Superior Thermal Barrier Coatings for Industrial Gas-Turbine Engines Using a Novel Solution-Precursor Plasma-Spray Process

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SCIES Project 03- 01- SR107

DOE COOPERATIVE AGREEMENT DE-FC26-02NT41431

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Project Awarded: 07/01/03 (36 Months Duration)

$546,000 Total Contract Value ($546,000 DOE)

Gas-Turbine Needs and Goals

- **Highly Durable Thermal Barrier Coatings (TBCs) for Improved Performance and Efficiency, at Low Cost**
- **Ultra-Thick TBCs for Combustors, Airfoils, Blades Out-of-Airseals**
- **Four-Fold Improvement in Spallation Life Over Conventional Air Plasma Spray (APS) Ultra-Thick TBCs**
- **Transfer Technology for Producing Ultra-Thick TBCs to Industrial Partners**

Objectives and Approach

- **To Demonstrate Feasibility of Ultra-Thick (~3 mm) TBCs Using Solution-Precursor Plasma-Spray (SPPS)**
- **To Determine Mechanical Properties, Thermal Cond., Durability, and Hot-Corrosion Resistance**
- **To Elucidate Failure Mechanisms and Microstructural Thermal Stability**
- **To Identify Microstructural and Architectural Characteristics for Optimum Ultra-Thick SPPS TBCs**
- **To Obtain TBCs with Improved Durability, Thermal Resistivity and Hot-Corrosion Resistance**

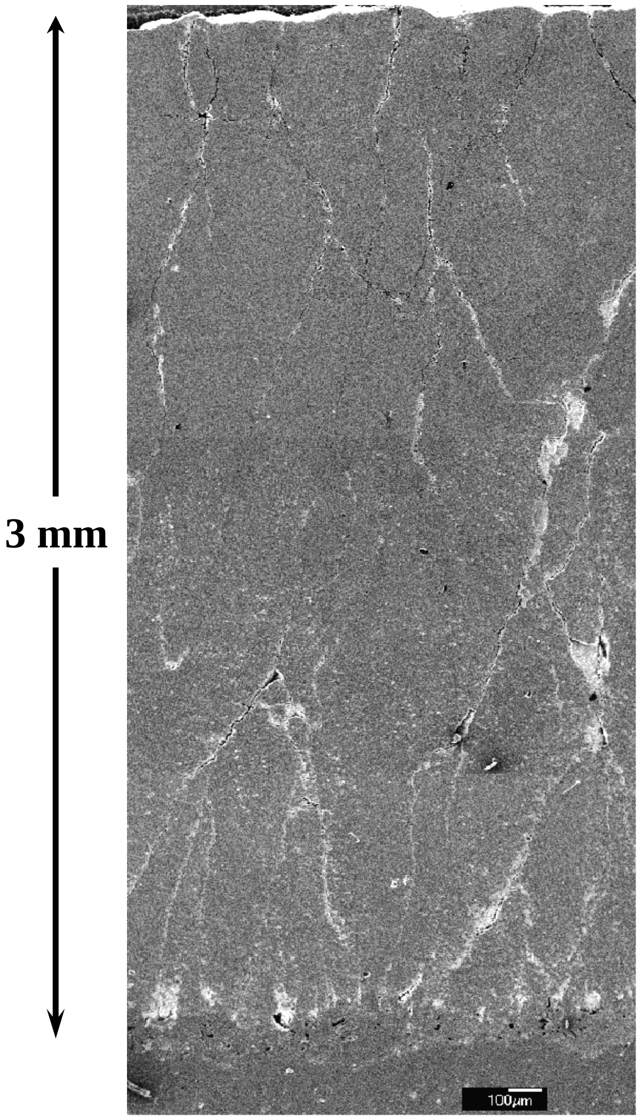
Accomplishments

- **Demonstrated the Feasibility of Depositing Ultra-Thick (~3 mm) TBCs Using the SPPS Process**

- **Determined Mechanical and Thermal Properties of SPPS Ultra-Thick TBCs**

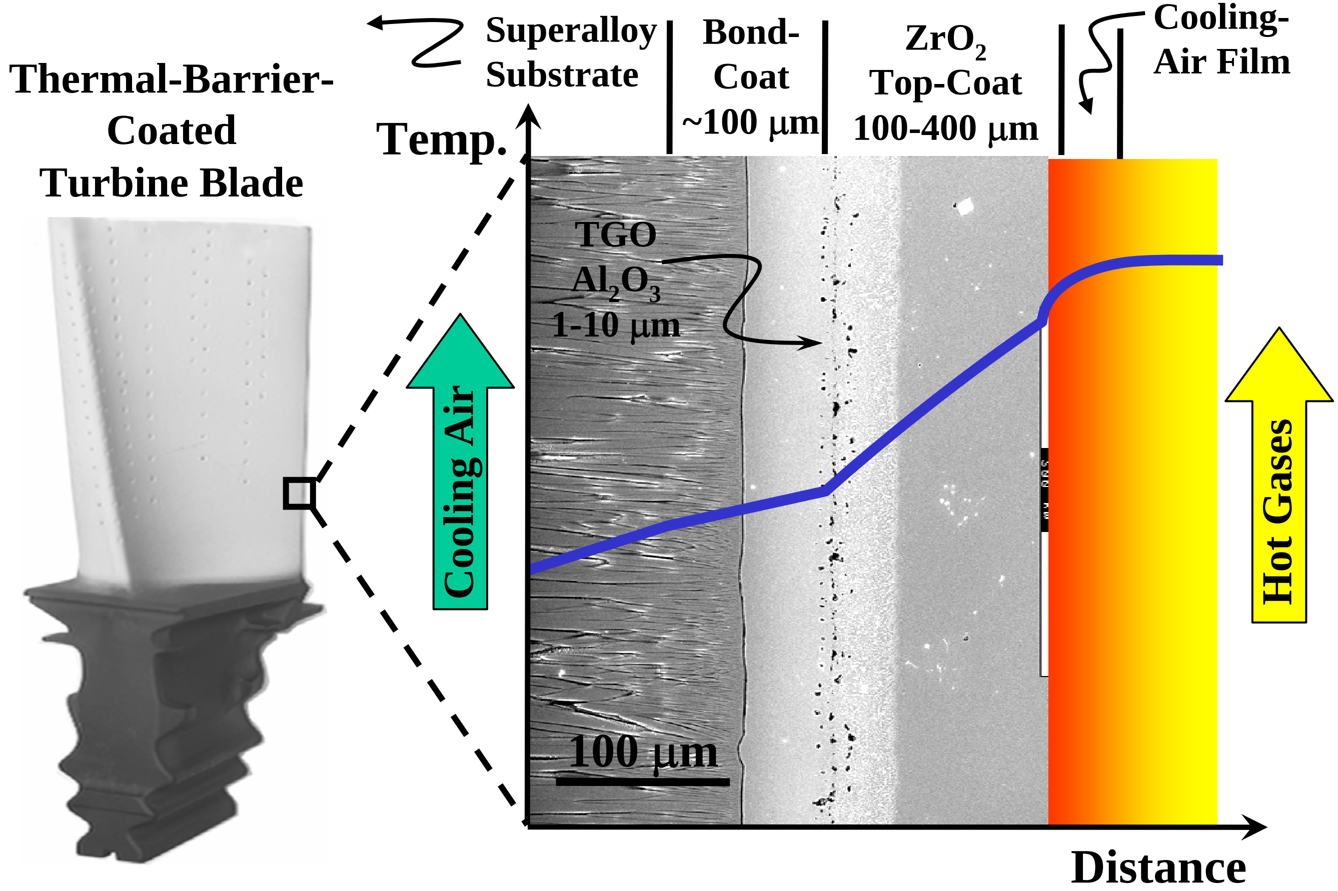
- **Demonstrated Improved Durability in SPPS Ultra-Thick TBCs**

- **Deposited Layered TBCs for Lower Thermal Conductivities**



Thermal Barrier Coatings

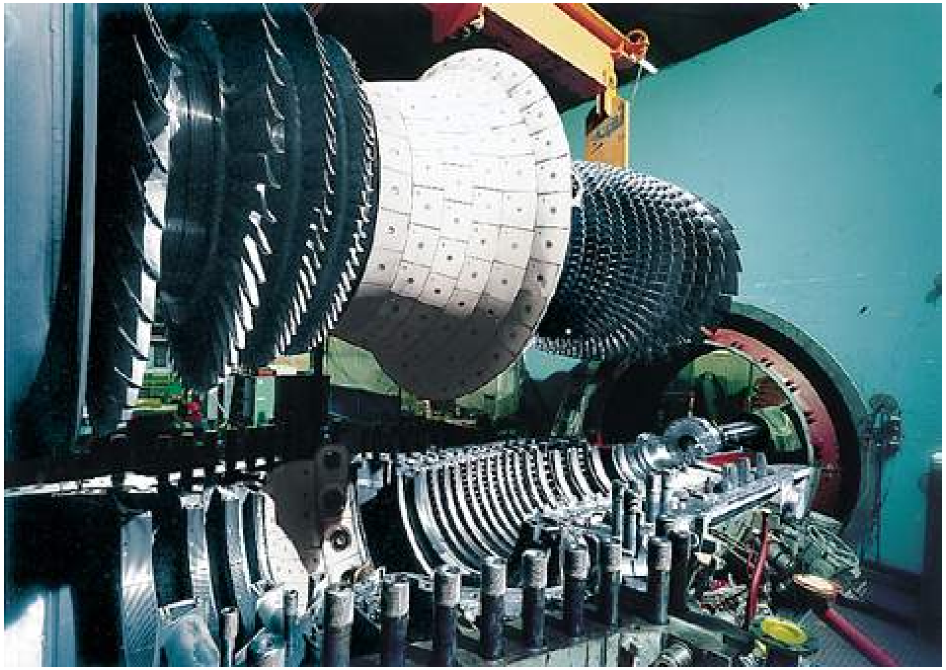
- Hot-Section Metal Comp.
- Blades
- Vanes
- Combustors
- Temp. Redn. Up to 300 ^{o}C



