

# Advanced Thermal Barrier Coatings for Operation in High Hydrogen Content Gas Turbines

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DOE UTSR Meeting, Oct 22<sup>nd</sup>, Purdue University

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AT STONY BROOK UNIVERSITY



DOE NETL UTSR

Contract #DE-FE0004771

2010-2014

Program Manager: Dr. Briggs while

Dwivedi et al., JACerS, DOI: 10.1111/jace.13021

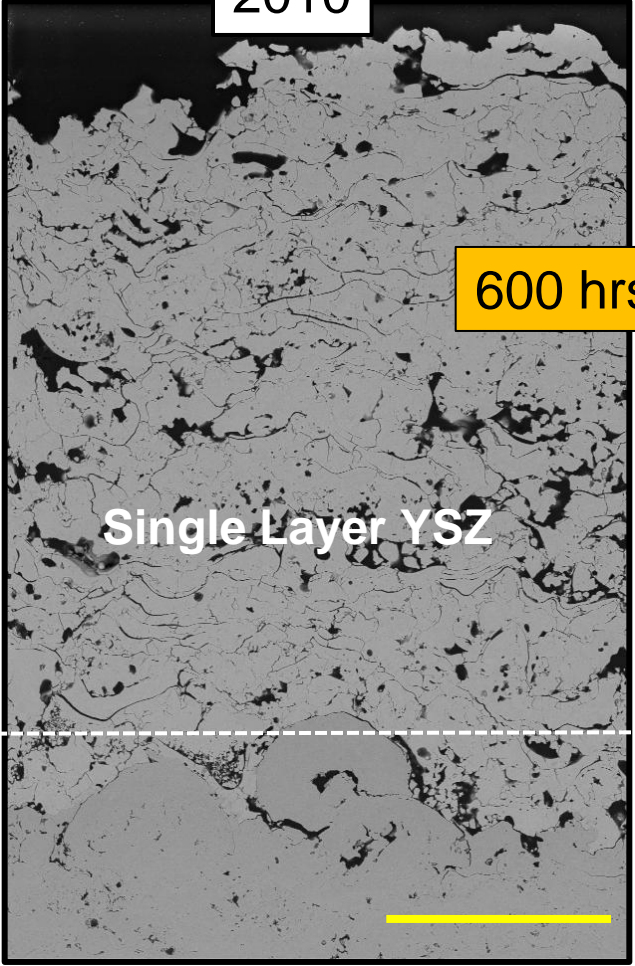
Viswanathan et al., JACerS, DOI: 10.1111/jace.13033

Dwivedi et al., JTST, Under Review

Viswanathan et al., JACerS, Under Review



2010



Single Layer YSZ

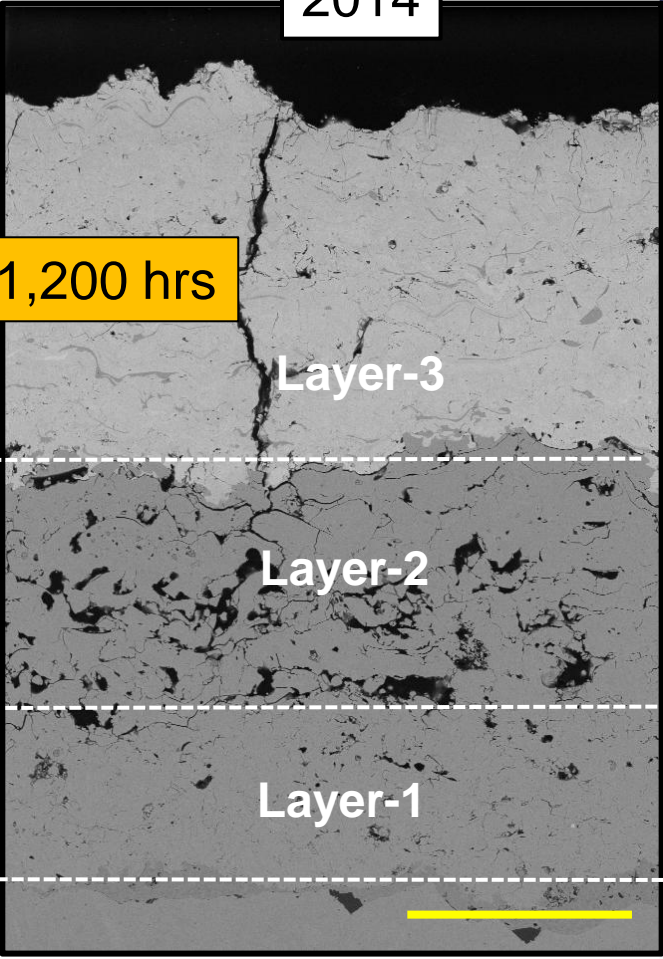
600 hrs

- 50 +coating conditions
- 40+ architectures
- 600+ FCT samples

4 years

- Adequate erosion resistance
- Significantly higher durability
- CMAS resistance
- Mechanisms and Methodology to incorporate any new composition

2014



Layer-3

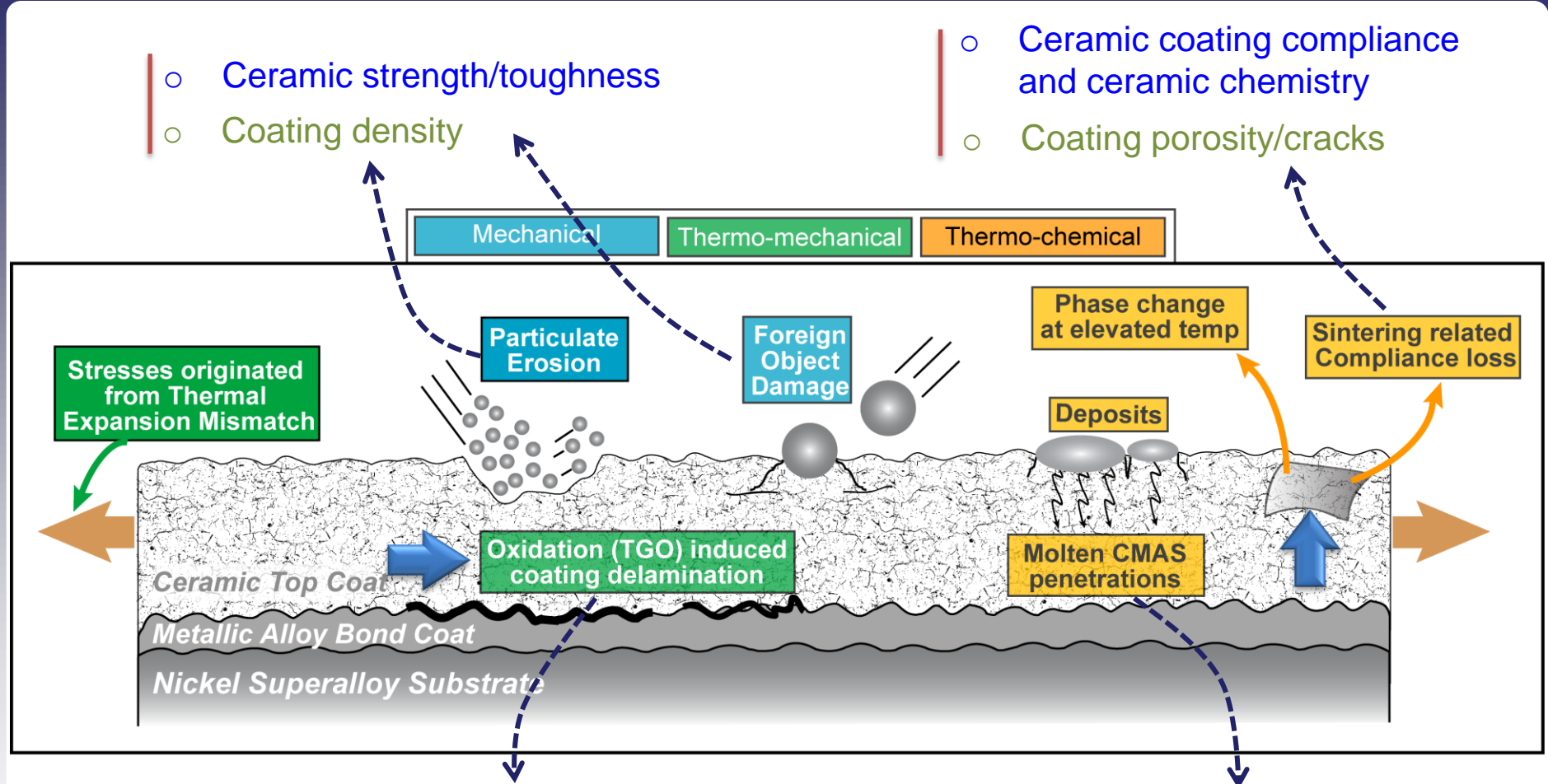
Layer-2

Layer-1

1,200 hrs



# Interplay between TBC durability and “manufactured” coating properties 3



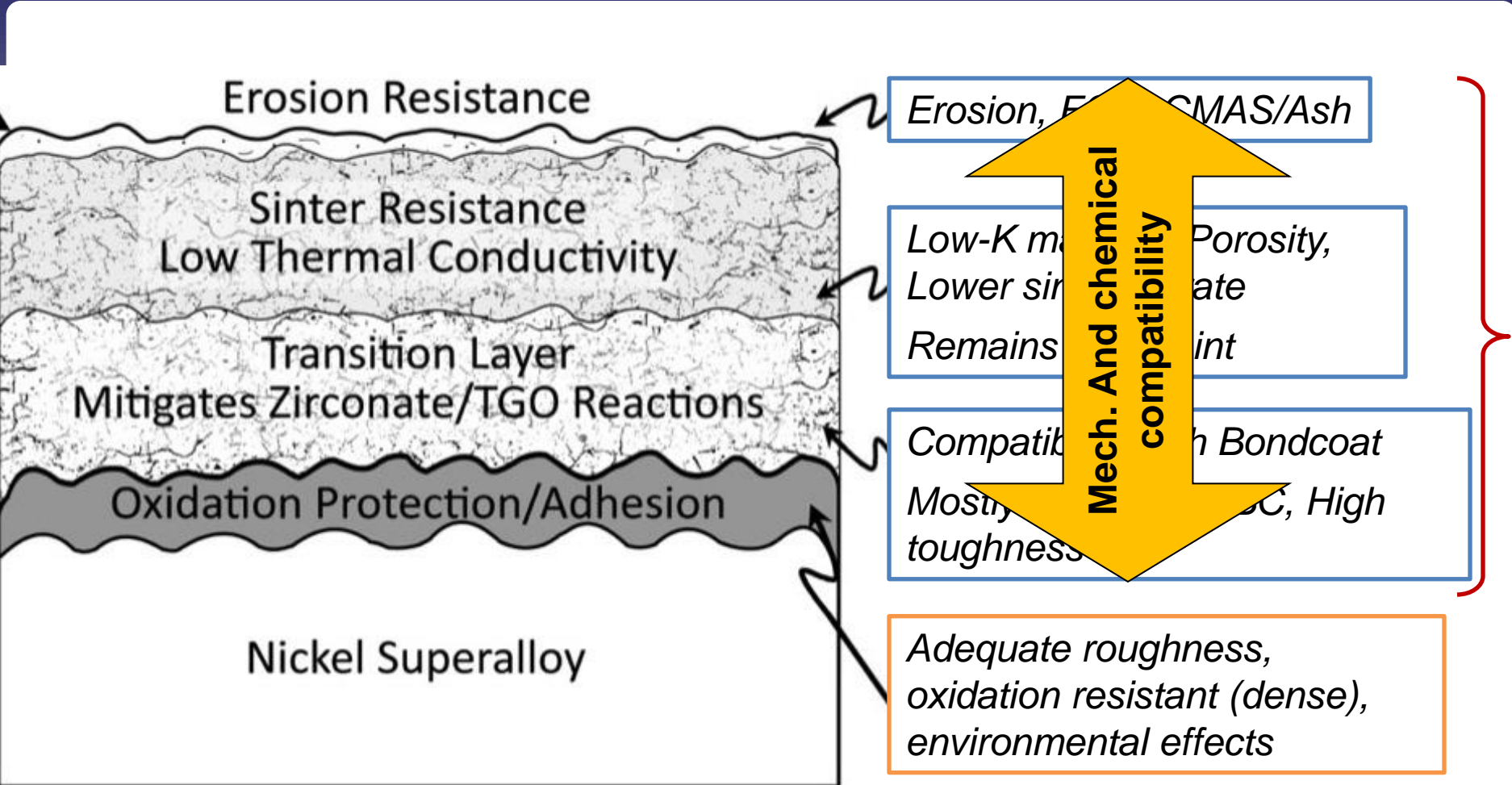
- Ceramic strength/toughness
- Coating density

- Ceramic coating compliance and ceramic chemistry
- Coating porosity/cracks

- Bond coat chemistry, Roughness
- Ceramic coating toughness
- Bond coat roughness
- Coating thickness

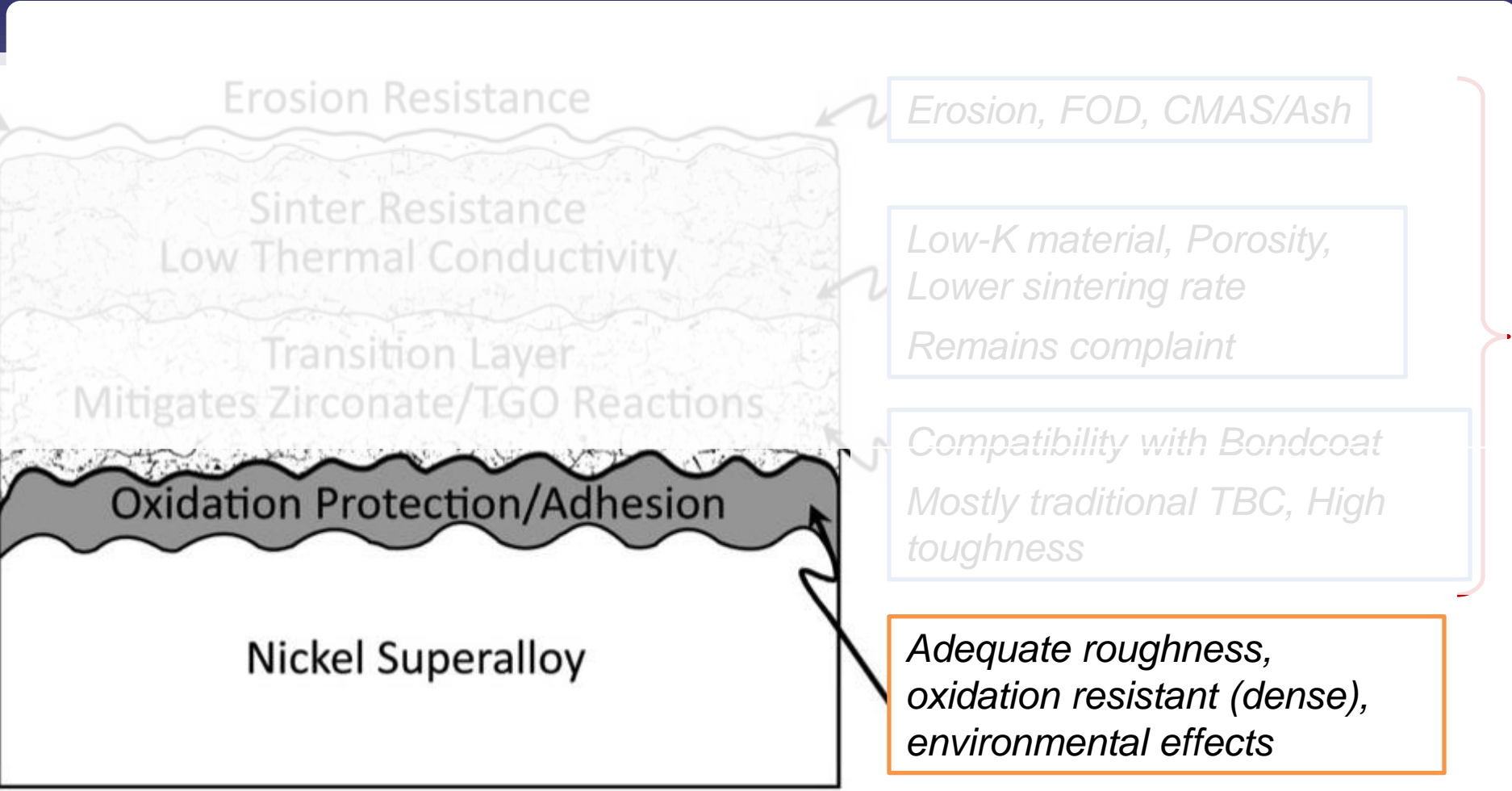
- Ceramic coating composition
- Pore architecture
- Coating thickness



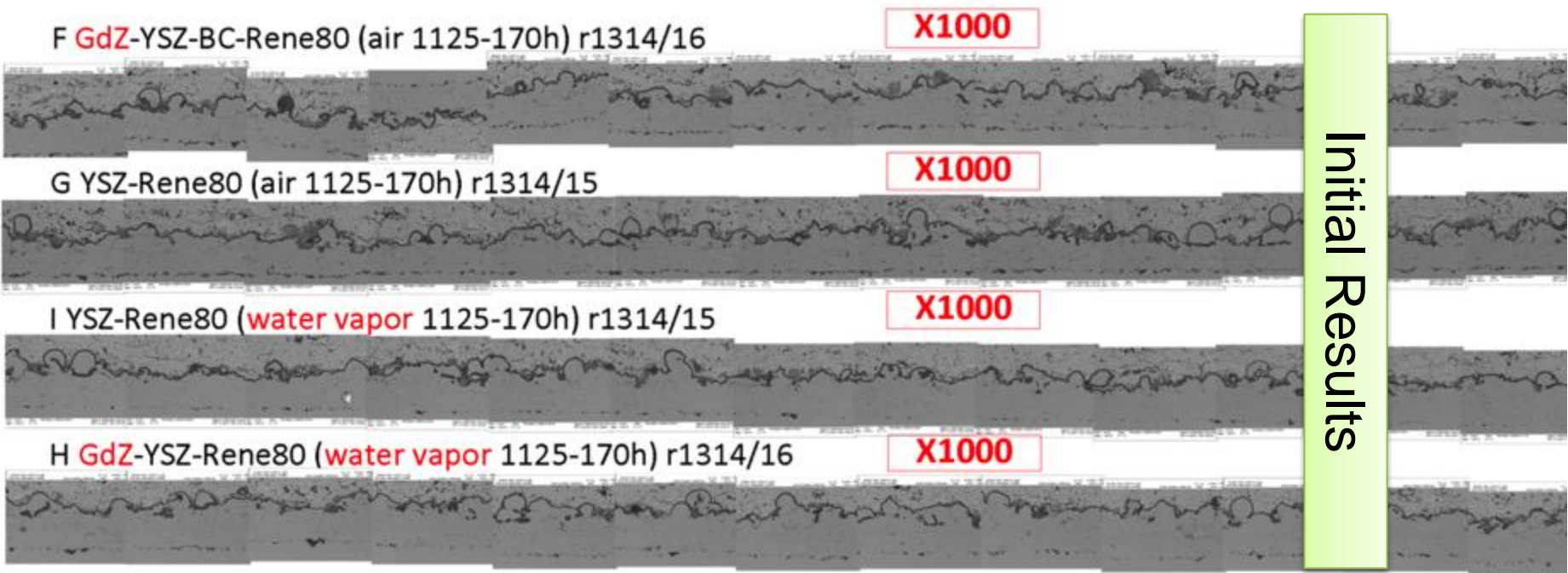


**Plasma spray is naturally suited for such layered manufacturing**





# Impact of water vapor on conv. & new TBC materials



**No significant difference found at this temperature, and long term exposures**

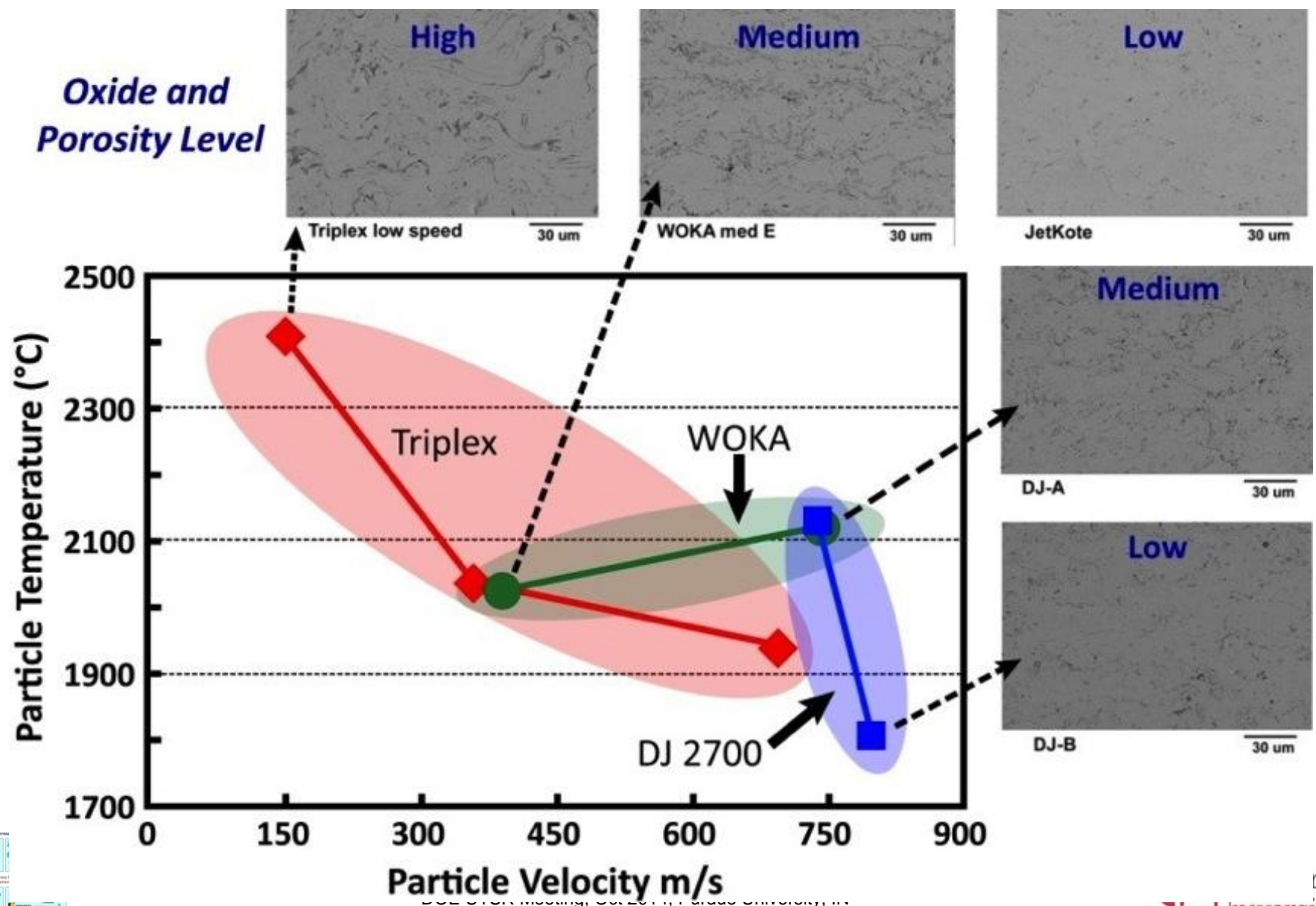
## Collaborative partnership with ORNL- Materials selection



