Improved Performance Thermal Barrier Coatings Using The Solution Precursor Plasma Spray Process

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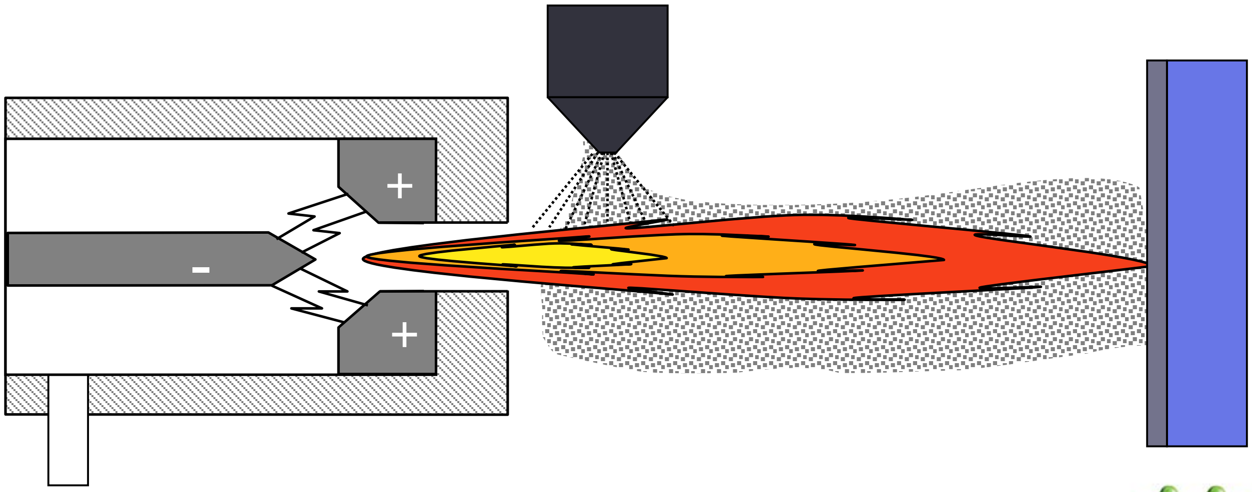
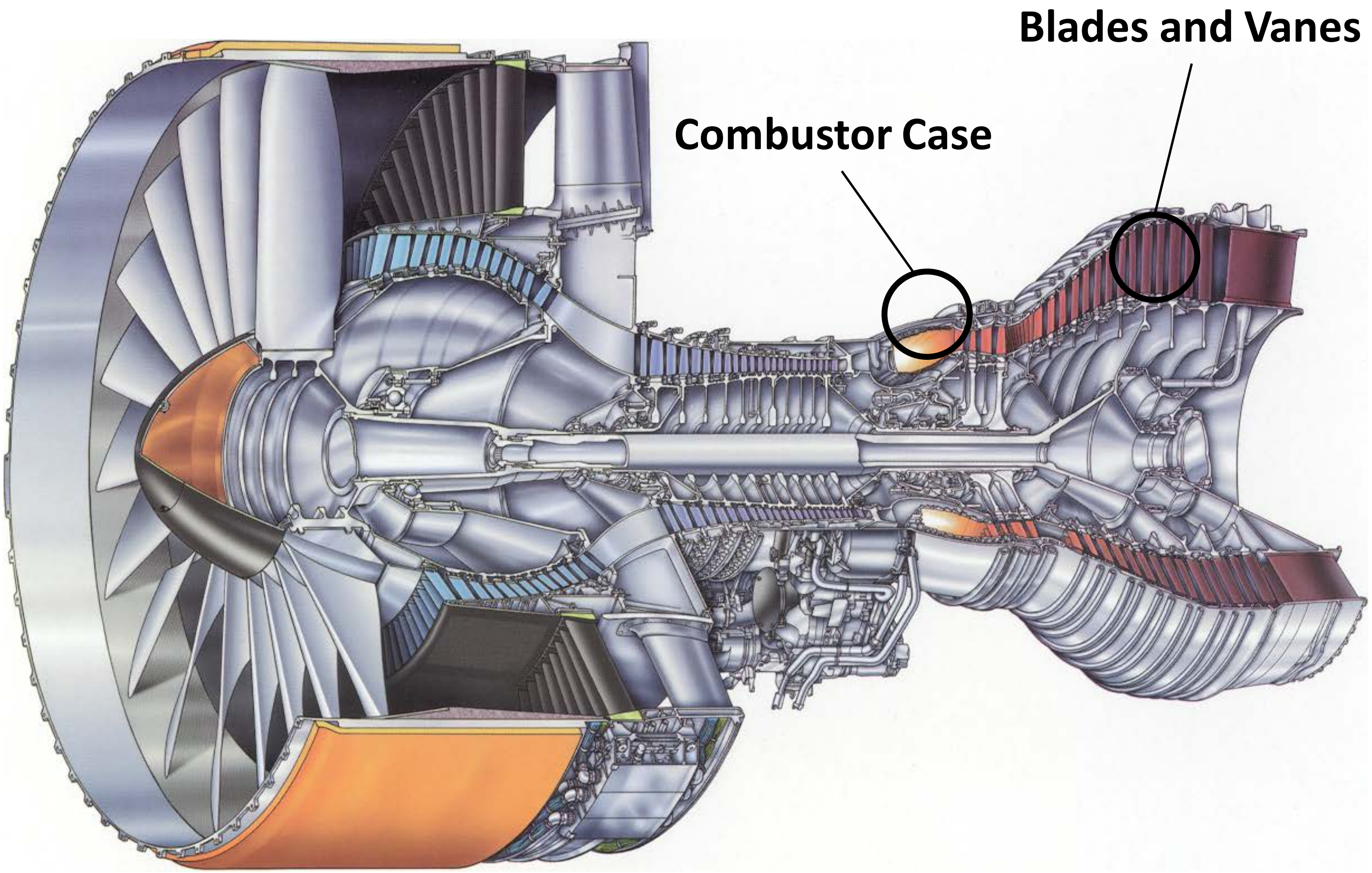


UTSR SBI

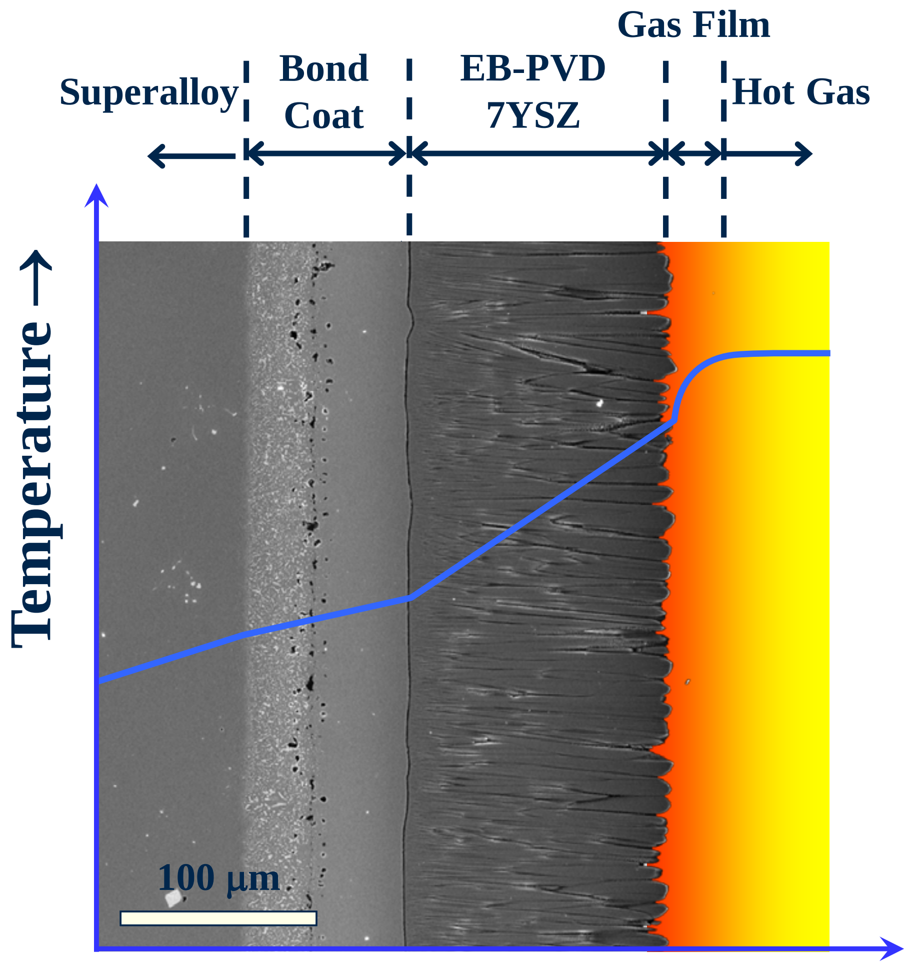
STTR Phase IIA Presentation
November 4, 2015

BACKGROUND

TBC Applications



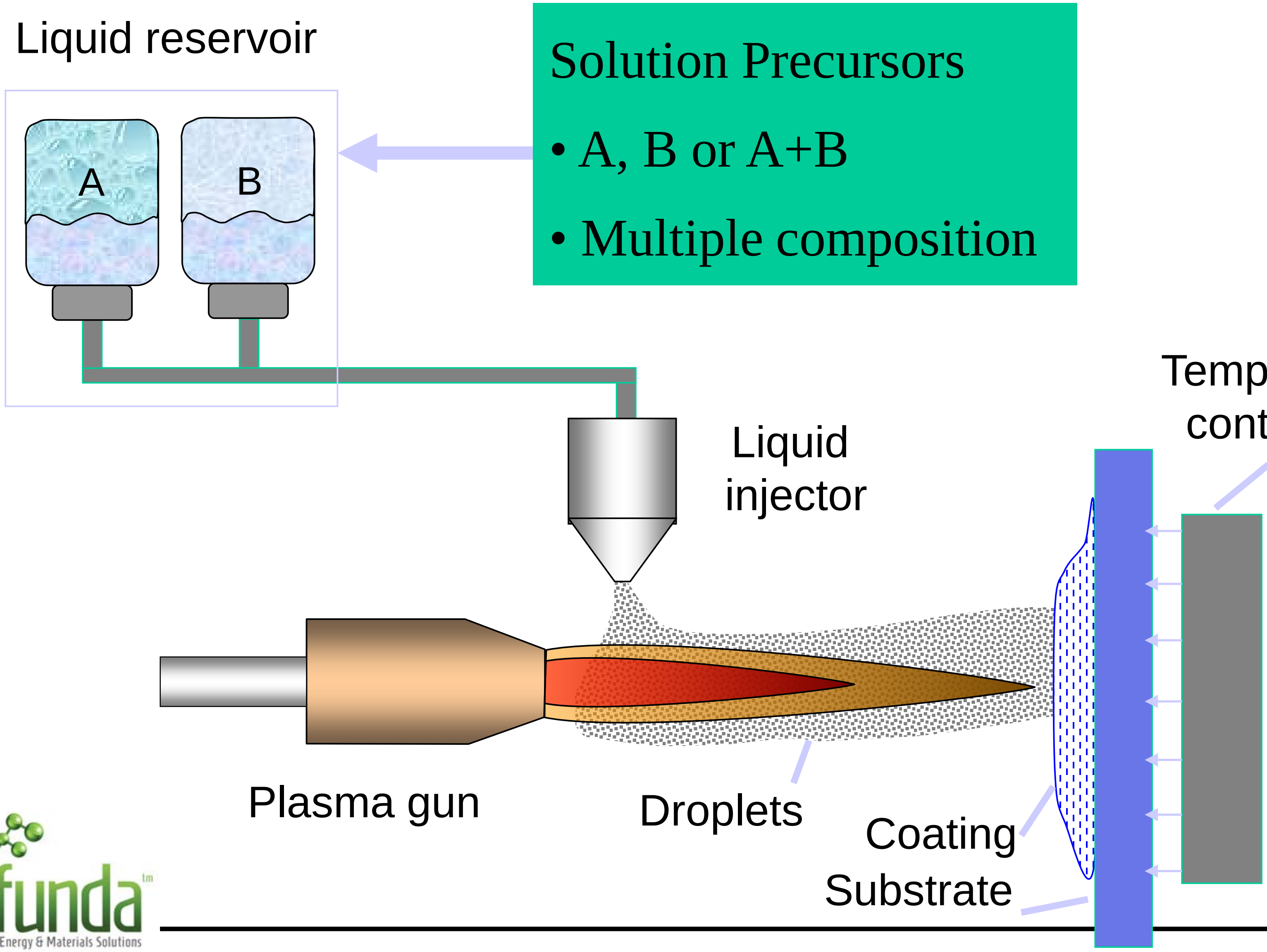
Microstructure & Requirements



Topcoat requirements:

- **Low thermal conductivity,**
- **High use temperature,**
- **High durability:**
  - ➢ **Toughness**
  - ➢ **Strain tolerance**

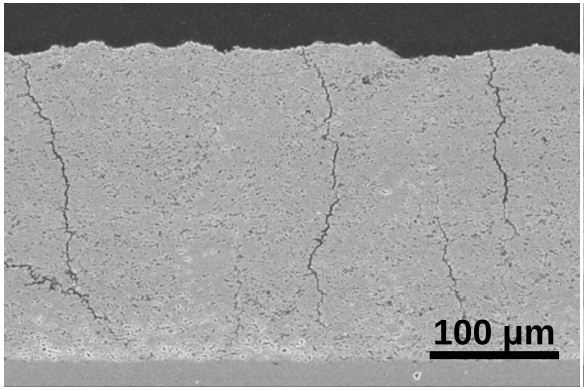
Solution Precursor Plasma Spray (SPPS) Process

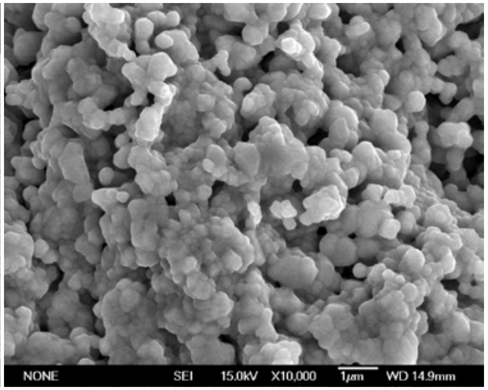


Solution Precursor Plasma Spray:

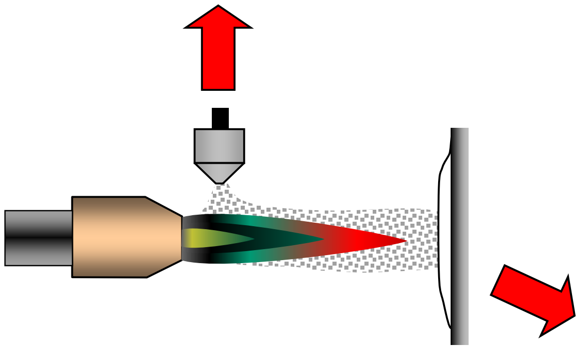
Unique Microstructural Features

Through-thickness vertical cracks

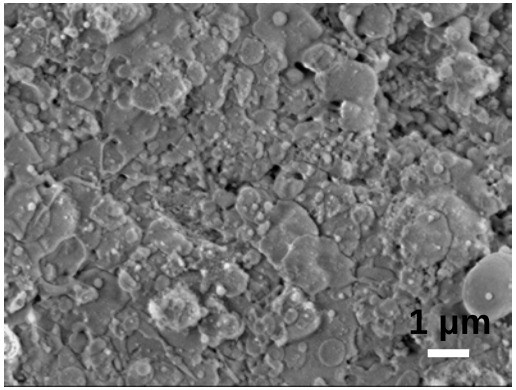




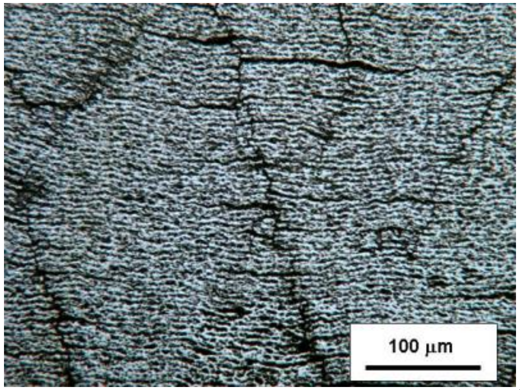
Varied nano/micro-scale porosity: 0~40%



Layered porosity: inter-pass boundaries.