Padture *et al.*, *Science*, 2002

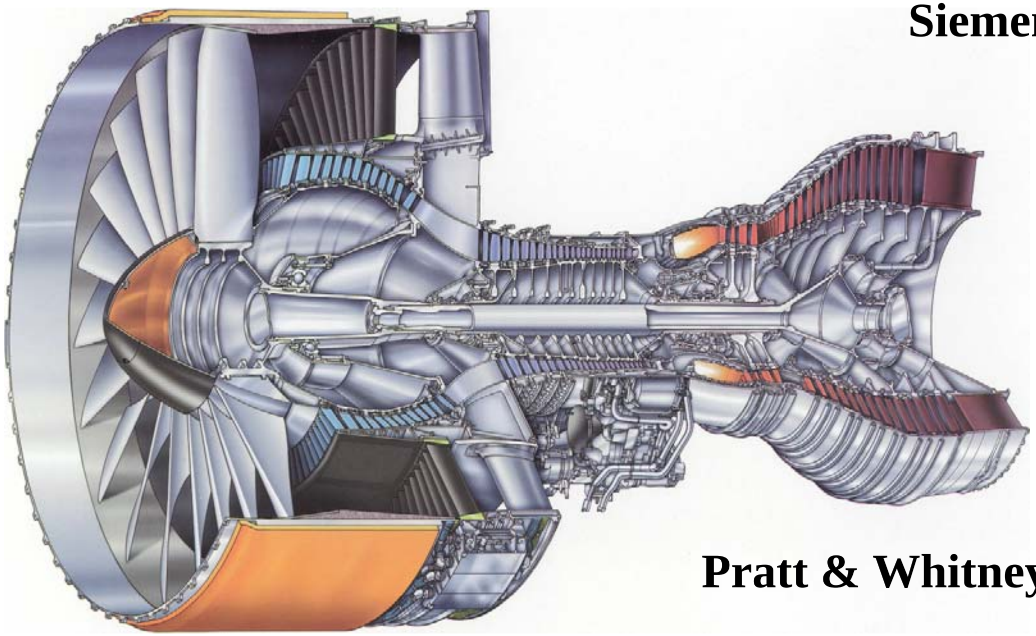
Gas-Turbine Engines

- Power Generation
- Marine Propulsion



Siemens-Westinghouse

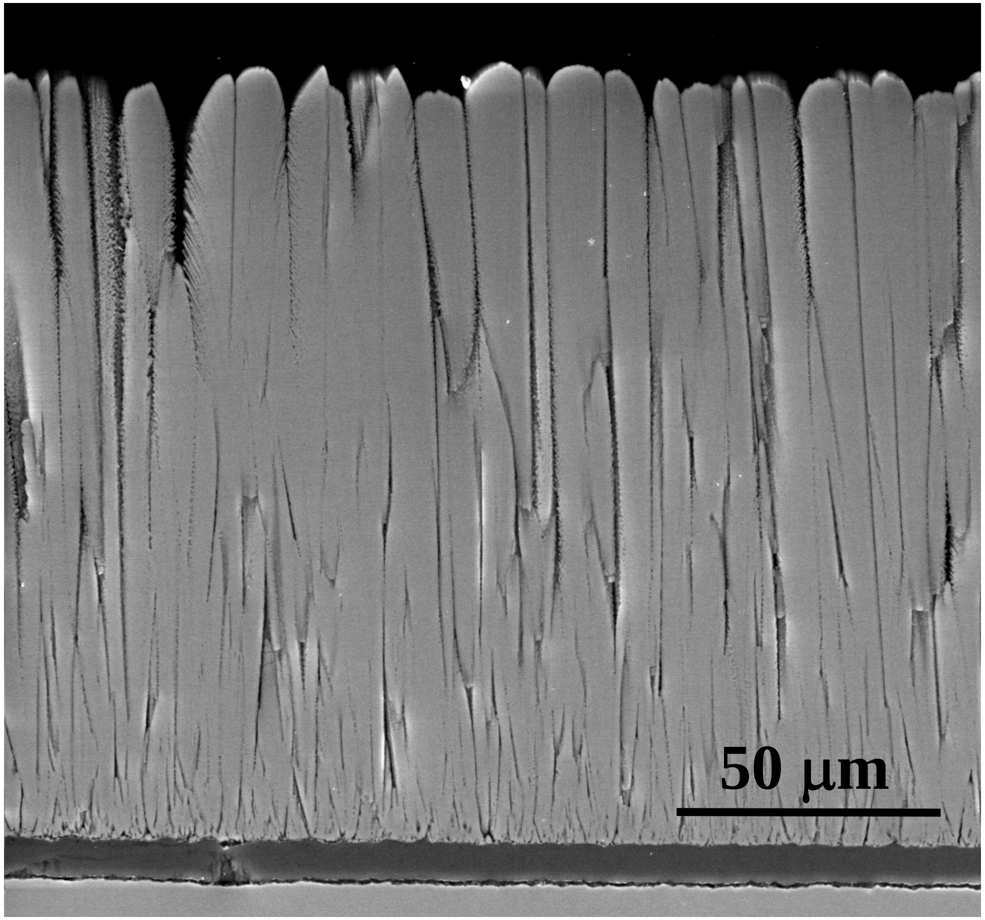
- Aircraft Propulsion



Pratt & Whitney

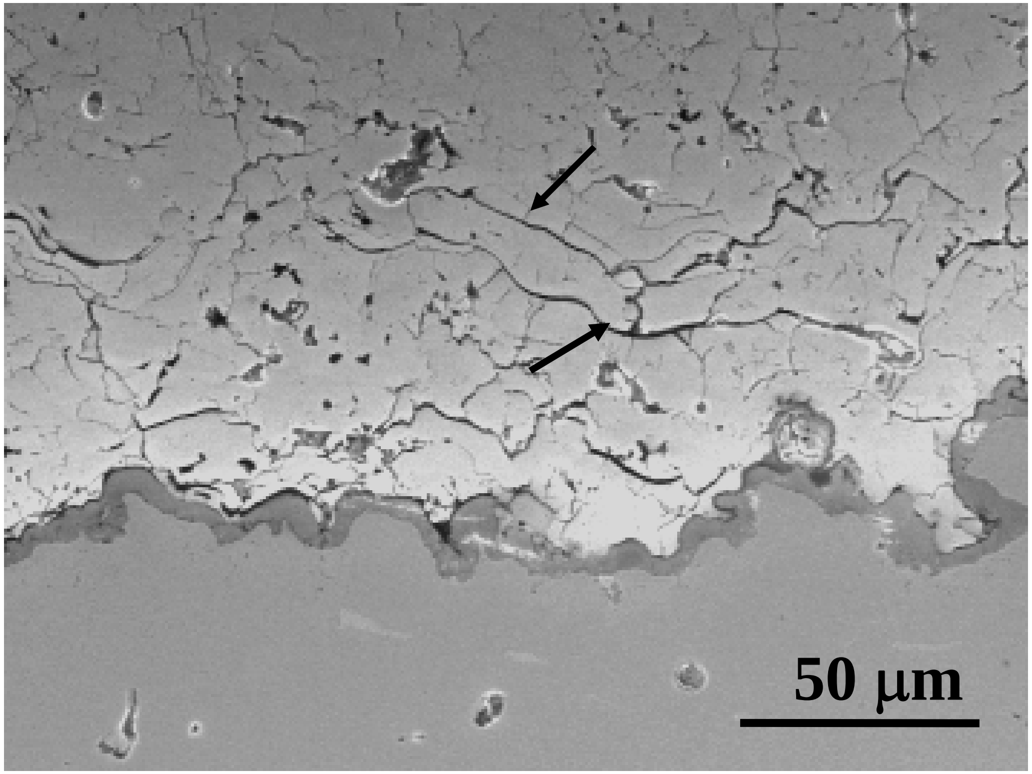
Electron-Beam PVD TBC

- Columnar Grains
- Porosity, Vertical Cracks
- Thinner (100-150 μm)
- Higher Strain Tolerance
- Higher Thermal Cond.
- Longer Spallation Life
- More Expensive
- No Hole Coverage

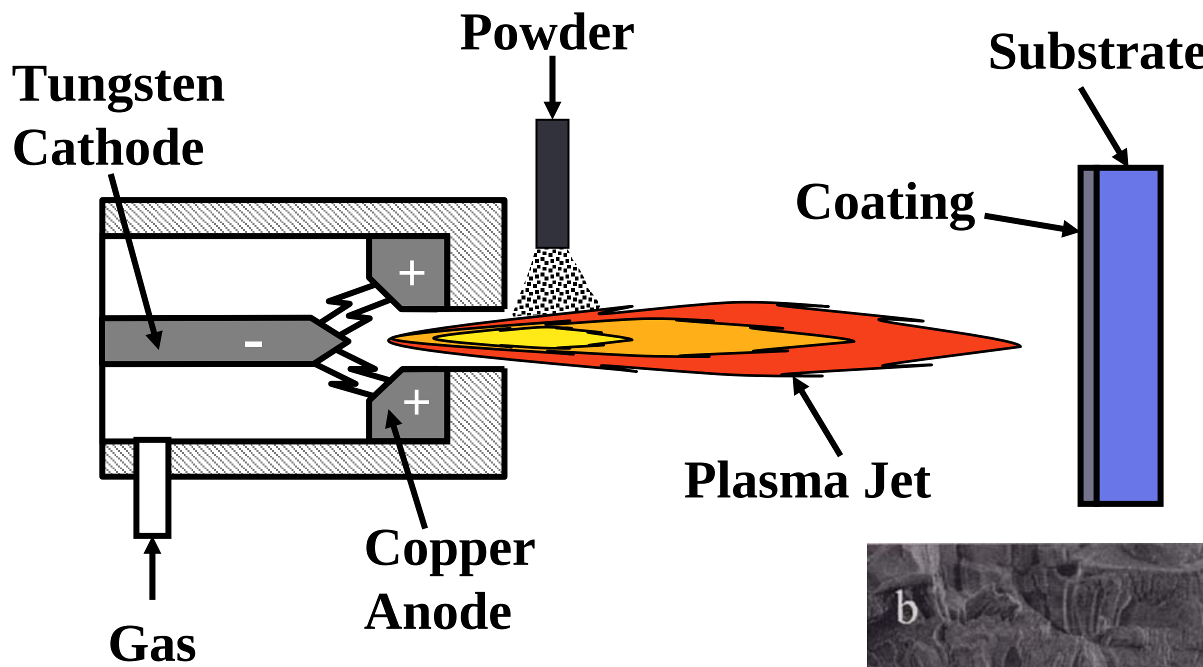


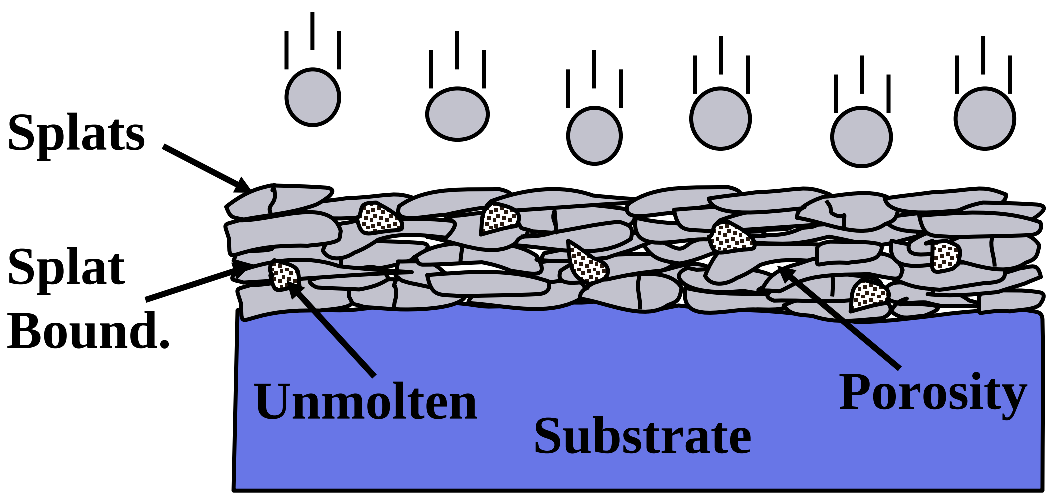
Air-Plasma Sprayed (APS) TBCs

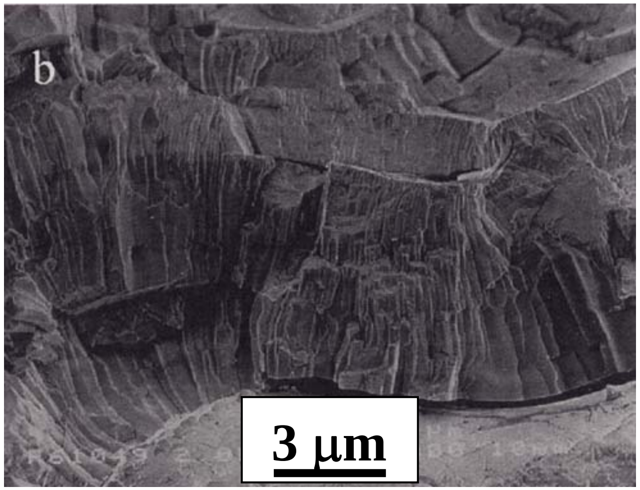
- "Splat" Grains
- Porosity, Horizontal Cracks, Splat Boundaries
- Thicker (200-400 μm)
- Rough Interface
- Lower Strain Tolerance
- Lower Thermal Cond.
- Shorter Spallation Life
- Less Expensive



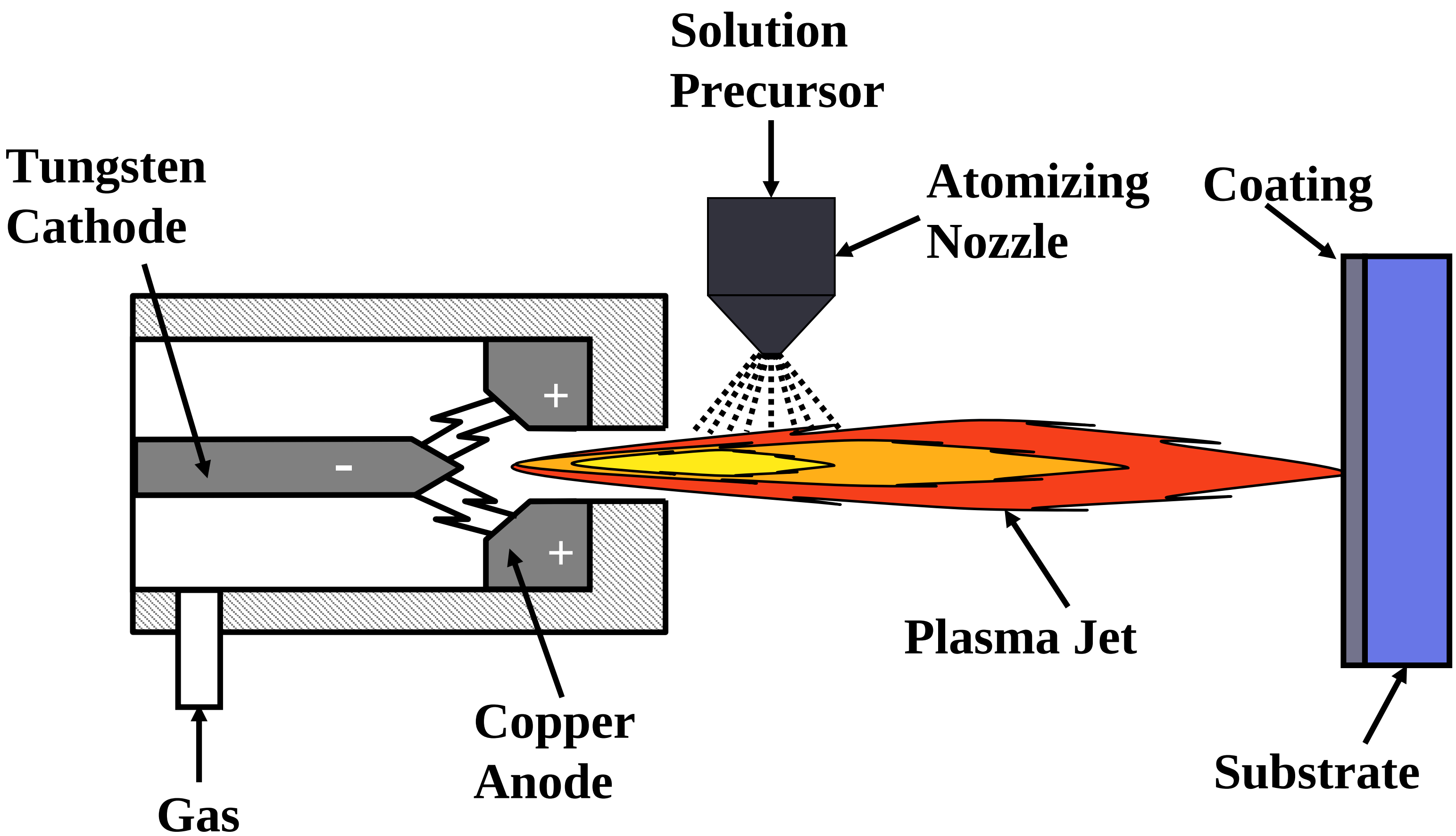
Conventional Air-Plasma Spray (APS)