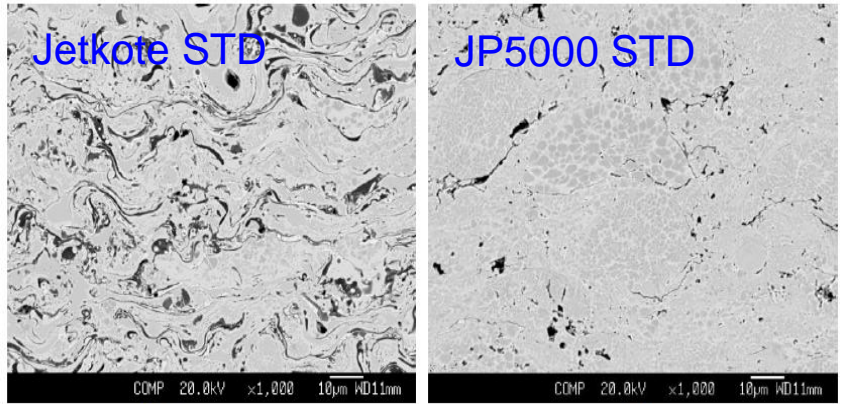
- HVOF bond coats (**NiCoCrAlY** & **NiCoCrAlYHfSi**) for ORNL testing
- ORNL is investigating the interactions with several different substrate materials



# Not all bond coats are the same! Processing plays a role

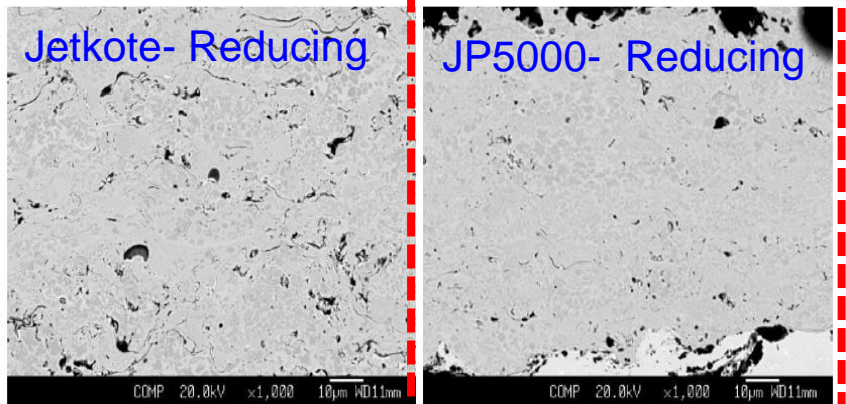


# Processing Effects on HVOF Bond Coats



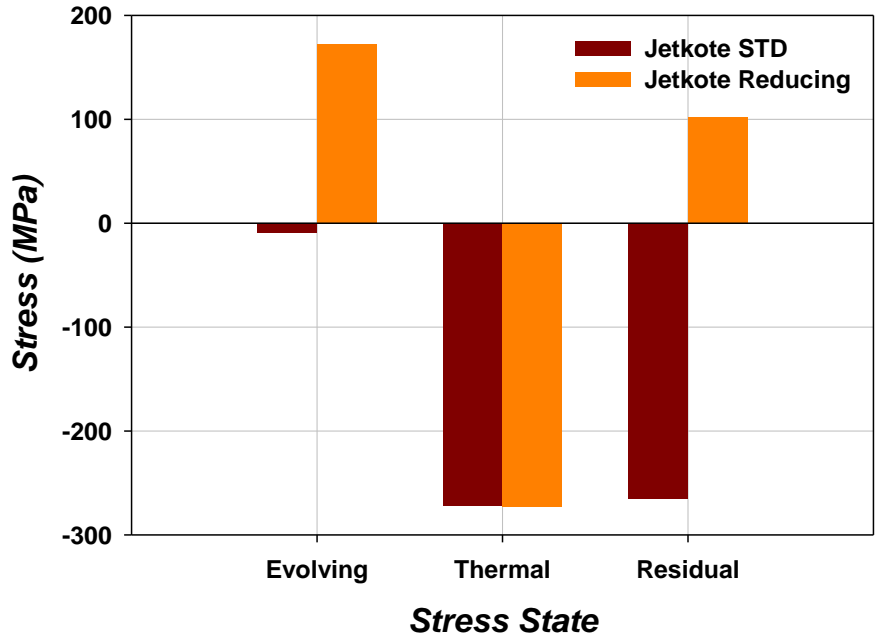
Jet1neu

JP2neu



Jet3 red

JP4red



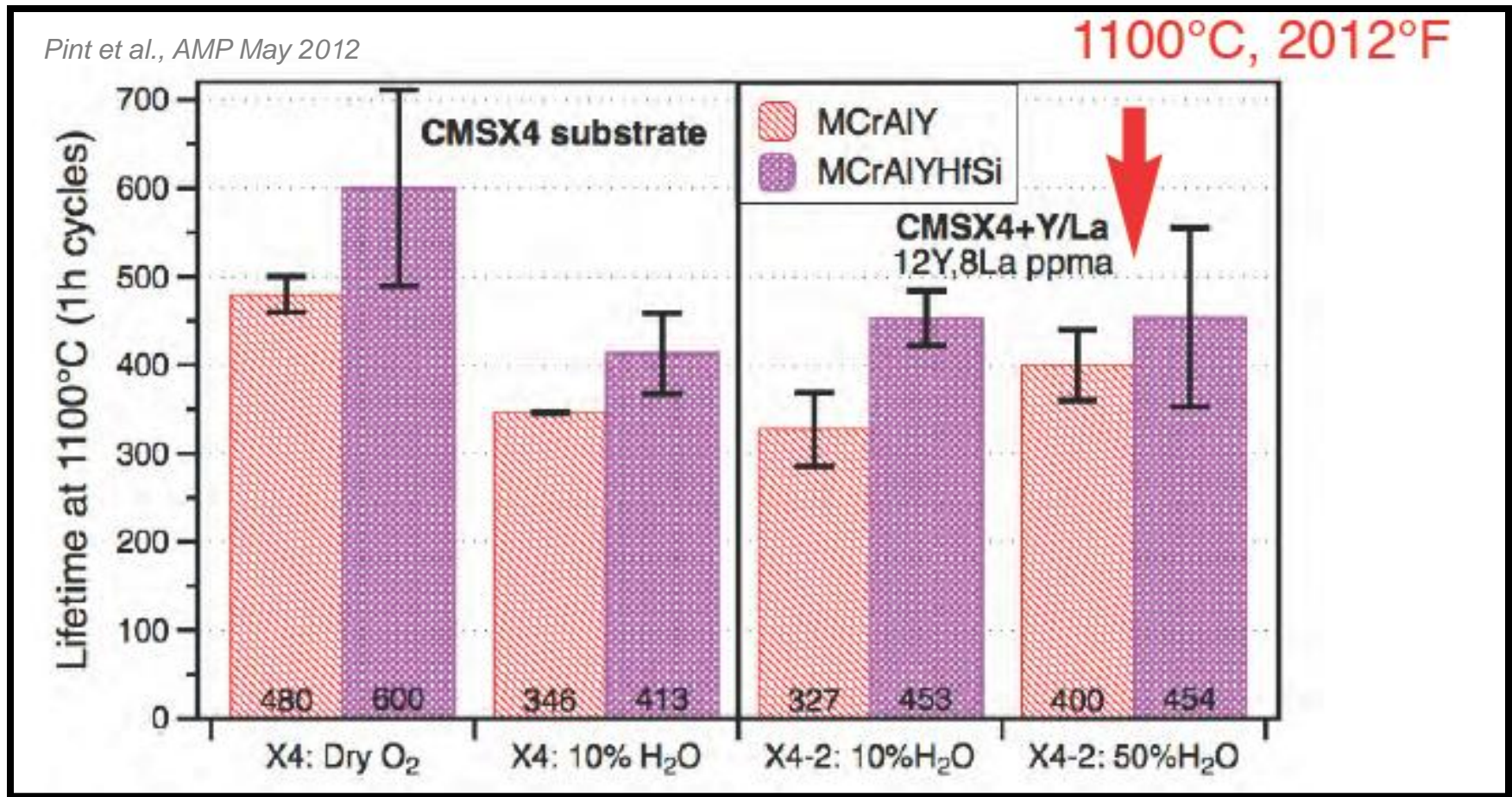
*HVOF process type and spray conditions significantly affect deposition stresses and final stress state of the coating.*

*JP5000 chosen due to microstructure and compressive stress state.*





# Down selection of bond coat material



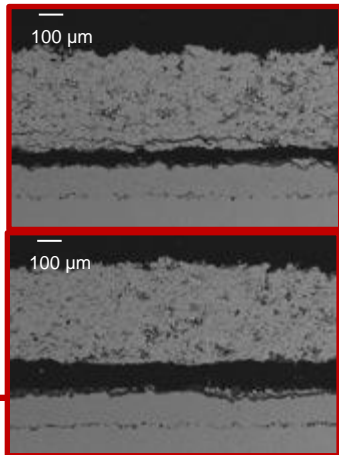
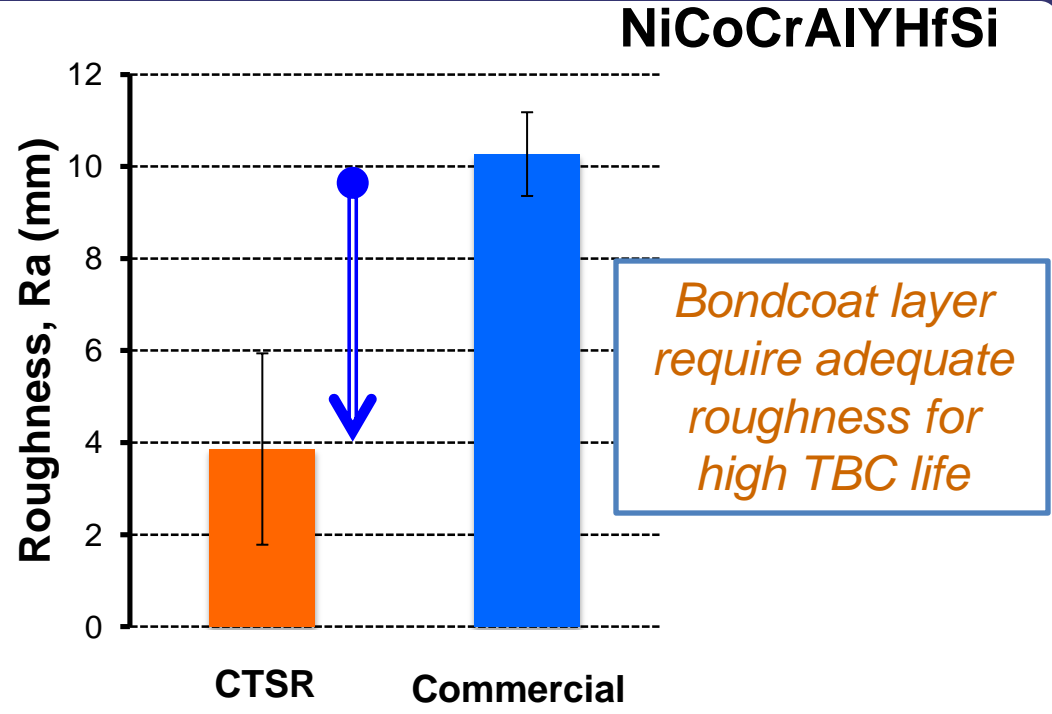
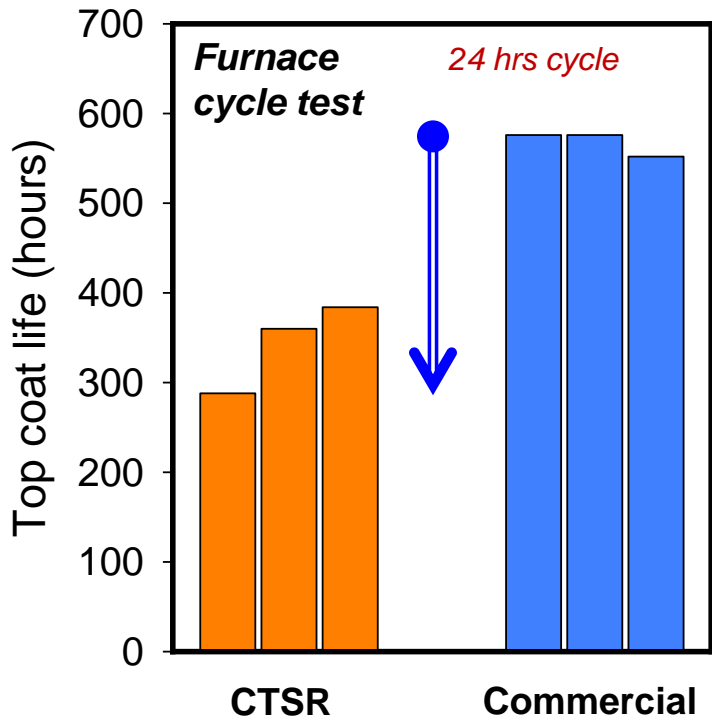
XPT: NiCoCrAlY

AMDRY: NiCoCrAlY-HfSi

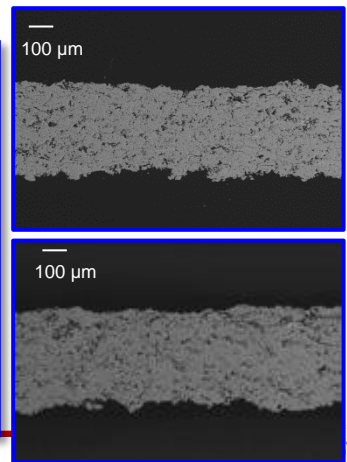
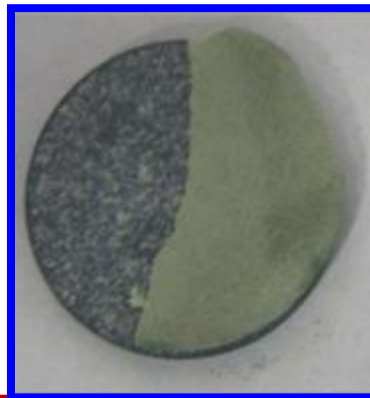
Reactive element bondcoat showed higher life under all the conditions

Collaboration with Dr. Bruce Pint and Dr. Allen Haynes at ORNL

# BC roughness effects may overshadow chemical effects? 10



Fracture in TGO



Fracture in topcoat



# Processing Strategies

Rough bond coat surface



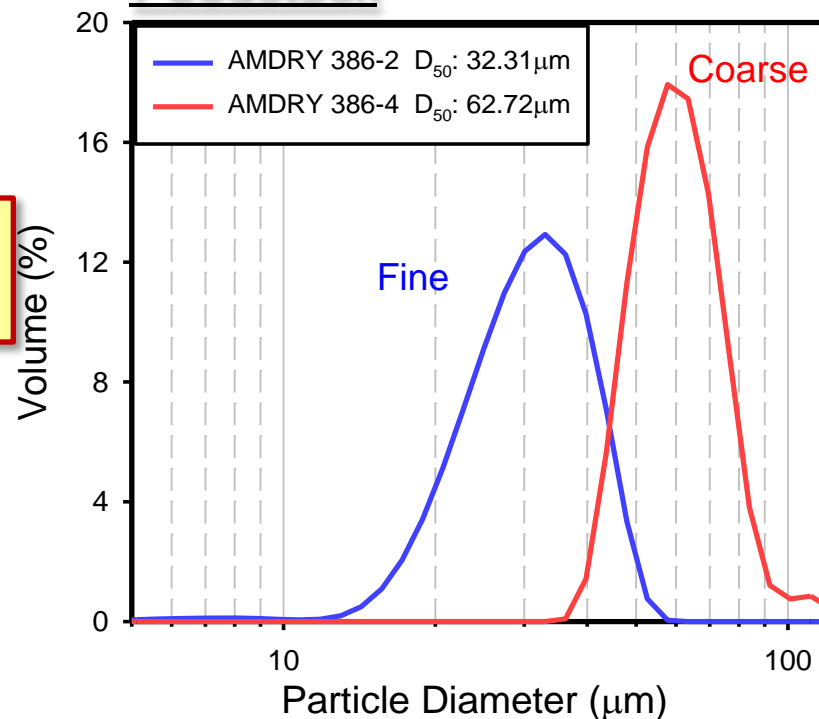
Particle size

Processing Control



Two layered architecture

## Feedstock

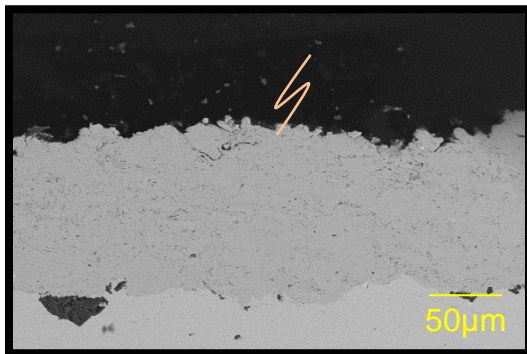
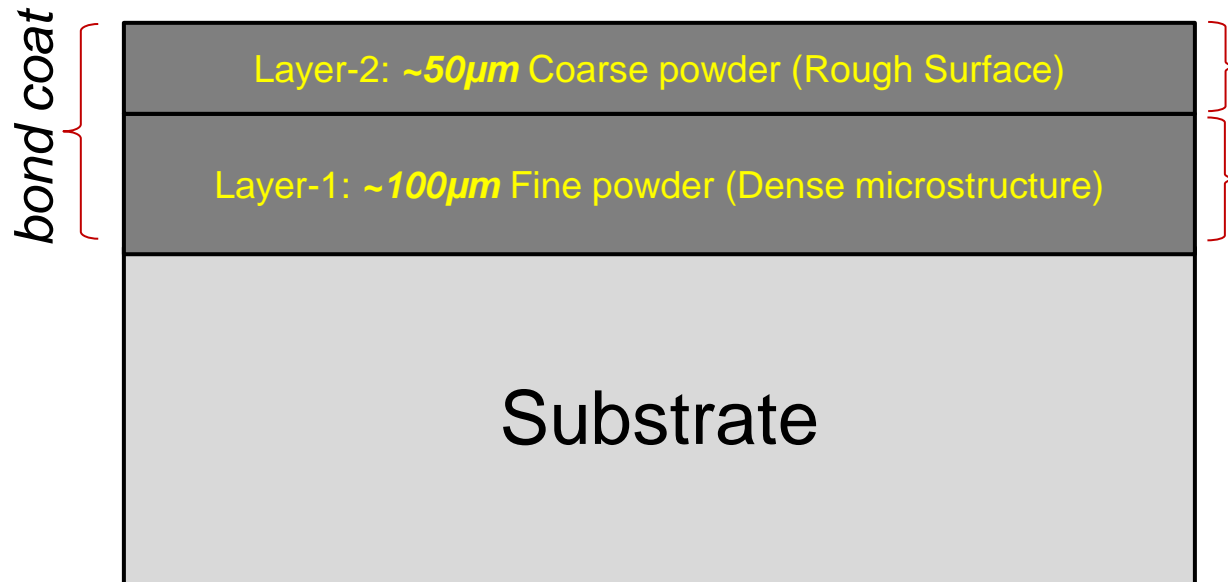