Splat diameter < 2 µm
Splat thickness < 1 µm
Splat area is 1/2500 of that in APS TBCs



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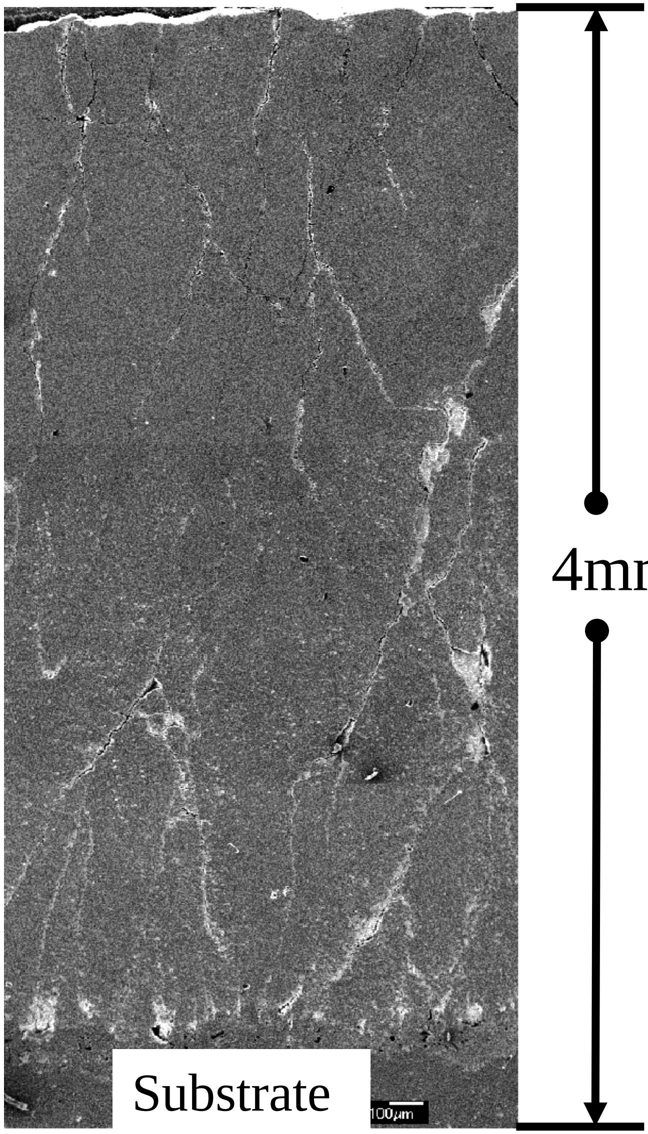
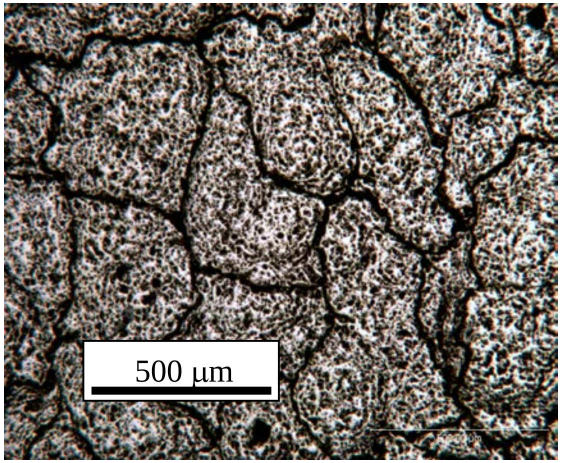
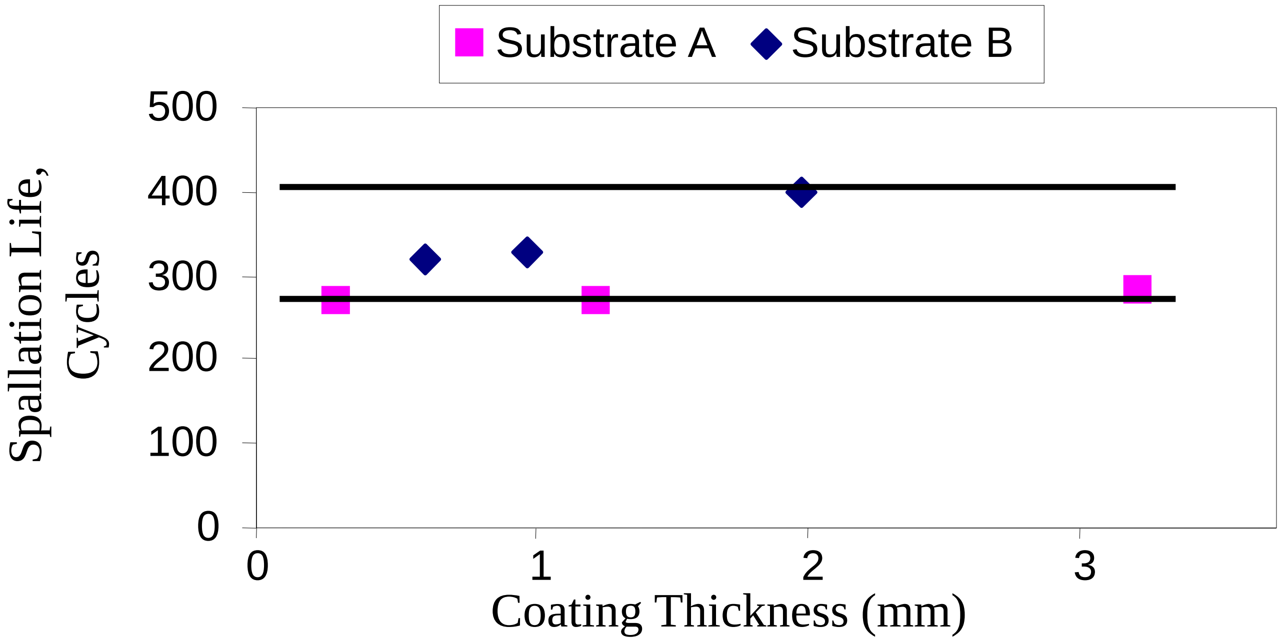
Thick SPPS Thermal Barrier Coatings



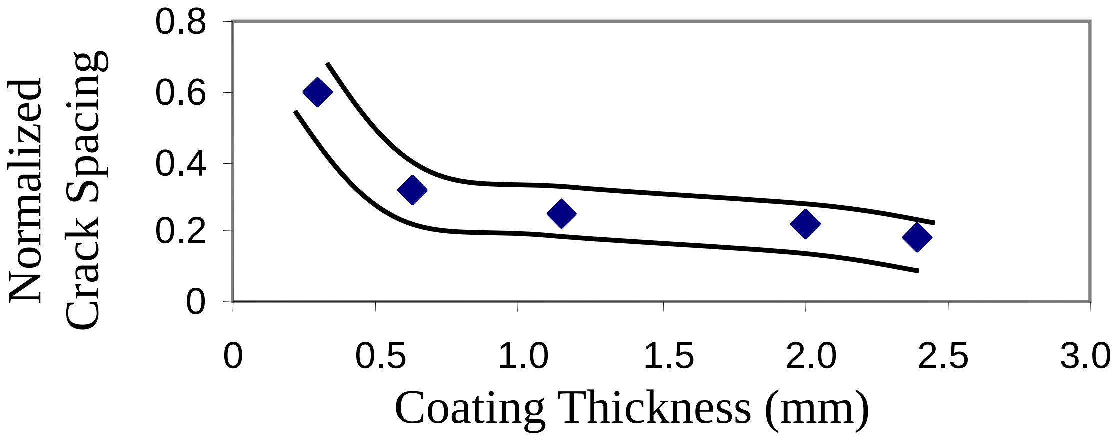


Surface

Effect of SPPS TBC Thickness On Durability



Thermal Cycle:
1121° C/1 hour



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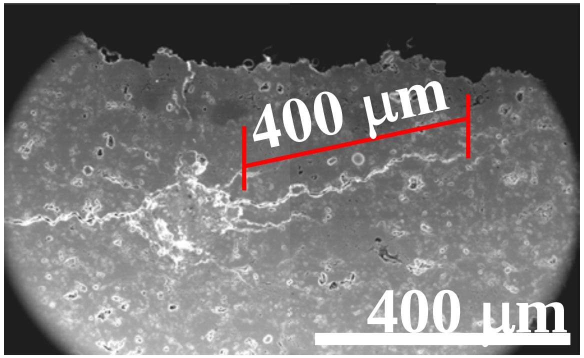
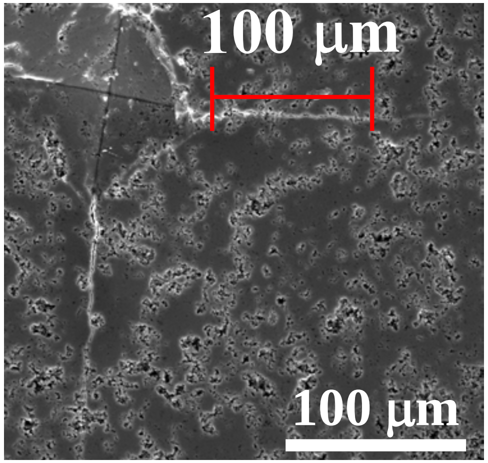
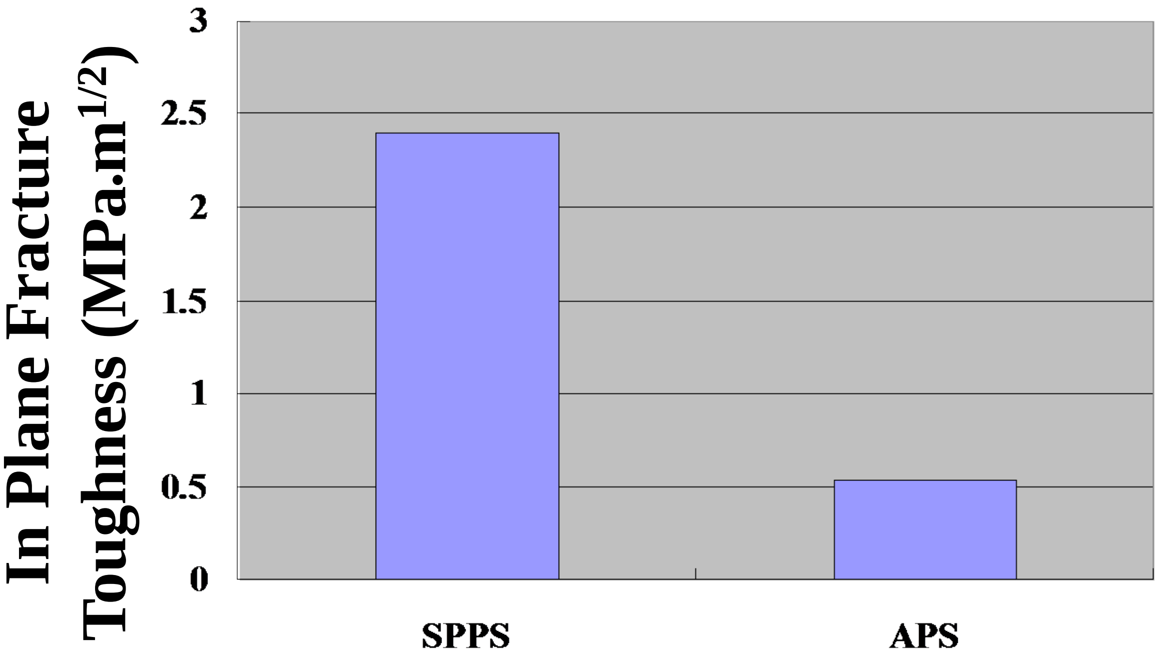
In-Plane Fracture Toughness

APS TBC

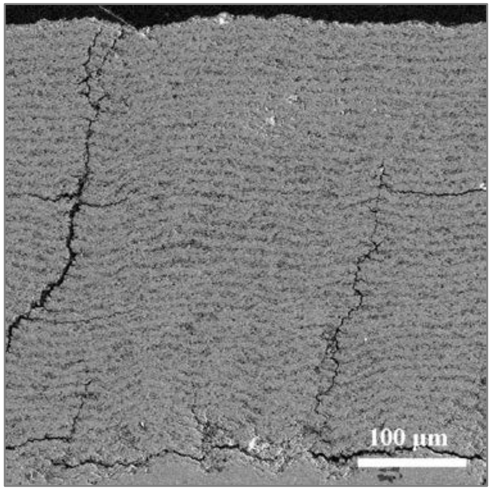


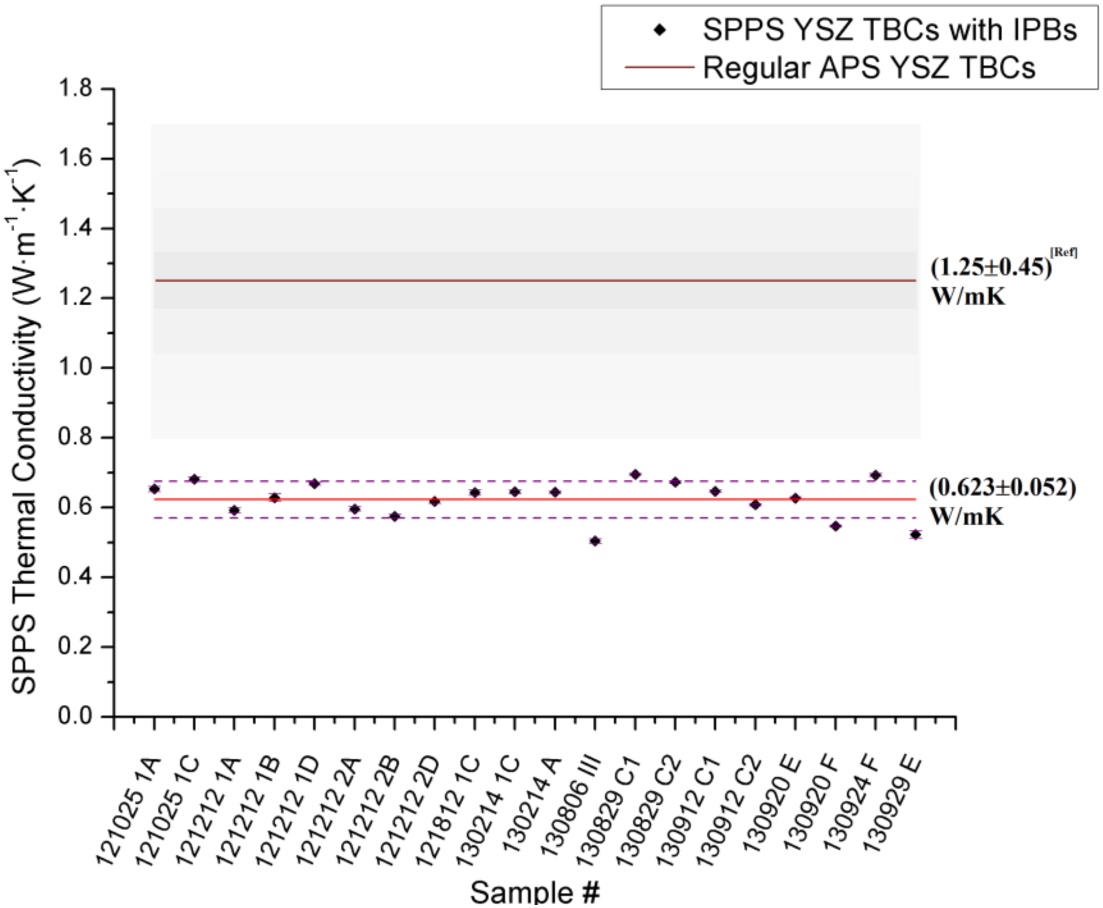


SPPS TBC



SPPS YSZ With IPBS: Thermal Conductivity





- **50% Reduction Demonstrated**

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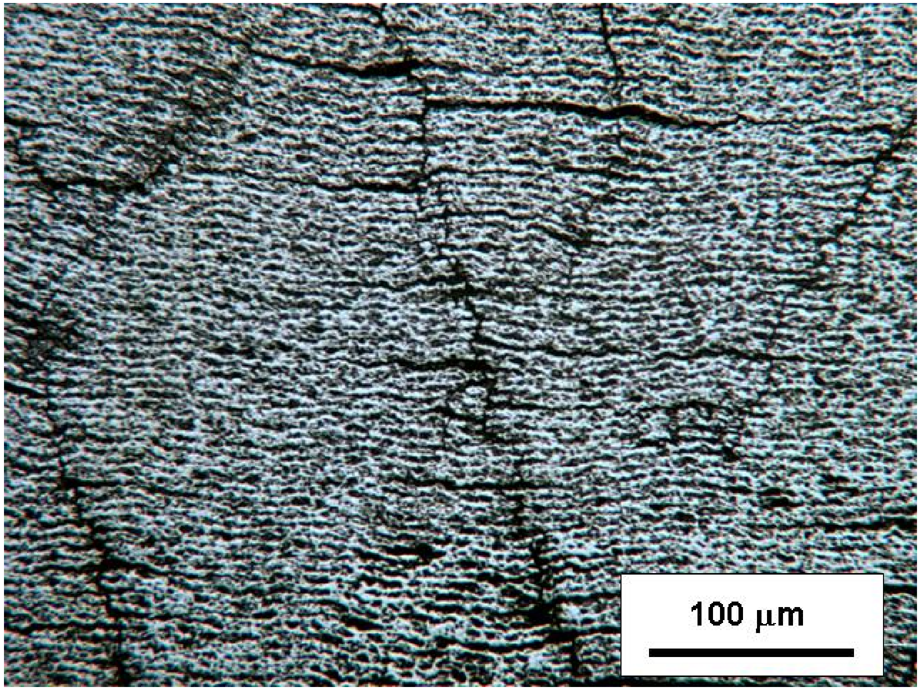
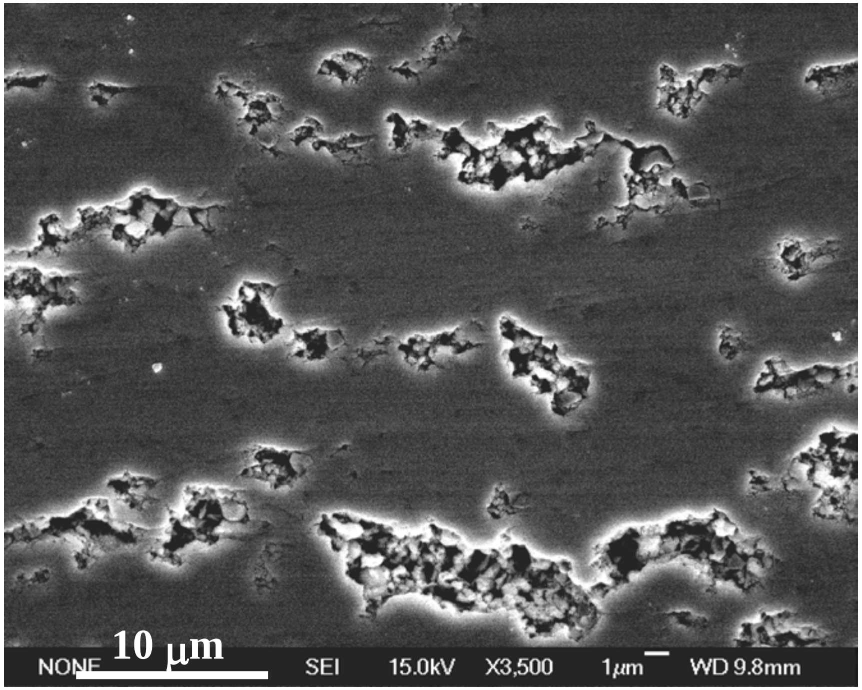
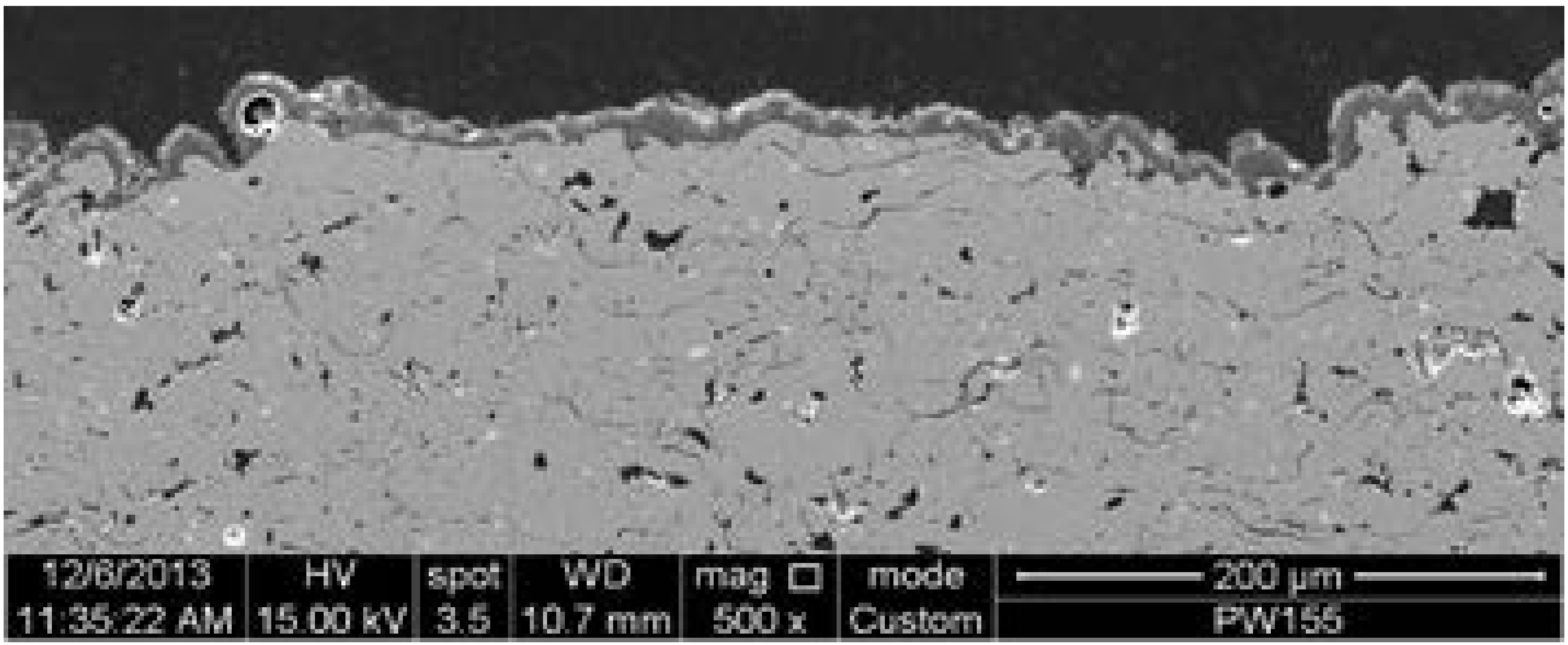
Engineered SPPS YSZ TBC Architecture