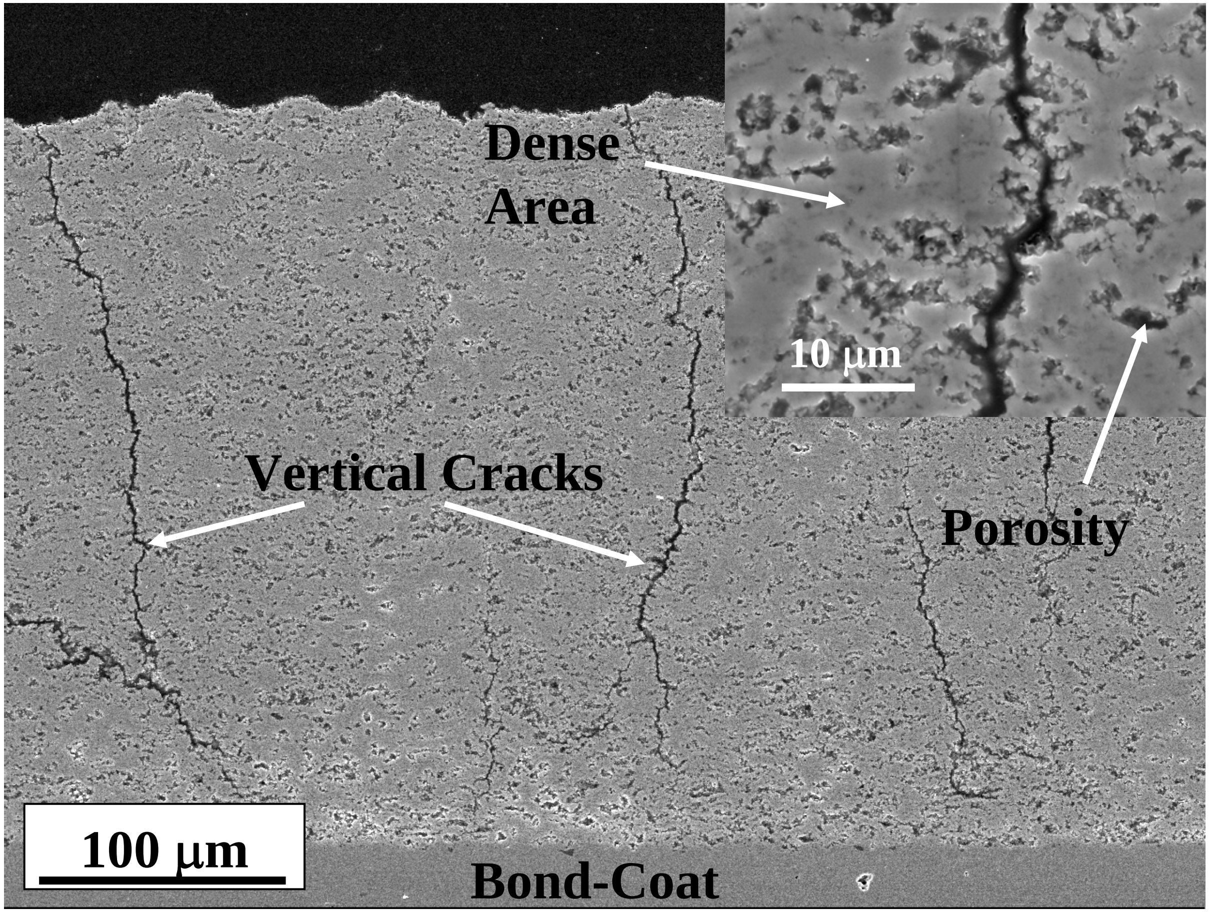
Solution-Precursor Plasma Spray (SPPS)



Solution Precursor: Aq Soln. Zr + Y Salts => 7YSZ

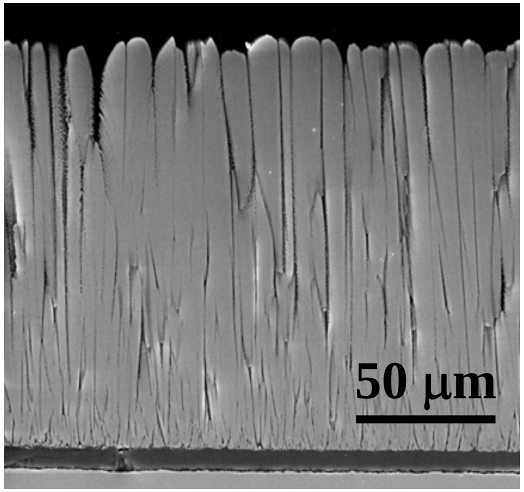
Acta Mater., 2001; *J. Mater. Res*., 2002; *Mater. Sci. Engr. A*, 2003

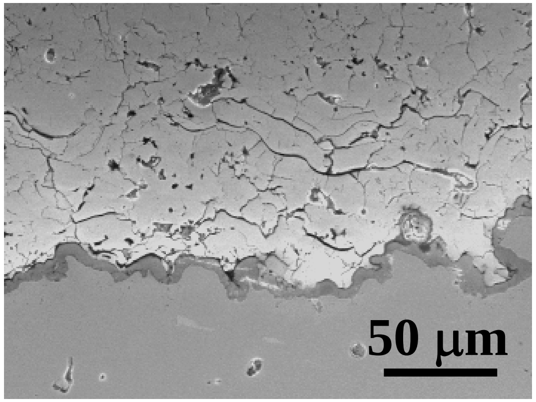
SPPS TBCs: ZrO_2-7 wt% Y_2O_3



- No Macro-Splat Boundaries
- Vertical Cracking
- Porosity (18-20%)

EB-PVD



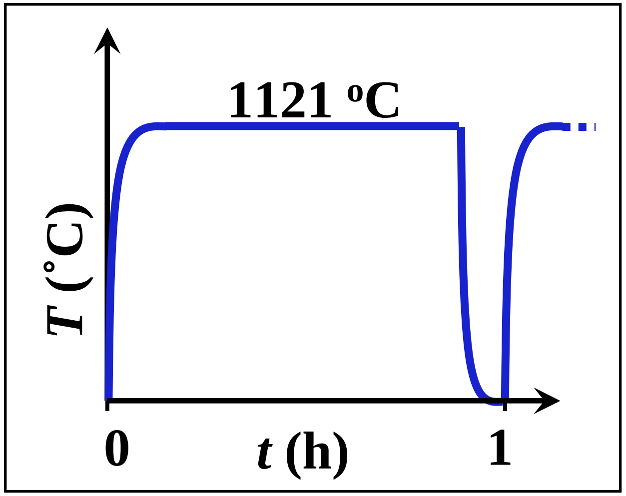


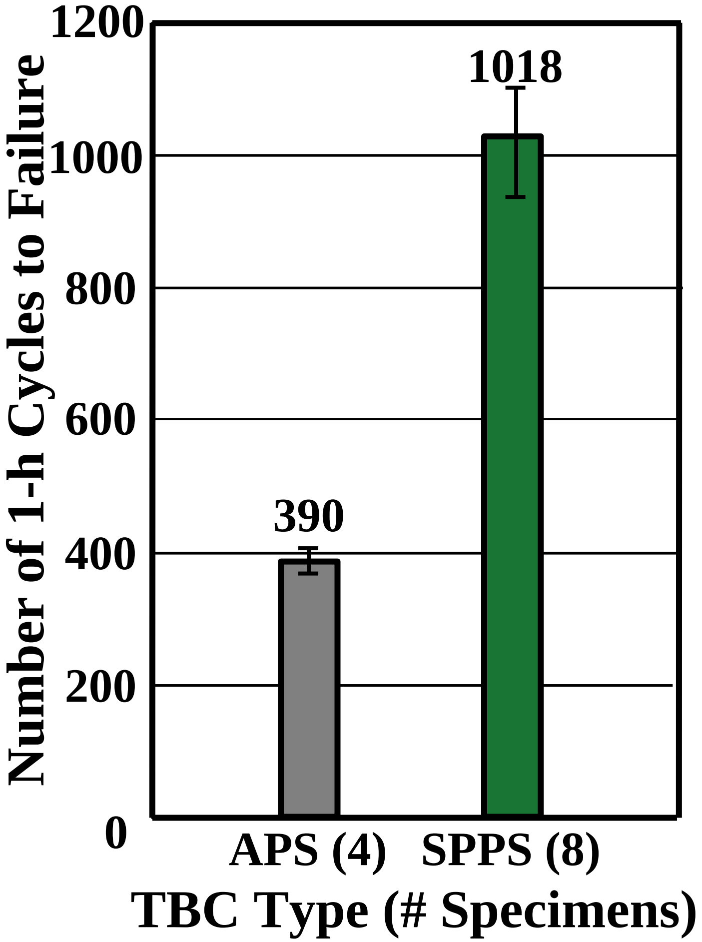
Conv. APS

Durability of SPPS TBCs

- **Same Bond-Coat for APS and SPPS**
- **TBC Thickness: ~250 μm**

Thermal-Cycling Life Test

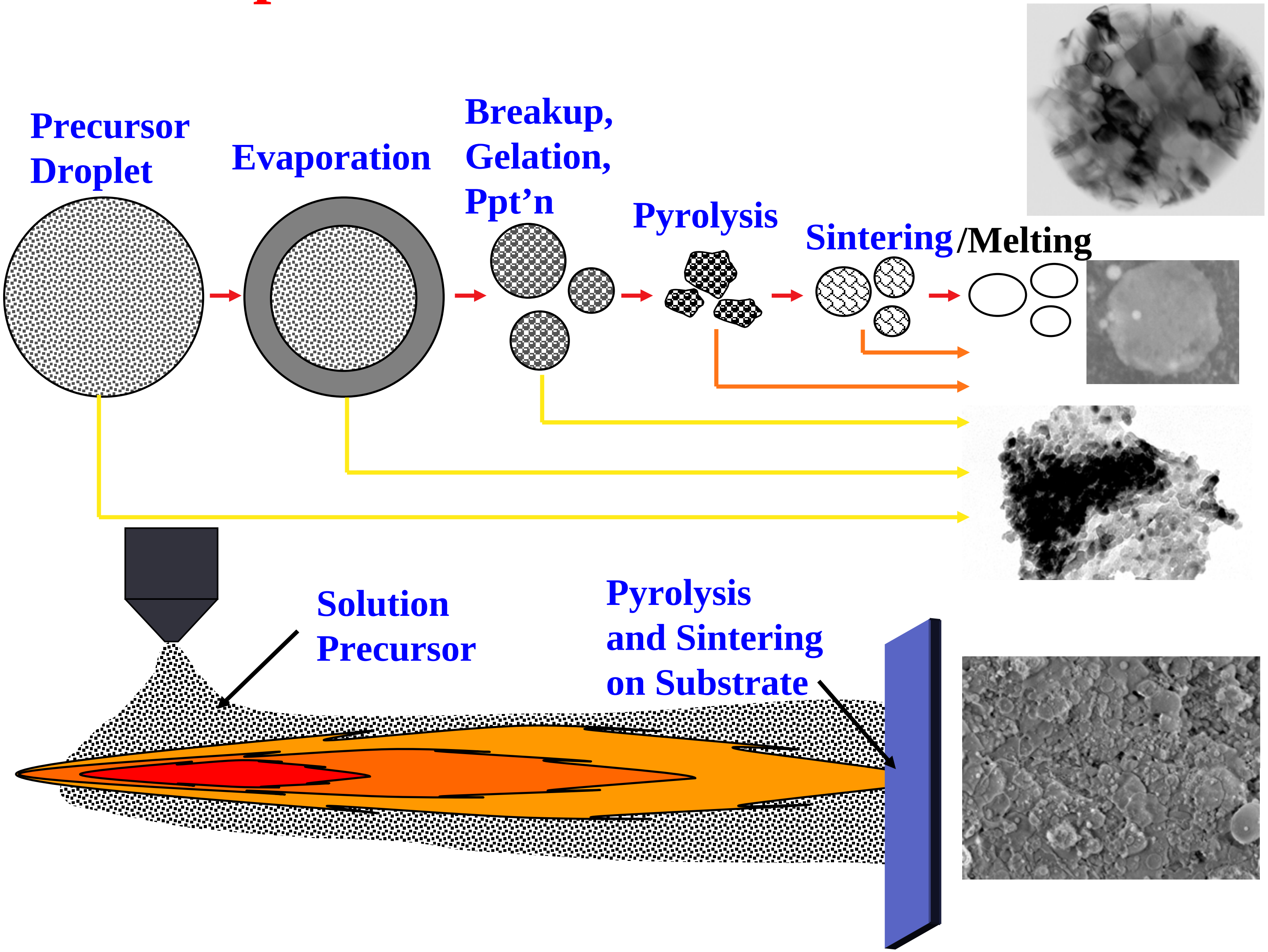




- **No Macro-Splat Boundaries**
- **Vertical Cracking**
- **Porosity (18-20%)**

Surf. & Coat. Techol., 2004

SPPS Deposition Mechanisms



Ultra-Thick TBCs

SPPS Process Uniquely Suited for Ultra-Thick TBCs

Advantages

- Lower Thermal Diffusivities
- Increased Engine Operating Temperatures
- Improved Efficiency
- Lower Cooling Requirements