## Strategy

- Utilize the *Fine* particle size for *Dense Oxidation Resistant* initial layer
- Utilize the *Coarse* particle size to tailor the topography for high *surface roughness*

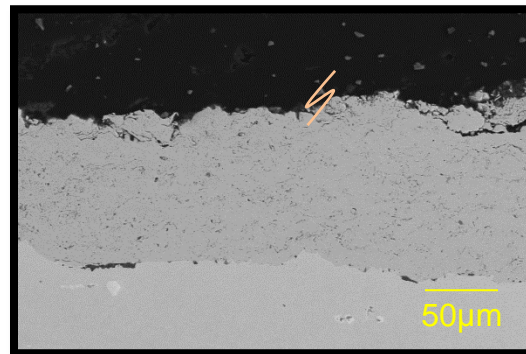
# Deposition Scheme

## Two layers bond coat deposition



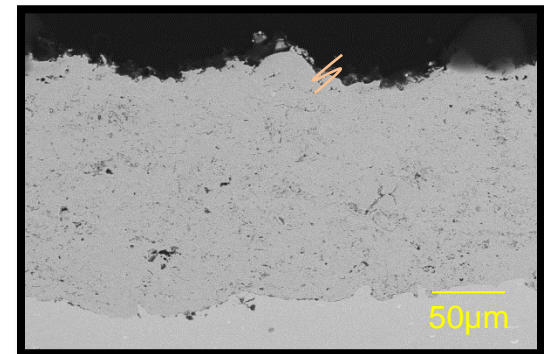
**Densest bottom layer**

Poor splat cohesion



**Denser bottom layer**

Poor splat cohesion and some cracking

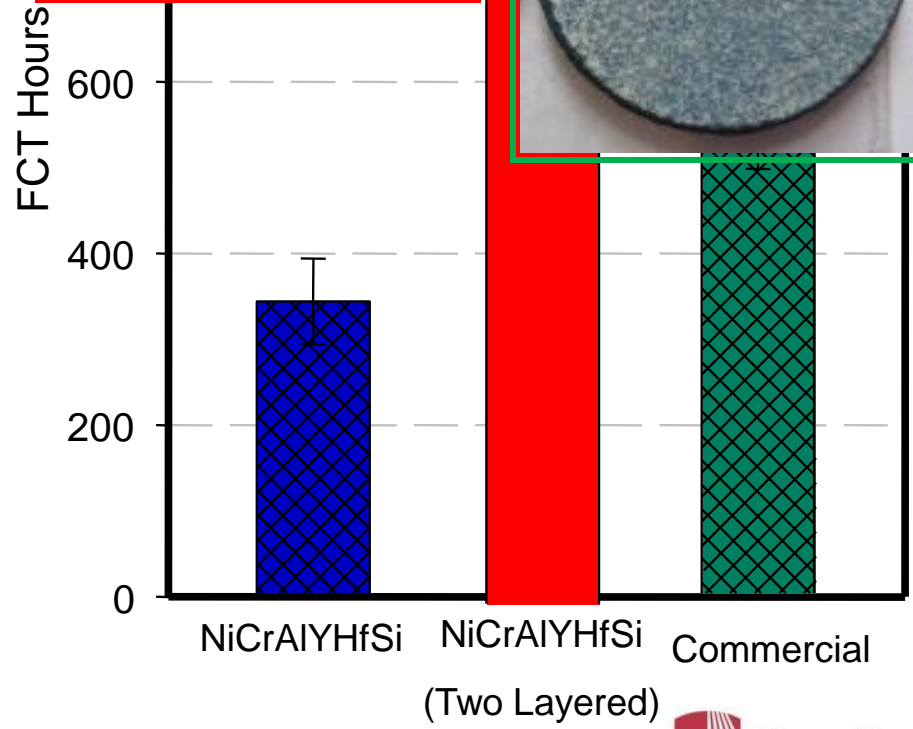
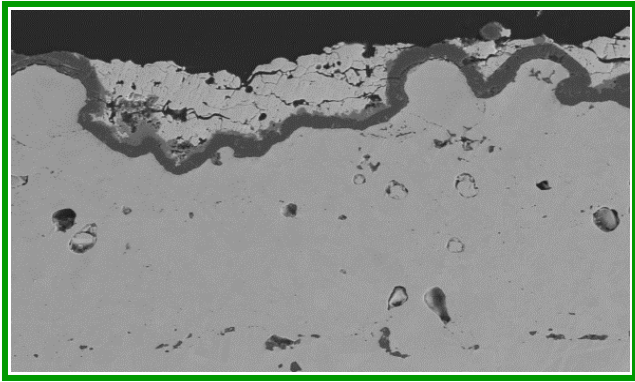
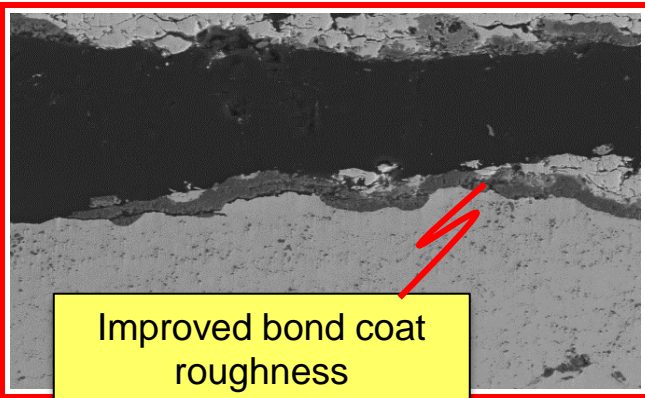


**Least dense bottom layer**

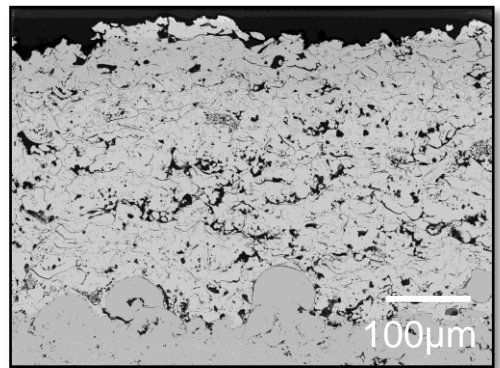
**Good particle melting and splat cohesion**

# Performance of the Two Layered Bond Coat

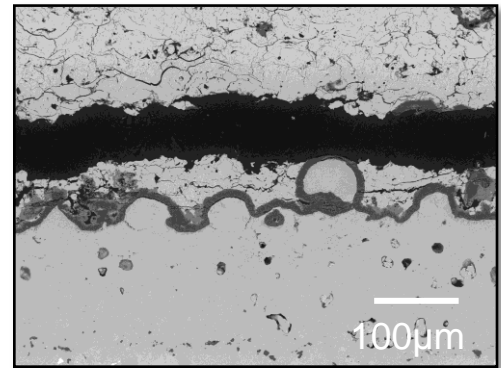
Similar top coats on 3 different bond coats  
**FOCUS : Two Layered Bond Coat**



As-deposited TBC



Failed (~600 hrs)

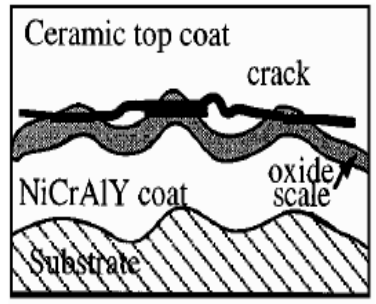
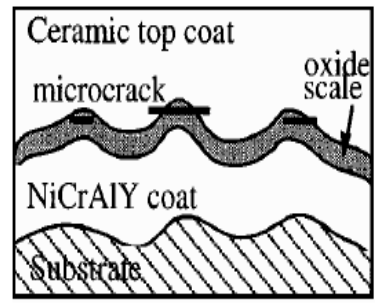
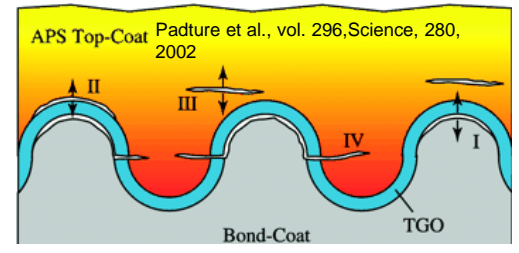


With extending service hours

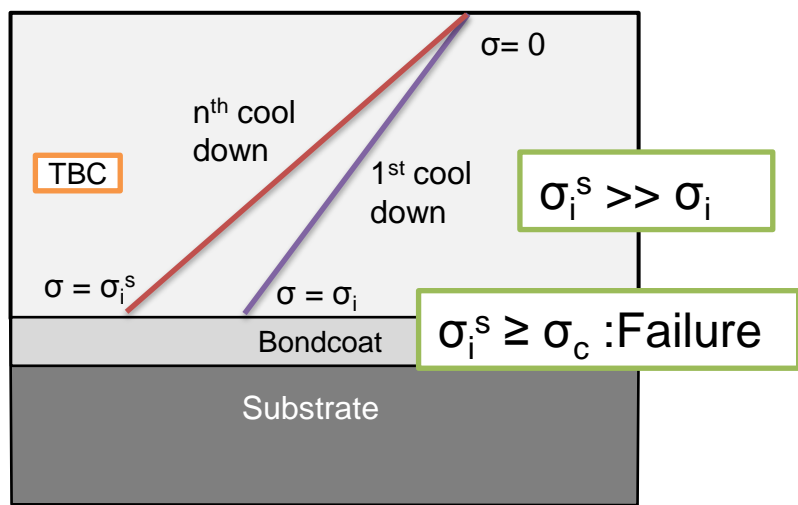
- ❑ **TGO Growth:** Additional Stress build up at the interface. (limited control)
- ❑ **Sintering:** loss in compliance => higher stress build up. Higher driving force for crack propagation. Process optimization to design coating with large compliance in as sprayed condition.

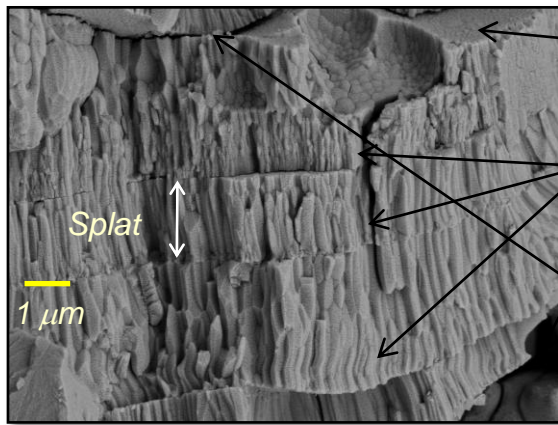
Majority of TBC failure occur at the BC-TC interface. **Parameter of interest is Fracture Toughness.**

Failure Mechanism



Teixeira et al., JTST, 9(2), 2000—191





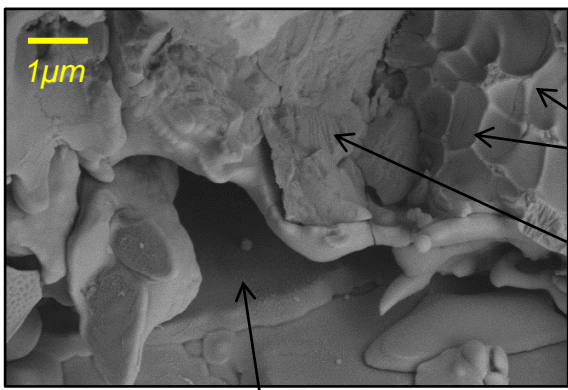
Intrasplat cracks  
 Intersplat boundaries  
 Pores or voids  
 Lamellar pores

The defect architecture governs Thermal conductivity and Coating compliance

Some defects present more tortuous path to a crack than others.

These defects can be controlled via processing.

Fractured X-section. APS YSZ coating



Splat detachment  
 Fracture through splats

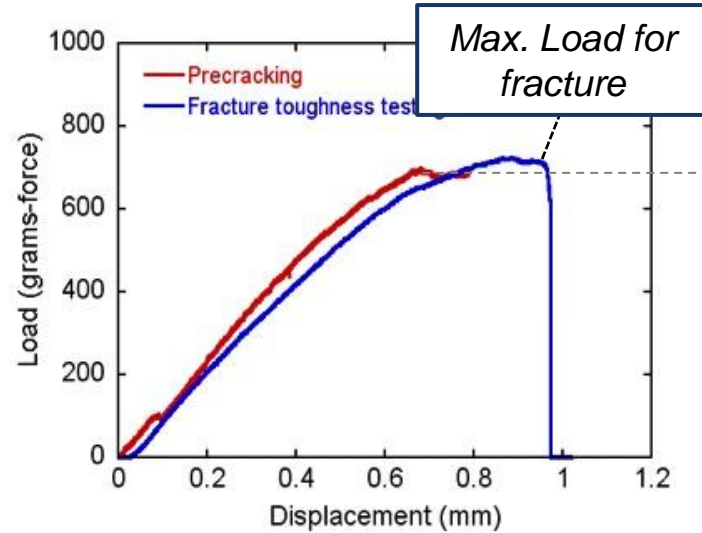
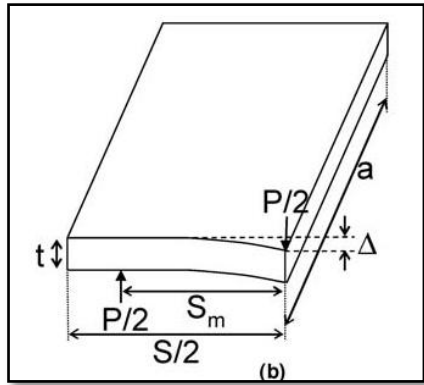
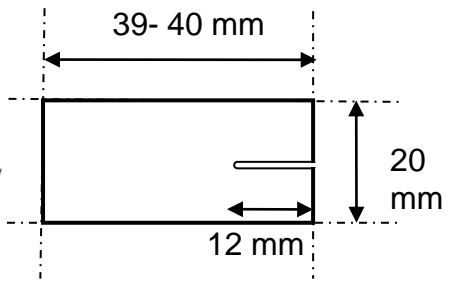
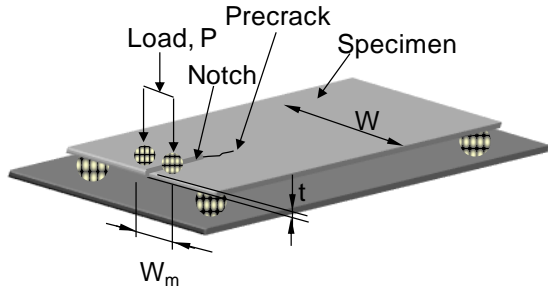
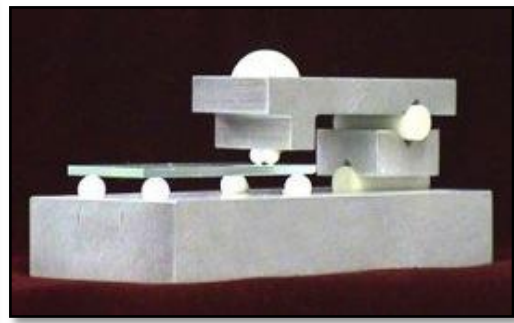
Interlamellar pore as a possible crack path

APS YSZ		
Abradables	Layered structures	Segmented Structures
 50µm	 50µm	 50µm
Large globular pores	Layered structure with thin splats	Vertical crack with high "local" density

Plasma spray can be utilized to produce significantly different microstructures.  
 Can we manipulate the effective fracture toughness of these structure?



# Fracture Toughness: Double Torsion Technique



$$K_{IC} = P_{IC} S_m \left[ \frac{3(1+\nu)}{S t^4 \xi} \right]^{1/2}$$

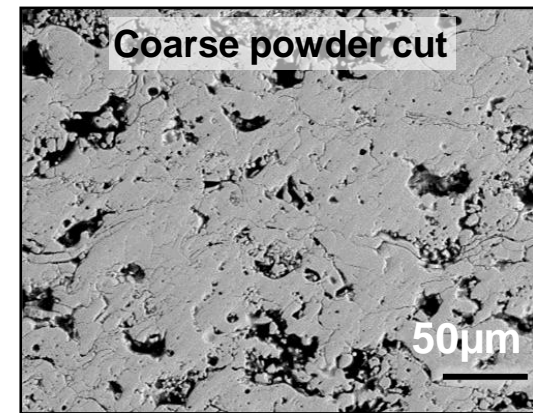
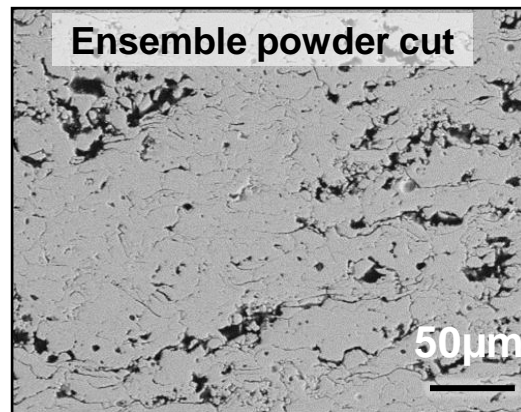
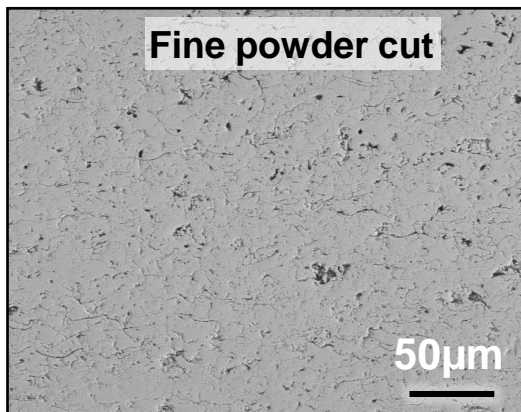
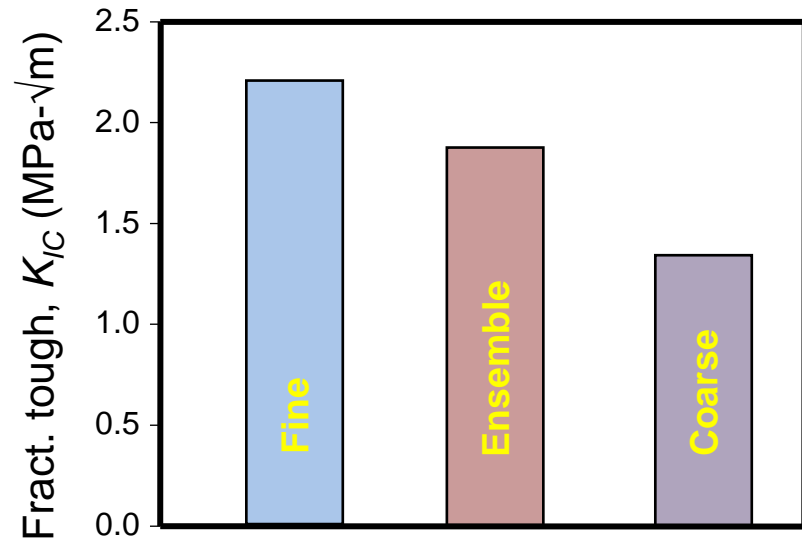
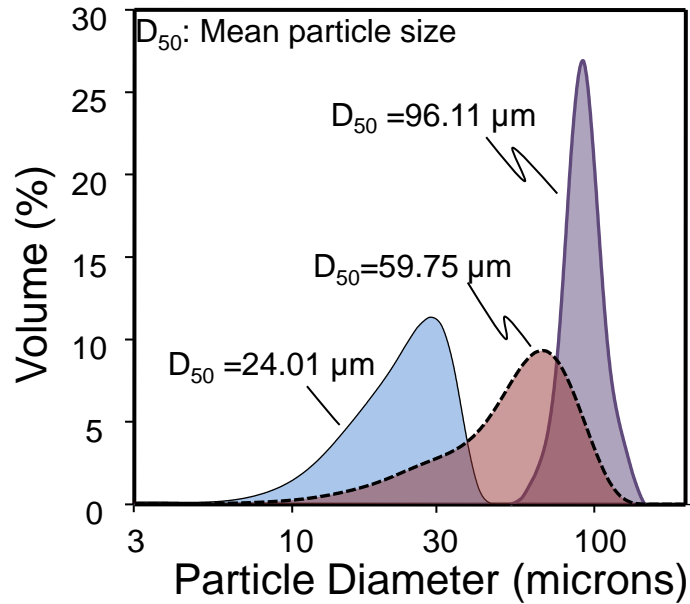
$P_{IC}$  - Maximum load at failure  
 $\nu$  - Poisson's ratio  
 $S$  - specimen width  
 $S_m$  - moment arm  
 $t$  - specimen thickness

- Advantages:**
- ✓ 4 point
  - ✓ Pre-crack
  - ✓ Load
  - ✓ Does not require crack length monitoring
  - ✓ Can be performed a low thickness specimen (~600µm).