- Vertical cracks for strain tolerance/thermal cycle durability
- Planar pores (IPBs) for low thermal conductivity

SPPS can Make Thin Dense Layers 10 Micron



YAG A CHALLNAGE AND OPPROTUNITY

Properties Of YSZ and YAG

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

3 SPPS TBCs Developed

SPPS TBC	**Benefits**
YSZ	High Durability
YSZ with IPBs	Lower K High Durability
YAG	Higher Temp. Similar K High Durability Lower Density

SPPS YAG TBCs: Project Objectives

- Develop a Higher Temperature (+200^{o}C), Lower Thermal Conductivity Thermal Barrier Coating Using Yttrium Alumina Garnet (YAG) and the Solution Precursor Plasma Spray Process (SPPS)
- Phase IIa Objective Improve Performance/Cost

- Lower Thermal Conductivity
- Increse deposition rate $ and efficiency
- Radically improve CMAS resistance

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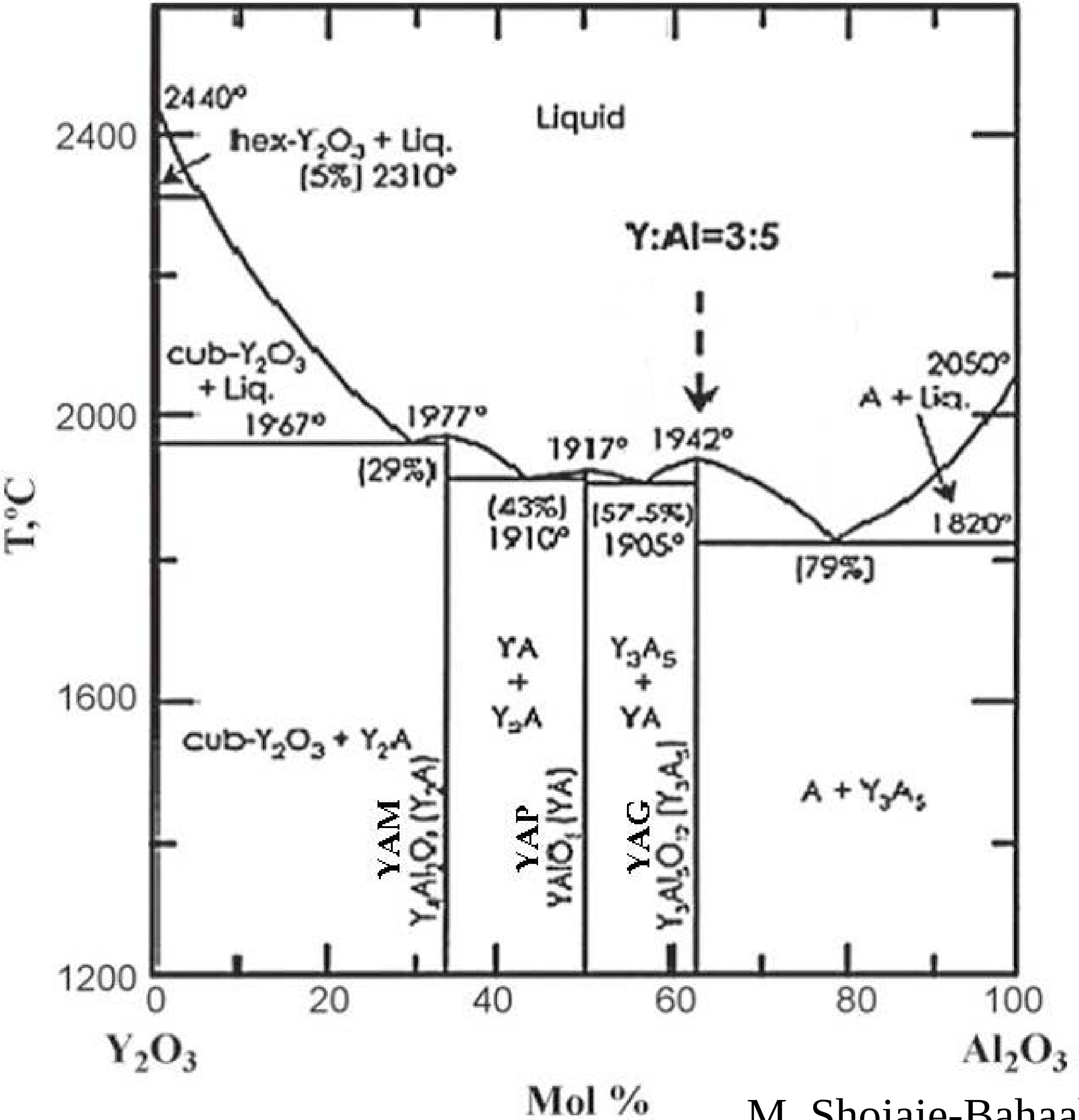
Anticipated Benefits

- **A New TBC That Can Tolerate Surface Temperatures of 1500^{o}C Can Be Game-Changing For the Gas Turbine Industry Due to Higher Turbine Efficiencies and Lower Fuel Consumption**

Yttria-Alumina Phase Diagram

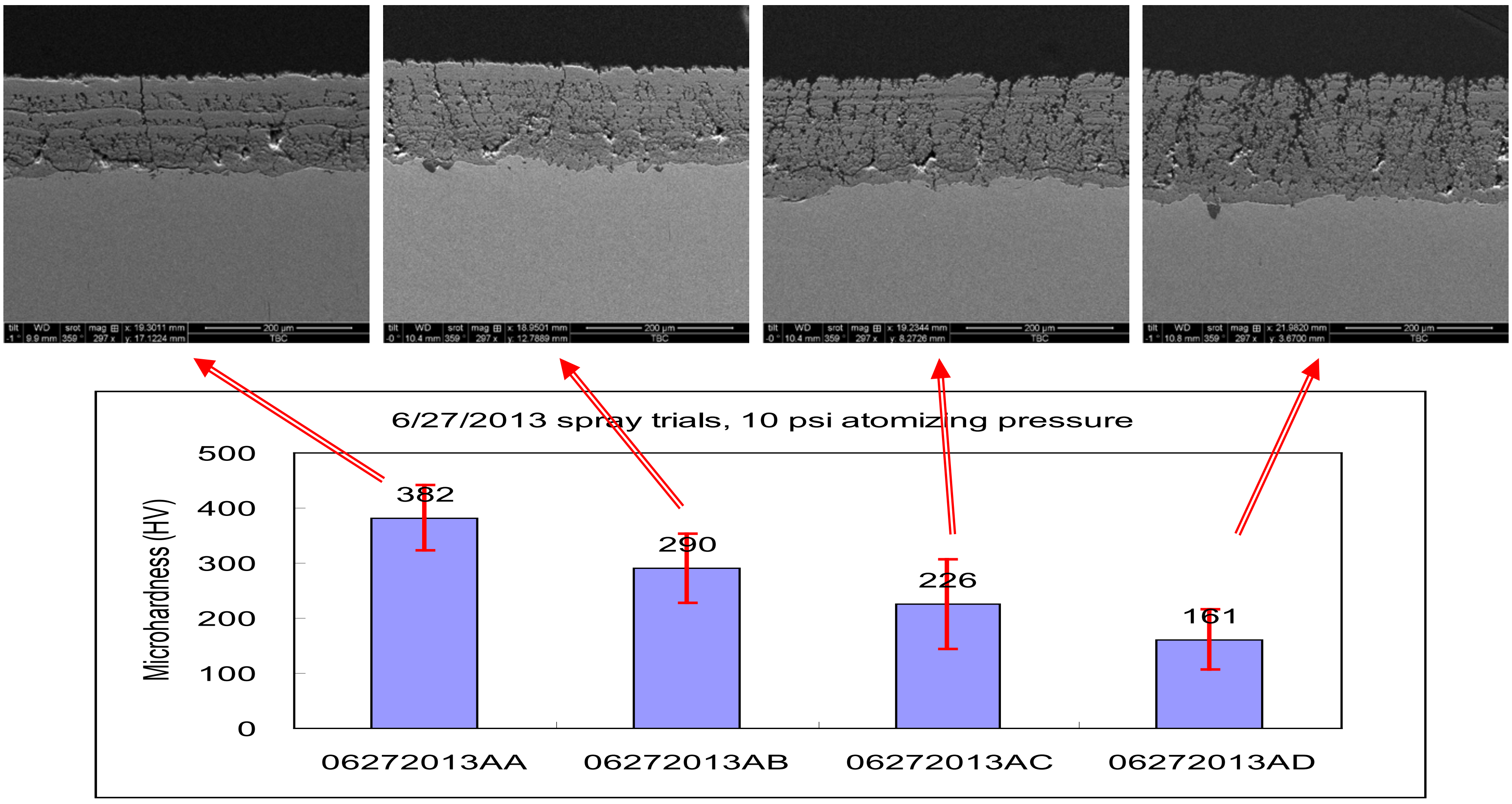


M. Shojaie-Bahaabad et al,
Ceramics Intl., Vol 35, 2009

Thermal Spray Optimization
Many Variables

- **Stand off Distance**
- **Precursor Composition**
- **Atomizing Gas Pressure**
- **Scan Speed and Step Height**
- **Injection Method, Stream vs. Atomizing**
- **Feed Rate**
- **Gun Power**
- **Gas Mix**
- **Gun Type**

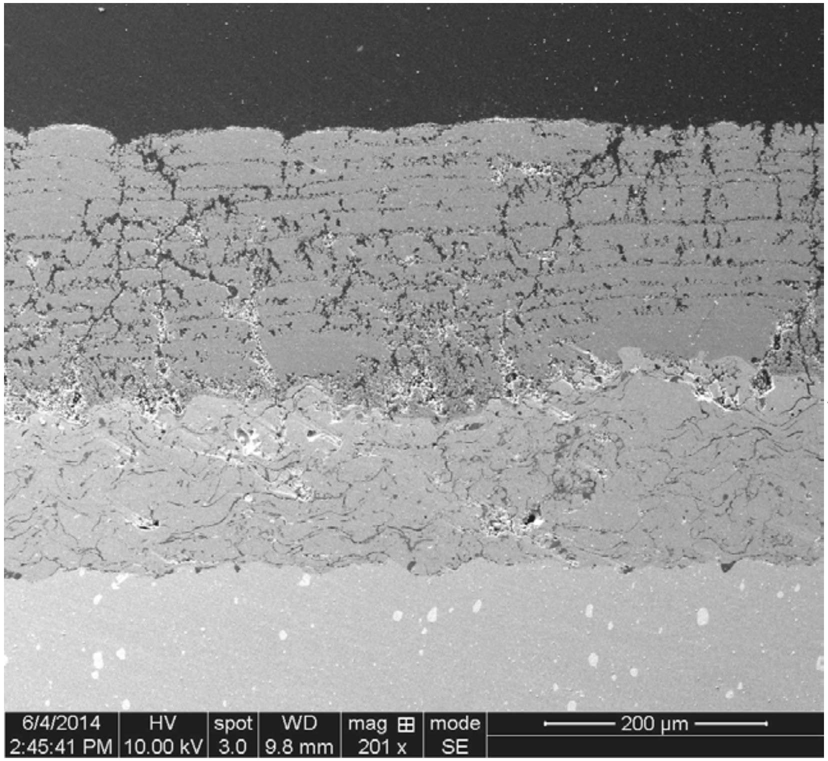
Increased Spray Distance at Lower Atomizing Pressure



SD = 1.375” 1.425” 1.5” 1.625”

Performance

SPPS YAG TBCs: Standard Microstructure
--Used for Engine-Critical Properties Tests--



SPPS YAG

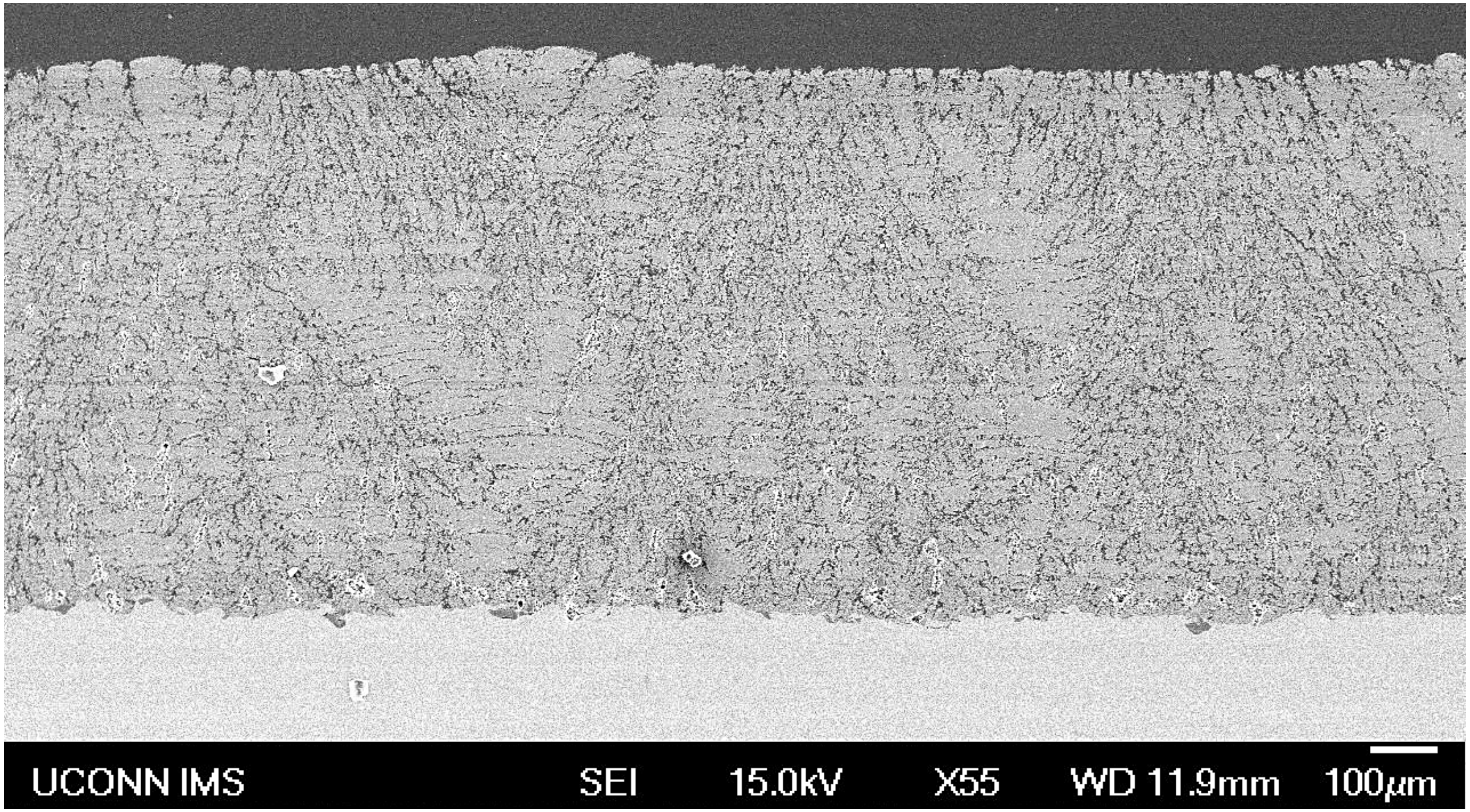
APS YSZ

Bond Coat

Superalloy

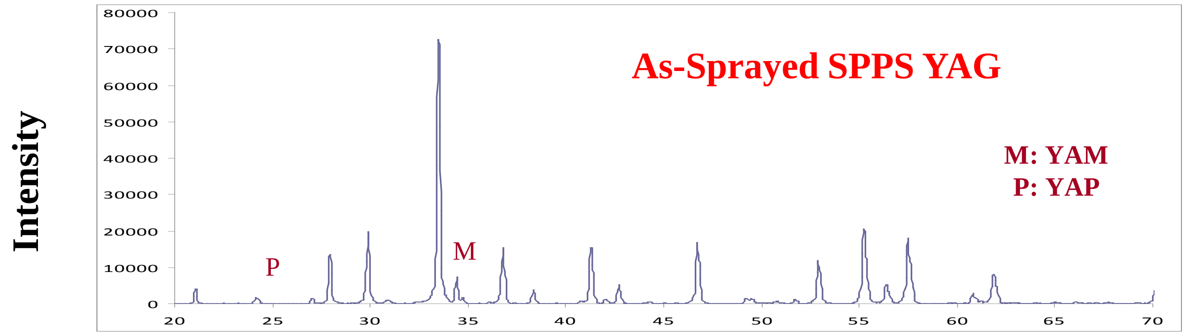
- **Vickers Hardness: 200-400**
- **Porosity: 15-20%**