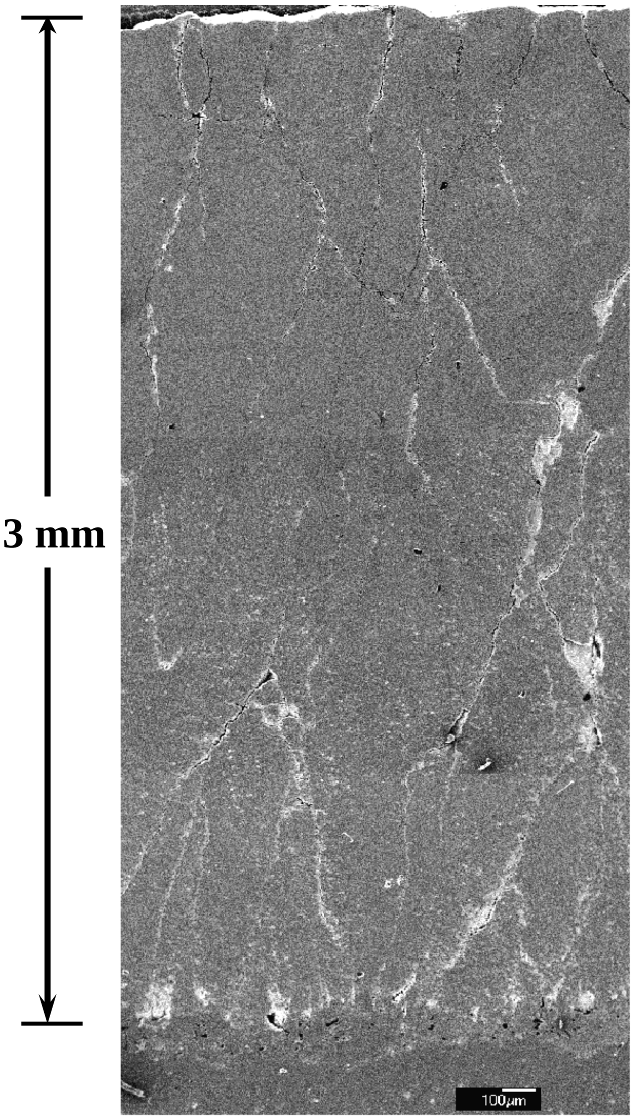
Applications

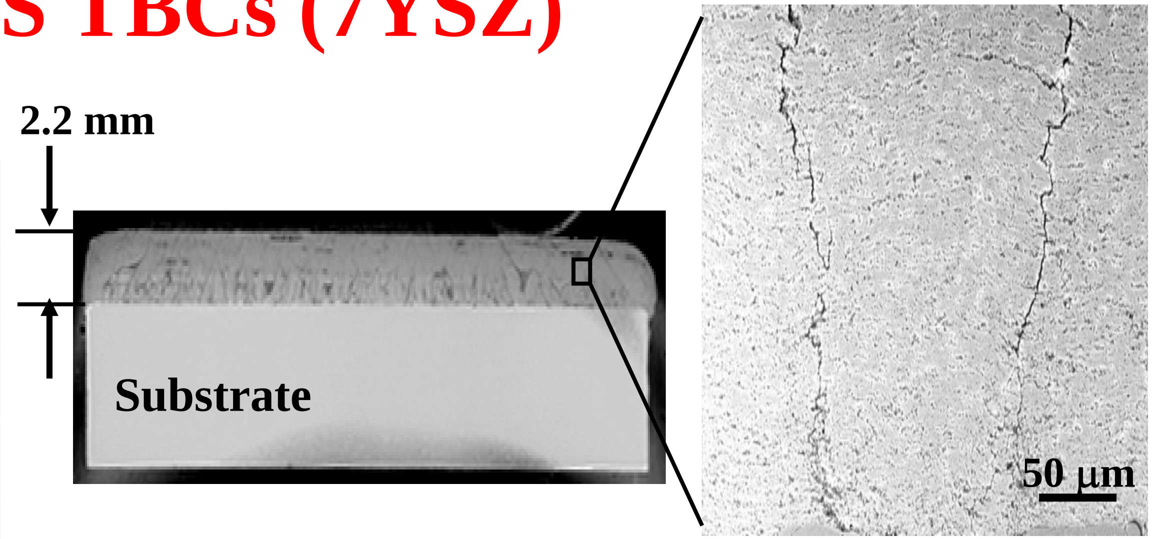
- Turbine Blades Out-of-Air-Seals
- Turbine Airfoils
- Combustors

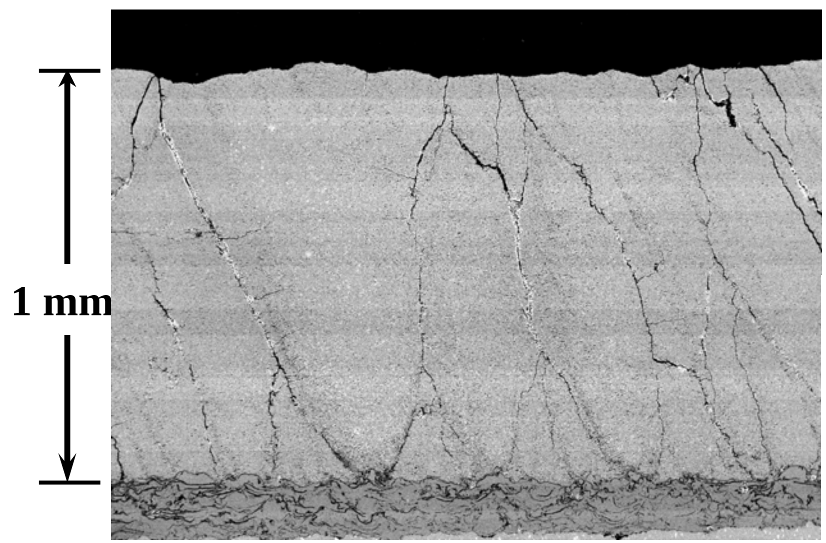
Current Limitations

- Ultra-Thick TBCs Difficult To Deposit Using APS
- Need Graded Interfaces

Ultra-Thick SPPS TBCs (7YSZ)



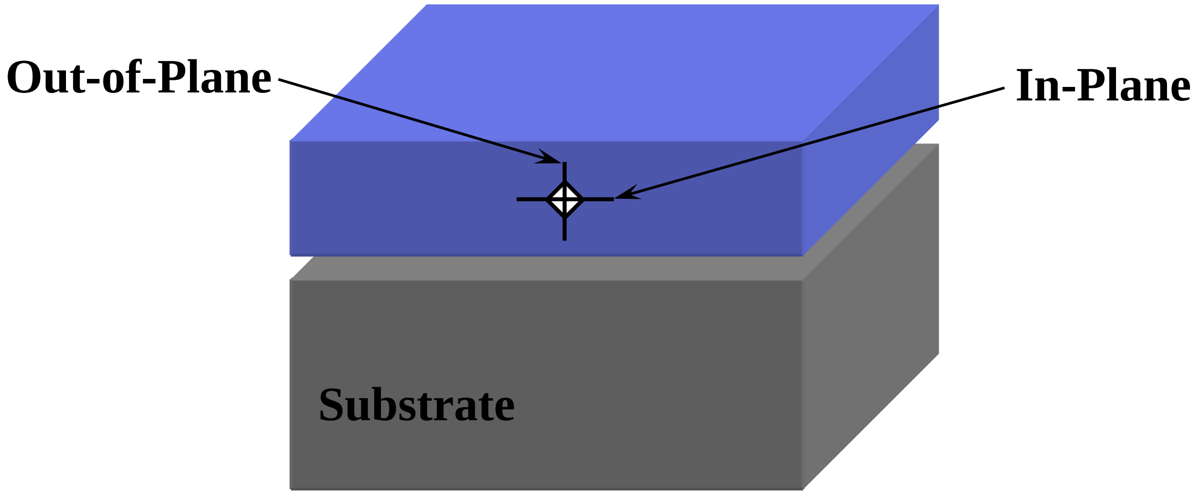




Toughness: Vickers Indentation

Free-Standing Coatings (~3 mm)

- **SPPS**
- **Conventional APS**



Vickers Indentation

SPPS

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

In-Plane

Out-of-Plane

APS

ckTime™ and a
ZW) decompressor
to see this picture.

Toughness

$$K_{IC} = 0.016(E/H)^{0.5} P c^{-1.5}$$ (Lawn *et al.*)

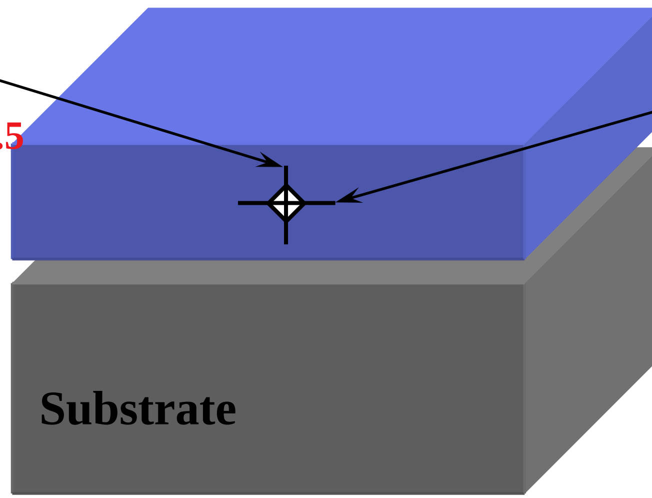
(P=49 N)

(H from Hardness Test and E from Comp. Test)

Out-of-Plane

SPPS: 1.17 MPa.m$^{0.5}$

APS: N/A



In-Plane

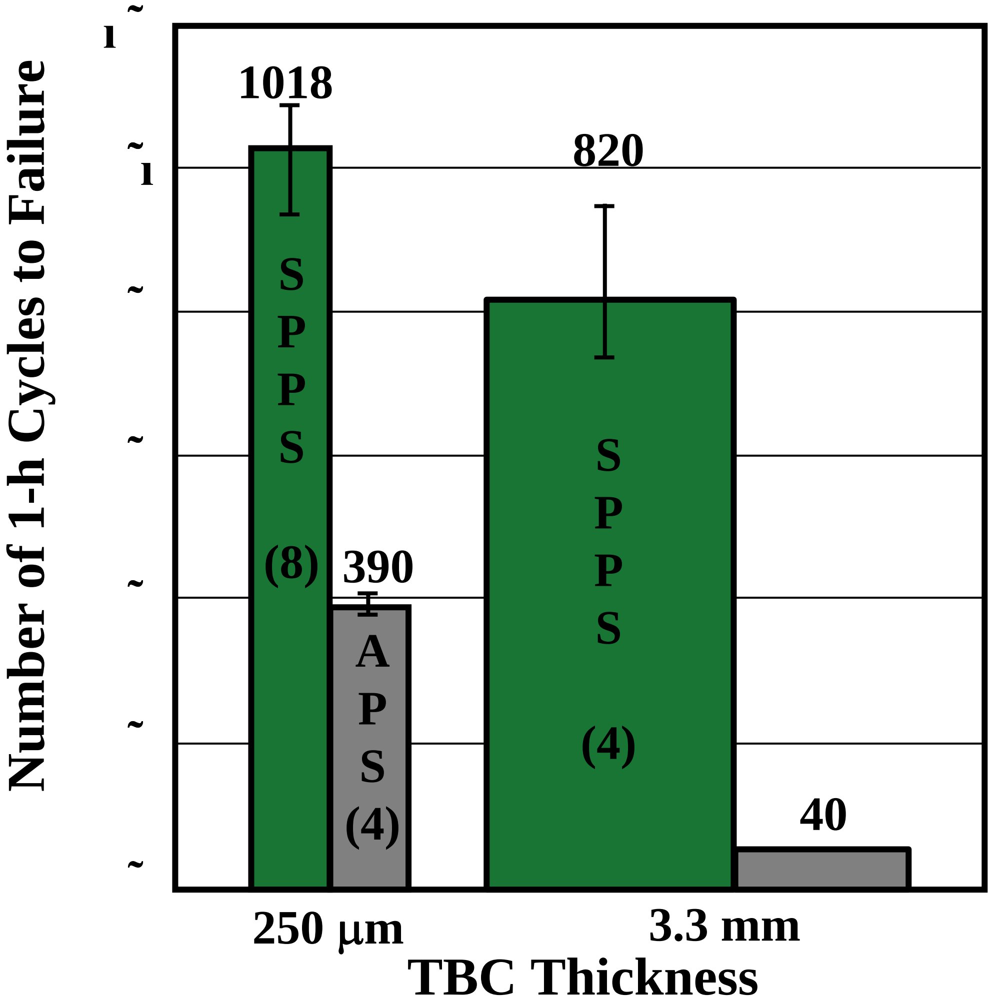
SPPS: 1.72 MPa.m$^{0.5}$

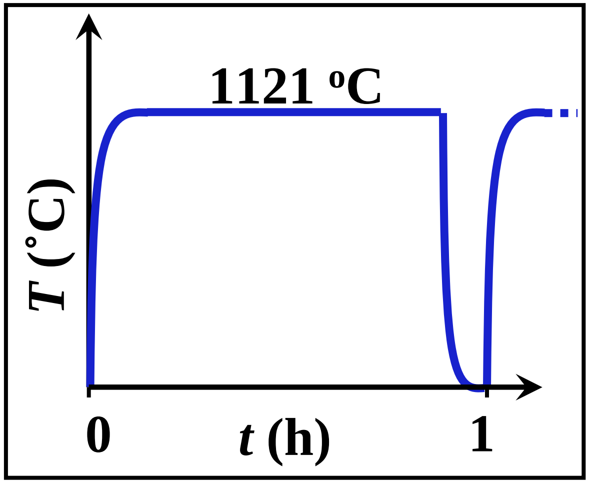
APS: 0.26 MPa.m$^{0.5}$

SPPS TBCs 6 Times Tougher in the Important In-Plane Direction: Lack of Macro-Splat Boundaries