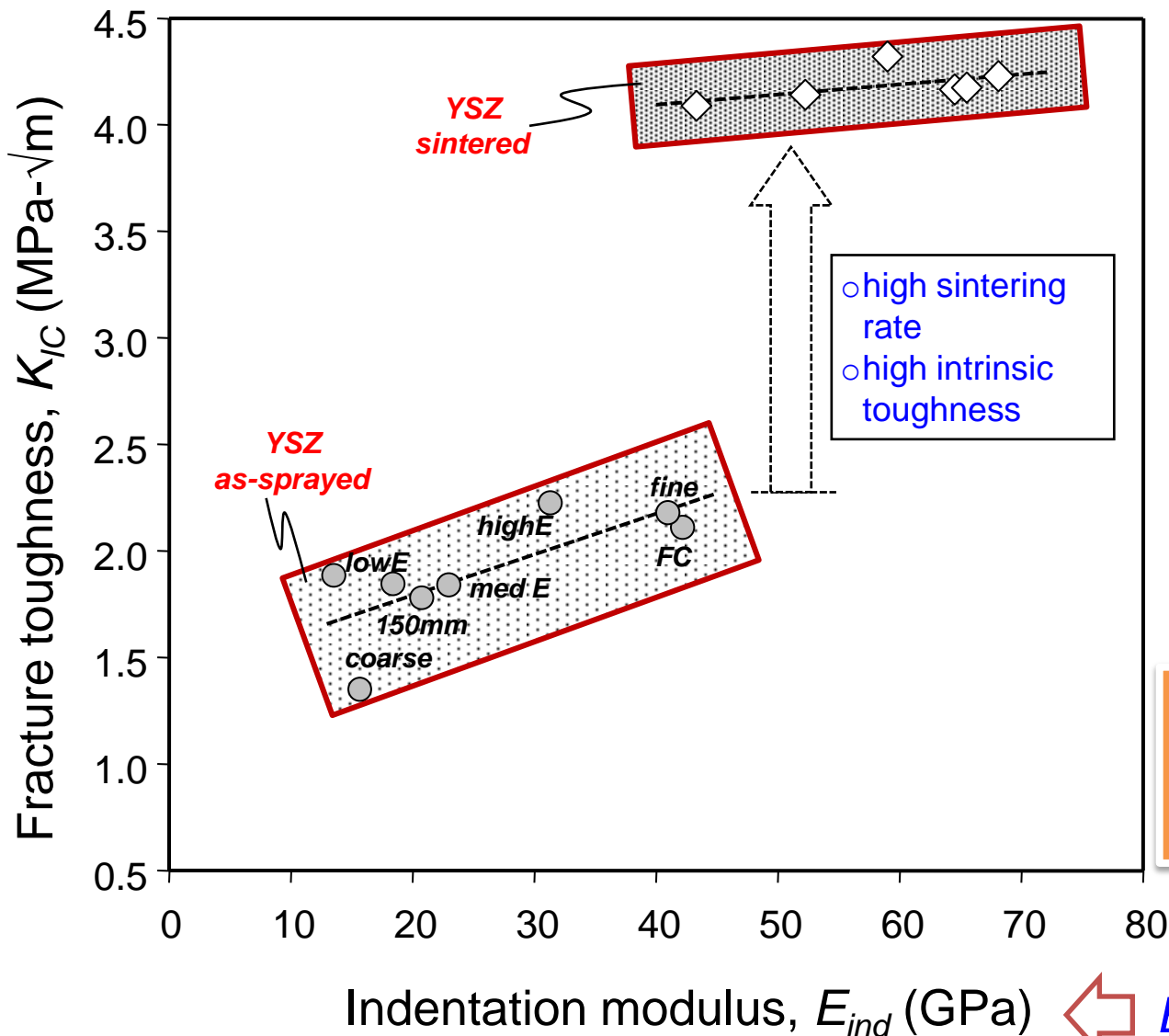
factor  
 $\exp(-\pi S/2t)$







# Fracture toughness and modulus relationship



- With sintering or densification of microstructure, fracture toughness increases.
- Toughness is more sensitive towards sintering

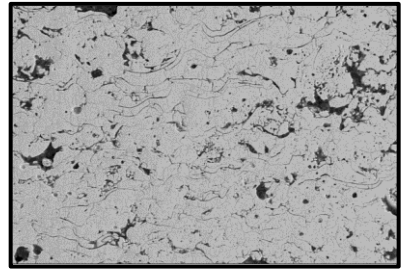
Fracture toughness is sensitive to coating microstructure

# FCT life of various APS YSZ architectures

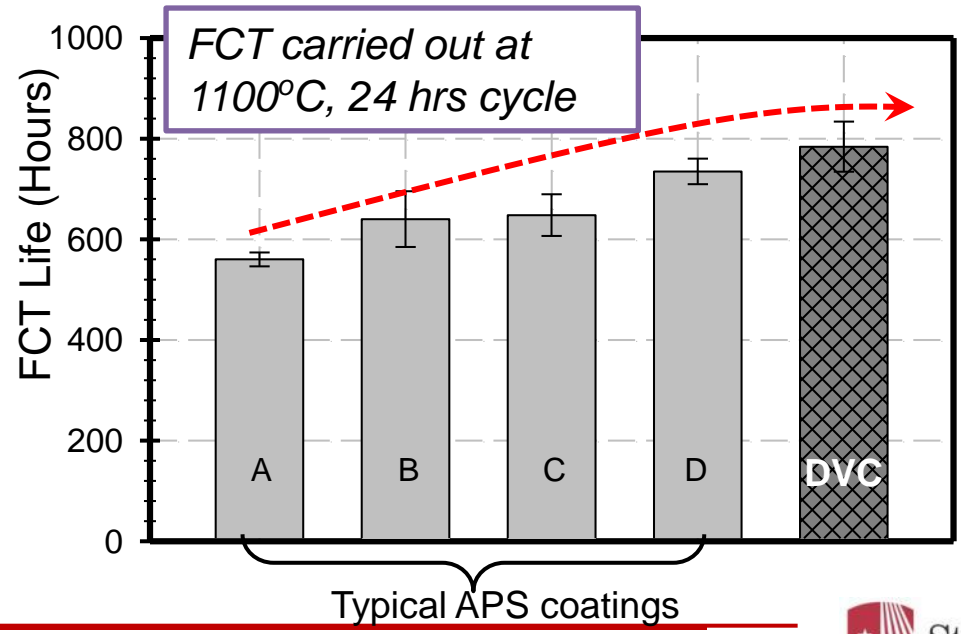
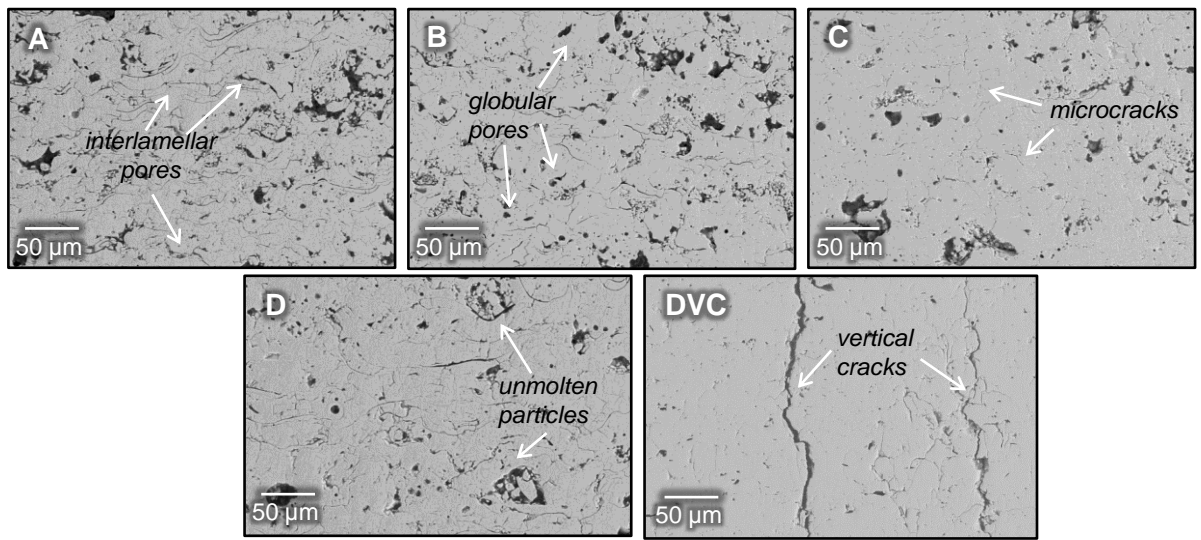
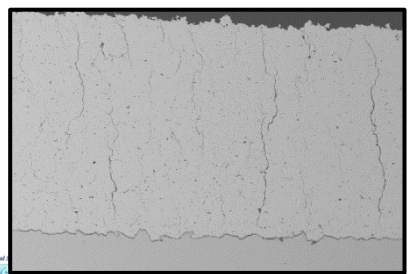
In order to limit the compliance loss

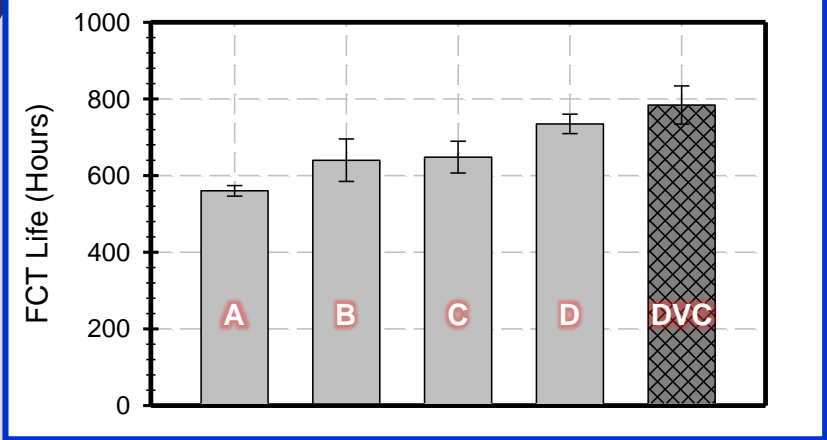
## 1. Porous coatings

*Generally, it has been believed that the porous TBCs last longer.*



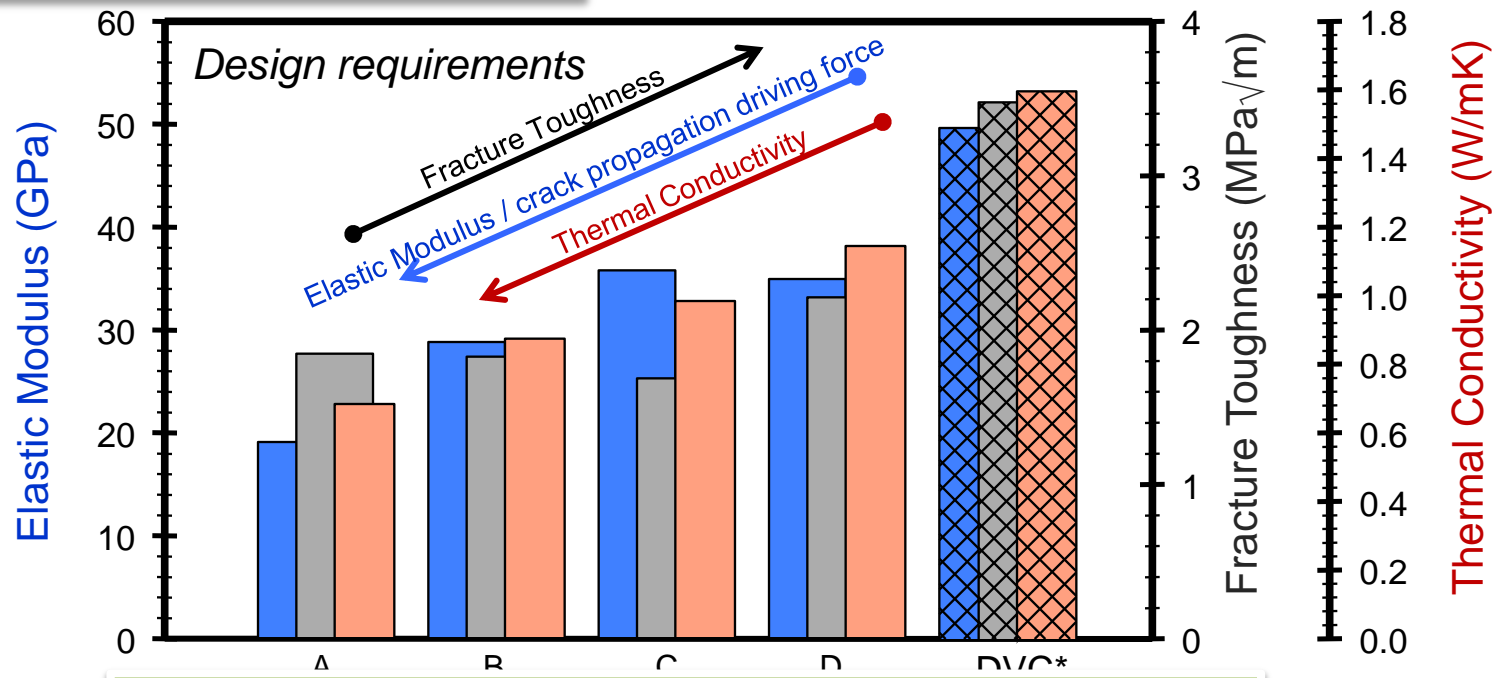
## 2. DVCs





### Design requirements

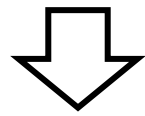
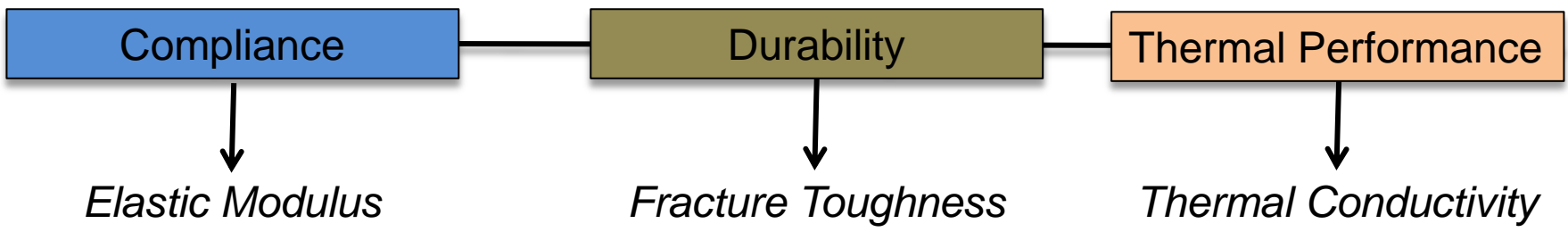
1. High toughness : Improved Cyclic Life
2. Low modulus : Less driving force to failure
3. Low thermal conductivity : Low substrate temperature



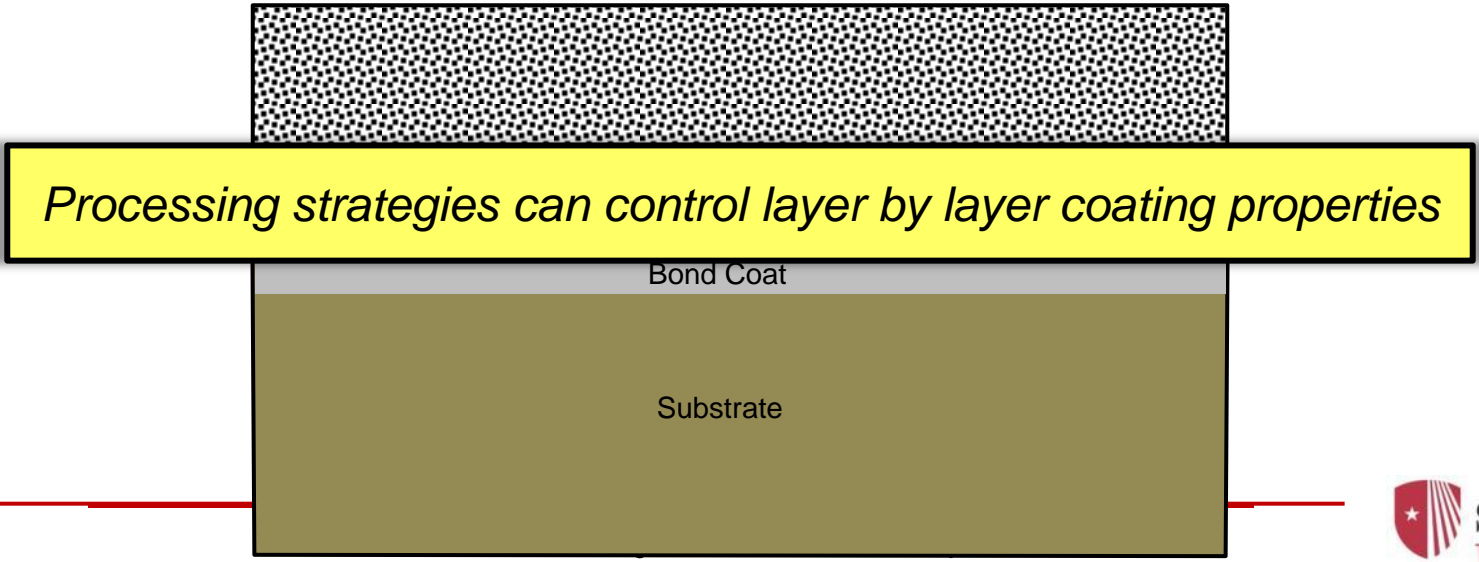
Need a strategic approach towards coating design for multi-functionality