Thick SPPS YAG TBCs Can Be Readily Fabricated

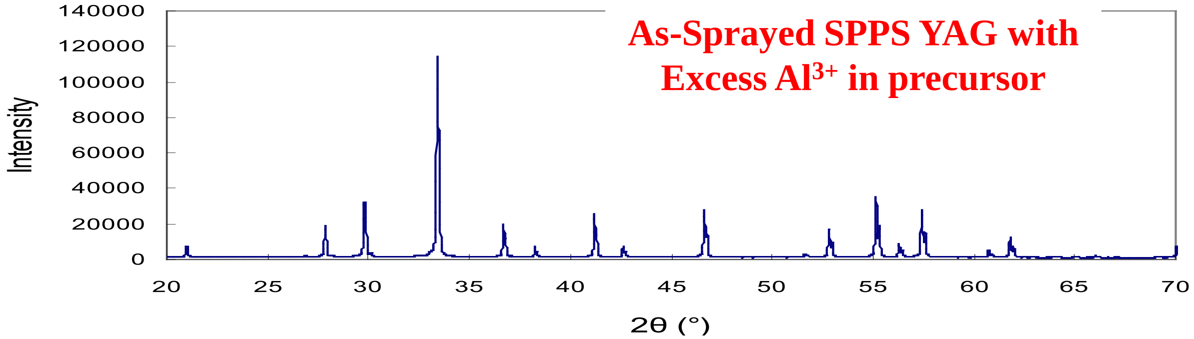


- 800 microns (33 mils) thick strain-tolerant microstructure
- Can be used for vanes, combustors and turbine outer air seals

Stoichiometric YAG Deposited By SPPS Process

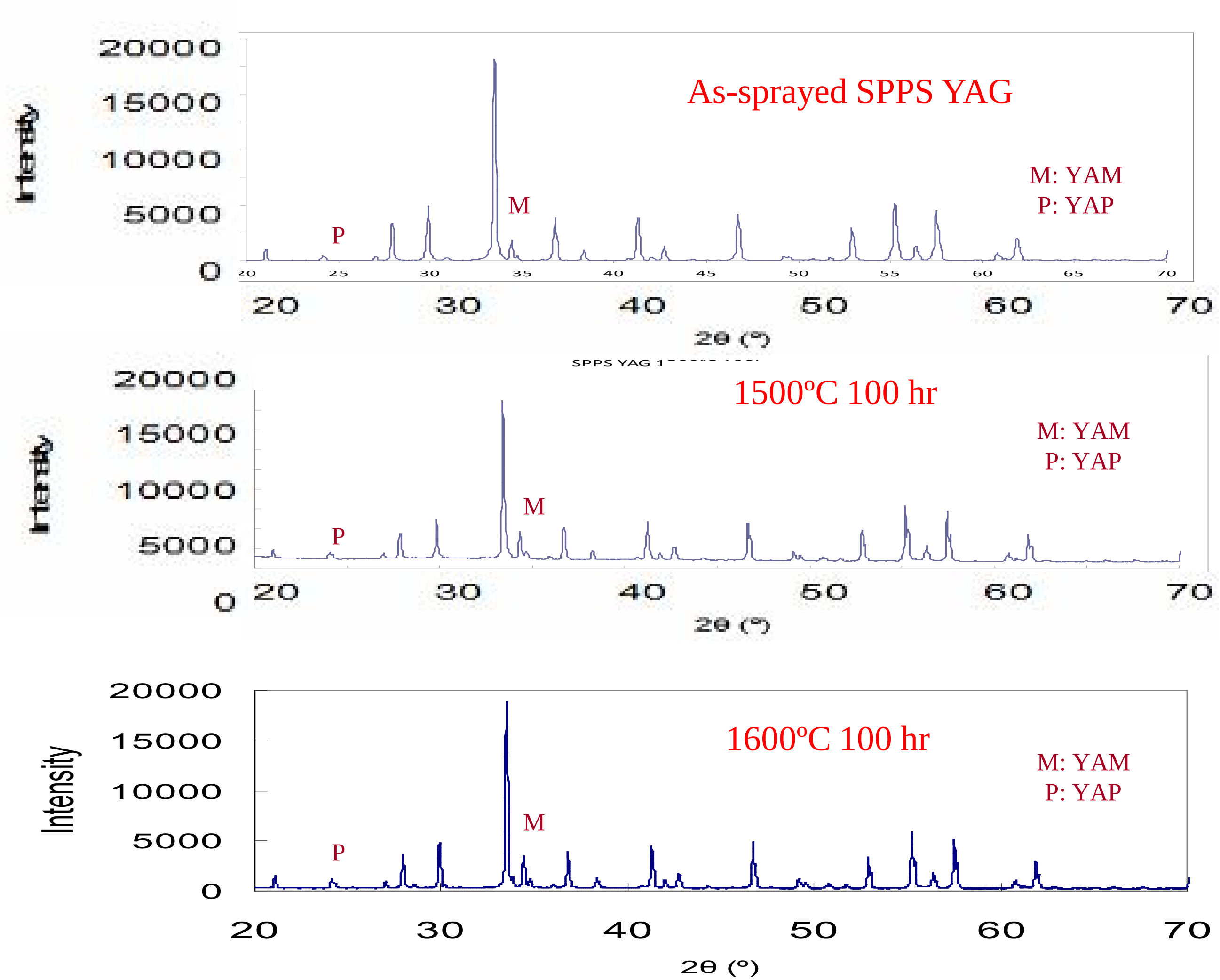


- **Predominantly YAG Phase with Minor Amounts of YAM and YAP**



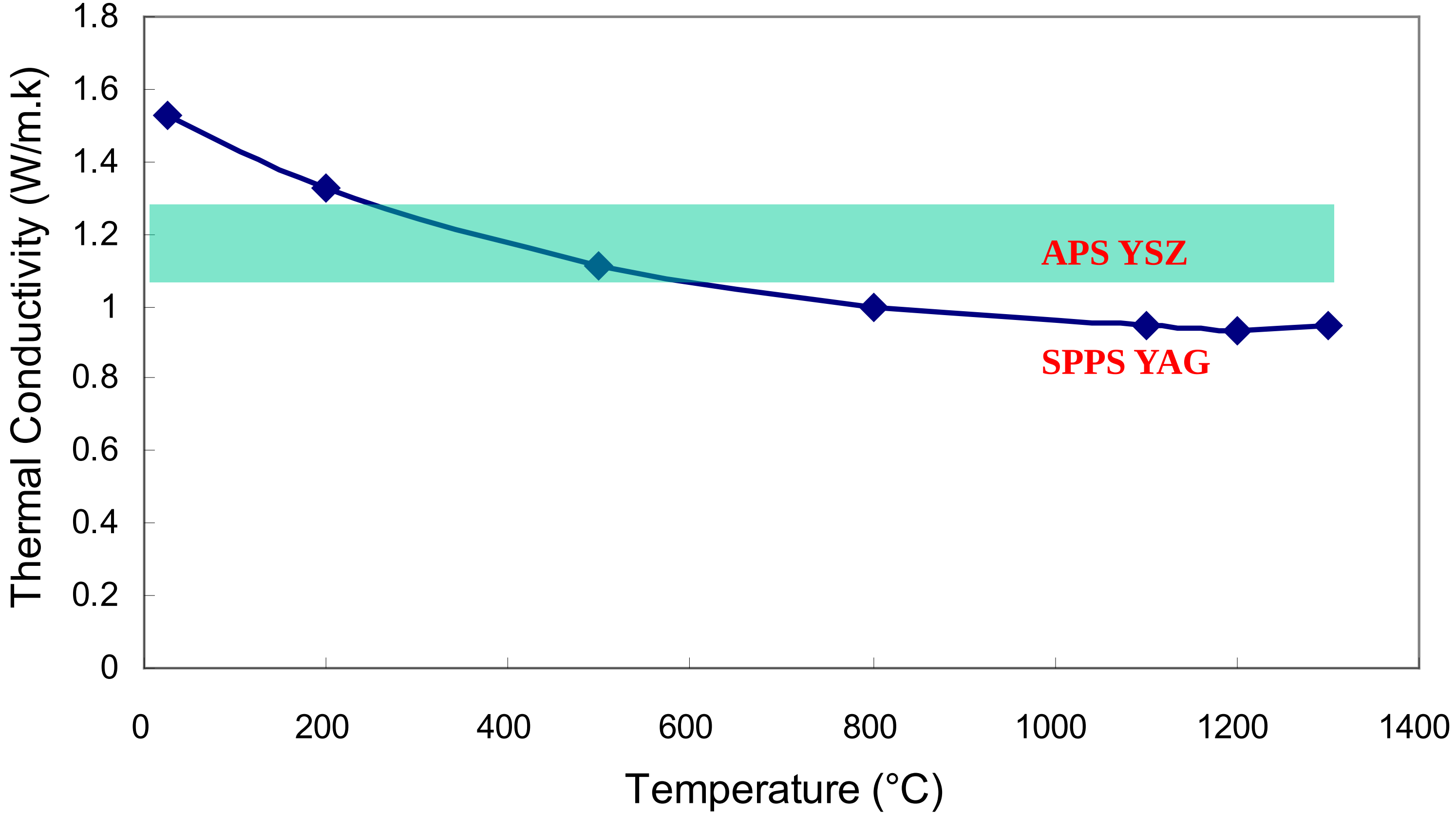
- **Pure YAG phase**

SPPS YAG TBCs: Phase Stability



- **SPPS YAG TBCs Are Phase Stable To At Least 1600ºC**

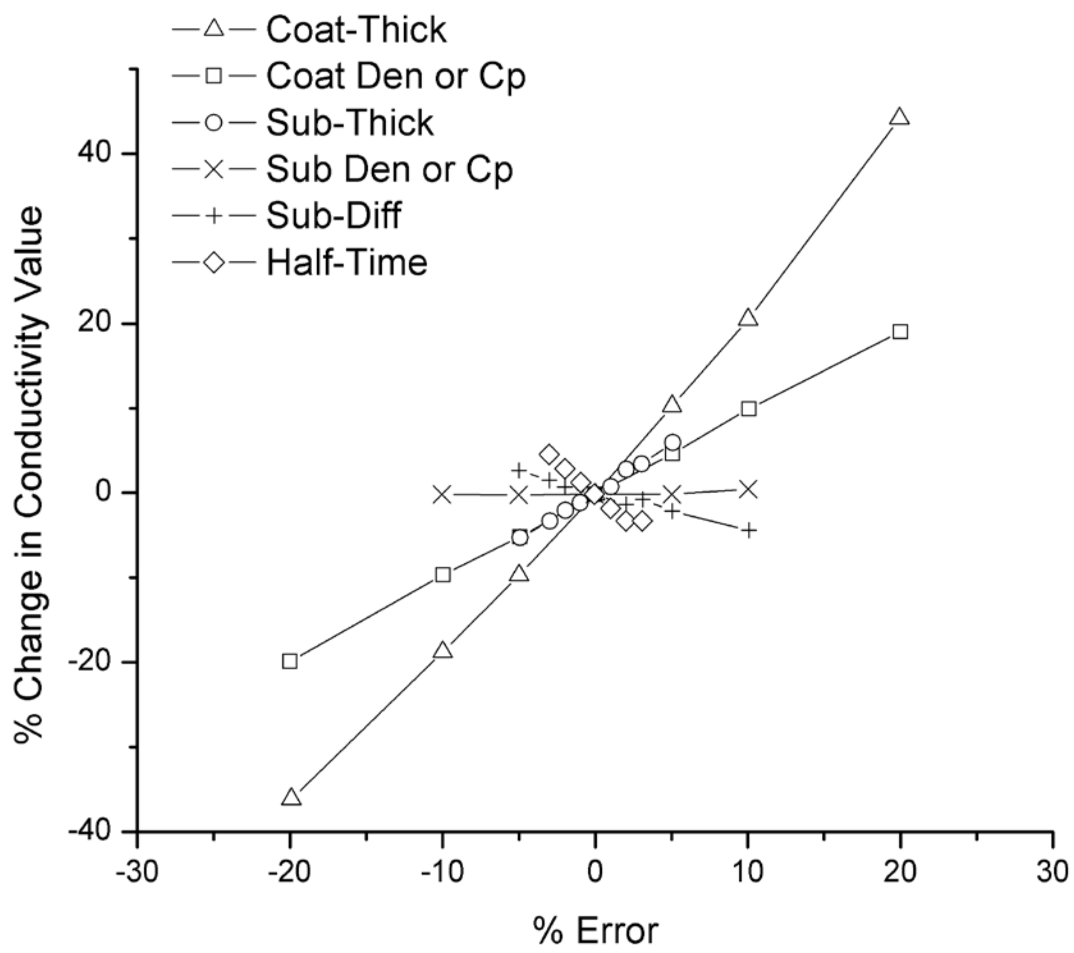
Thermal Conductivity of SPPS YAG TBCs



- **Measured by Netzsch Instruments Using Laser Flash**
- **1 mm thick sample with Vickers Hardness of 246**

Flash Method

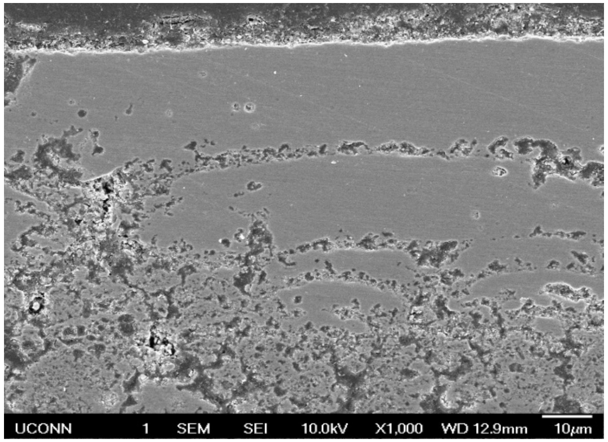
Error



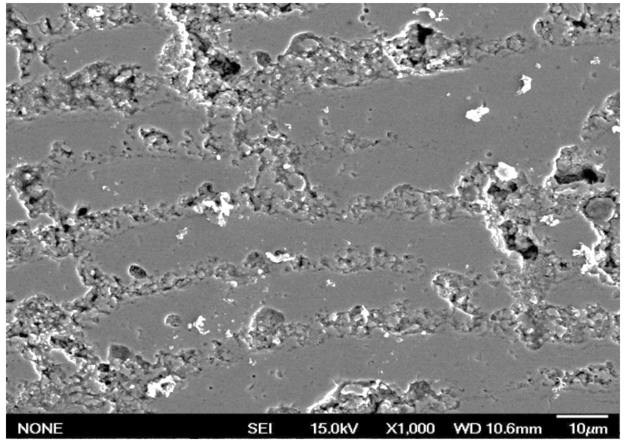
[4] Taylor RE. Thermal conductivity determinations of thermal barrier coatings. *Materials Science and Engineering A*245.1998: 160–167

