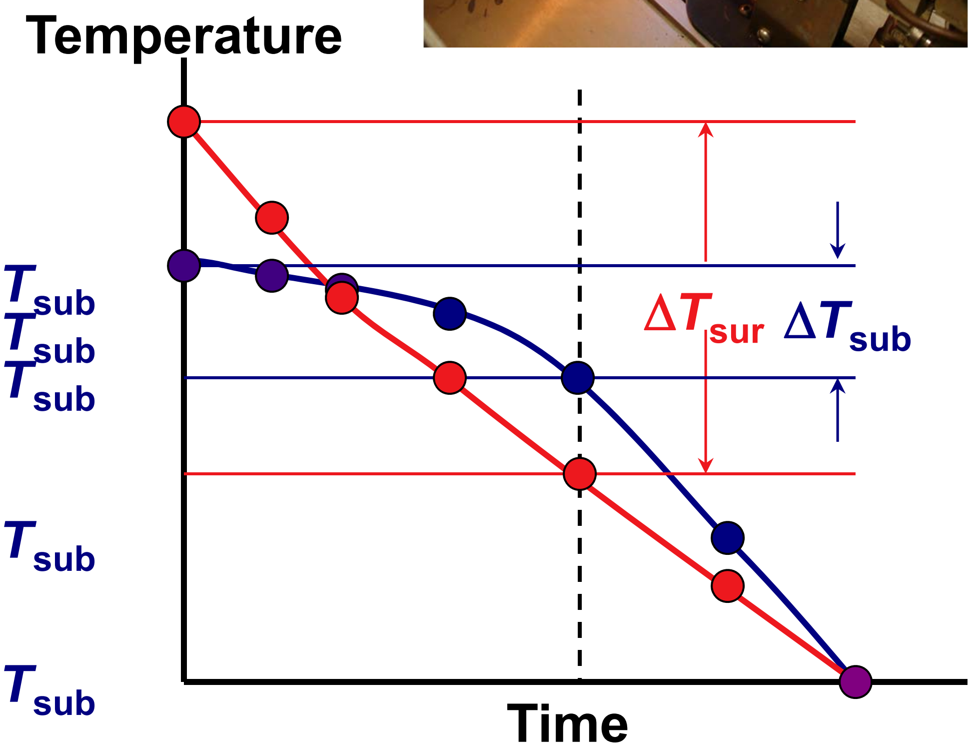
* **Substrate at Lower Temperature**





5 min. Heating, 2 min. Cooling

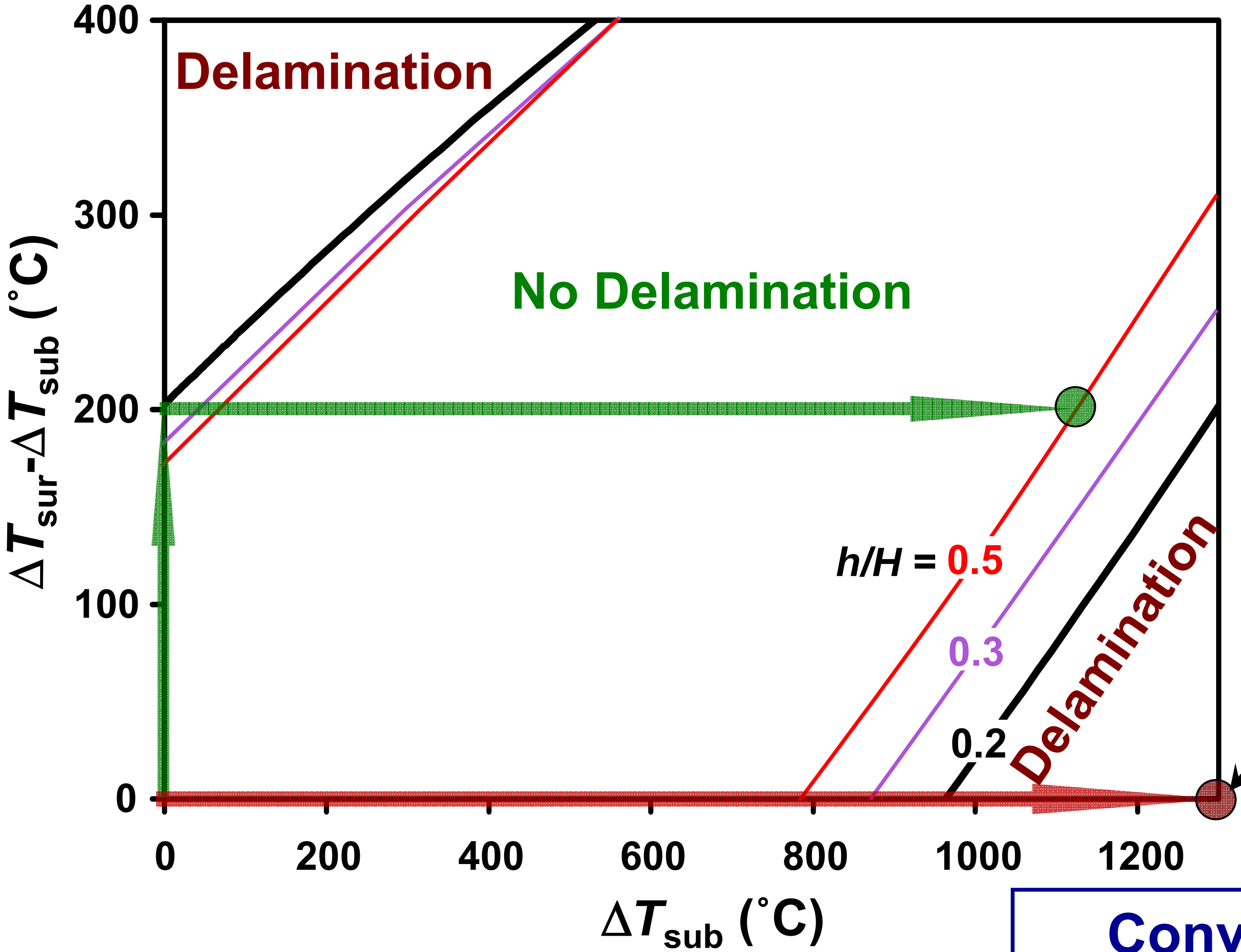


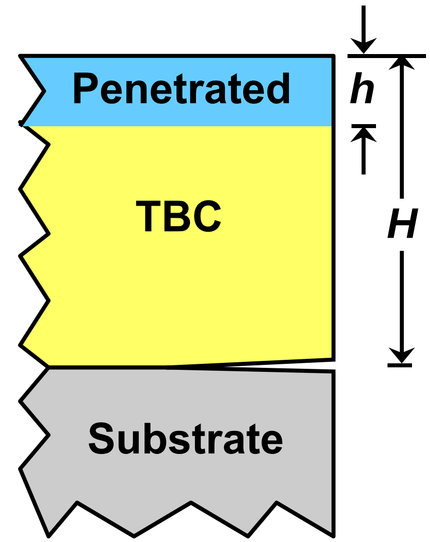


$\Delta T_{sur} - \Delta T_{sub} > 0$

Mechanics & Testing of Deposits-Penetrated TBCs

G_{IC}=30 J/m^2; λ=0.25; Deep Delamination





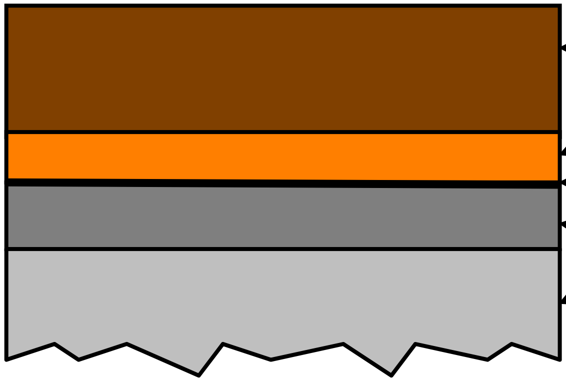
No Thermal Gradient: Spontaneous Failure