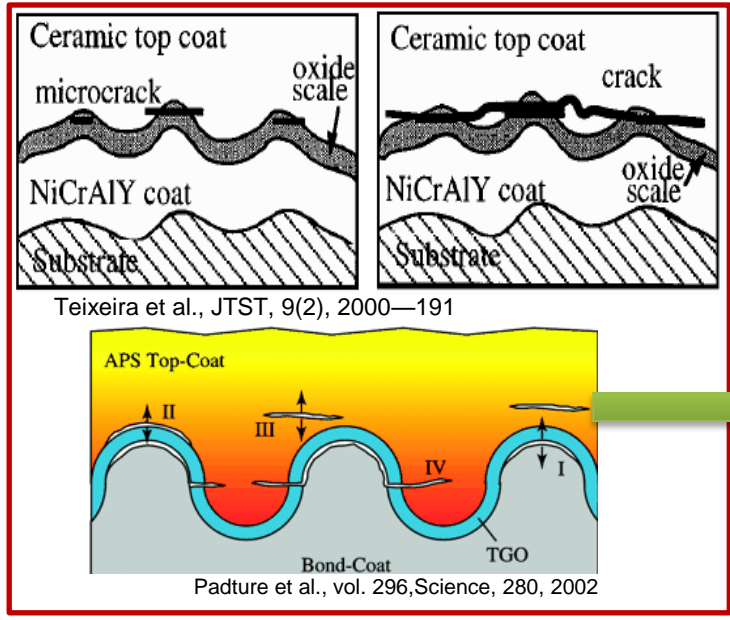


## Primary Requirement

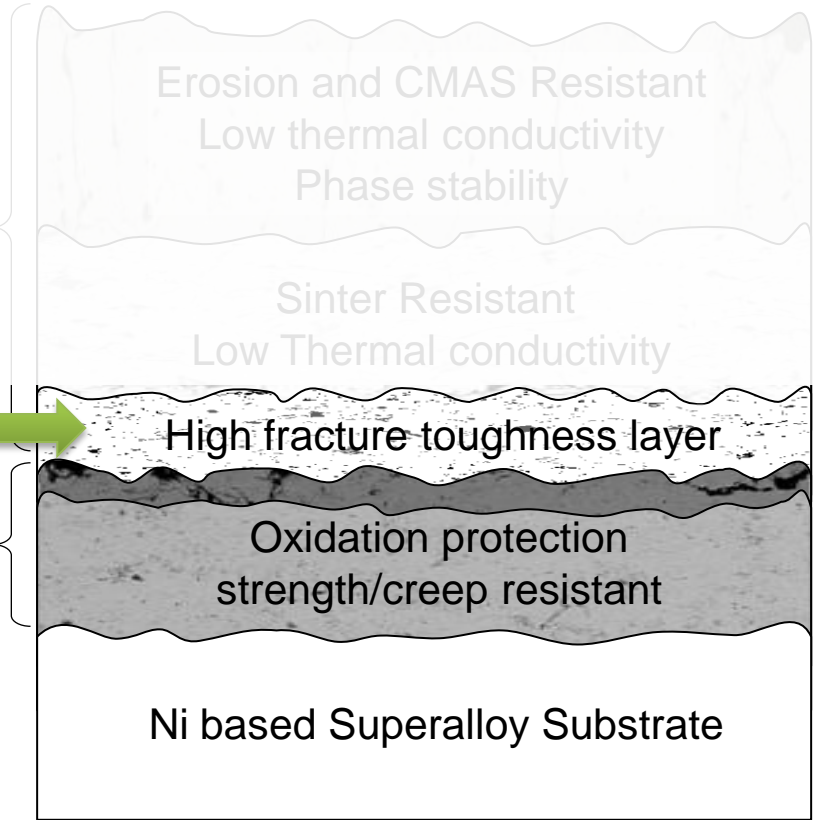


Function of coating microstructure





Multilayer Topcoat  
Bondcoat



$\sigma_i^s \geq \sigma_c$  : Failure



Approach: Higher toughness with denser coatings...

Total Elastic Energy available for interfacial crack propagation

$$U_{isothermal} = \frac{(1 + \nu)}{2(1 - \nu_c)} (\Delta\alpha_c \Delta T_{sub})^2 (E_c h_c)$$

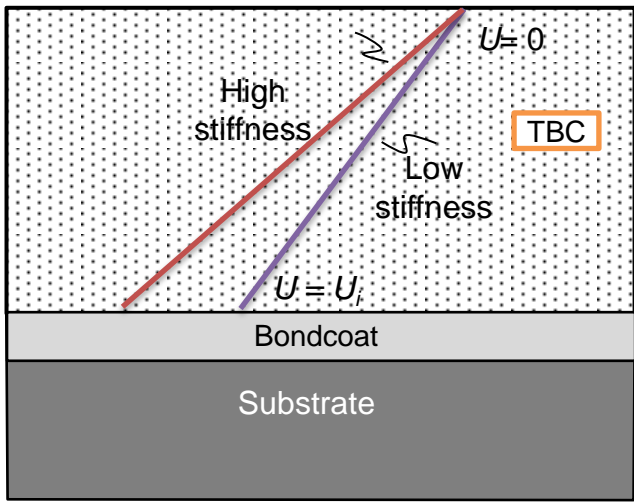
Levi et al., MRS Bulletin, 2012

For constant  $h_c$   
 $U_{interface} \propto E$  (modulus)

Failure occurs when  
 $U_{interface} \geq Gc$

$E^{Dense} > E^{Porous}$

$U_i^{Dense} > U_i^{Porous}$



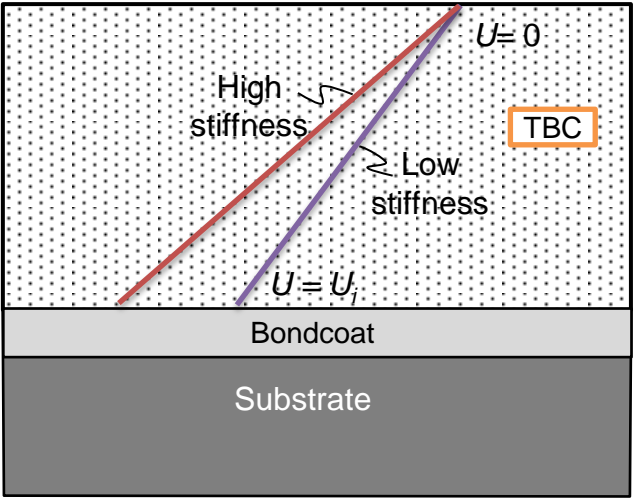
Total Elastic Energy available for interfacial crack propagation

$$U_{isothermal} = \frac{(1 + \nu)}{2(1 - \nu_c)} (\Delta\alpha_c \Delta T_{sub})^2 (E_c h_c)$$

Levi et al., MRS Bulletin, 2012

For constant  $h_c$   
 $U_{interface} \propto E$  (modulus)

Failure occurs when  
 $U_{interface} \geq Gc$



For multilayer coatings

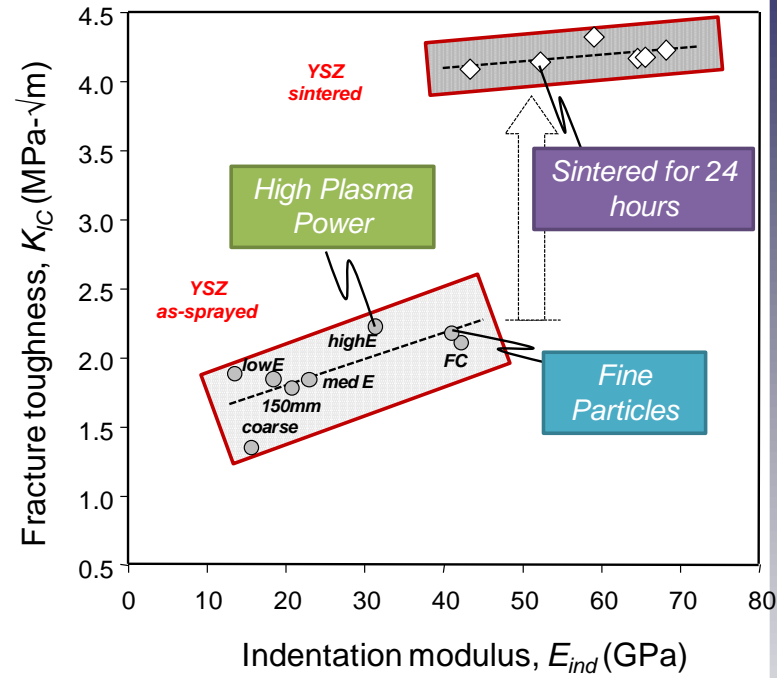
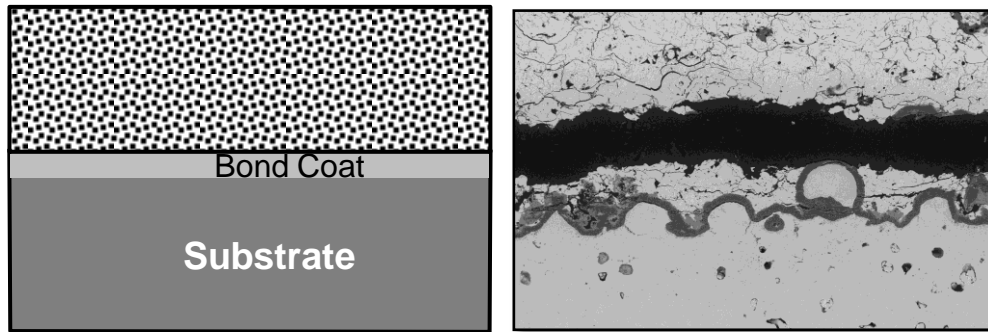
$$U_{isothermal} = \frac{(1 + \nu)}{2(1 - \nu_c)} (\Delta\alpha_c \Delta T_{sub})^2 (E_{c1} h_{c1} + E_{c2} h_{c2} + E_{c3} h_{c3} \dots)$$

Derived from Levi et al., MRS Bulletin, 2012

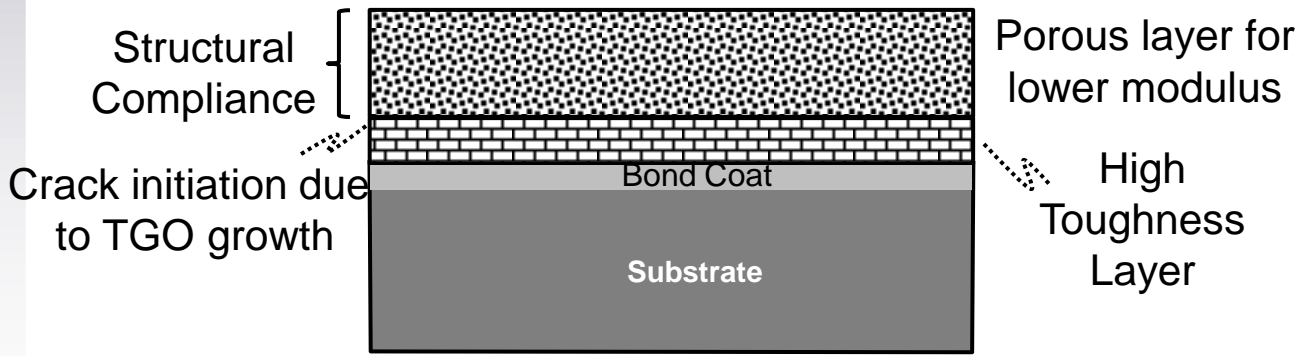


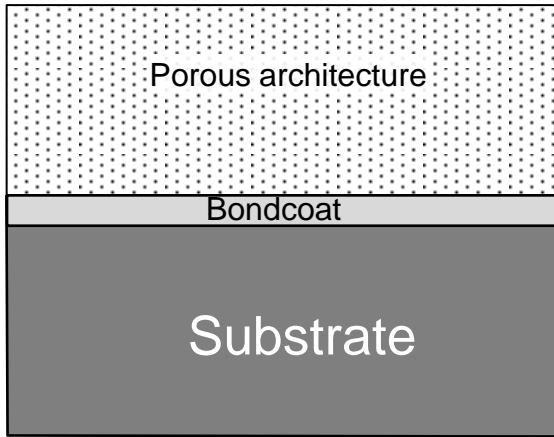


Typical APS TBC

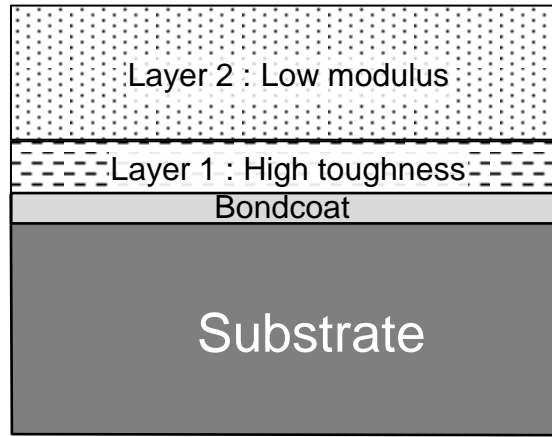


Functionally Optimized TBC with high fracture toughness interface layer

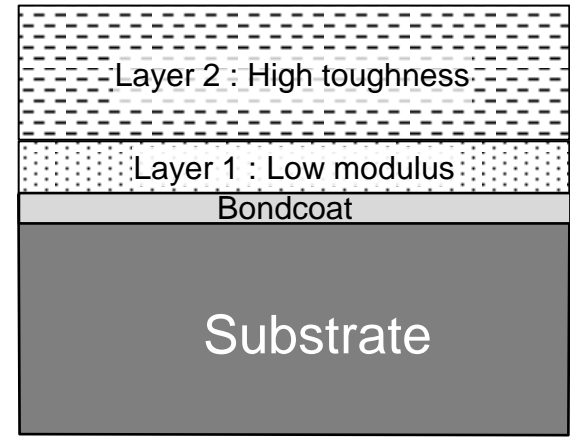




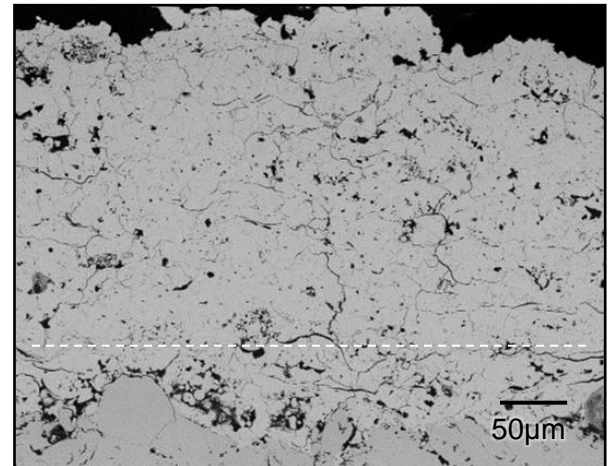
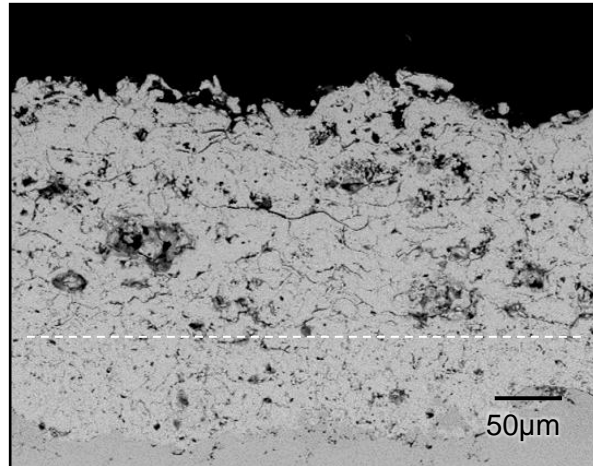
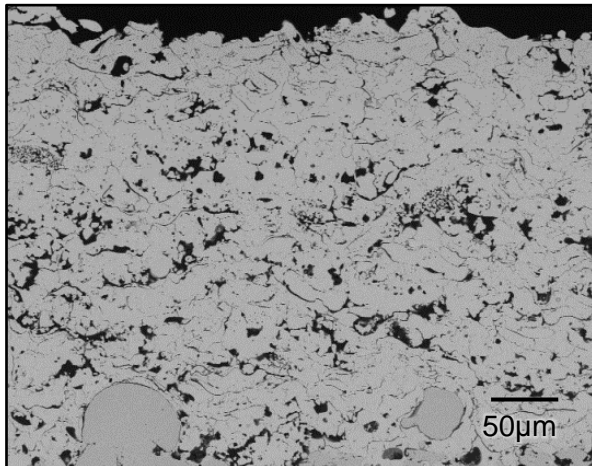
Conventional TBC  
Porous single layer

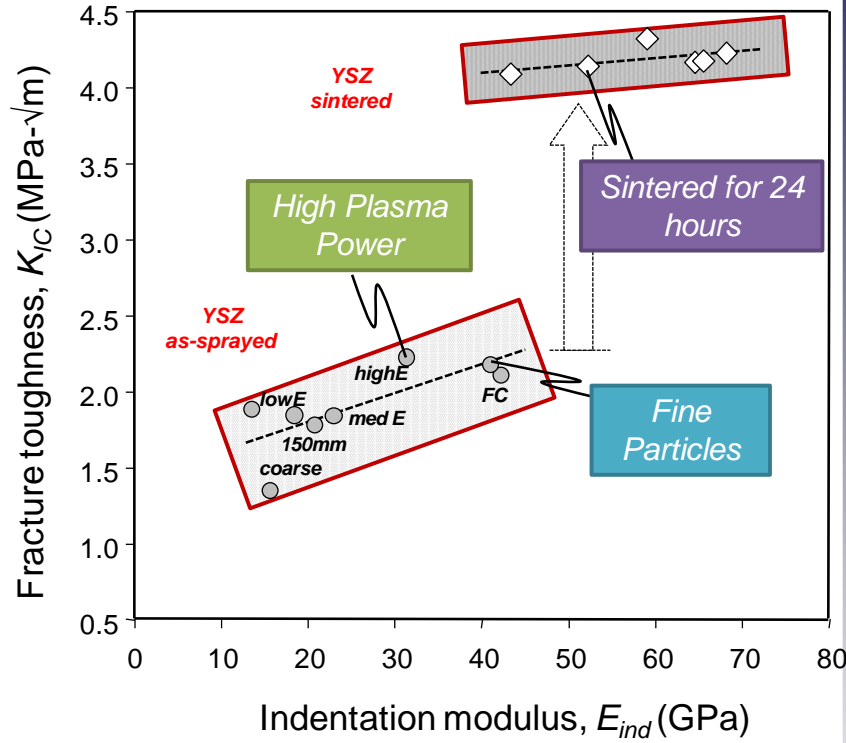
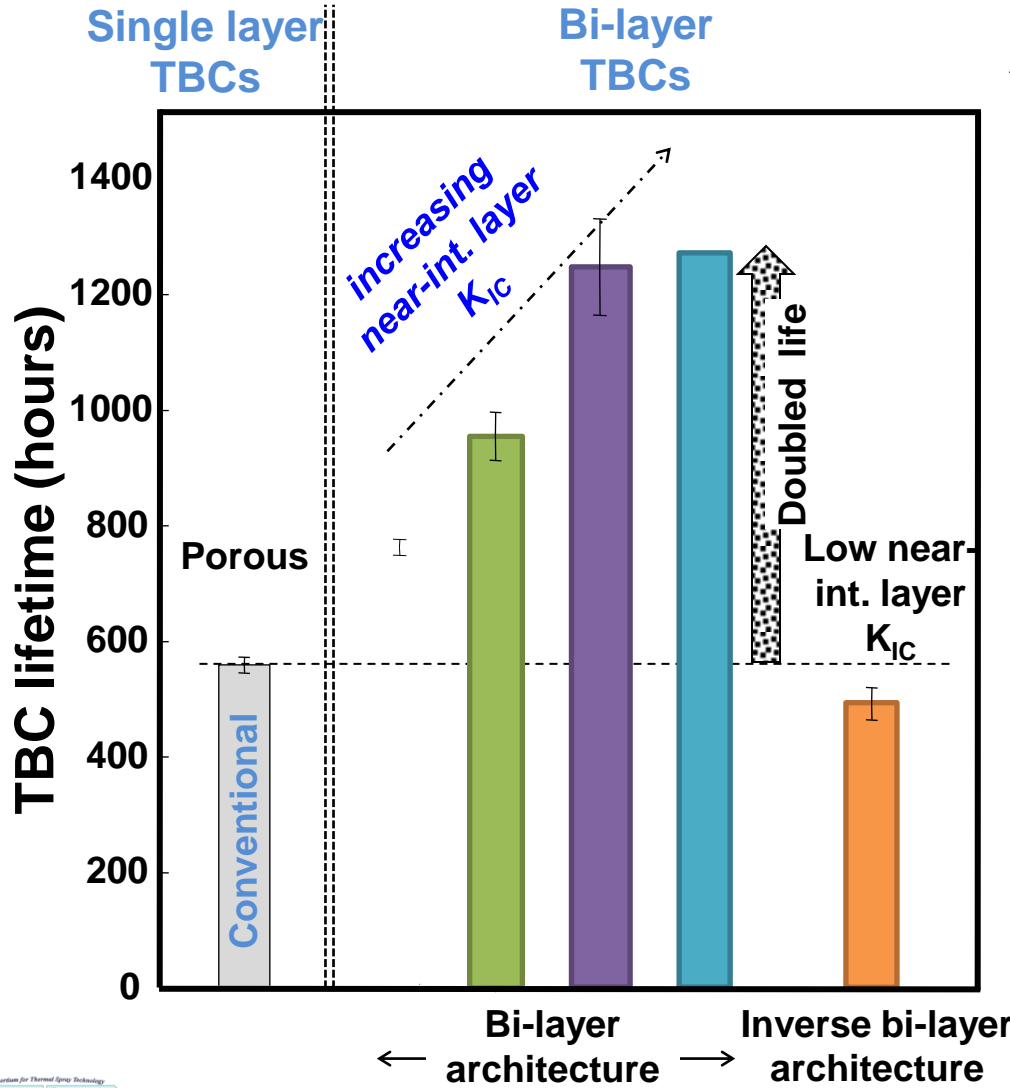