Mater. Sci. Engr. A, 2005

Thermo-Mechanical Durability



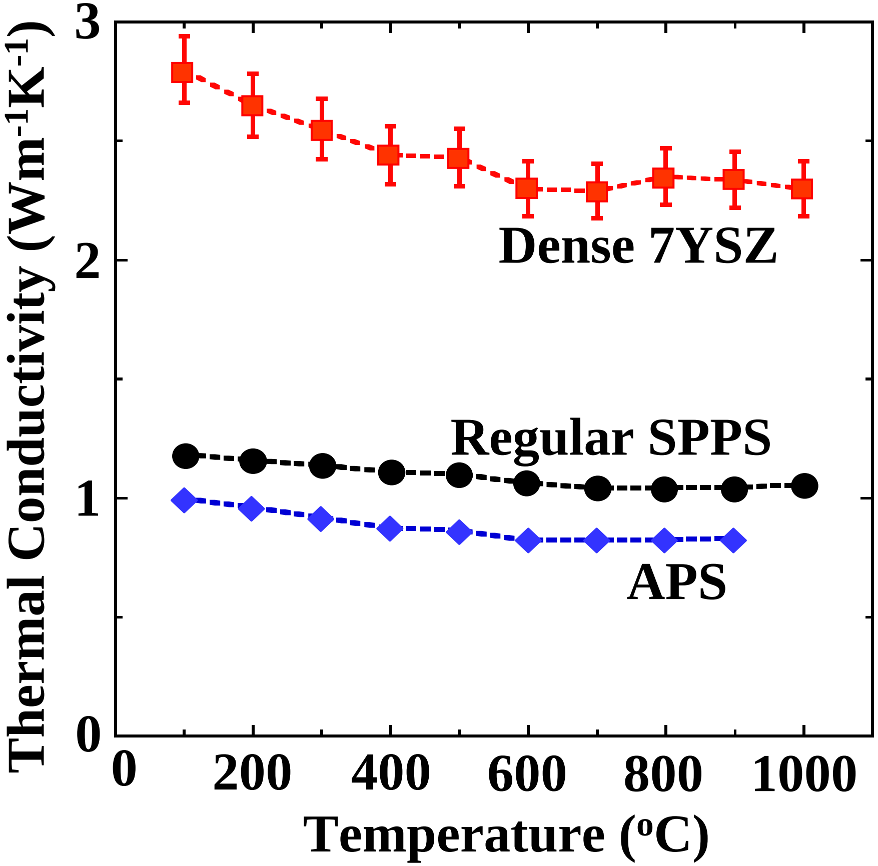


- **Vertical Cracks: Strain Tolerance**
- **Lack of Macro-Splat Boundaries: In-Plane Toughness**

***Mater. Sci. Engr. A*, 2005**

Thermal Conductivity

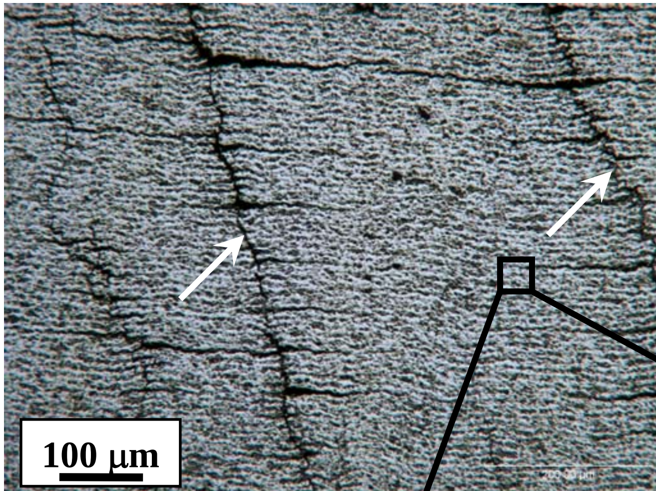
- Free-Standing Coatings (~1 mm)
- Laser-Flash Method

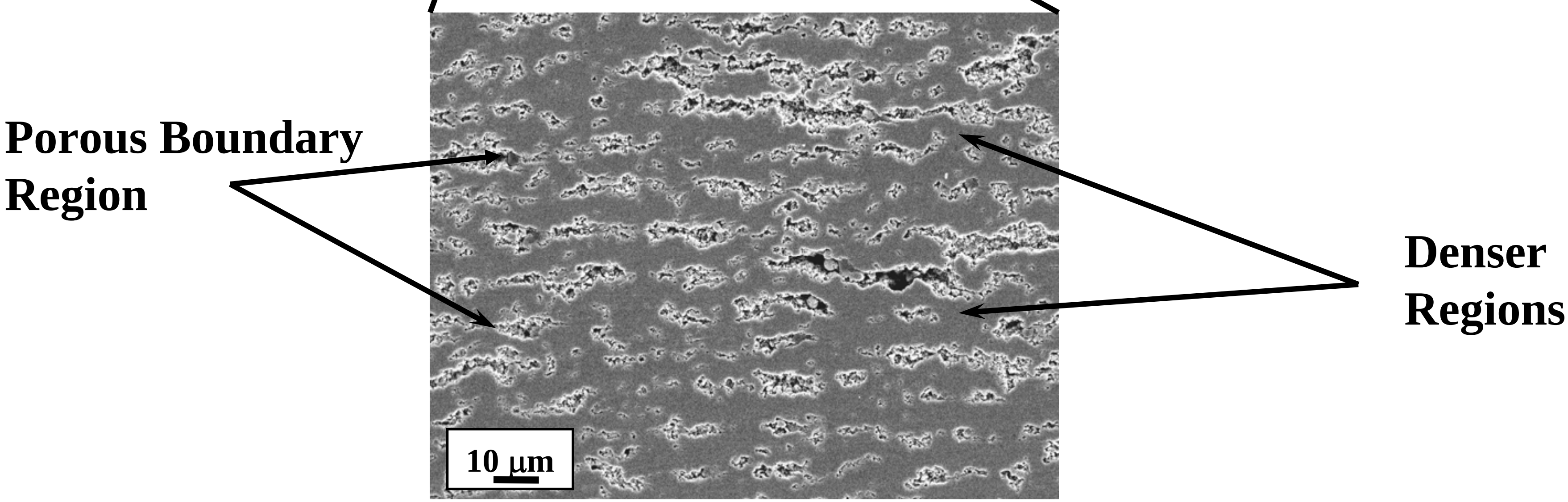


- SPPS Conductivity Higher Than APS
- Lack of Macro-Splat Boundaries

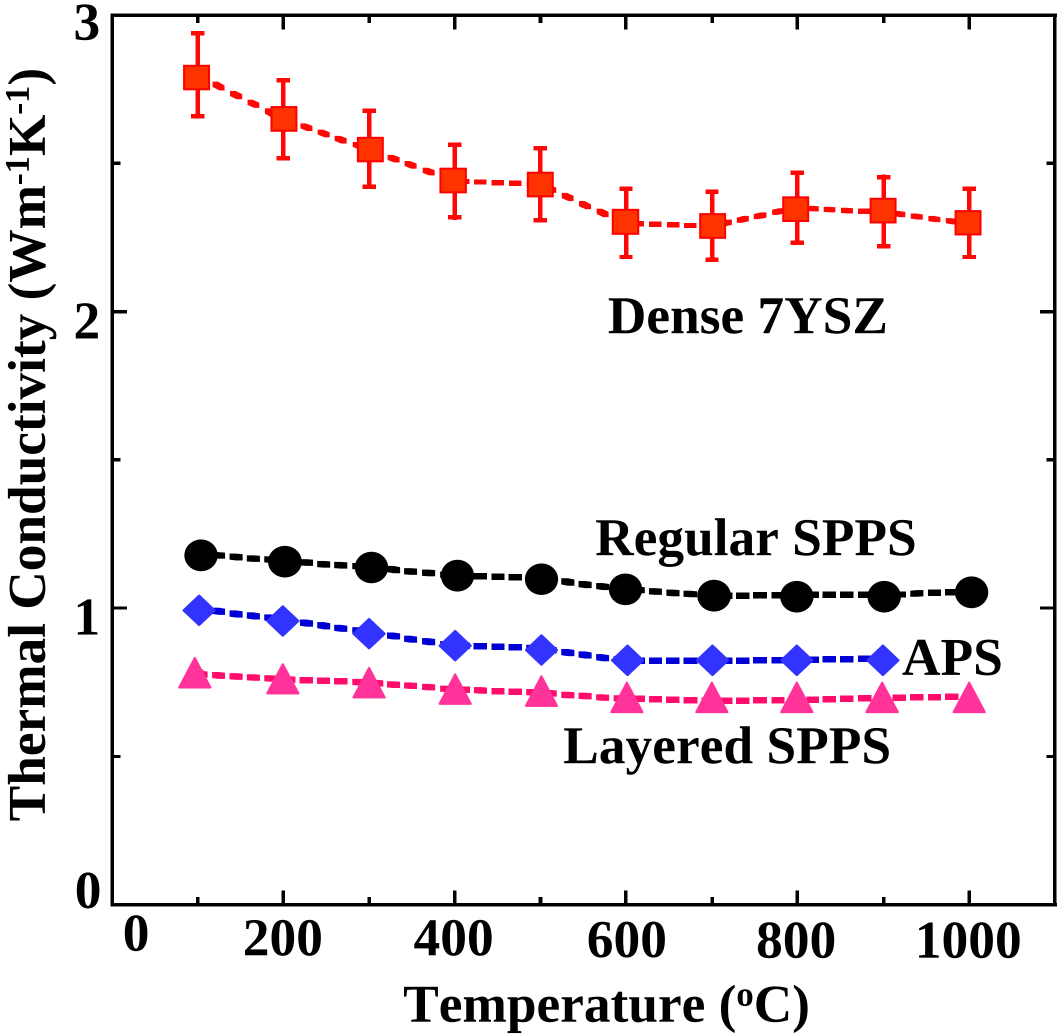
Engineering of SPPS Coating Microstructures: Layered SPPS

- **SPPS Process Modification**
- **Alternating Layers of Low and High Porosity**





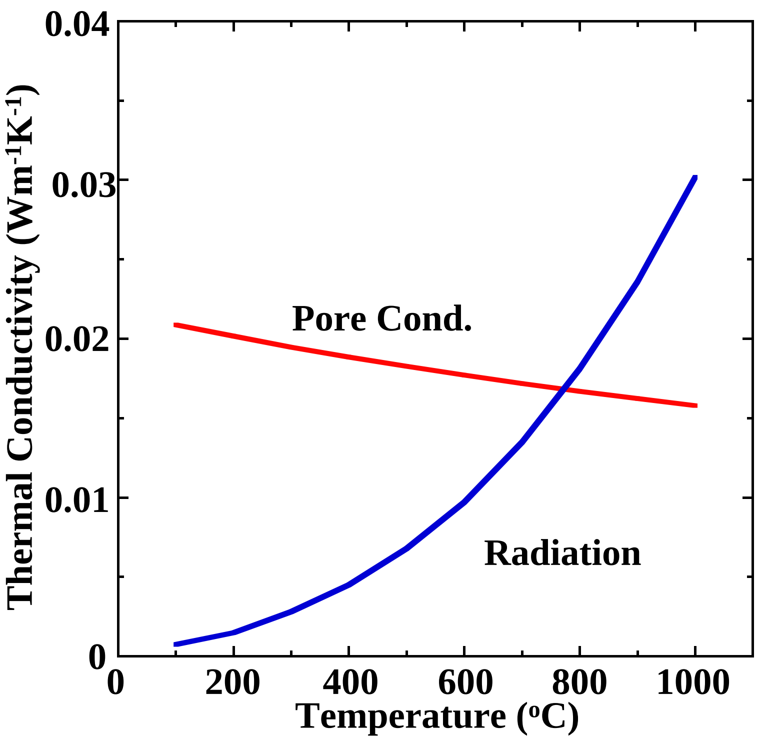
Thermal Conductivity



- Layered-SPPS Conductivity Lower than SPPS and APS
- Elongated Pores in High Porosity Layers

Thermal Conductivity Modeling: Guidelines for Microstructural Tailoring

- **Analytical Modeling**
- **Assumptions**
  - * Ignore Cond. of Pores
  - * Ignore Radiation



Conductivity of Gas Phase Confined in a Pore

$$k_g = \frac{k_g^0}{1 + BT/(d_t P)}$$

$k_g^0 \sim 0.0241$

$d_t = 0.6\mu m$

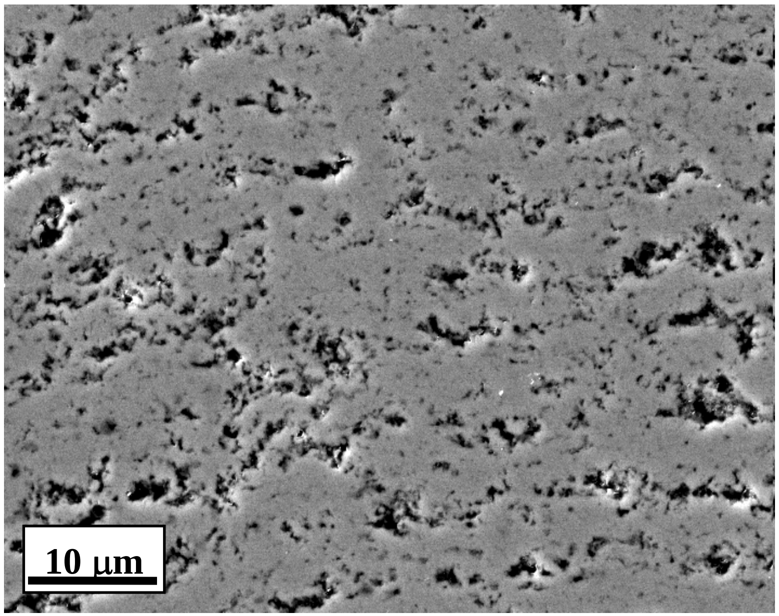
Radiation

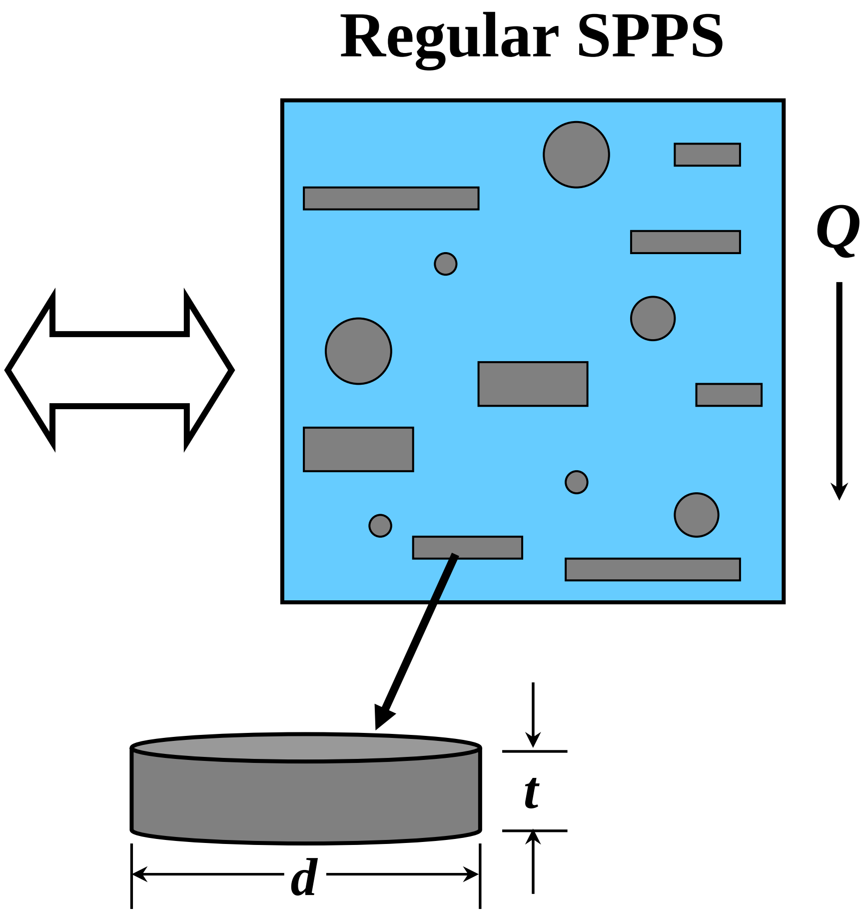
$$k_{rad} \approx \frac{16n^2}{3\alpha}\sigma_{SB}T^3$$