Model by Evans and Hutchinson, 2007

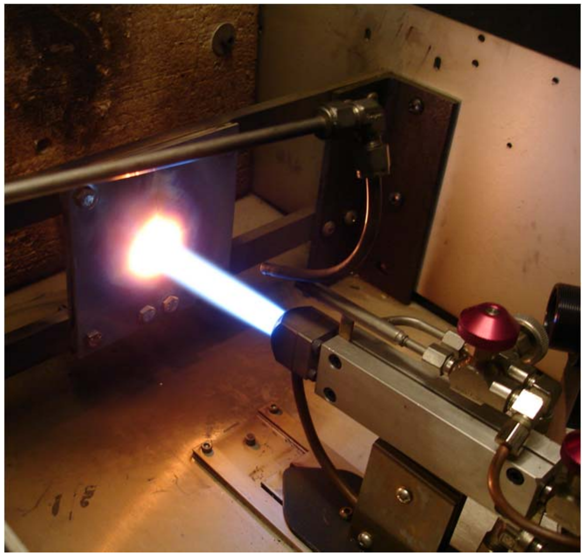
Conventional Furnace Cyclic Testing Not Suitable

Ongoing and Future Work

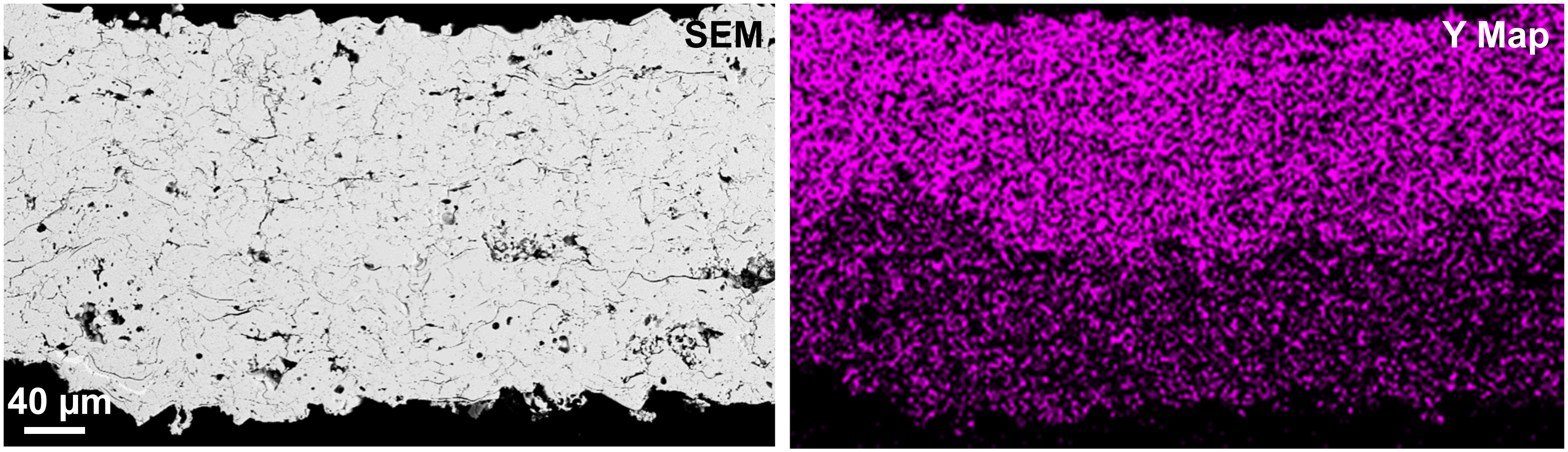
* $Y_2O_3.2ZrO_2$(*ss*) Toughness ~15 $J.m^{-2}$
* 7YSZ Toughness ~30 $J.m^{-2}$ (*t'*-ZrO_2 Ferroelastic Toughening)
* Exploit High Toughness of 7YSZ Near Metal/Ceramic Interface
* Bi-Layer APS $Y_2O_3.2ZrO_2$-7YSZ TBCs
    - CMAS-Resistant Top Layer, High Toughness Bottom Layer