Optimal bi-layered TBC  
Bi-layer with tough near-interface layer



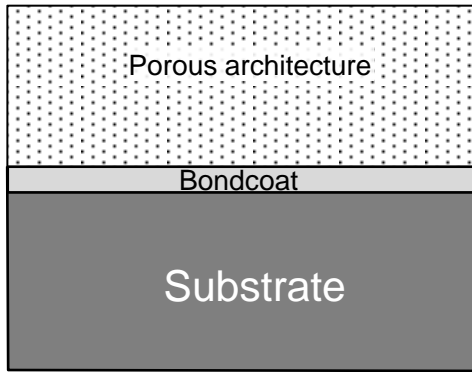
Inverse bi-layered TBC  
Bi-layer with inverse architecture



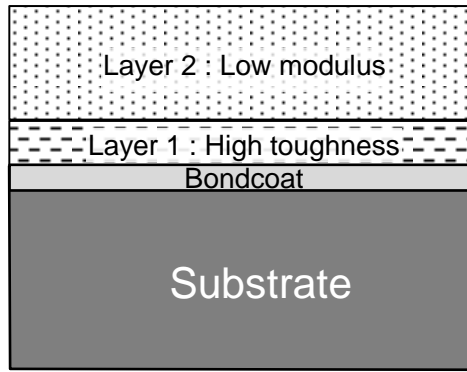


Consistent improvement in TBC life for bi-layer coatings  
With high toughness interface layer

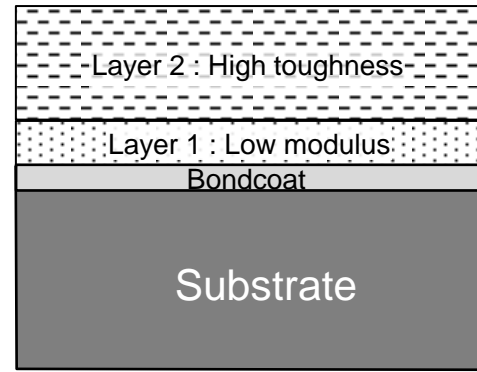




Conventional TBC



Optimal bi-layered TBC



Inverse bi-layered TBC

Failed Specimens

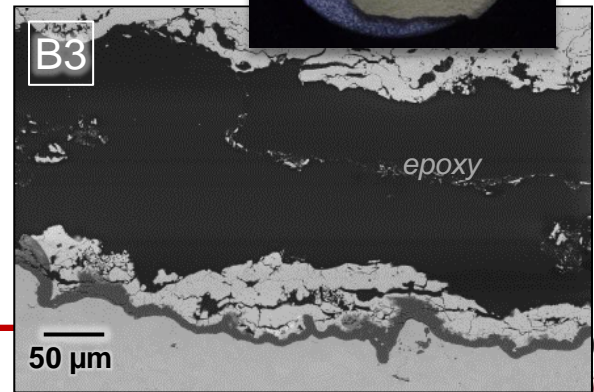
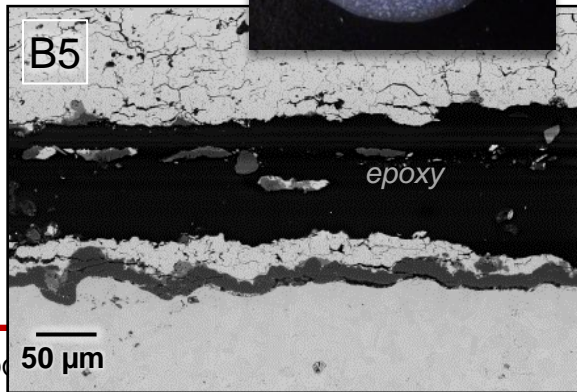
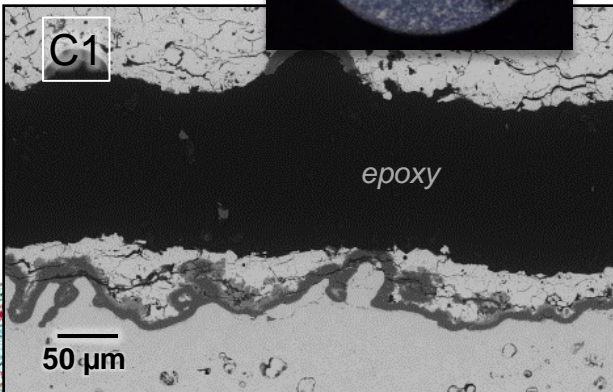
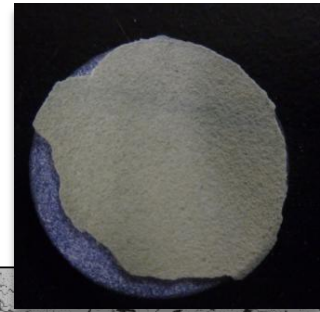
Conventional porous single layer



bi-layer with dense near-interface layer

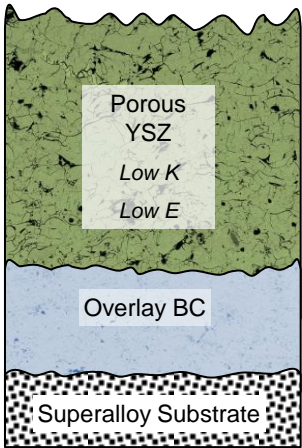


bi-layer with inverse architecture

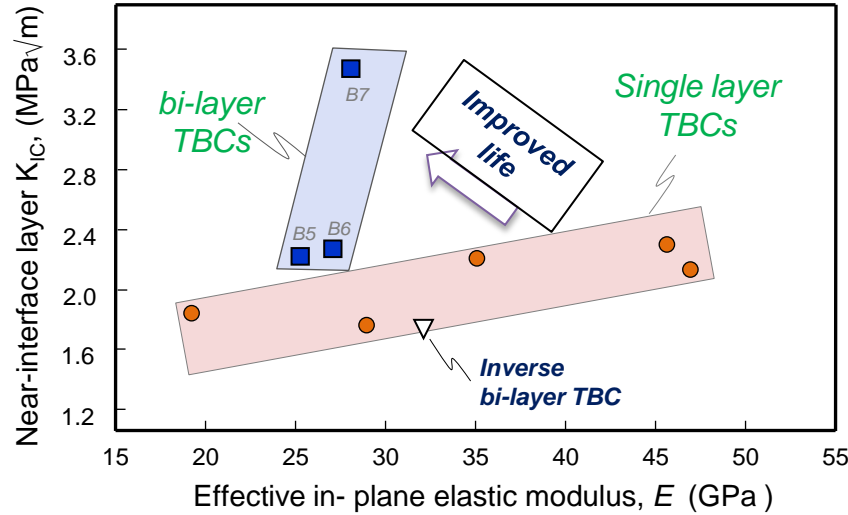
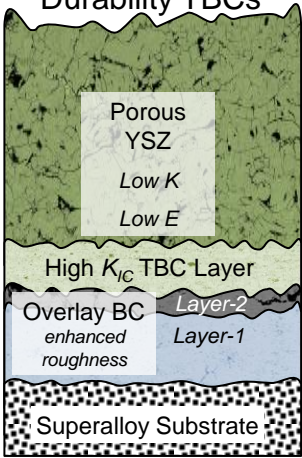


# Process optimization strategies

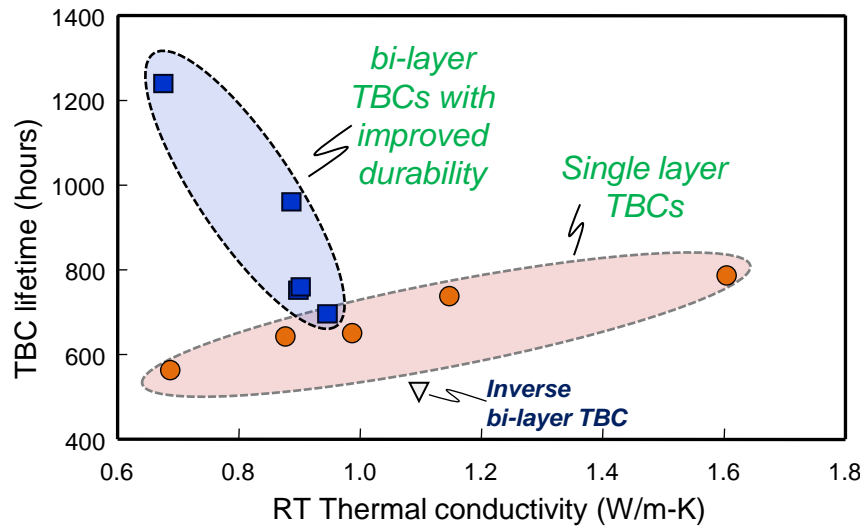
Conventional TBCs



Enhanced Durability TBCs

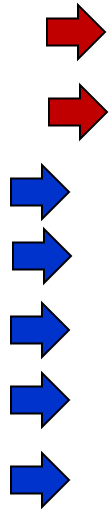


Property based design map for coatings with enhanced durability



Simultaneous optimization of coating durability and functionality





	<b>Traditional YSZ</b>	<b>New TBC Requirement</b>
Phase Stability	Good < 1200C	Good<1300-1400C
Thermal Expansion	Fair	Challenging
Thermal Conductivity*	Low	Lower
Sintering Resistance*	Fair	Good
Erosion Resistance*	Good	Challenging
Fracture Toughness*	Good	Challenging
<b>Mechanical Compliance</b>	known	To be explored

➔ *Materials' intrinsic properties*

➔ *Can be optimized via processing strategies\**



## TBC Materials under considerations

Material	Composition	Advantages	Powder
<b>YSZ</b>	7-8wt% YSZ	Stable below 1200 C, cost effective, properties well-characterized	Various sources, different levels of purity
<b>Zirconate</b>	$\text{La}_2\text{Zr}_2\text{O}_7$	Pyrochlore, low thermal conductivity, phase stability to 1400 C	Julich
<b>Zirconate</b>	$\text{Gd}_2\text{Zr}_2\text{O}_7$	Pyrochlore, low thermal conductivity, phase stability to 1400 C, compatible with YSZ	Saint Gobain, Julich,
<b>Co-doped</b>	1.5mol% $\text{Yb}_2\text{O}_3$ 1.5mol% $\text{Gd}_2\text{O}_3$ 2.1mol% $\text{Y}_2\text{O}_3$ $\text{ZrO}_2$	t' phase, low thermal conductivity, sintering resistant, compatible with MCrAlY bond coat, high erosion resistance	NASA
<b>YSZ-Al-Ti</b>	YSZ+20mol%Al +5mol%Ti	<i>CMAS resistant</i>	<i>Ohio State Univ</i>

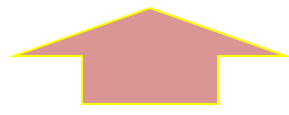
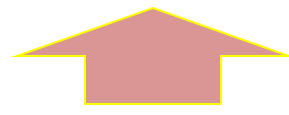
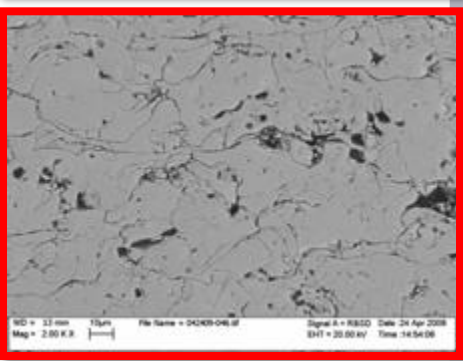
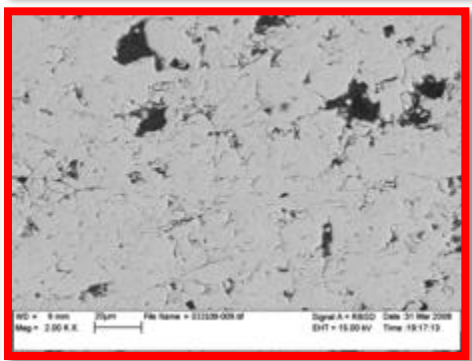
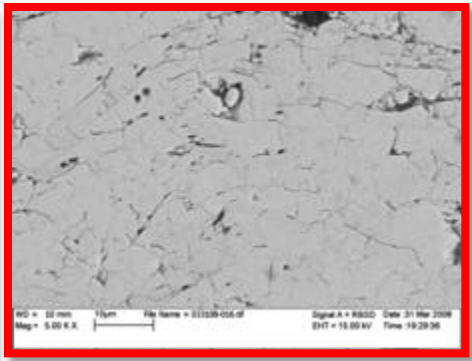
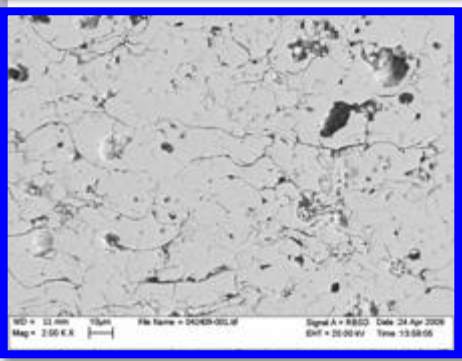
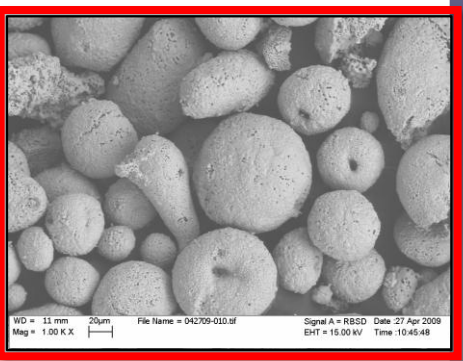
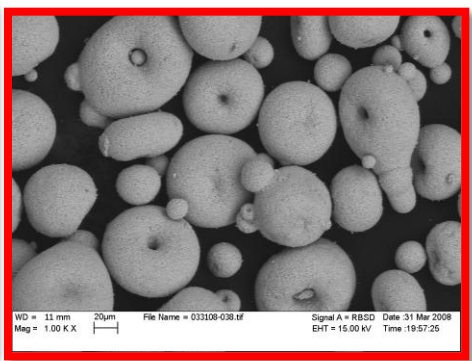
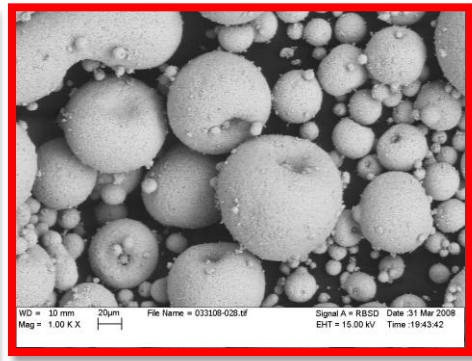
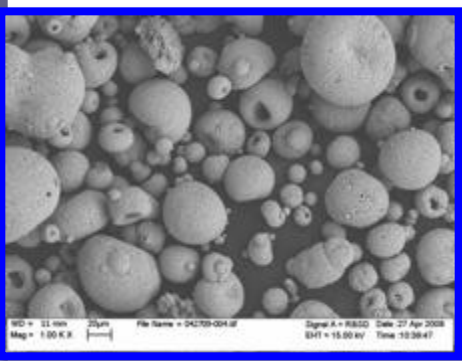


YSZ

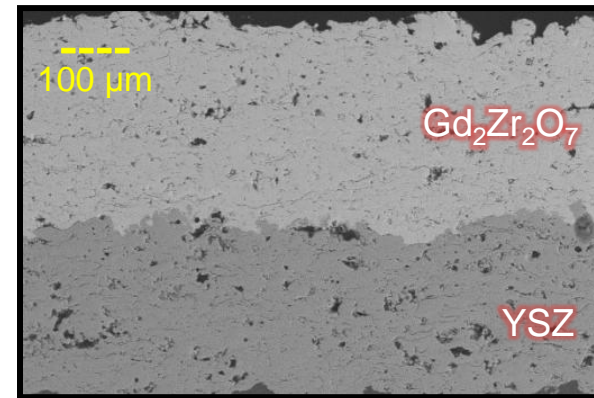
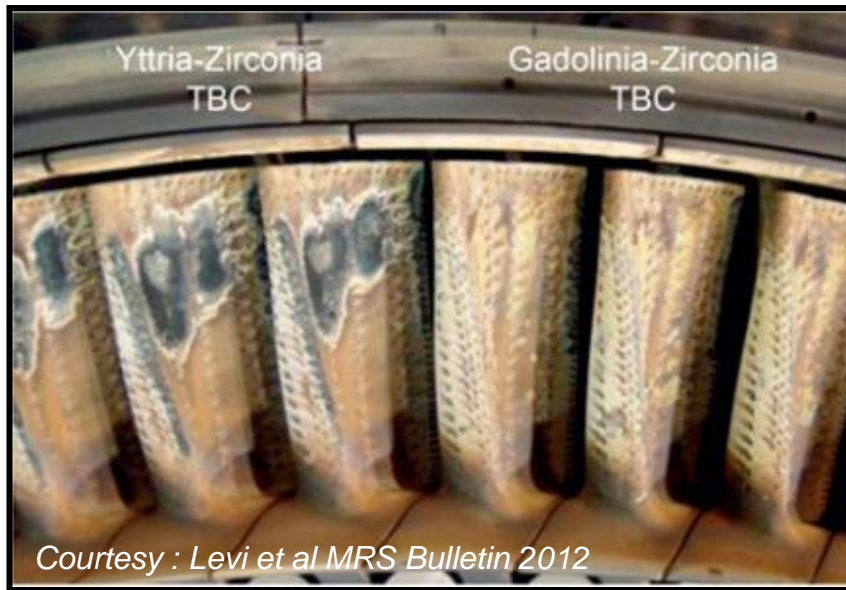
$\text{La}_2\text{Zr}_2\text{O}_7$