Thermal Conductivity of different YAG samples

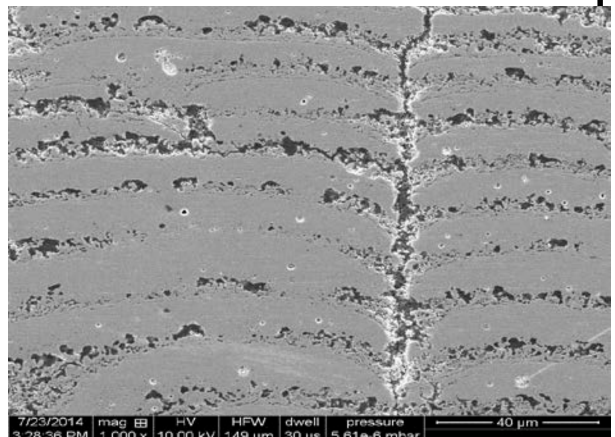
Porosity ~15%
HV= 249±175

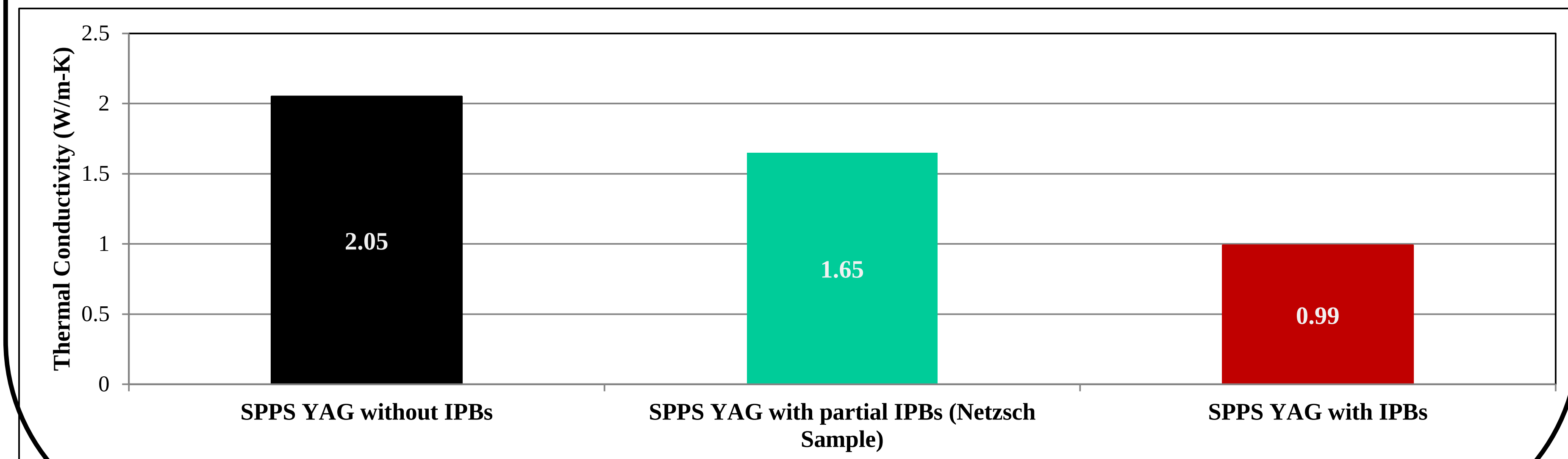


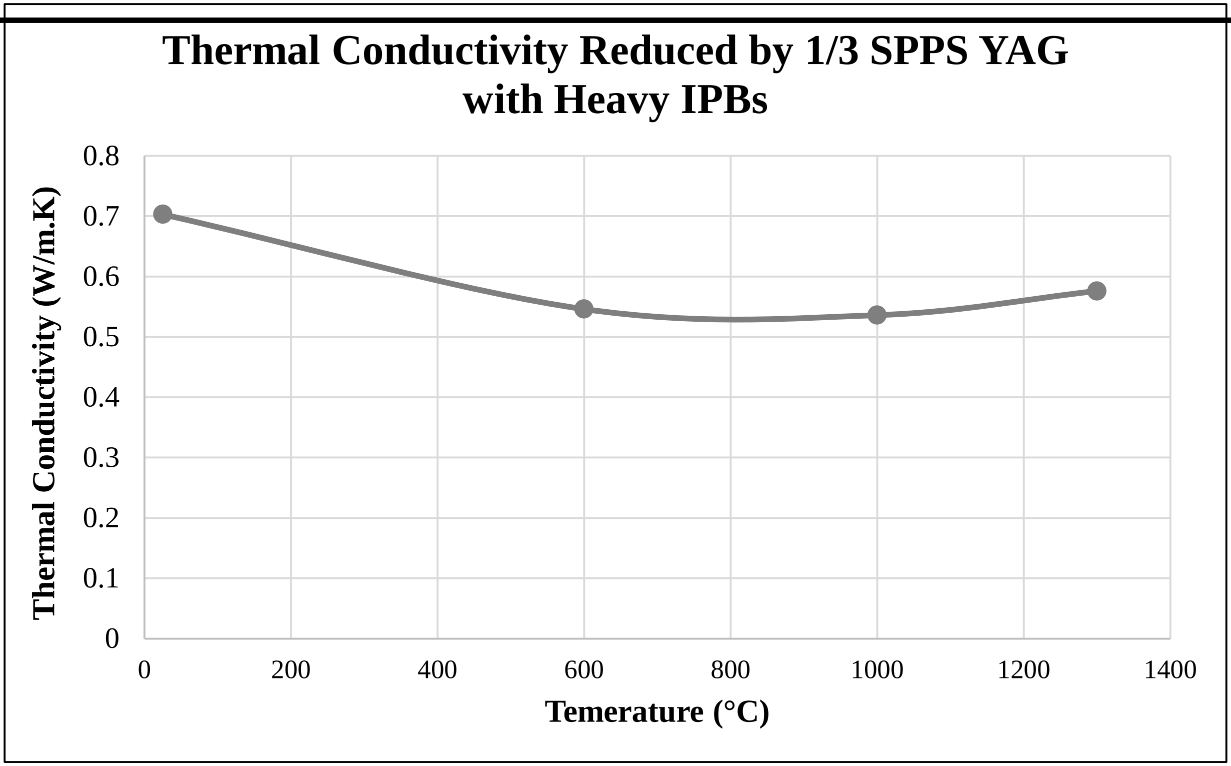
Porosity ~33%
HV= 260 ±33

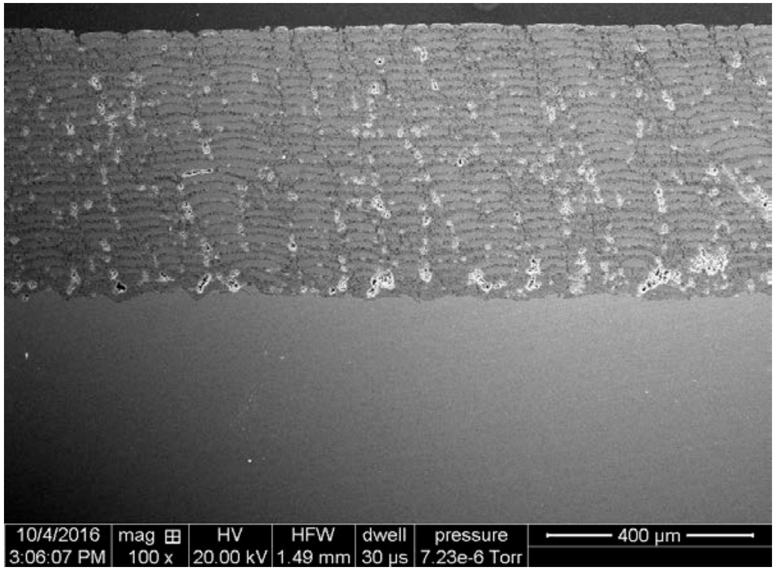


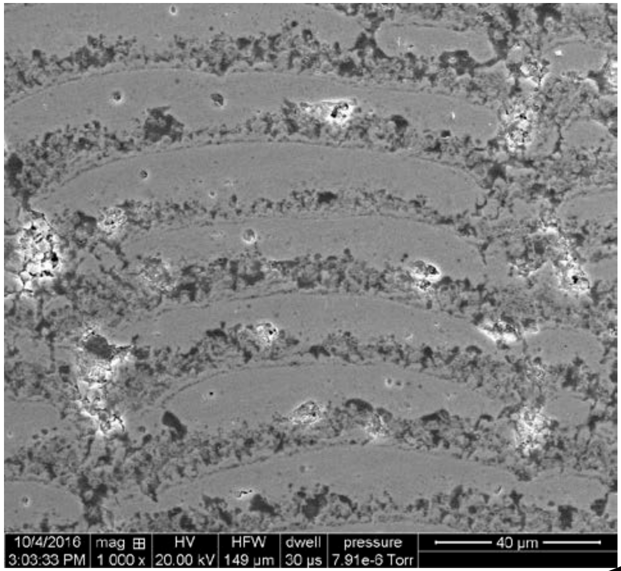
Porosity ~23%
HV= 324±60



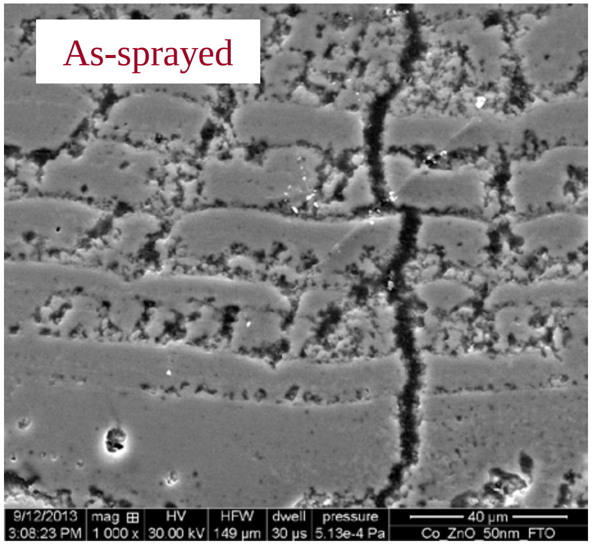



Thermal Conductivity Reduced by 1/3 SPPS YAG
with Heavy IPBs
Thermal Conductivity (W/m.K)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
200
400
600
800
1000
1200
1400
Temerature (°C)

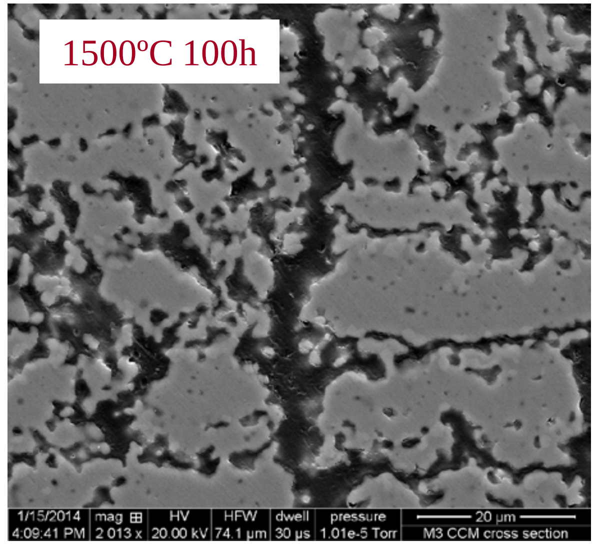

10/4/2016 3:06:07 PM
mag 100 x
HV 20.00 kV
HFW 1.49 mm
dwell 30 μs
pressure 7.23e-6 Torr
400 μm


10/4/2016 3:03:33 PM
mag 1 000 x
HV 20.00 kV
HFW 149 μm
dwell 30 μs
pressure 7.91e-6 Torr
40 μm

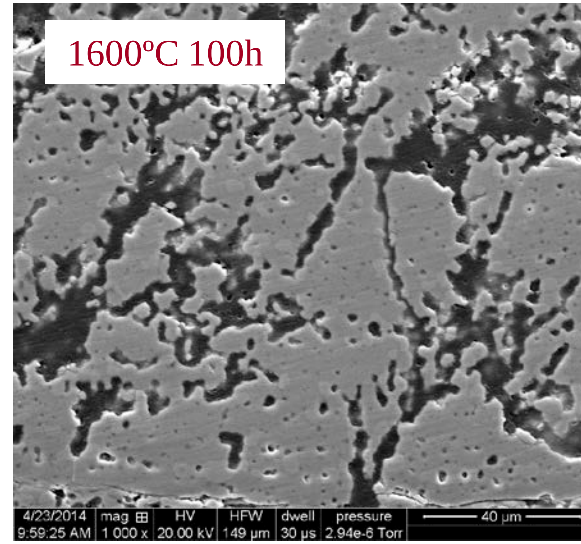
SPPS YAG TBCs: Sintering Resistance



HV = 380±185



HV = 324±122



HV = 378±139

Sintering Effects Are Small Up to 1600°C

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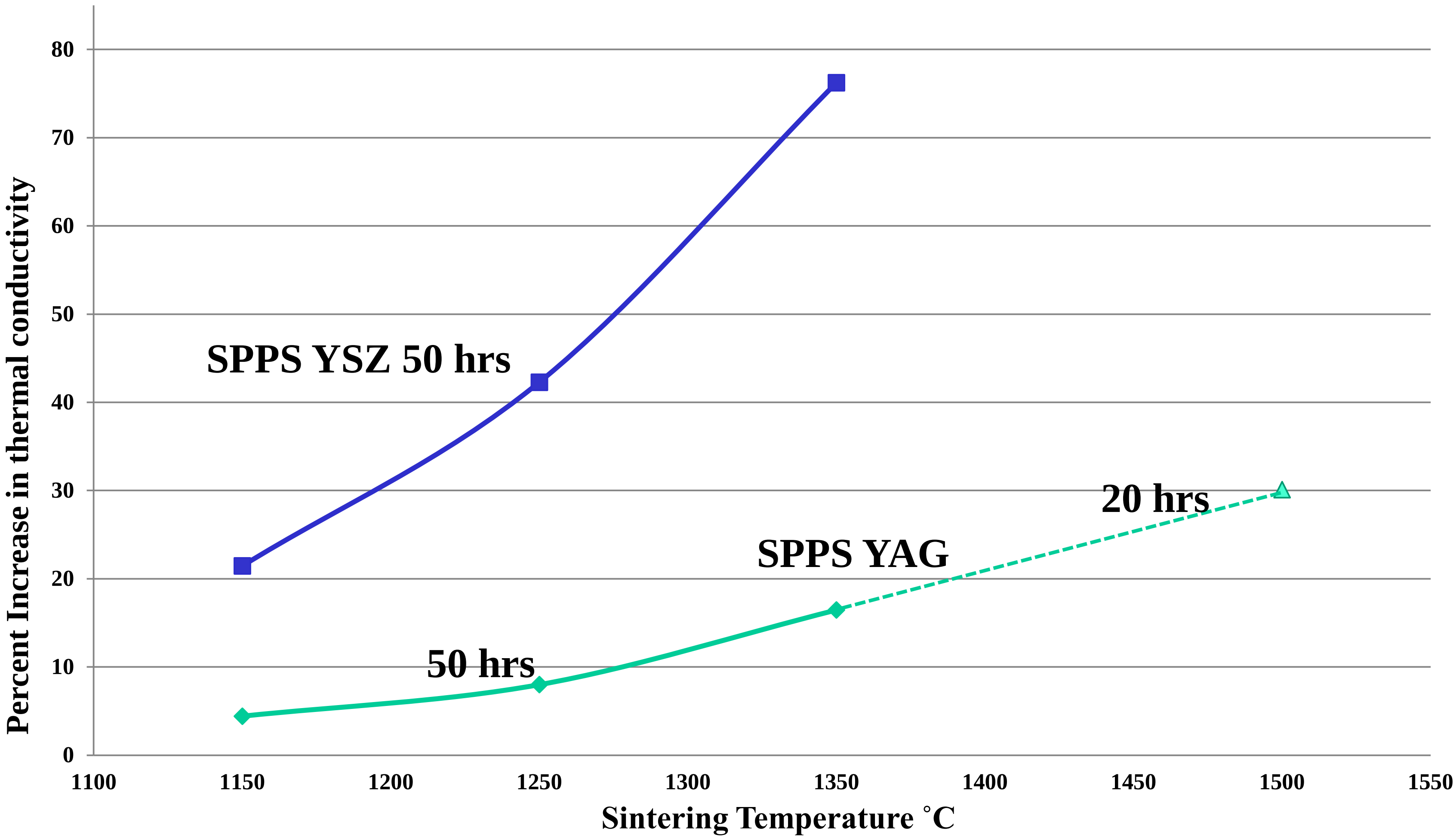
SPPS TBCs: Sintering & Thermal Conductivity



- **SPPS YAG TBCs More Sinter Resistant Than SPPS and APS YSZ**

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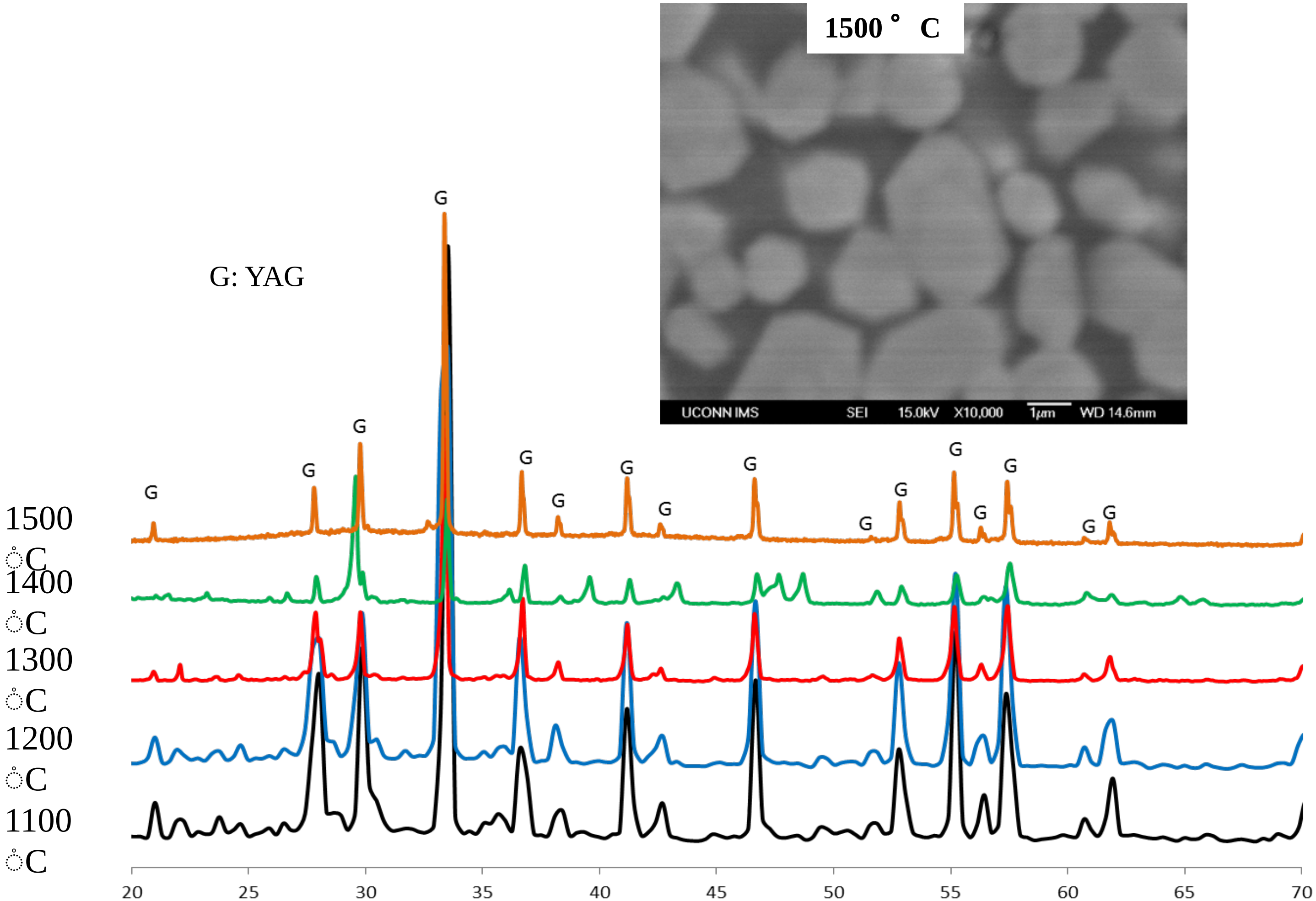
Innovations - Ideas - Solutions