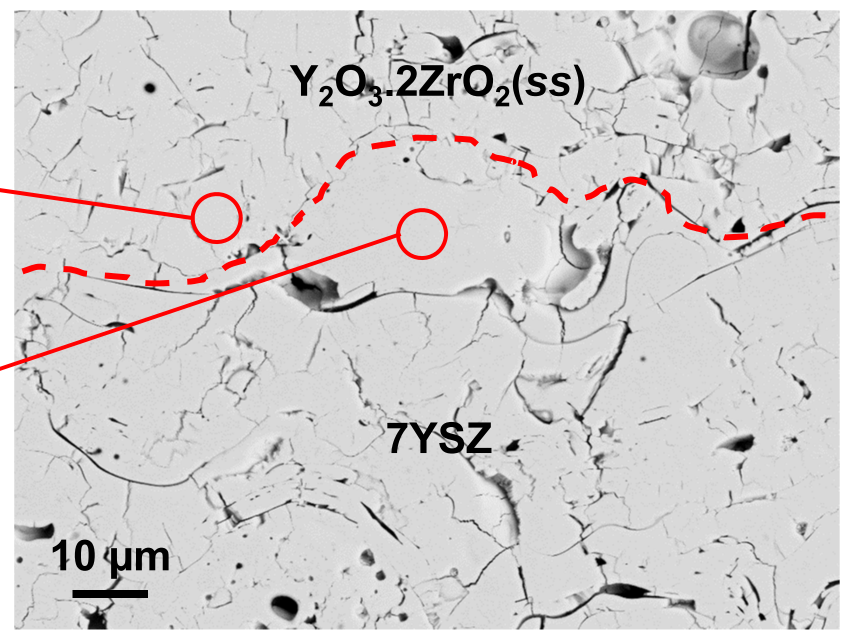
* Testing of Bi-Layer TBCs and 7YSZ TBCs
    - Gradient Rig
    - Fly Ash CMAS and Water Injection
* Characterization of Tested TBCs
    - Understanding of Damage and Mitigation Mechanisms
* Characterization of Tested TBCs