$n=2.2$

$\alpha = 10^7\ m^{-1}$

Thermal Conductivity Modeling: Analytical, Regular SPPS





- Mixture of Disk-Shaped and Spherical Pores
- Total Porosity ~22%

Thermal Conductivity Modeling: Analytical, Regular SPPS

Image Analysis

• Pore Vol. Fraction, Disk-Shaped Pores (ϕ_{Disk})	0.17
• Pore Vol. Fraction, Spherical Pores (ϕ_{Sphere})	0.07
• Aspect Ratio of Disk-Shaped Pores (d/t)	2.84
• Measured Density (Archimedes Principle)	4.73 Mg/m^3
• Av. Orientation of Disk-Shaped Pores	88^o

Thermal Conductivity Modeling: Analytical, Regular SPPS

Non-interacting Spherical Pores

$$\frac{k_{SphericalPores}}{k_{Dense}} = 1 - \frac{3}{2}\phi_{Sphere}$$

Aligned Disk-Shaped Pores

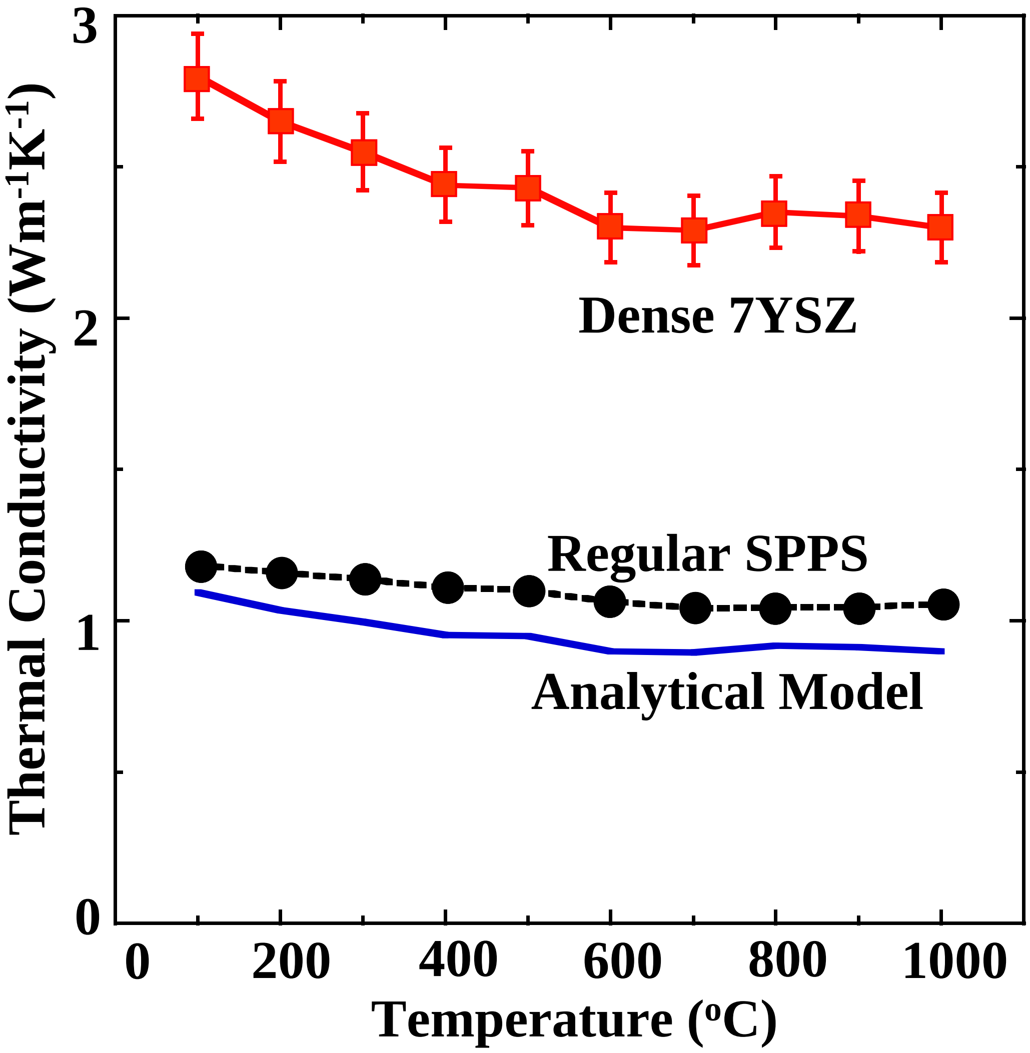
$$\frac{k_{DiskPores}}{k_{Dense}} = 1 - \left(\frac{2\phi_{Disk}}{\pi}\right)\left(\frac{d}{t}\right)$$

Effective Thermal Conductivity of Mixture

$$k_{SPPS} = \frac{1}{2}\left\{ f_2\left(\frac{\phi_{Disk}}{1-\phi_{Sphere}}\right) f_1\left(\phi_{Sphere}\right) + f_1\left(\frac{\phi_{Sphere}}{1-\phi_{Disk}}\right) f_2\left(\phi_{Disk}\right)\right\} k_{Dense}$$

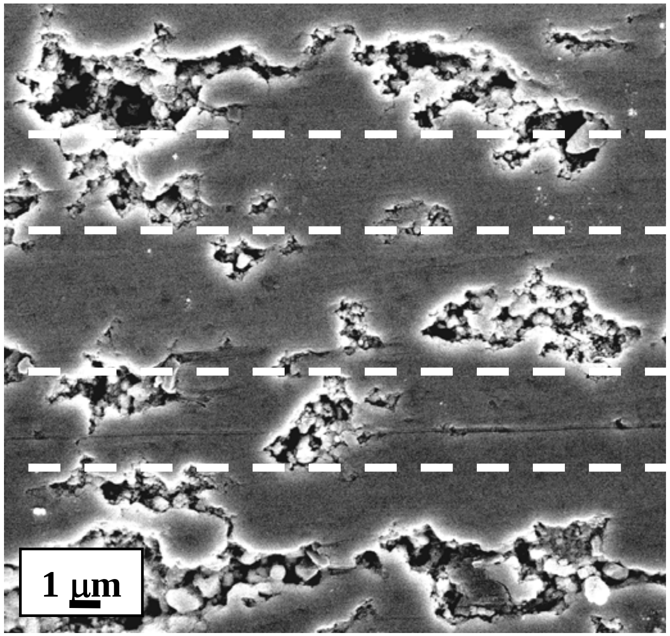
Shafiro et al., 2000; Lu et al., 2001; Cernuschi et al., 2004

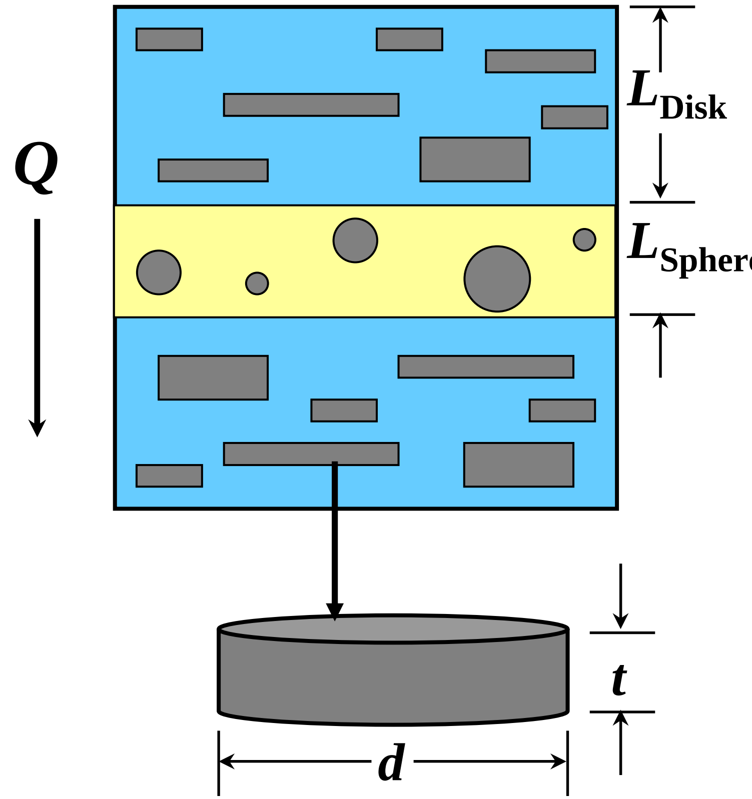
Thermal Conductivity Modeling: Analytical, Regular SPPS



- Calculated Th. Cond. within 13% of Expt.
- No Adjustable Param.
- Idealized Micro-structures

Thermal Conductivity Modeling: Analytical, Layered SPPS





- **Alternate Layers of:**
  - * Low, Spherical Porosity
  - * High, Disk-Shaped Porosity
- **Total Porosity ~33%**

Thermal Conductivity Modeling: Analytical, Layered SPPS

Image Analysis

- **Pore Vol. Fraction, Disk-Shaped Pores (ϕ_{Disk})** **0.24**
- **Pore Vol. Fraction, Spherical Pores (ϕ_{Sphere})** **0.06**
- **Aspect Ratio of Disk-Shaped Pores (d/t)** **3.34**
- **Av. Thickness of High-Porosity Layer (L_{Disk})** **6 μm**
- **Av. Thickness of Low-Porosity Layer (L_{Sphere})** **4 μm**
- **Measured Density (Archimedes Principle)** **4.13 Mg/m^3**
- **Av. Orientation of Disk-Shaped Pores** **89^o**

Thermal Conductivity Modeling: Analytical, Layered SPPS

Non-interacting Spherical Pores

$$\frac{k_{SphericalPores}}{k_{Dense}} = 1 - \frac{3}{2}\phi_{Sphere}$$

Aligned Disk-Shaped Pores

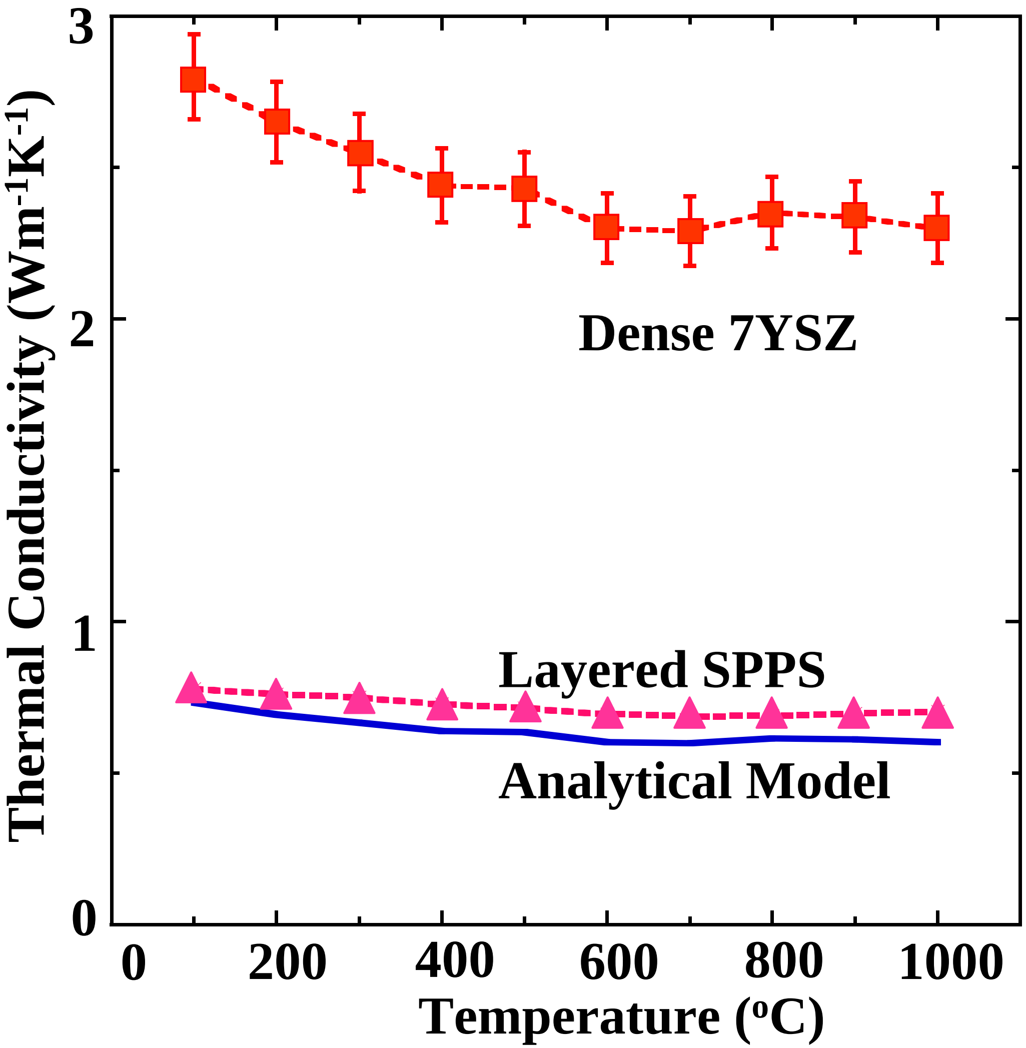
$$\frac{k_{DiskPores}}{k_{Dense}} = 1 - \left(\frac{2\phi_{Disk}}{\pi}\right)\left(\frac{d}{t}\right)$$