Phase Stability: 50:50 w/o YAG/CMAS Powder



- **YAG Phase Stable To 1500ºC In Presence of CMAS**

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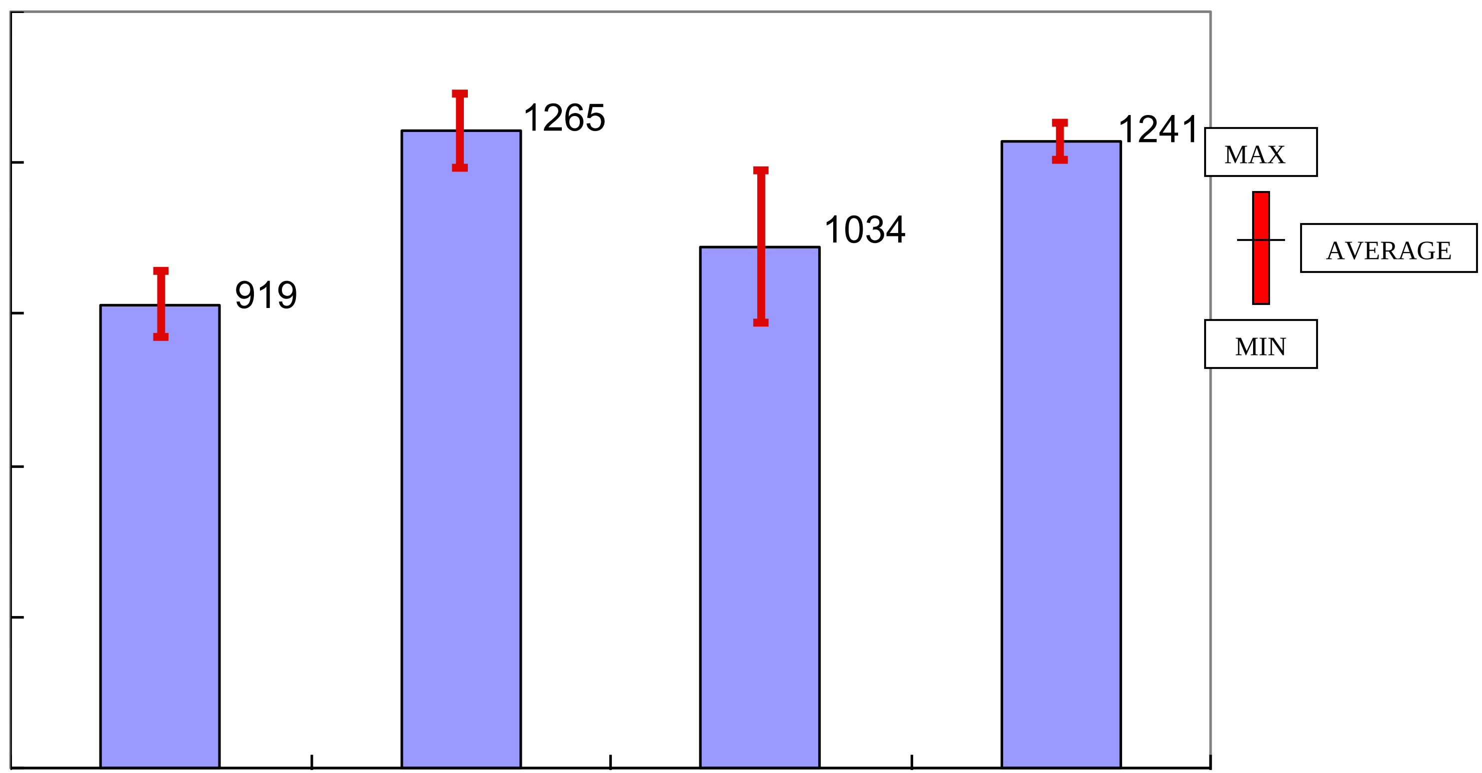
SPPS YAG TBCs: Thermal Cycle Life vs Hardness



- **SPPS Strain-Tolerant Microstructure Overcomes Higher Thermal Expansion Mismatch Stresses**

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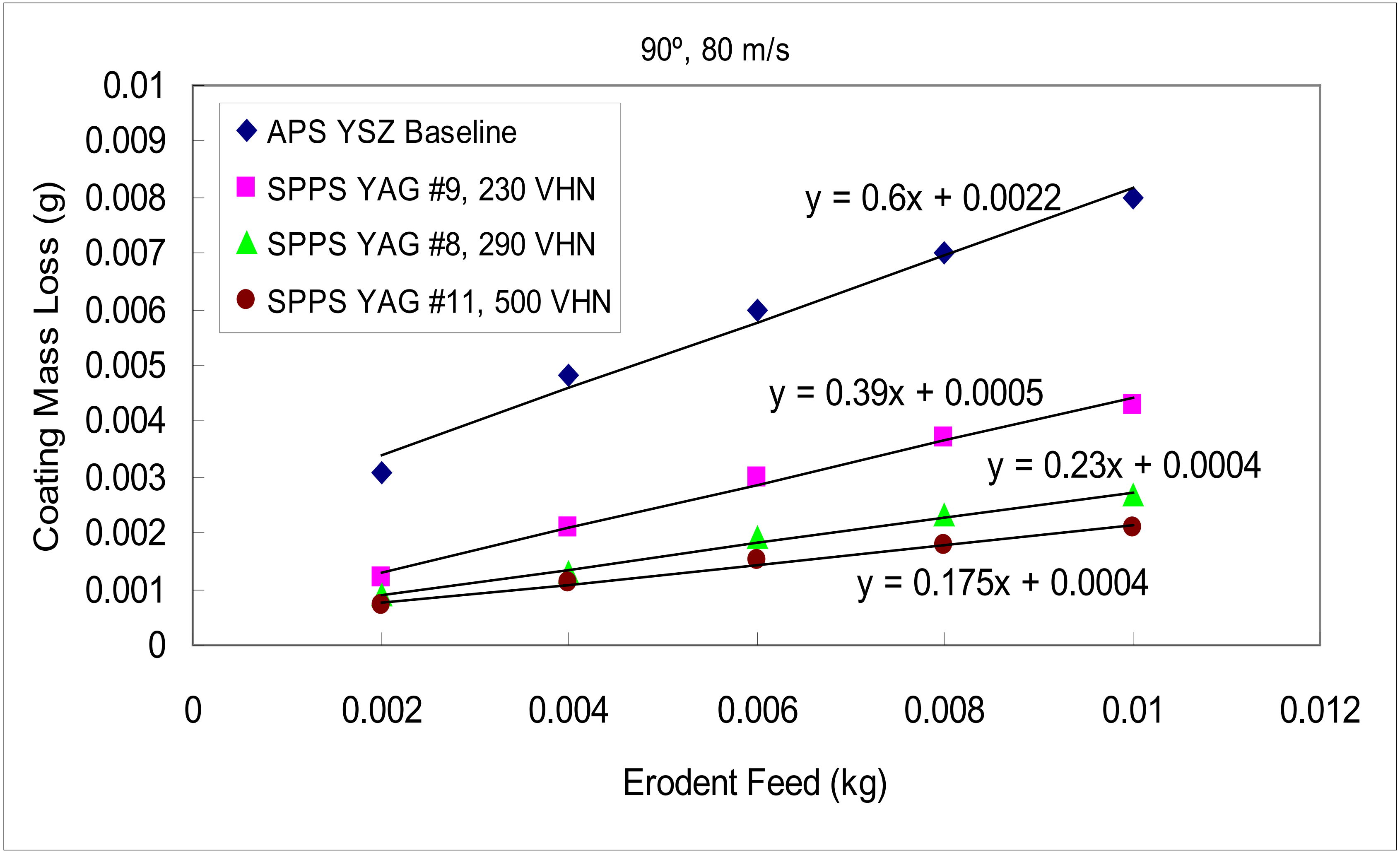
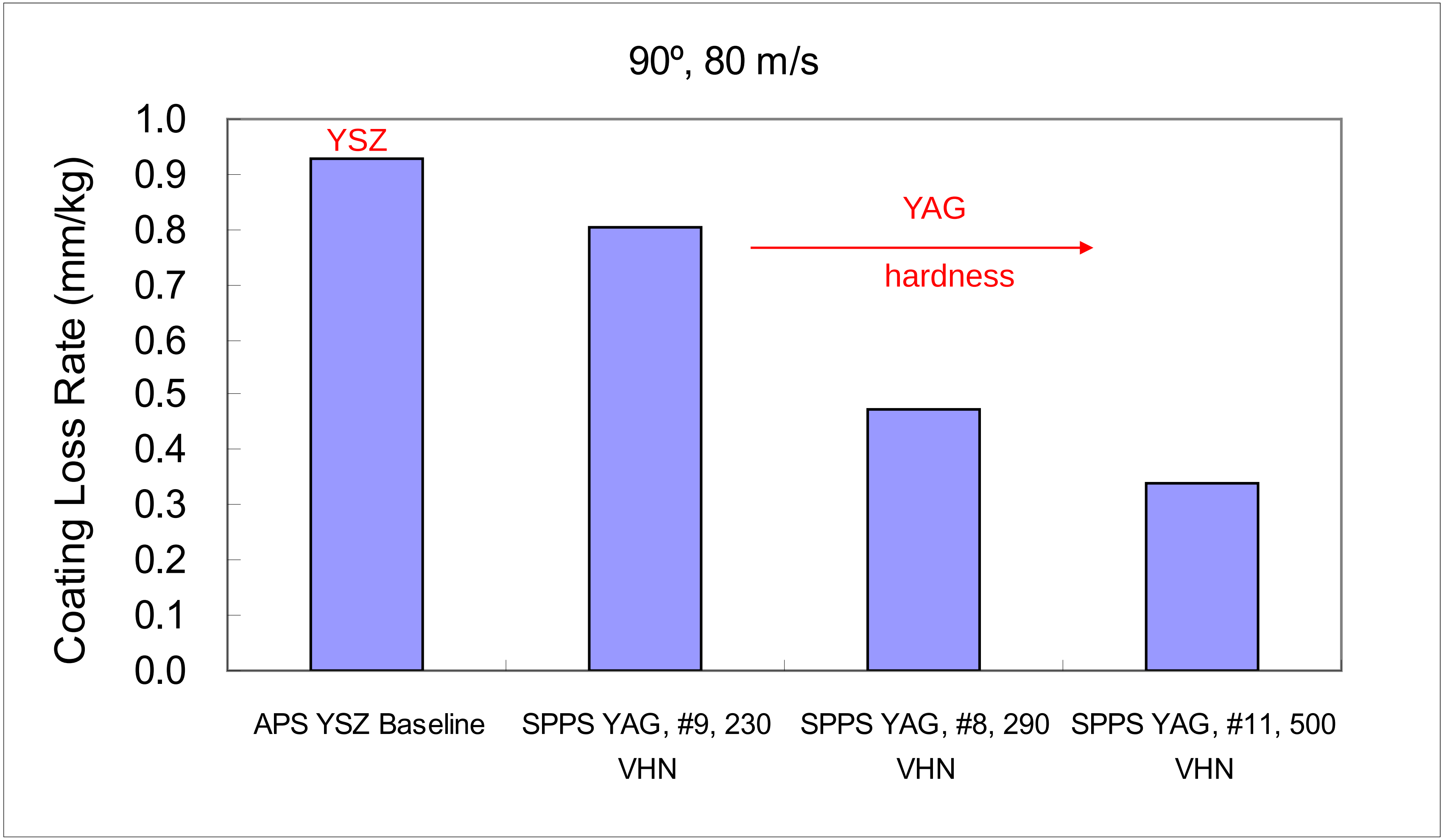
SPPS YAG TBCs: Erosion Rate vs Hardness

(Tests Performed at Penn State Univ. By Dr. D Wolfe)



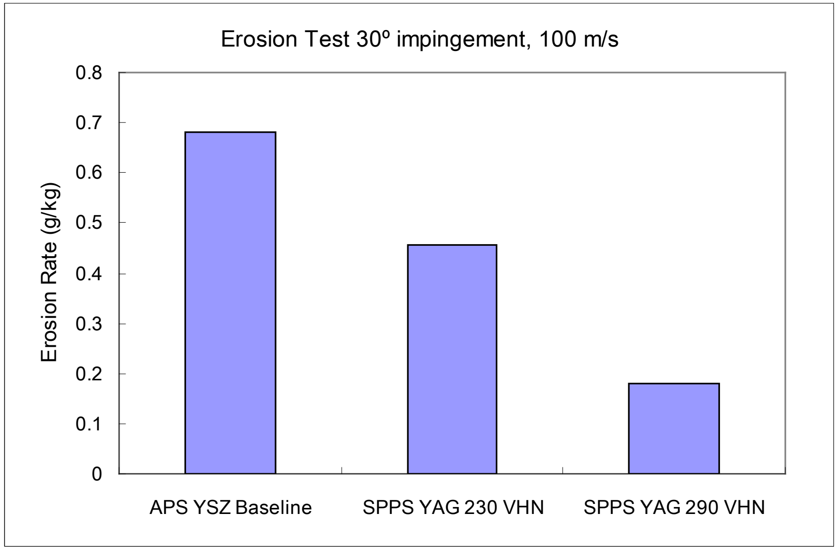
SPPS YAG TBCs: Erosion Rate vs Hardness

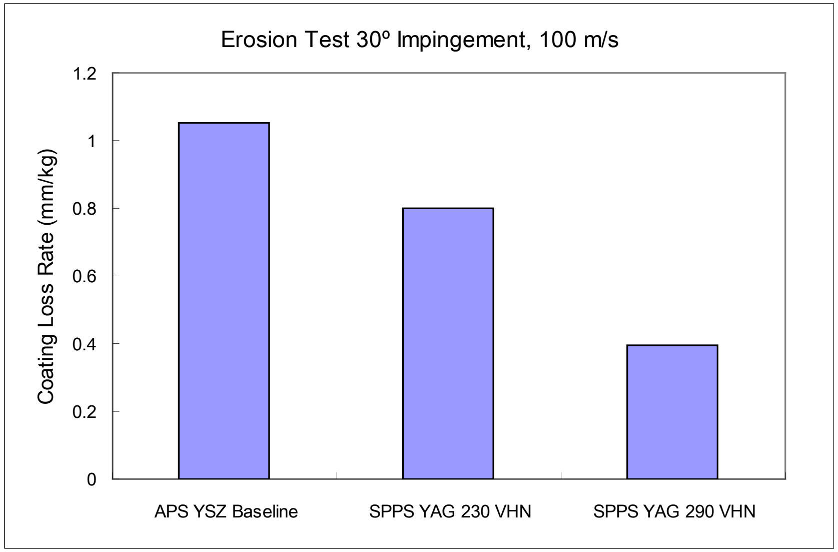
(Tests Performed at Penn State Univ. By Dr. D Wolfe)



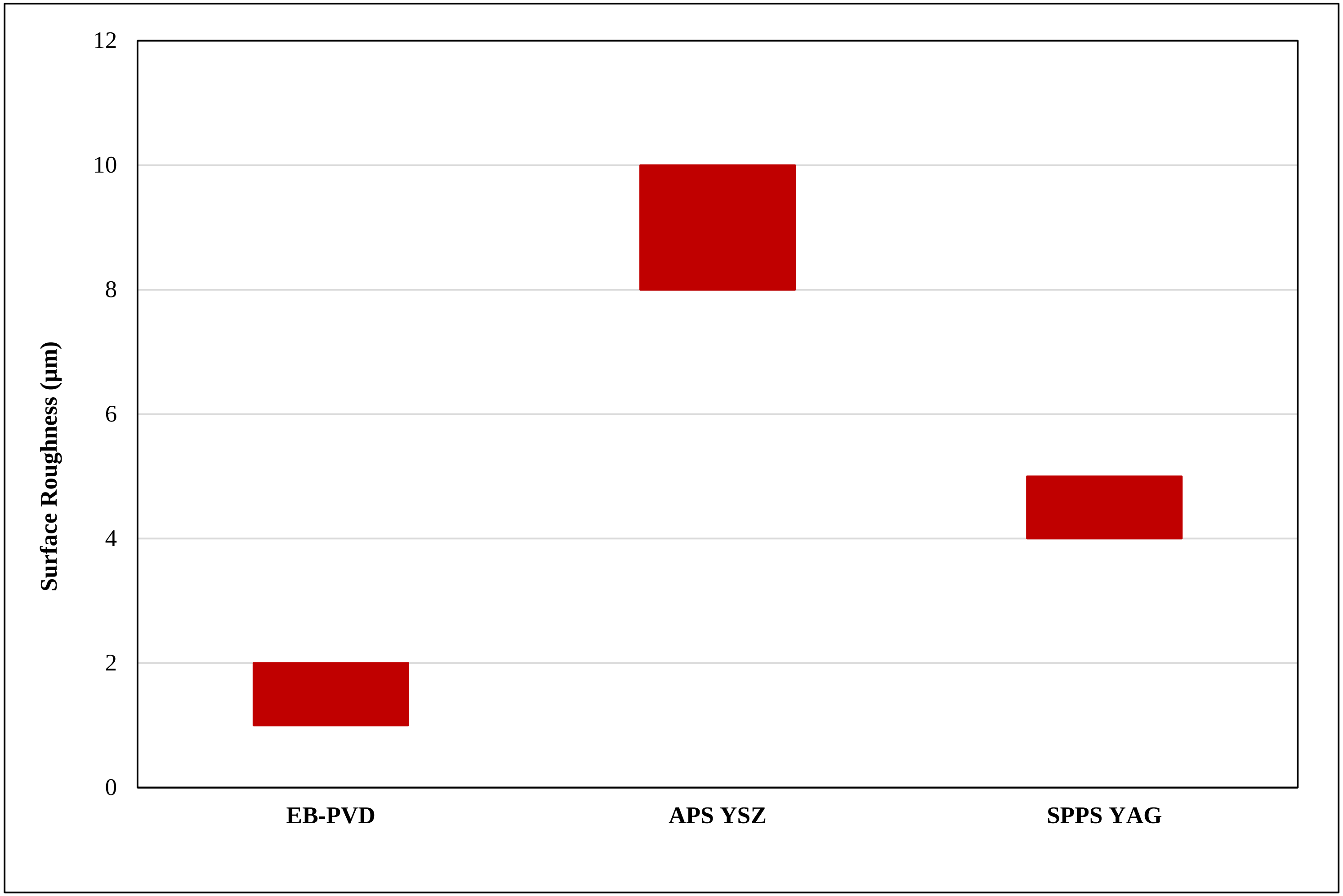
SPPS YAG TBCs: Erosion Rate vs Hardness -30º Impingement-

(Tests Performed at Penn State Univ. By Dr. D Wolfe)





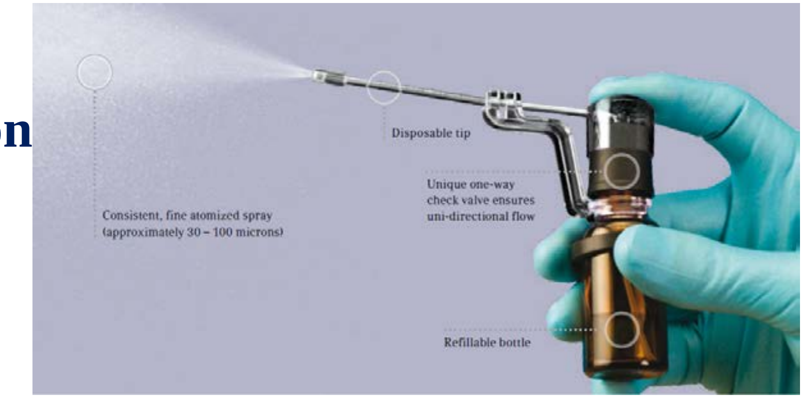
- **SPPS YAG Has Superior Erosion Resistance To APS YSZ In Both 30º 90º Impingement Erosion Tests.**