$Y_2O_3.2ZrO_2$(*ss*)-7YSZ Bi-Layer APS TBCs



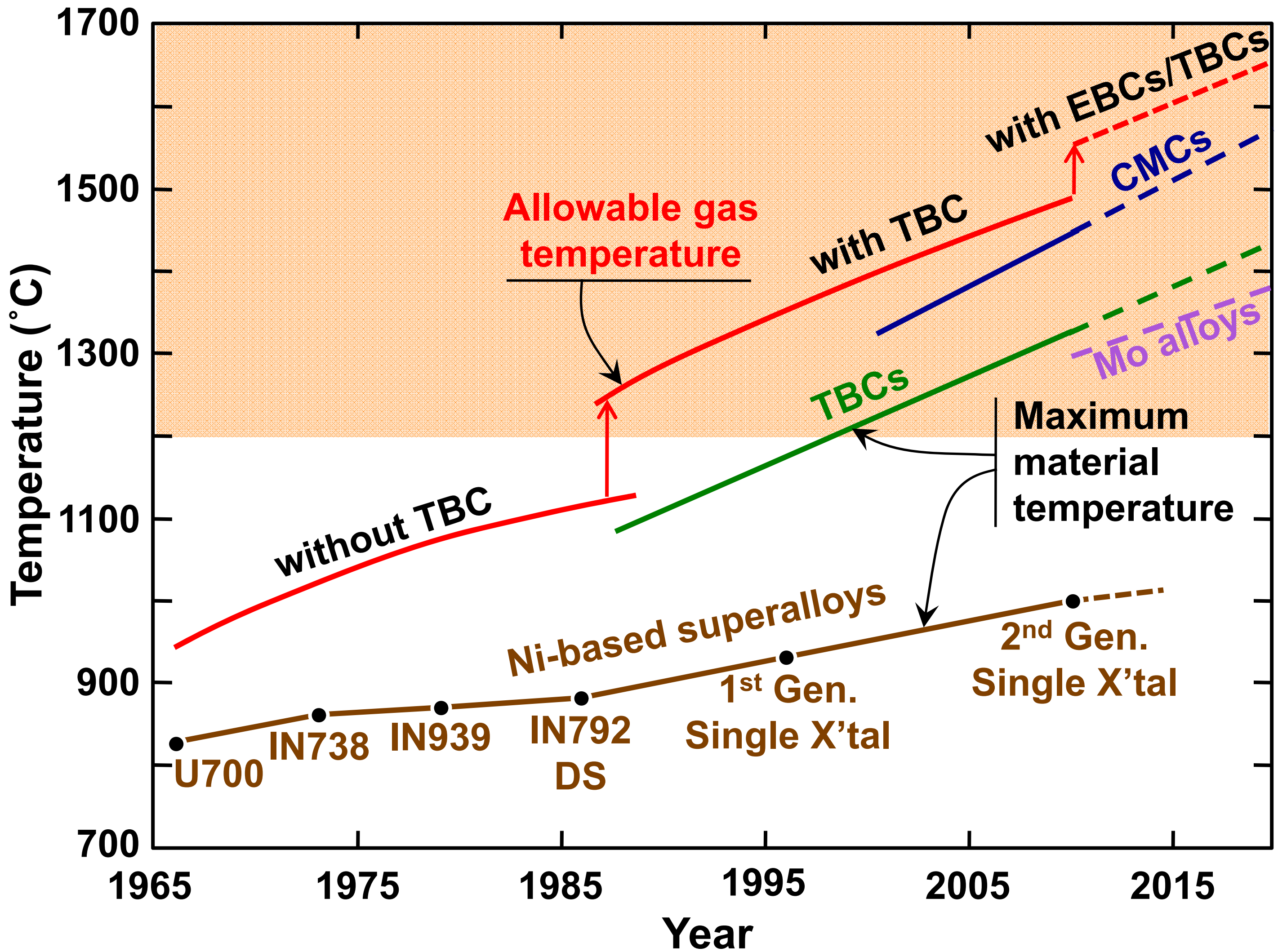
Y	53
Zr	47



Y	9
Zr	91

EDS Composition
Atom % Cation Basis

Outlook



Evans, 2008

Need Resistance to CMAS in TBCs, EBCs

CMAS-Resistant EBCs

* Dense Coatings; Good CTE Match with CMCs; High-Temp. Stability
* Optical Basicity (OB) Concept Could be Applied to EBCs
* No Reactivity Between CMAS and EBC: Opposite of TBCs Case
* Match OBs of EBCs and Expected CMAS
* Water Vapor Causes Si-Depletion, Increases CMAS Λ: Dynamic

EBC	Λ	$\Delta\Lambda$ (Fly Ash Λ 0.63)	Reference
$Y_4Al_2O_9$	0.87	0.24	Fu *et al.*, 2011
$Gd_4Al_2O_9$	0.99	0.36	Fu *et al.*, 2011
$YAlO_3$	0.80	0.17	Hazel *et al.*, 2008
$GdAlO_3$	0.89	0.26	Fu *et al.*, 2011
Y_2SiO_5	0.79	0.16	Grant *et al.*, 2010
Yb_2SiO_5	0.76	0.13	Toohey *et al.*, 2011
$Y_2Si_2O_7$	0.70	0.07	Ahlborg *et al.*, 2013
$Yb_2Si_2O_7$	0.68	0.05	Toohey *et al.*, 2011
$Sc_2Si_2O_7$	0.66	0.03	Liu *et al.*, 2013

Summary

* Molten CMAS attack of TBCs is a growing issue with rising temperatures in both aero and power gas-turbine engines.

* 7YSZ TBCs are not well-suited to repel fly ash CMAS attack.

* The Optical Basicity concept can be used to screen CMAS-resistant TBC compositions.

* "Model" experiments indicate that high "solute" content, especially Y^{3+}, in TBCs is necessary for mitigation of attack. Other TBC ceramics?

* Demonstrated processing and fly ash CMAS-resistance of $Y_2O_3.2ZrO_2$ APS TBCs

* Gradient testing is necessary to capture thermo-chemo-mechanical response of partially-penetrated TBCs.

* Optimization of CMAS resistance and other required properties in TBCs is necessary: bi-layer TBCs.

* The Optical Basicity concept could be applied to screening CMAS-resistant EBC compositions.

* Resistance to molten CMAS will remain a challenge as gas-turbine engine operating temperatures continue to increase.

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