Effective Thermal Conductivity of Layered Composite

$$k_{LayeredSPPS} = \left(\frac{f_1(\phi_{Sphere})\, f_2(\phi_{Disk})\left(L_{Sphere} + L_{Disk}\right)}{f_1(\phi_{Sphere})\, L_{Disk} + f_2(\phi_{Disk})\, L_{Sphere}}\right) k_{Dense}$$

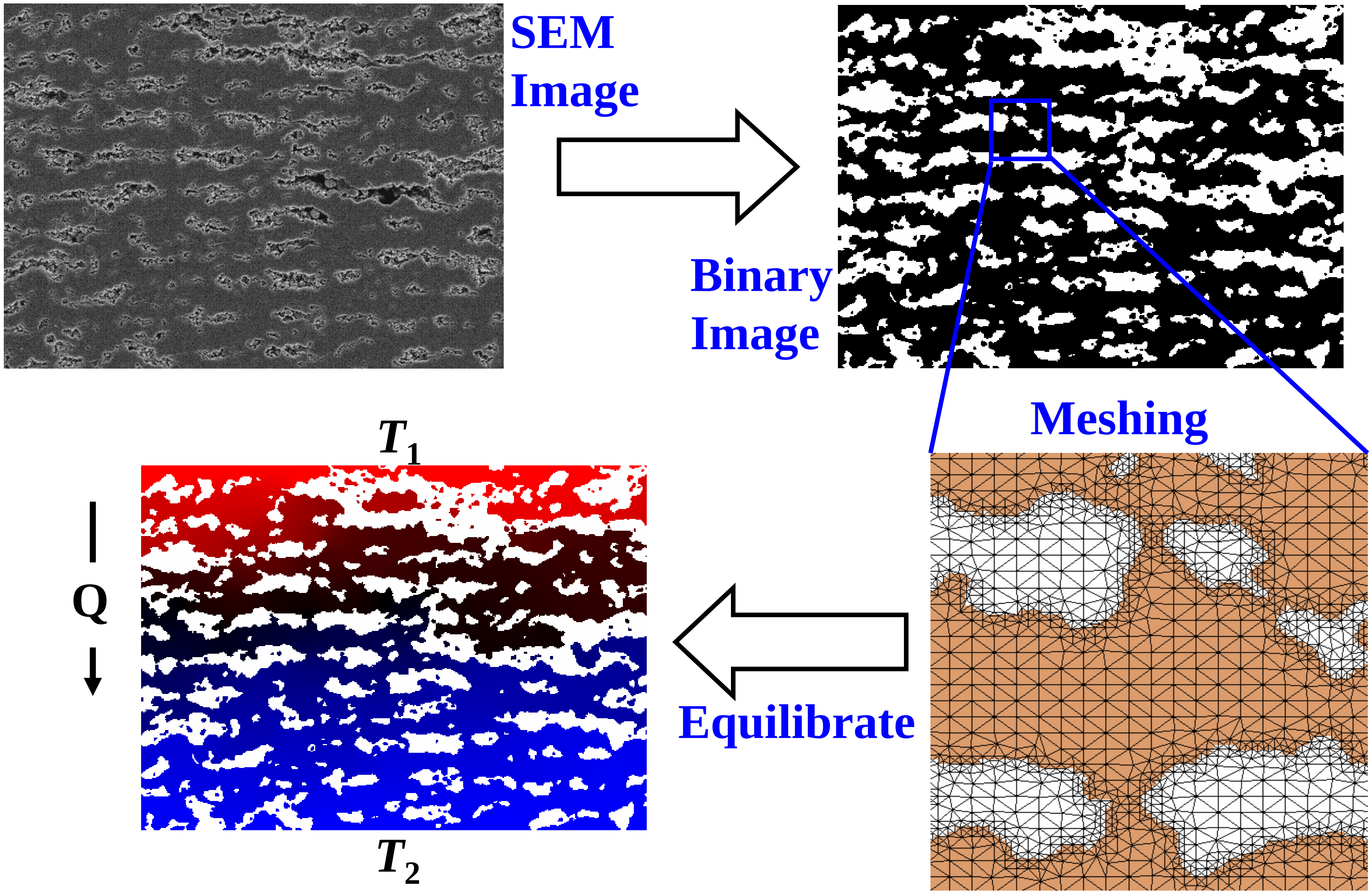
Shafiro et al., 2000; Lu et al., 2001

Thermal Conductivity Modeling: Analytical, Layered SPPS



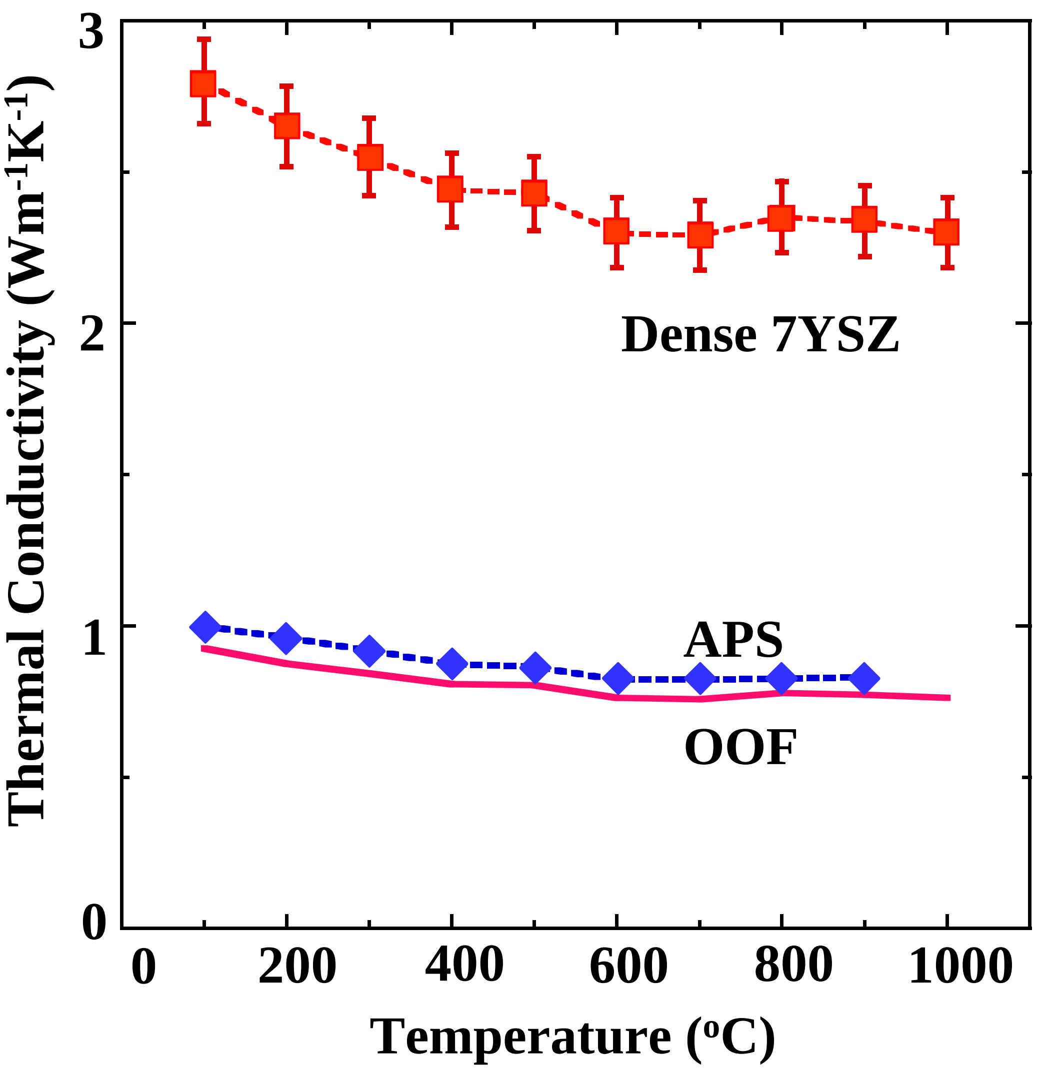
- Calculated Th. Cond. within 11% of Expt.
- No Adjustable Param.
- Idealized Micro-structures

Thermal Conductivity Modeling: OOF (2-D)