$\text{Gd}_2\text{Zr}_2\text{O}_7$

Cluster-doped





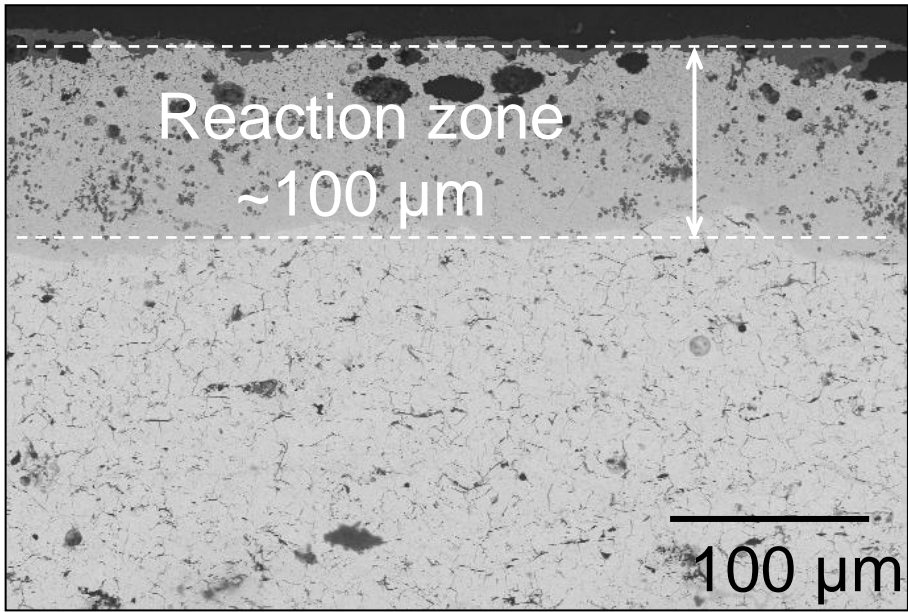


## Challenges:

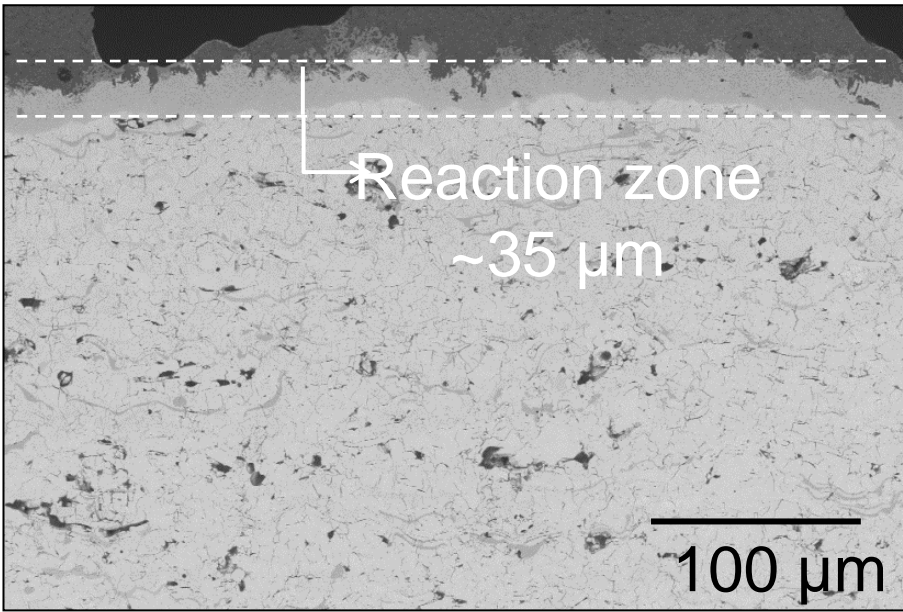
1. CMAS mitigation
2. High erosion/FOD resistance
3. Compatibility with YSZ

All have significant dependency on processing

Porous GDZ



Dense GDZ



SiO <sub>2</sub>	CaO	FeO	Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>	TiO <sub>2</sub>	SrO	MnO	K <sub>2</sub> O	Na <sub>2</sub> O	P <sub>2</sub> O <sub>6</sub>
29.7	25.4	14.8	14.7	5.1	3.6	1.8	1.1	1.0	0.9	0.8	0.6	0.2

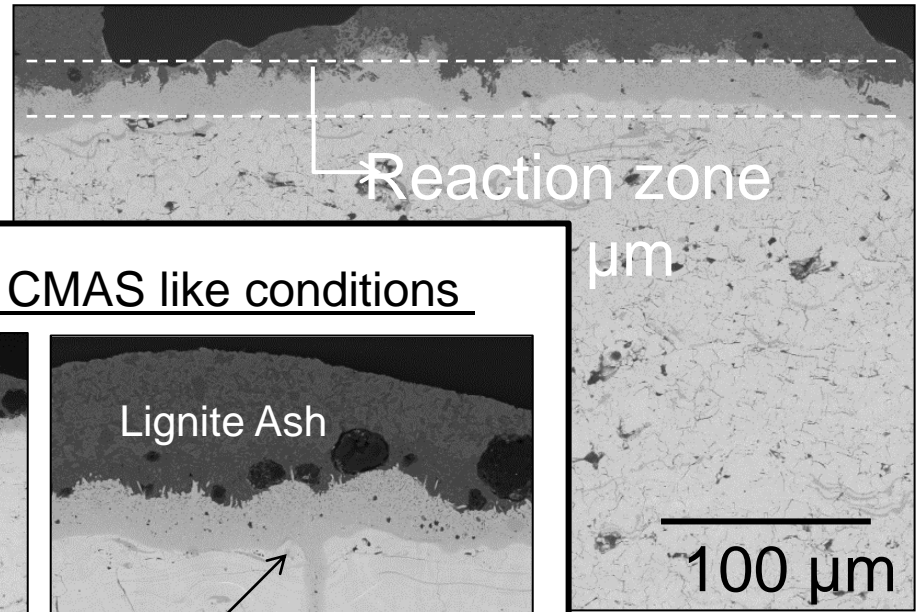
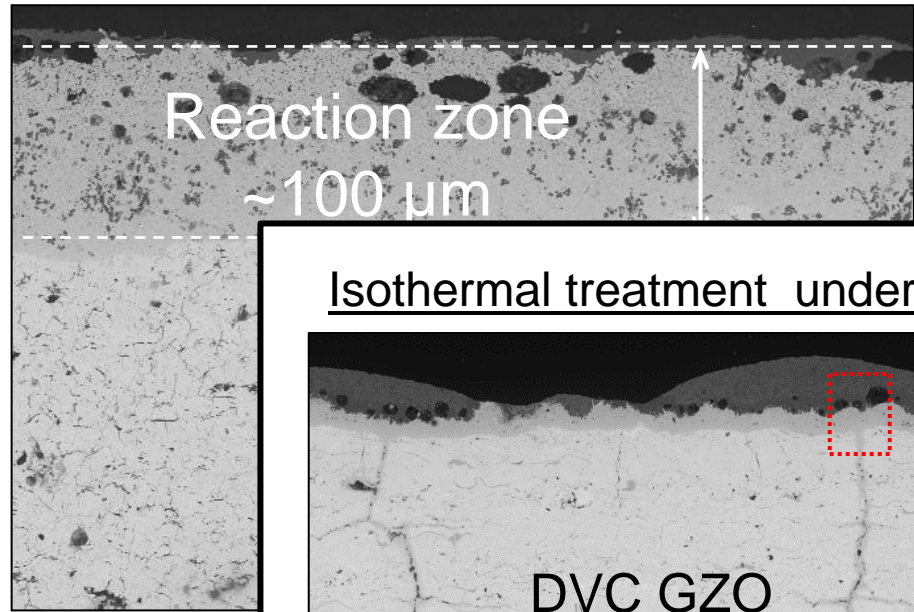
Courtesy: Prof. Nitin Padture

- Dense GDZ seems to offer lesser Lignite ash penetration depth.
- It also offer benefits in terms of erosion resistance.
- However, it has high modulus, which will increase the overall strain energy



Porous GDZ

Dense GDZ



Isothermal treatment under CMAS like conditions

DVC GZO

Lignite Ash

Molten ash wicking

**Potential candidate for Top layer**

SiO <sub>2</sub>
29.7

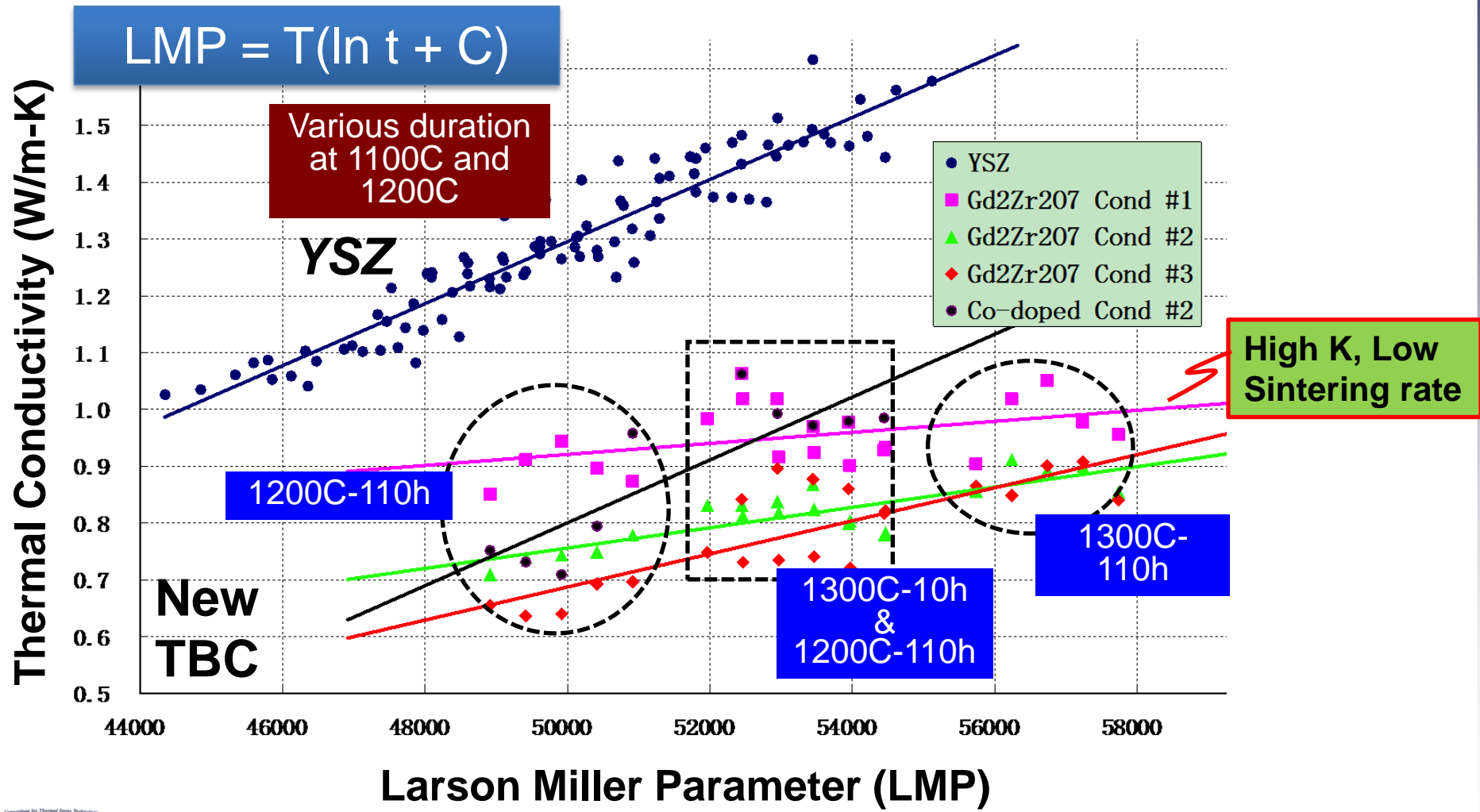
Na <sub>2</sub> O	P <sub>2</sub> O <sub>6</sub>
0.6	0.2

Courtesy: Prof. Nitin Padture

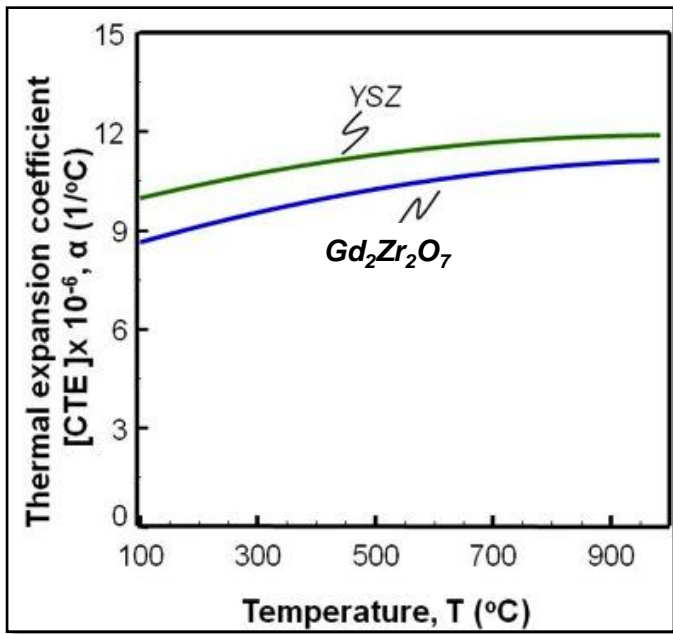
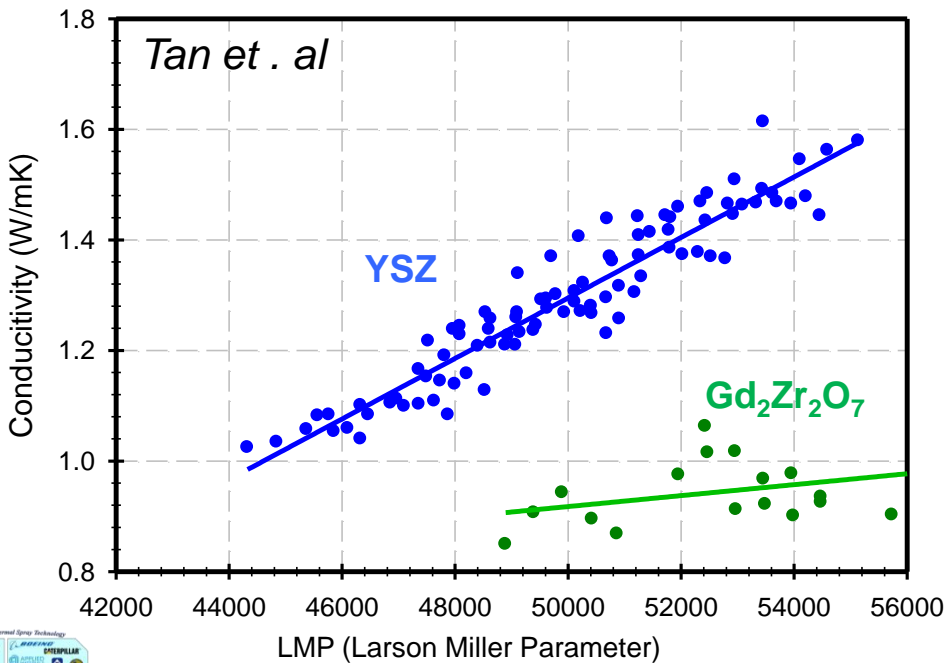
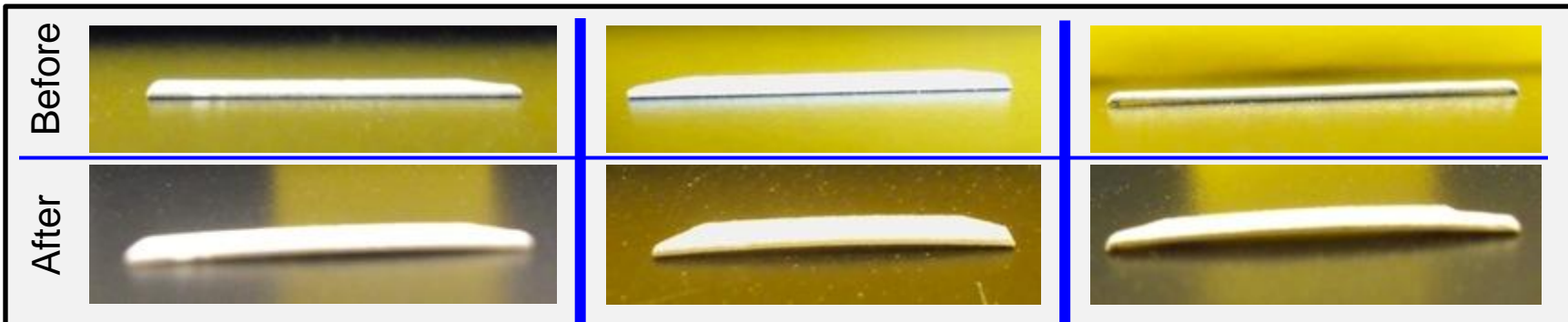
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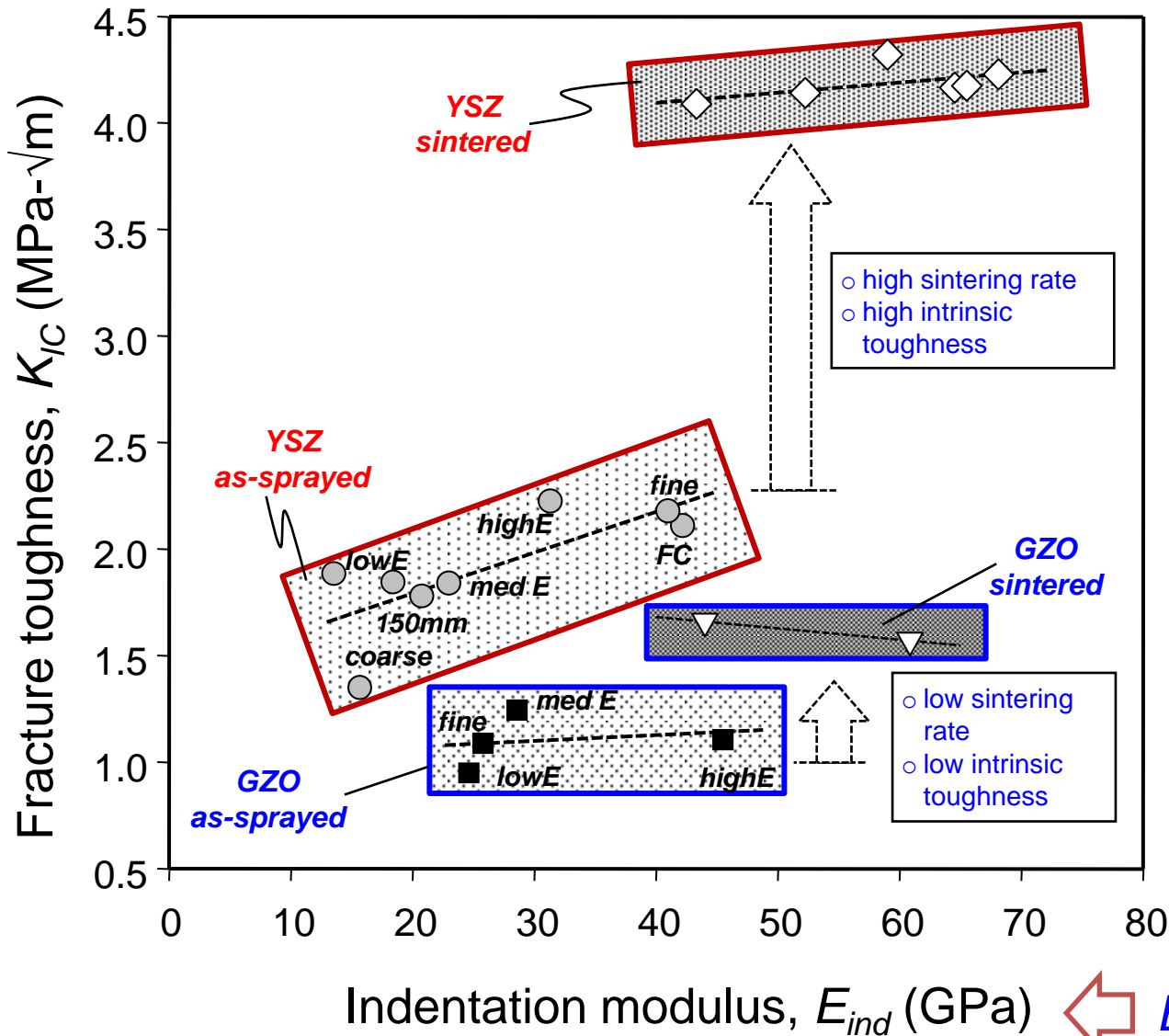


Larson Miller Parameter (LMP): Temp and Time for thermal exposure



Free standing bi-layer coatings  
Isothermal exposure at 1200°C for 24 hours





- YSZ more sensitive to processing than GDZ
- Equivalent sintering affects YSZ fracture toughness more than GDZ