Surface Roughness (µm)
0
2
4
6
8
10
12
EB-PVD
APS YSZ
SPPS YAG

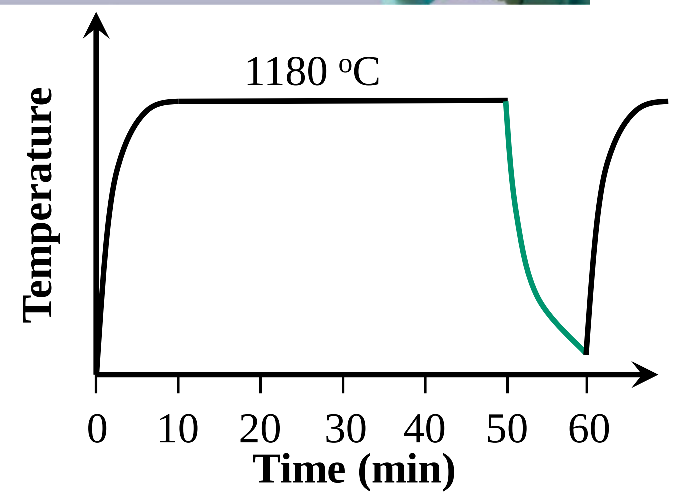
Spritz/Atomizer Test Conditions

- **1 wt% CMAS Aqueous Solution**
- **0.1 mL/spray**



- **4-CMAS (M.P. ~1200 ^oC)**

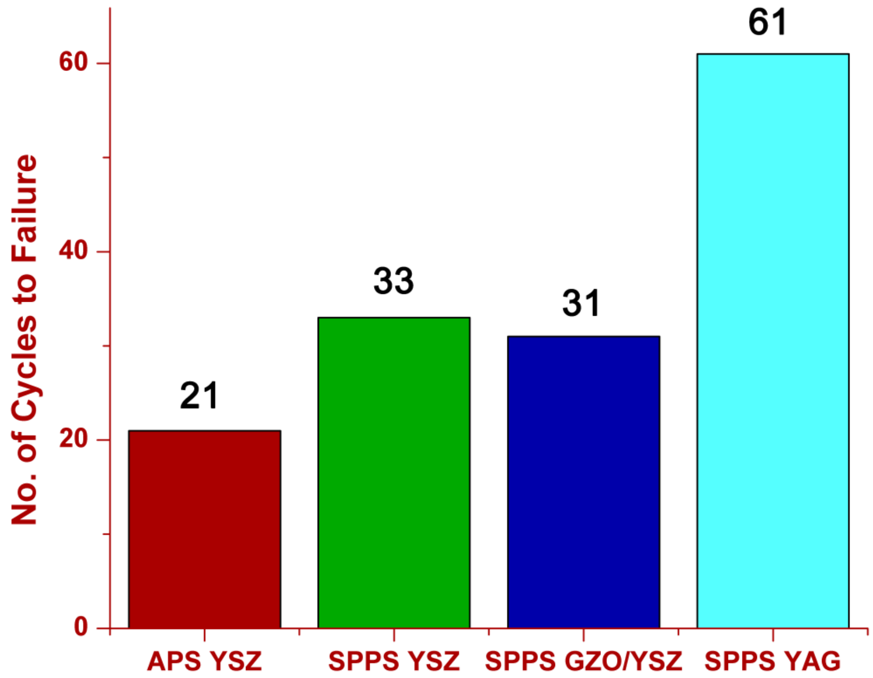
Oxide	SiO_2	CaO	Al_2O_3	MgO
Wt.%	52.3	37.1	7.1	3.5
Mol.%	51.5	39.2	4.1	5.2



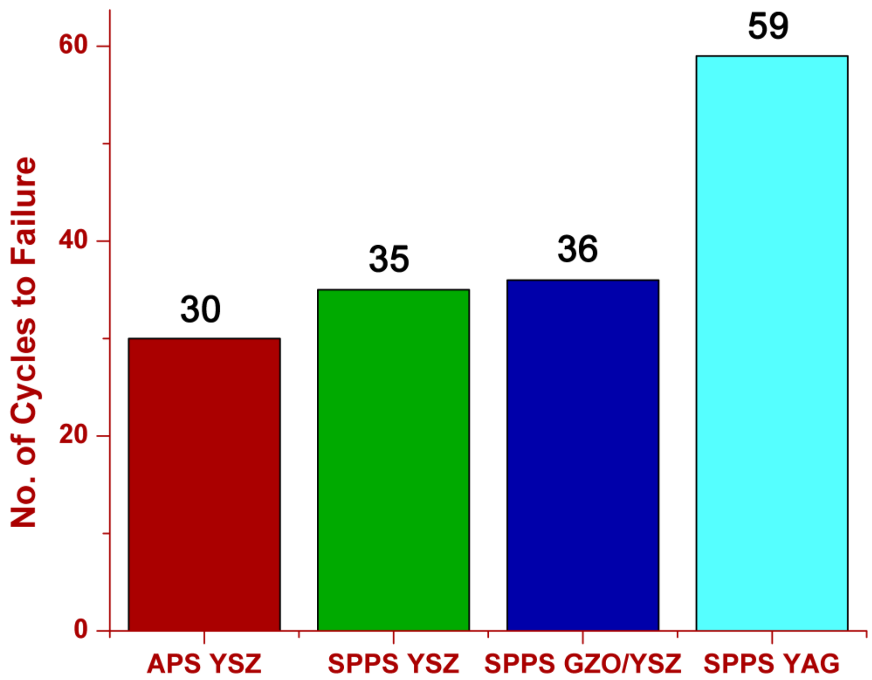
- **9-CMAS (M.P. ~1180 ^oC)**

Oxide	$CaSO_4$	SiO_2	CaO	Al_2O_3	MgO	Fe_2O_3	K_2O	TiO_2	Na_2O
Wt.%	42.00	31.57	1.54	16.50	2.66	1.54	1.54	1.33	1.32
Mol.%	26.75	45.56	2.38	14.03	5.72	0.84	1.42	1.44	1.8

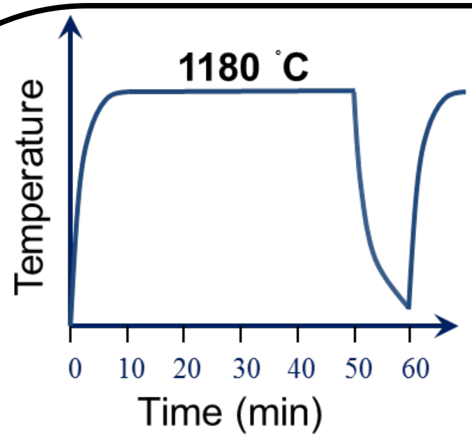
Spritz Test: Cyclic Lives



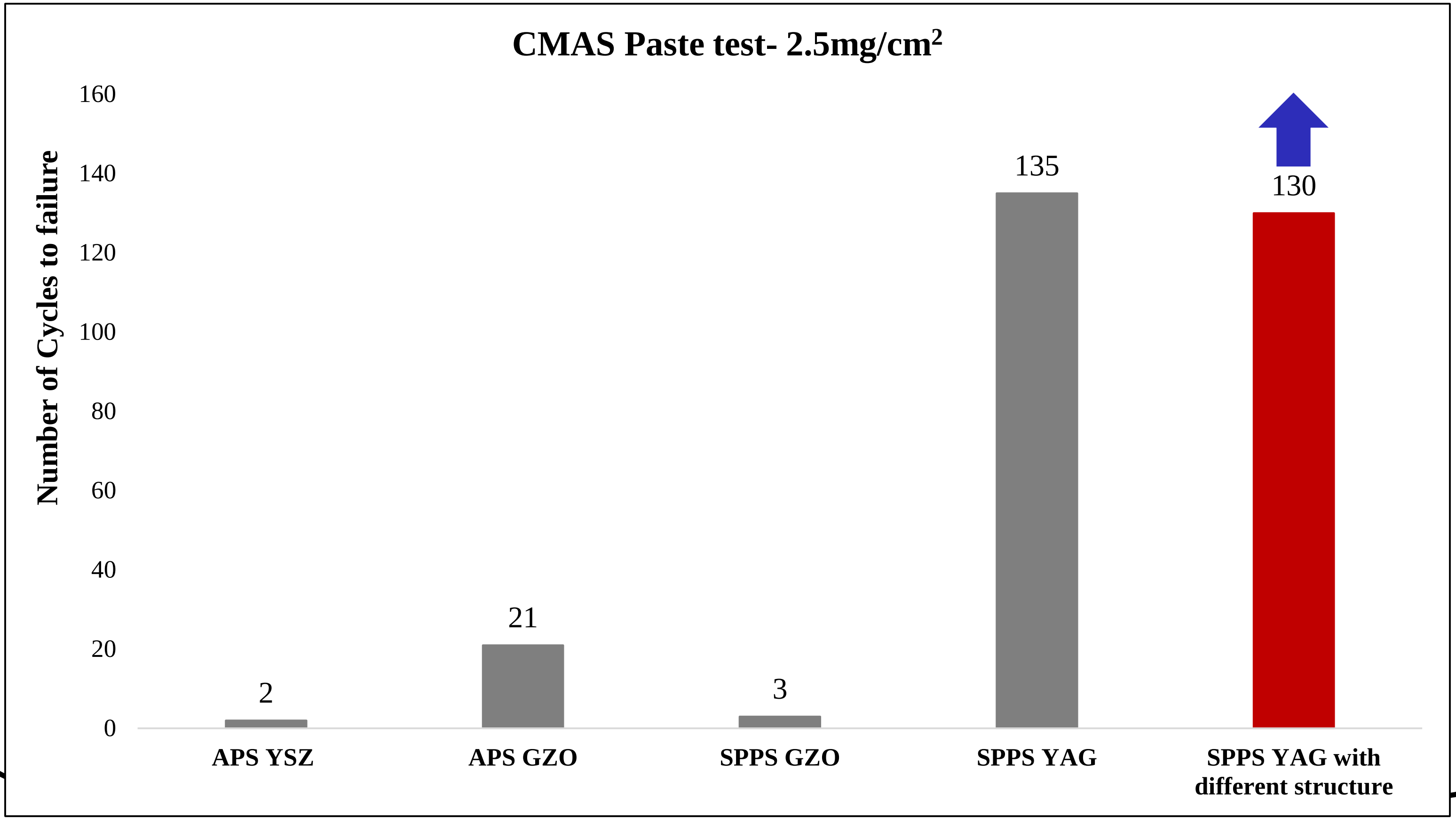
4 Component CMAS

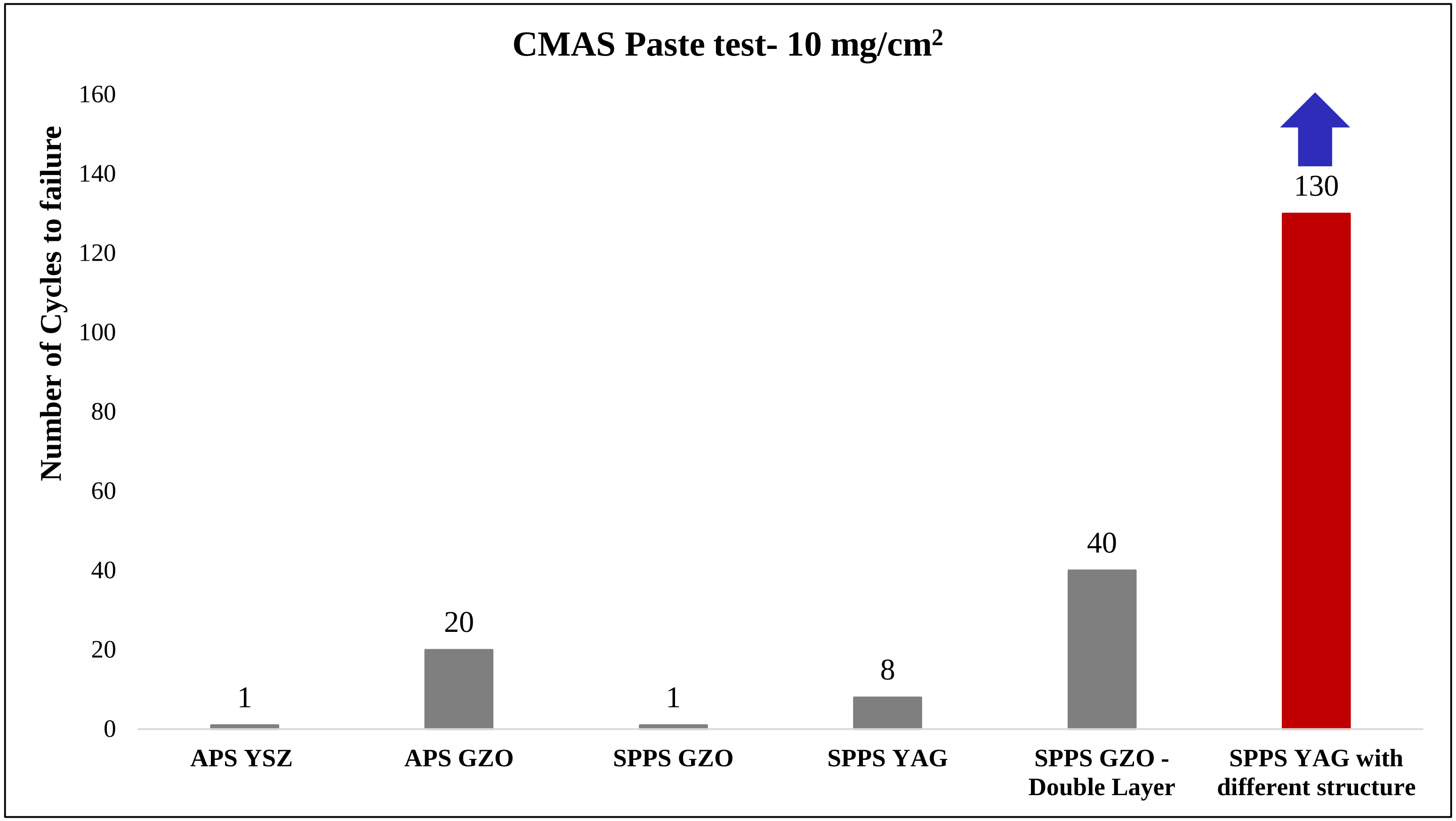


9 Component CMAS



Thermal Cycling Temperature Profile





CMAS Paste test- 10 mg/cm²
Number of Cycles to failure
0
20
40
60
80
100
120
140
160
1
20
1
8
40
130
APS YSZ
APS GZO
SPPS GZO
SPPS YAG
SPPS GZO - Double Layer
SPPS YAG with different structure

SPPS YAG TBCs: Critical Engine Properties

<u>200^{o}C Temperature Advantage</u>

- **Phase Stability**
- **Sinter Resistance**
- **CMAS Resistance**

<u>Improved Durability</u>

- **Thermal Cycle Resistance**
- **Erosion Resistance**

<u>Other Significant Properties</u>

- **Lower Thermal Conductivity**
- **Reduced Density**
- **Surface Smoothness**

Cost Reduction- Utility Improvements

Phase IIA Industry Partners

- **Solar Turbines**
- **Siemens Energy**
- **Pratt & Whitney**
- **Praxair**
- **Progressive Surface**
- **Chromalloy**
- **General Electric Power**
- **Rolls-Royce**
- **Oerlikon-Metco**

Industrial Partners Activities

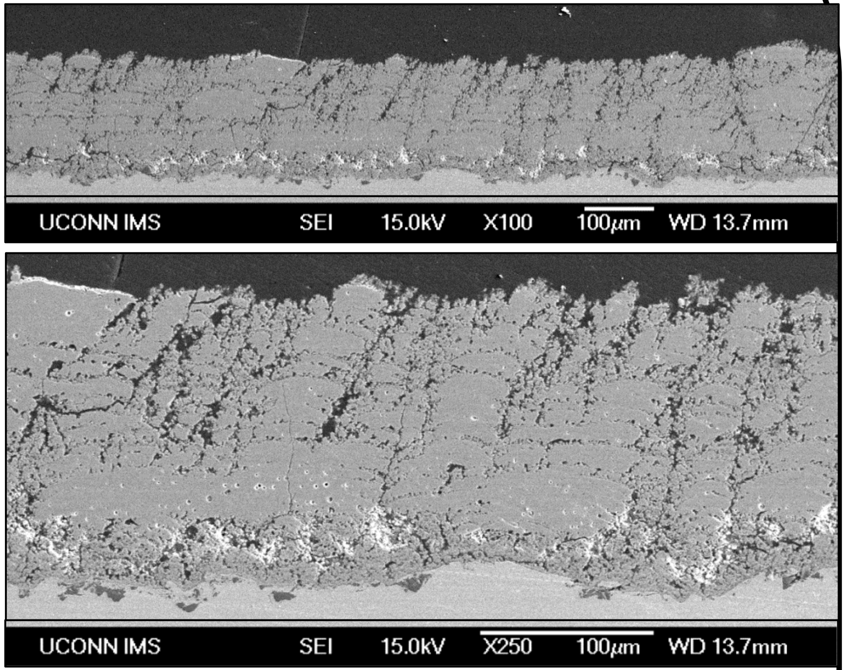
- **Olikon Metco spray trials done**
- **Praxair spray trials done**
- **Solar Engine Parts sprayed and tested**
- **Progressive Spray trials done**
- **Outside of Phase IIa we are involved in Tech Transfer**

Goals Related to Industrialization Benefits Cost Ratio

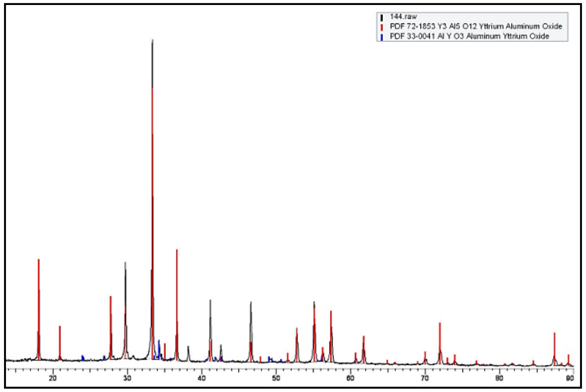
- Lower Thermal Conductivity(less thickness)
- Higher Deposition Efficiency
- **Higher Deposition Rate
- Larger Stand off Distance

Conductivity reduction via rare earth Doping

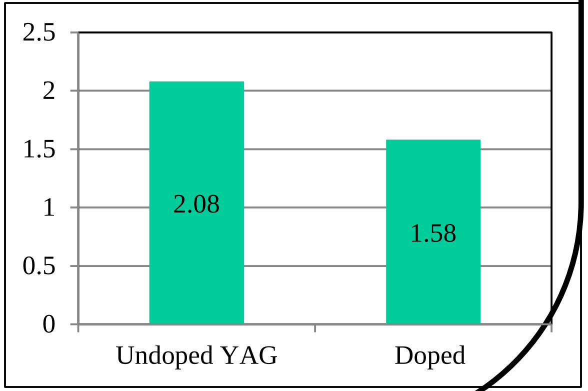
- SPPS YAG coatings were produced with 1 atm.% doping of a Rare Earth
- ~24% reduction in thermal conductivity was achieved at RT