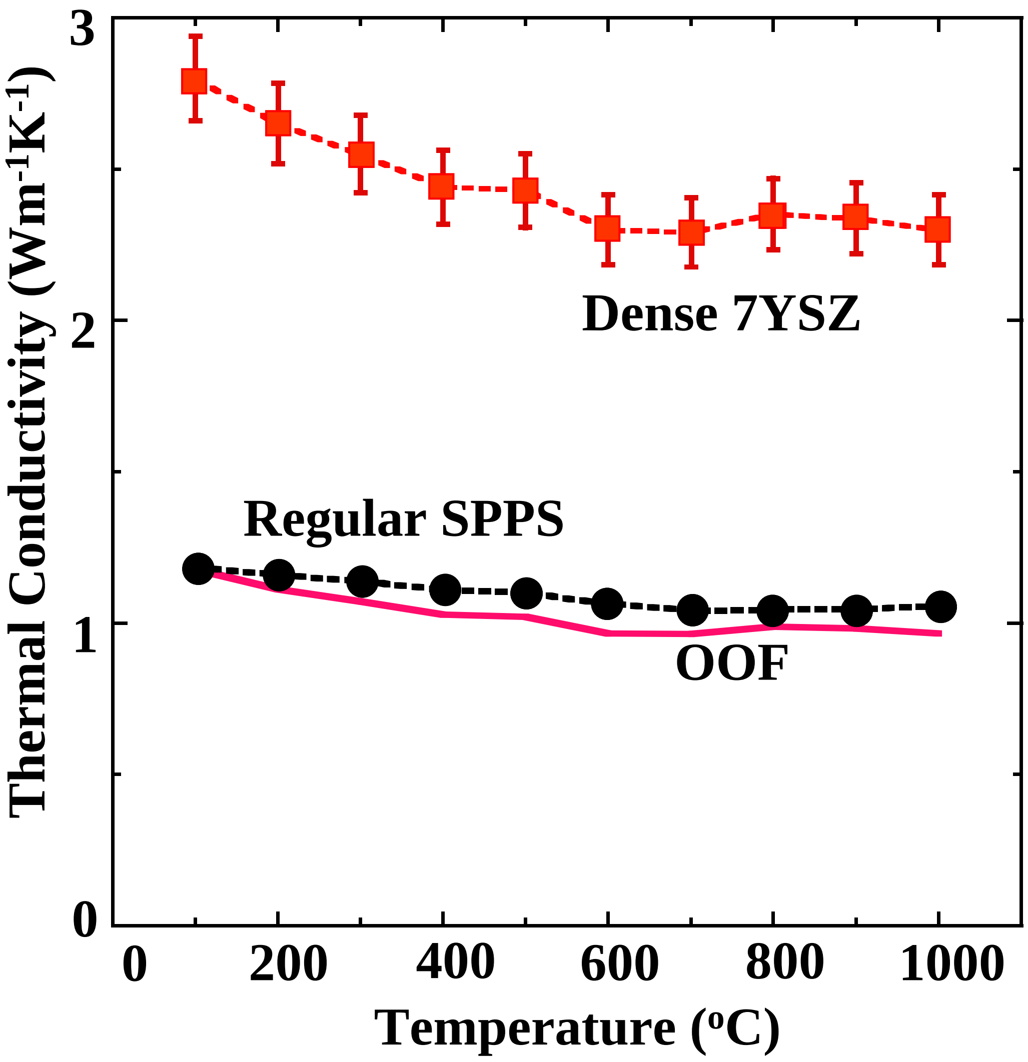
OOF Source: www.ctcms.nist.gov/oof

Thermal Conductivity Modeling: OOF, APS



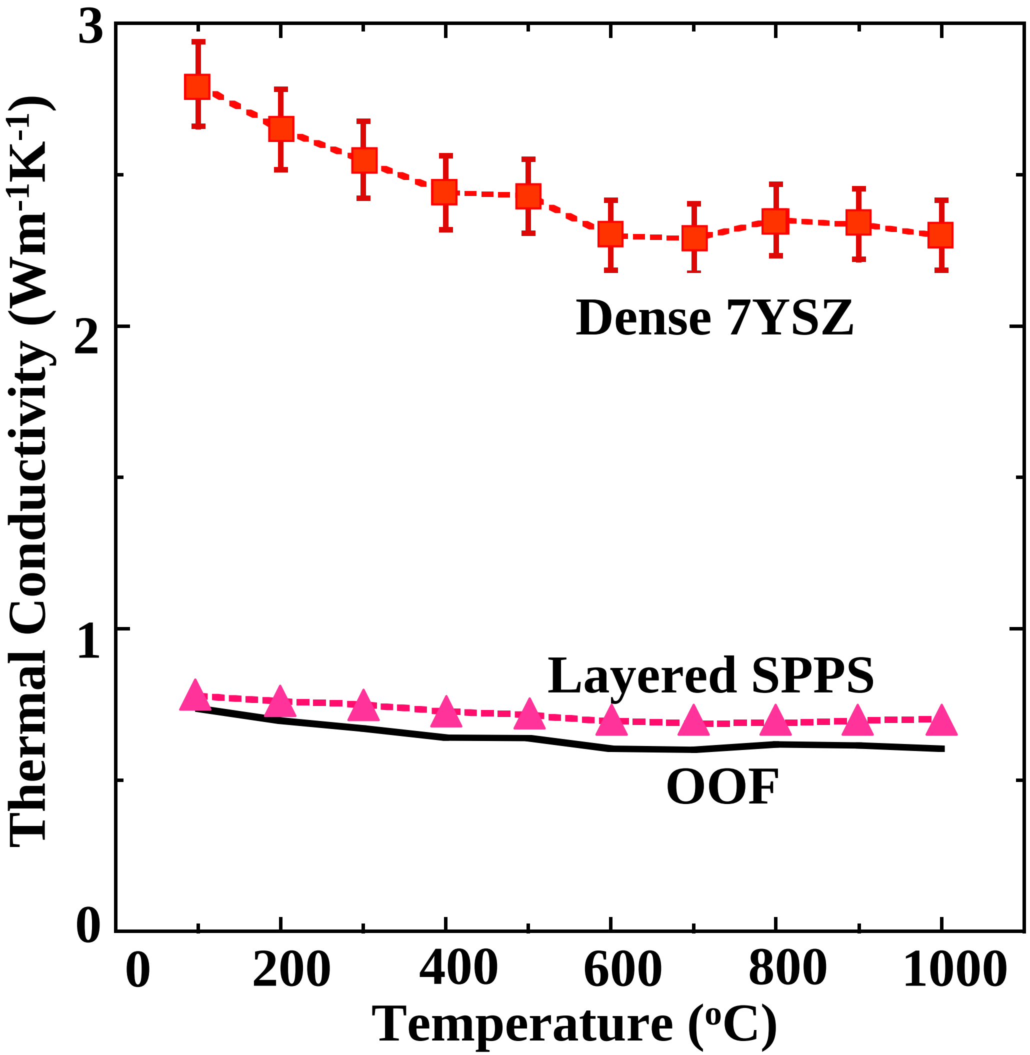
- Calculated Th. Cond. within 7% of Expt.

Thermal Conductivity Modeling: OOF, Regular SPPS



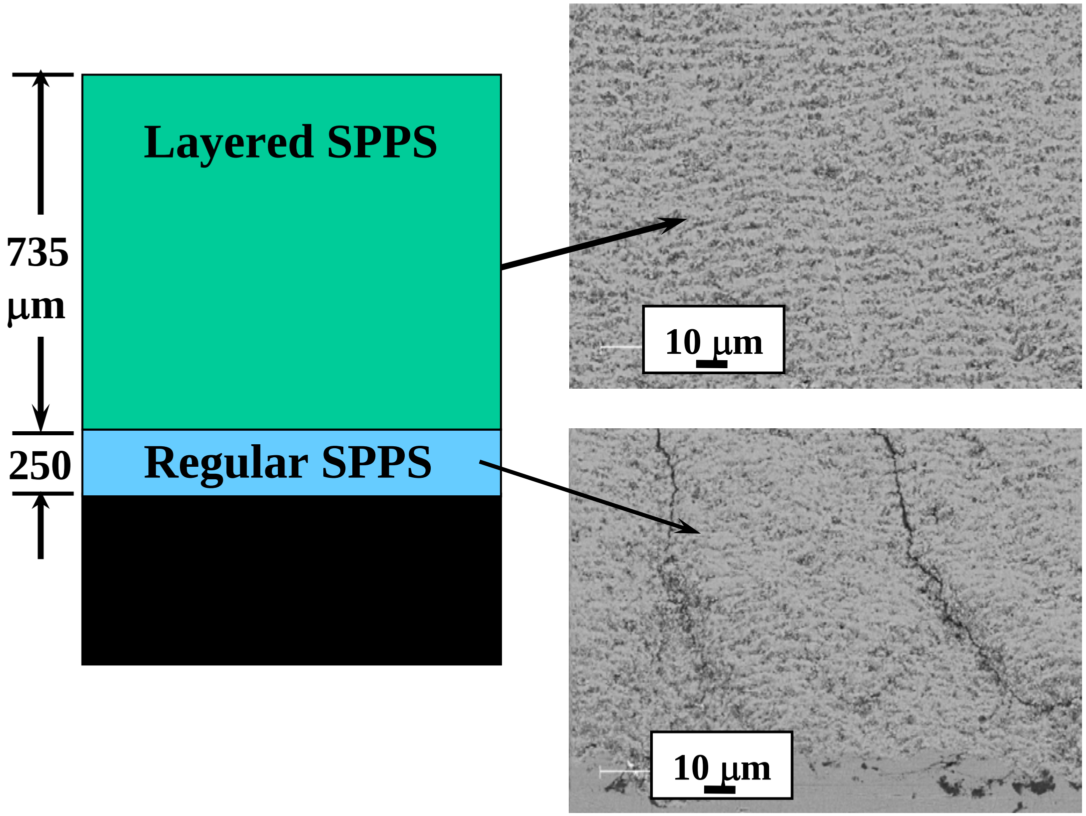
- **Calculated Th. Cond. within 6% of Expt.**
- **Better Than Analytical Model**

Thermal Conductivity Modeling: OOF, Layered SPPS

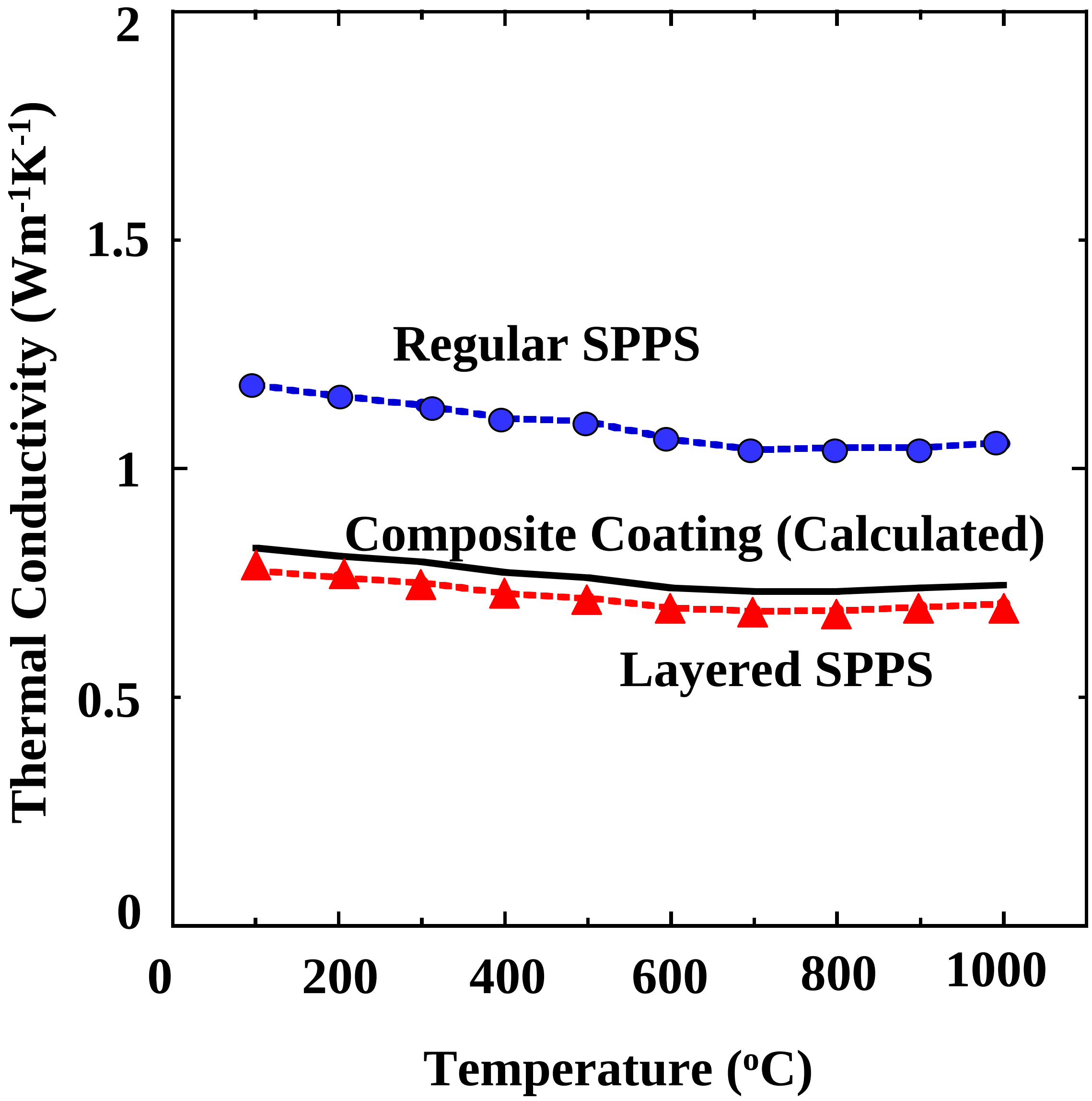


- **Calculated Th. Cond. within 10% of Expt.**
- **Better Than Analytical Model**

Low Thermal Conductivity, Improved Durability: SPPS TBCs with Layered Architecture



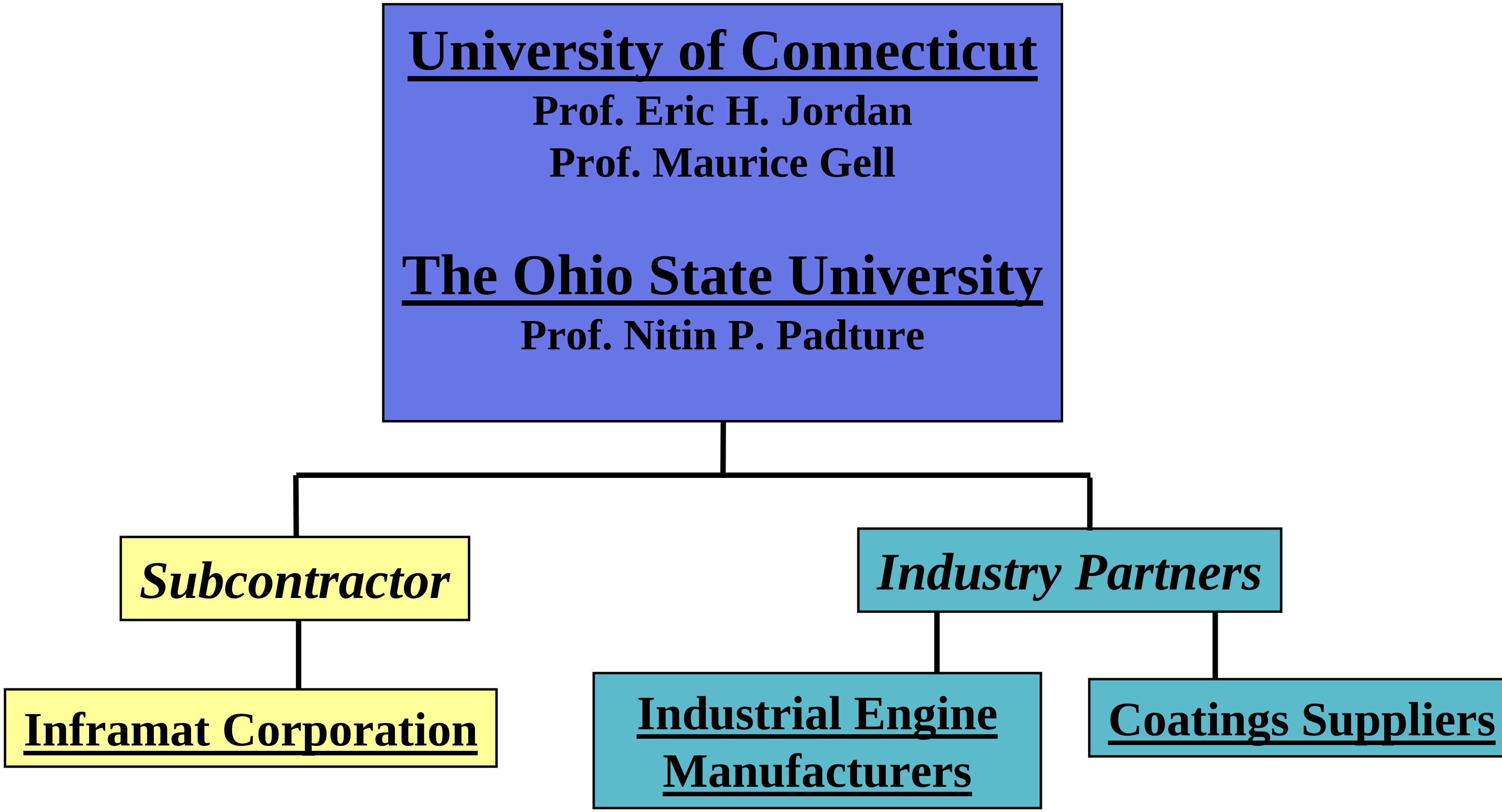
Low Thermal Conductivity, Improved Durability: SPPS TBCs with Layered Architecture



Summary

- **Demonstrated Feasibility of Depositing Ultra-Thick (~3 mm) TBCs Using the SPPS Process**
- **Demonstrated High Durability in Ultra-Thick TBCs**
- **Demonstrated Feasibility of Depositing Layered TBCs with Low Thermal Conductivities**
- **Modeled Effect of Microstructure on Th. Cond.**
- **Demonstrated Feasibility of Depositing SPPS TBCs with Layered Architecture for Low Th. Cond. and High Durability**

Teaming Arrangements



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- SCIES/DoE