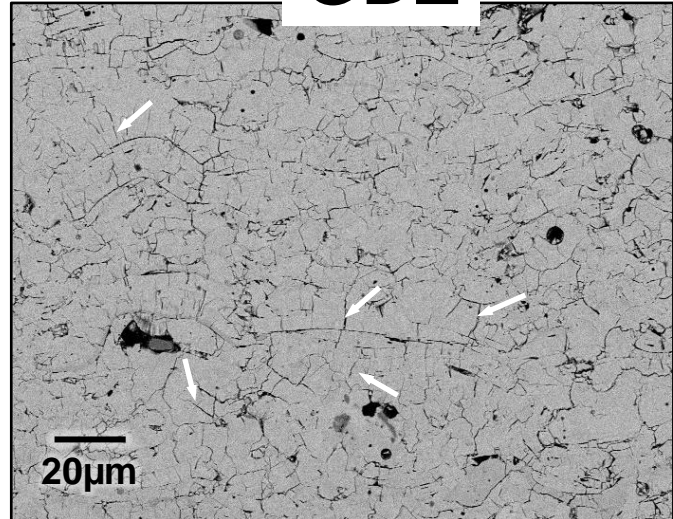
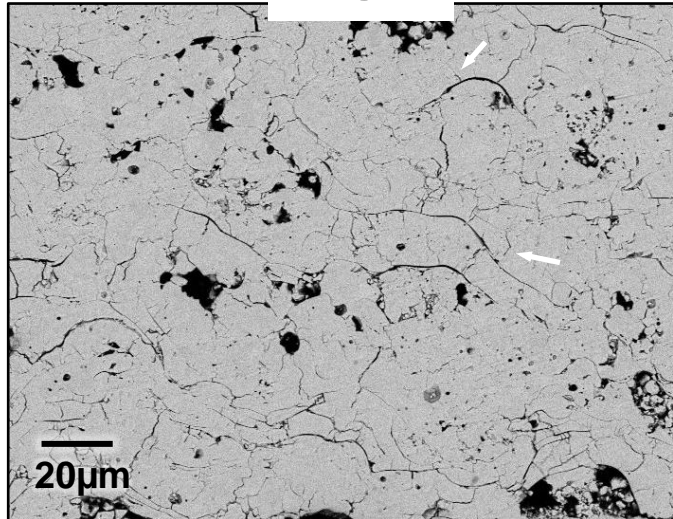


# Larger microcracking in GDZ due to low toughness

SEM

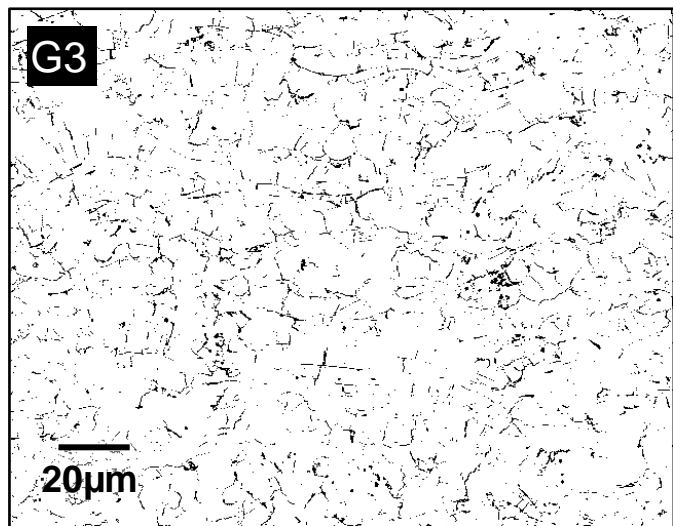
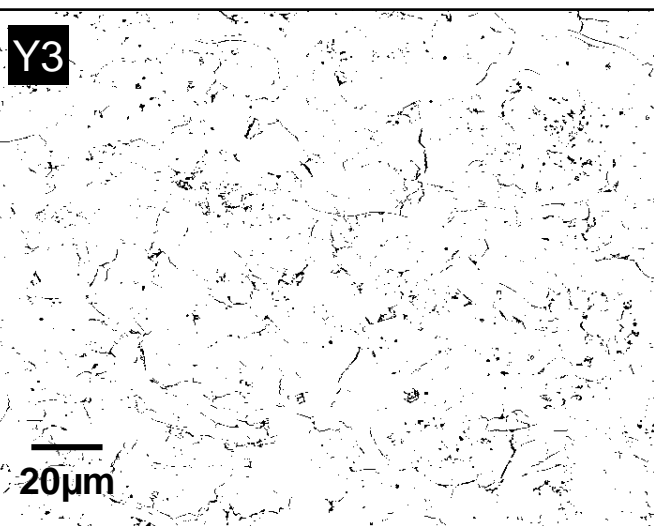
YSZ

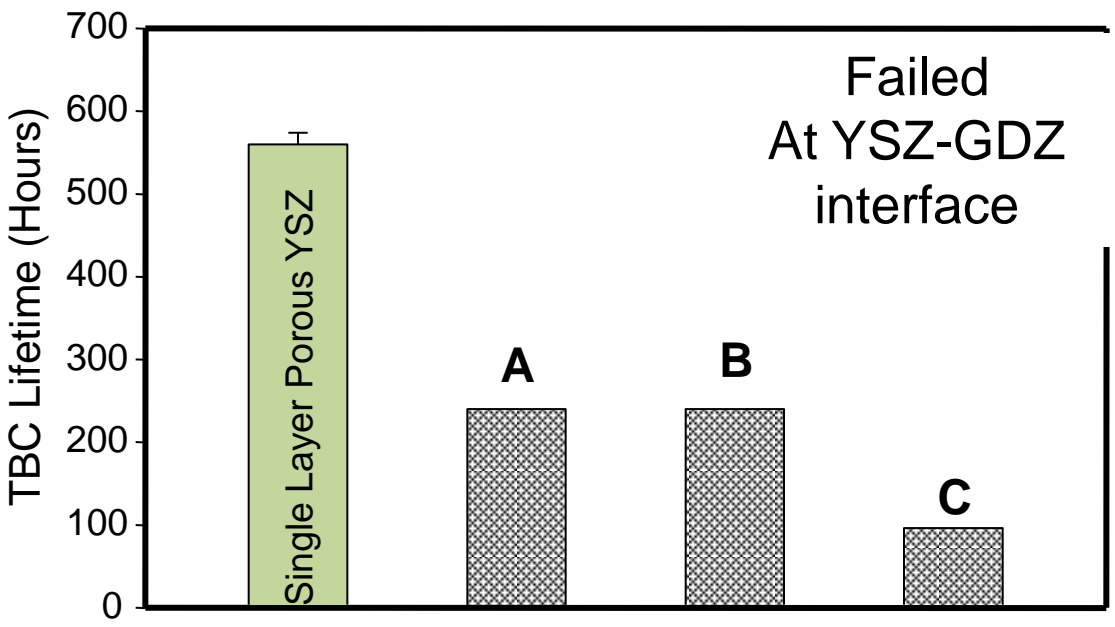
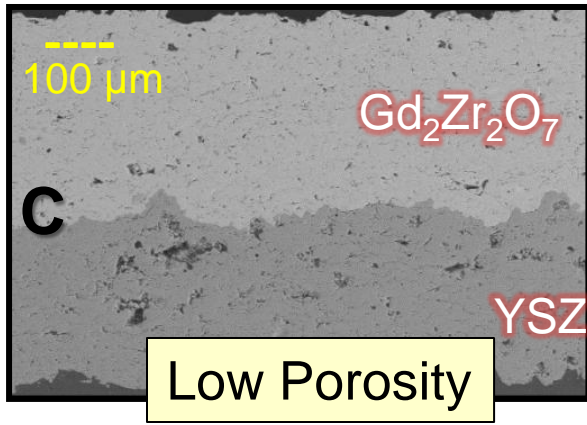
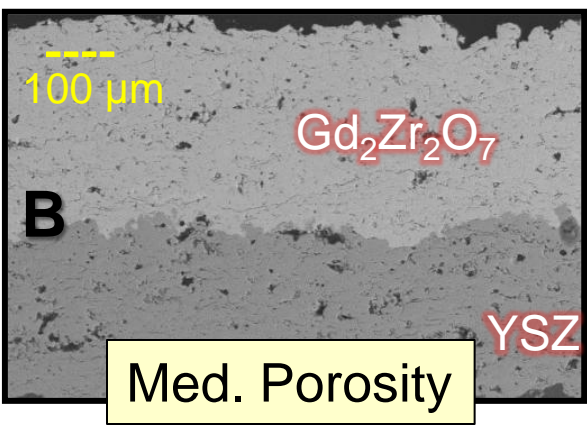
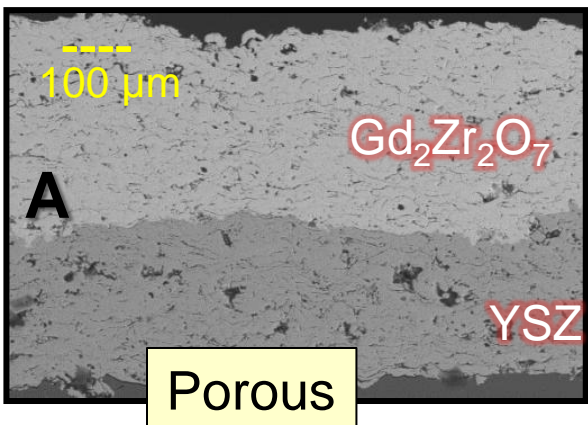
GDZ



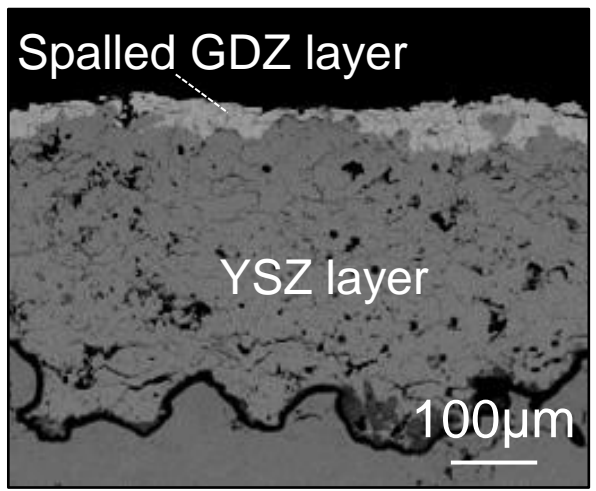
**Introduces processing challenges**

Filtered



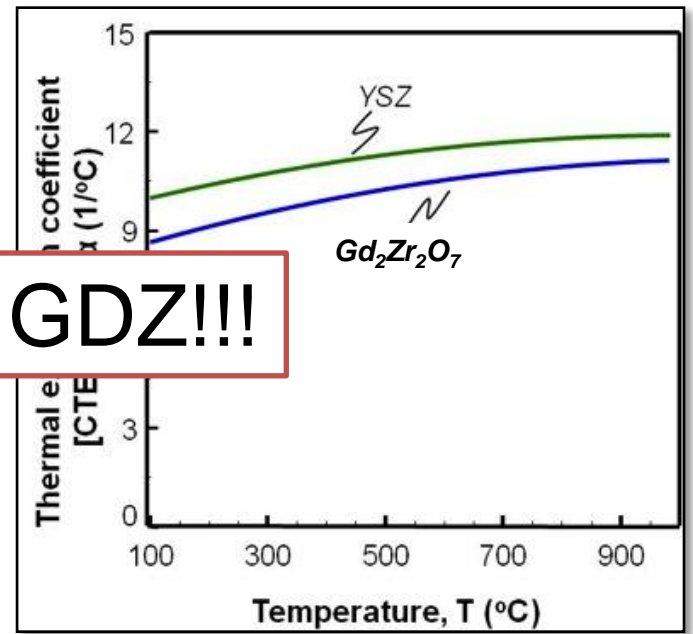
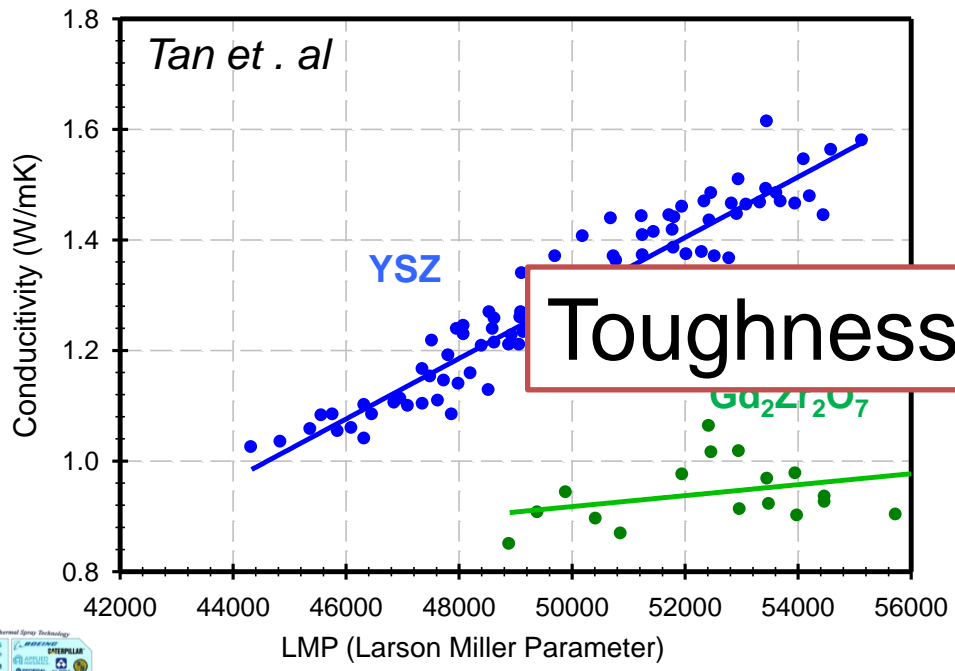
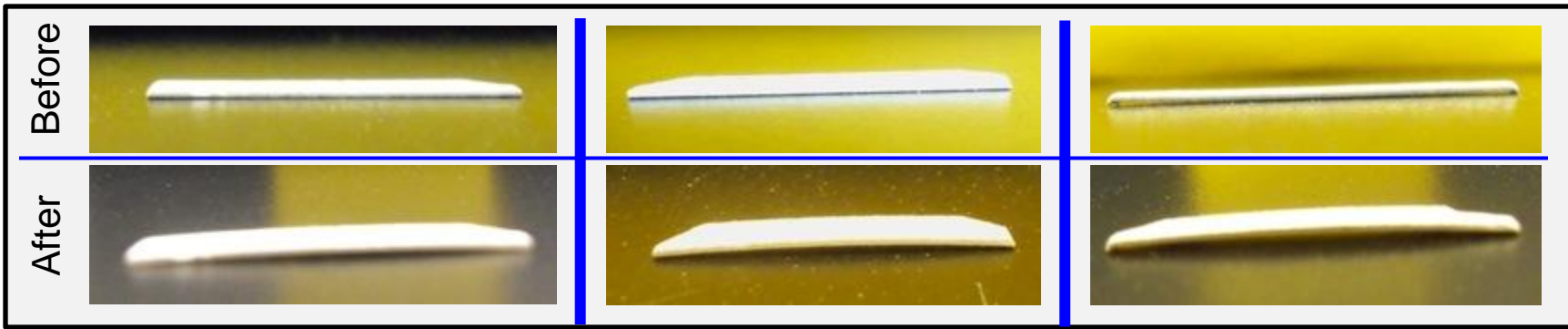


**Failed microstructure (C)**





Free standing bi-layer coatings  
Isothermal exposure at 1200°C for 24 hours



# Systematic progress over past four years

Y1

- YSZ and GDZ process property relationships
- Process Map development
- **Toughness, Lignite ash penetration depth, erosion**

Y2

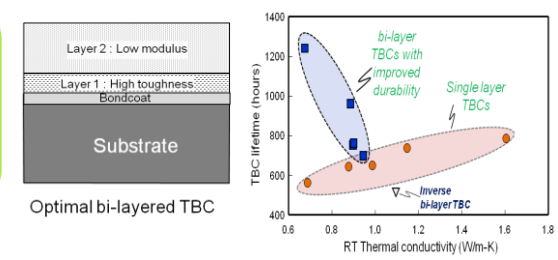
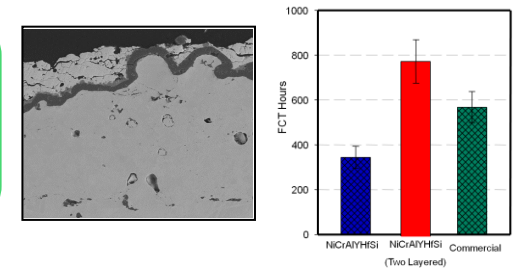
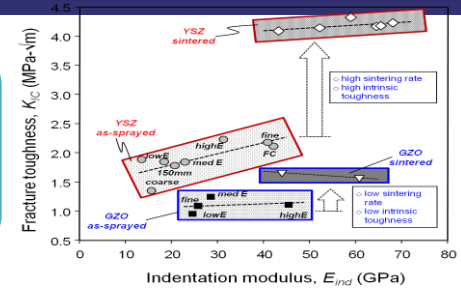
- Rough bond coat process optimization with 40% increase in FCT life
- **Two layer dense BC layer**

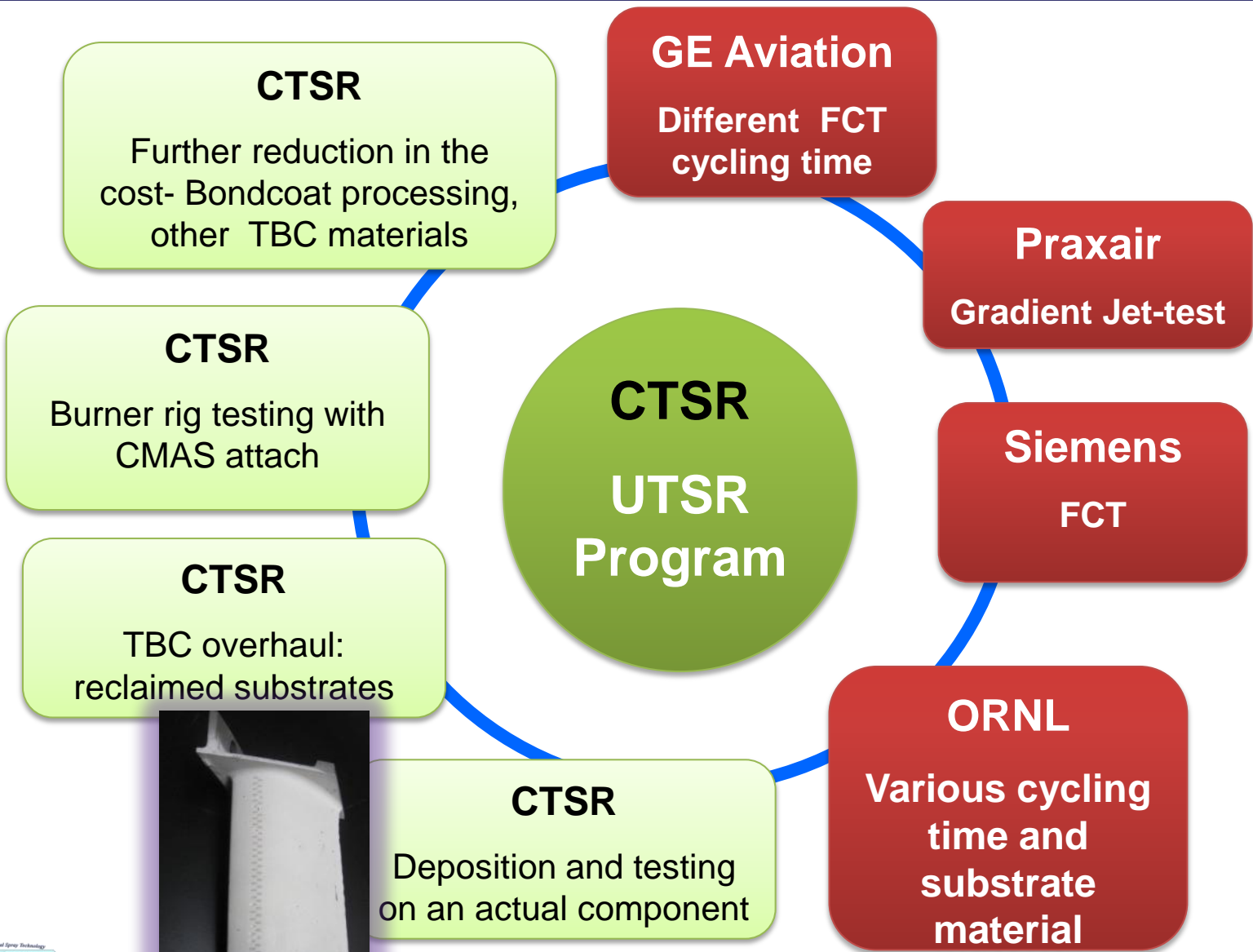
Y3

- bi-layer YSZ coating with two fold increase in FCT life, and maintaining low  $K$
- **High toughness interface layer, Elastic energy model**

Y4

- Multilayer YSZ-GDZ coating system
- **enhanced life, Lignite ash penetration minimization, erosion resistance**





# Gratefully acknowledged



Consortium is operated by the Center for Thermal Spray Research at Stony Brook University

Prof. Nitin Padture



Dr. Briggs While, Program Manager

Prof. Toshio Nakamura, Stony Brook University

Dr. Curtis Johnson, Rtd. GE GRC

Prof. John Hutchinson, Harvard university