SEM images of SPPS YAG coatings with 1 atm.% doping

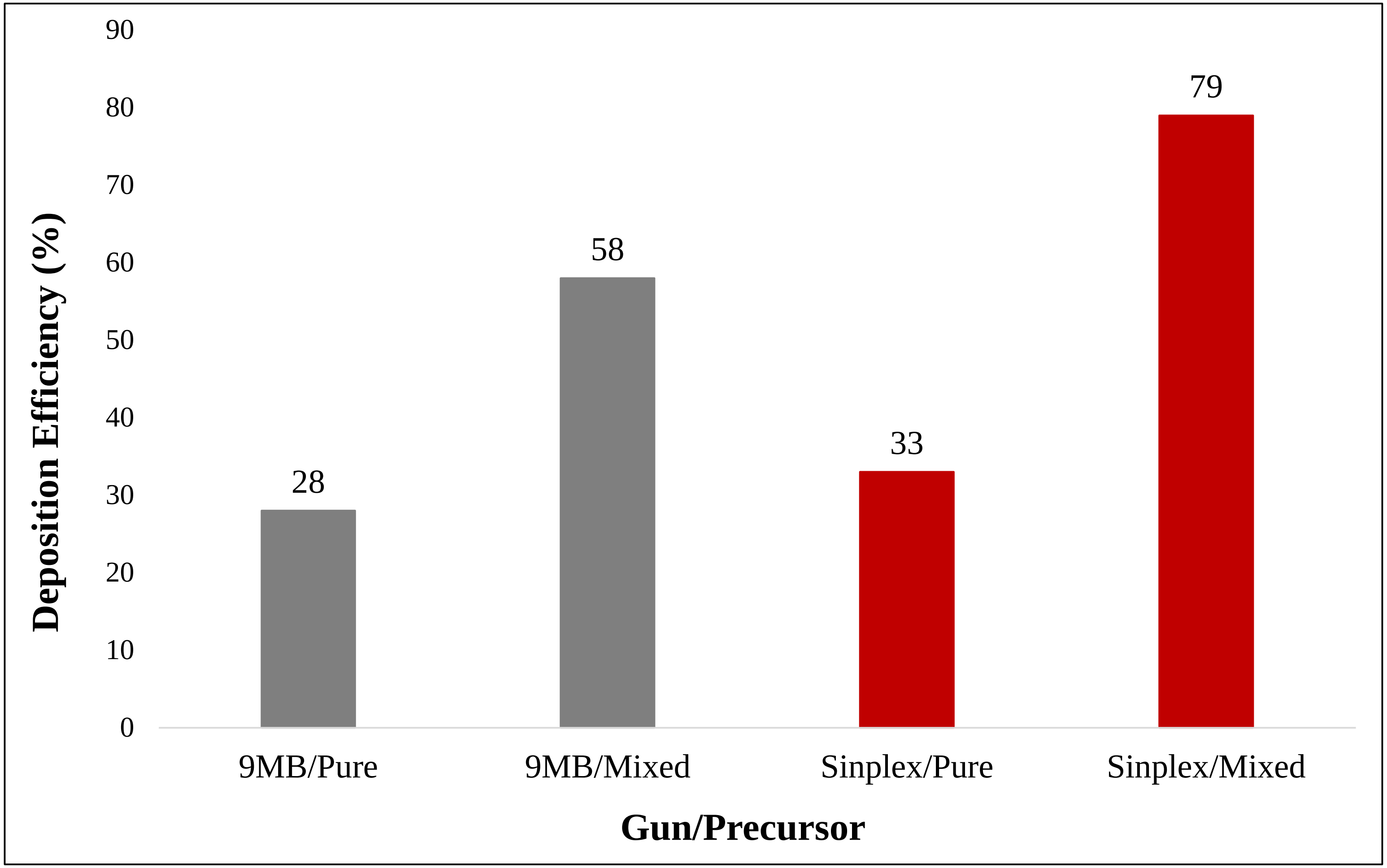


XRD showing phase stability

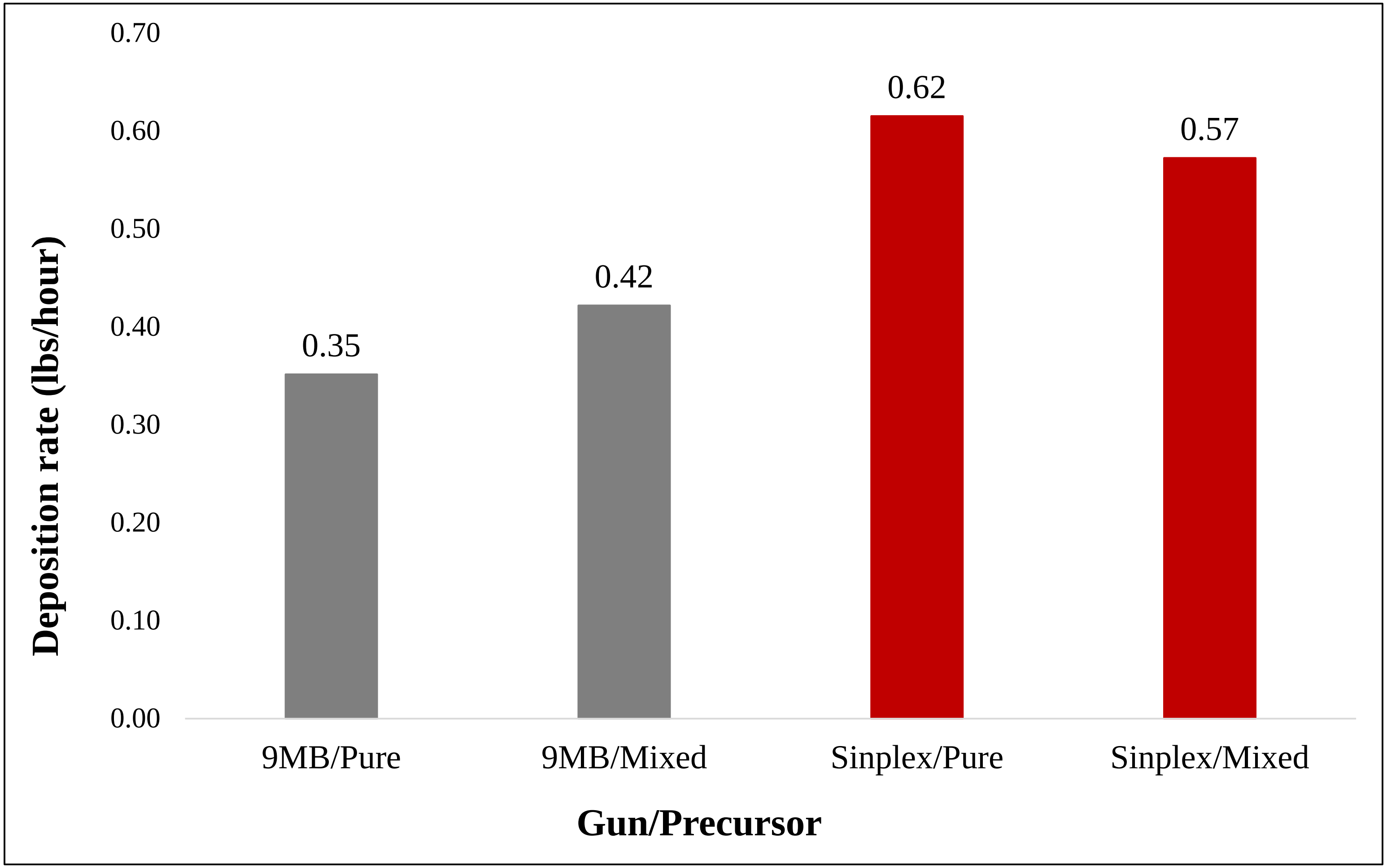


Comparison of Thermal conductivity

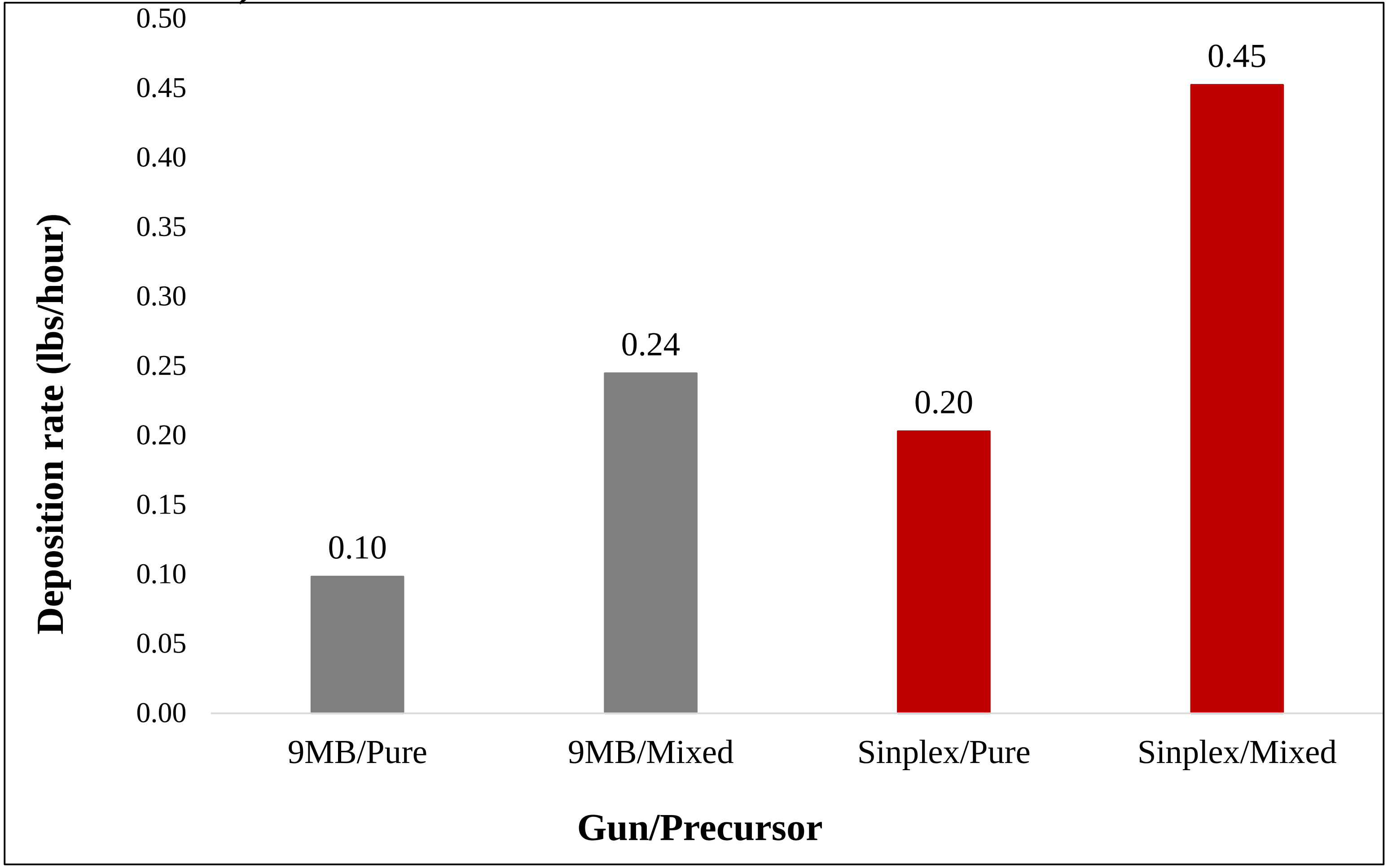
Modified Precursor + Sinplex Gun Nearly 30 % Deposition Efficiency Improvement



Sinplex Gun with Modified Precursor Increases Deposition Rate 30%



Deposition Rate Deposited (Feedrate * g/ml * 60 / 454 * DE/100) Doubled

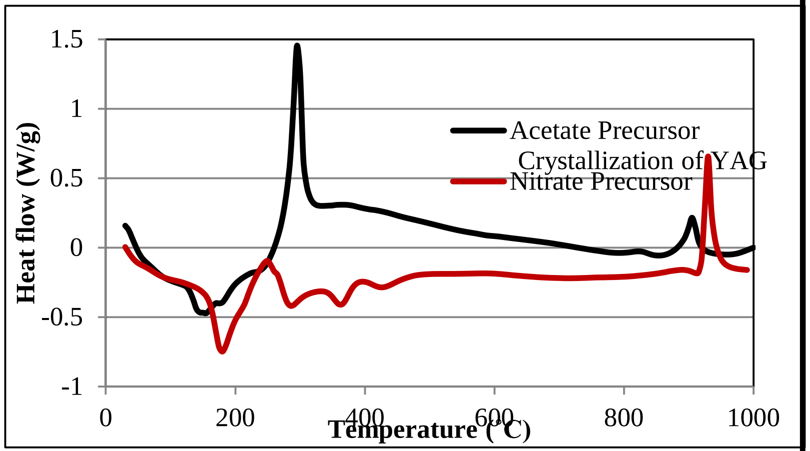


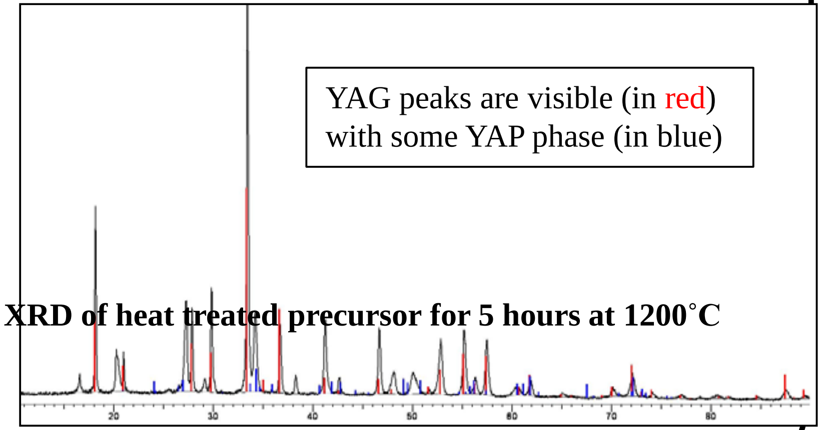
Have done 0.67 but working on microstucure

Improved Using Acetate Vs. Nitrate Precursor

- Substantial increase in DE and DR leads to a 45% reduction in production cost of SPPS YAG coatings with Acetate precursor
- Lower Viscosity helps in more uniform flow, less clogging and buildup at the nozzle
- Stronger exothermic peaks during decomposition aids in melting of YAG particles in plasma

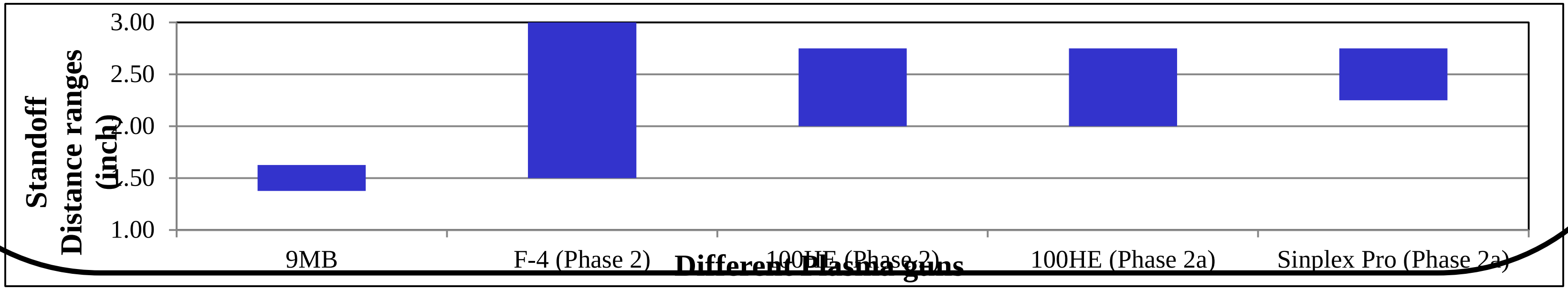
DSC



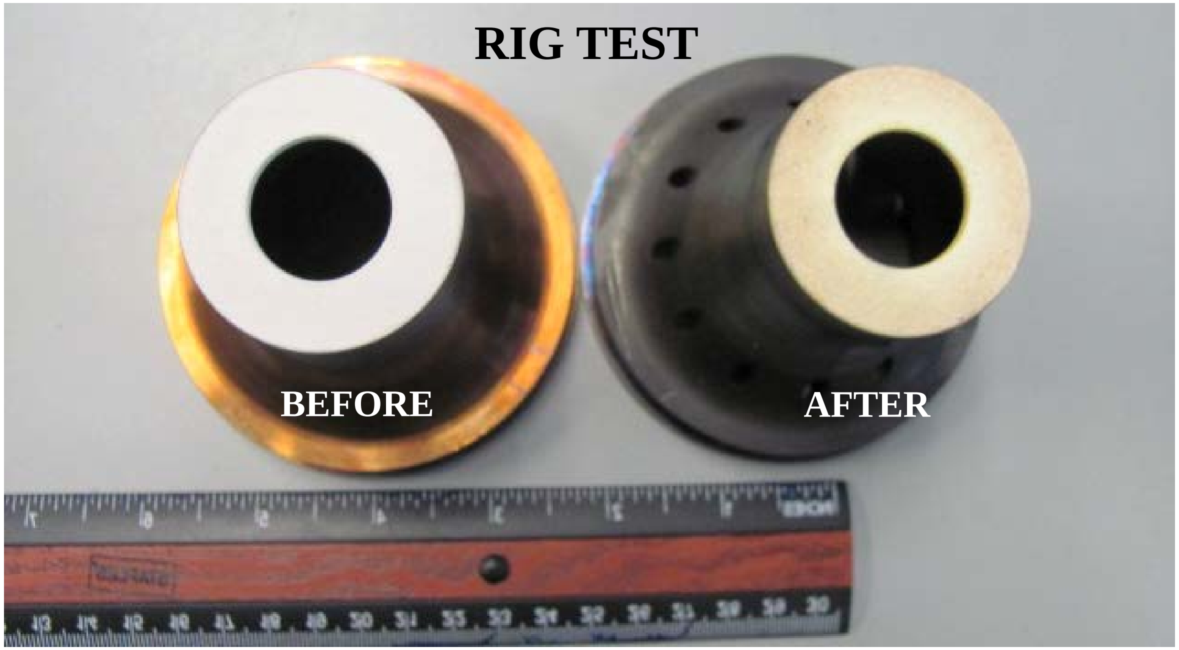


Standoff Distances

Industrial Partner Visits	STTR Phase	Plasma Gun Used	Standoff Distance (inch)	Results/ Comments	Future work
Praxair 11/2014	2	F-4	1.5-3.0	Poor- Fair initial results	F-4, 100HE, Plazjet, HE1100
Progressive 02/2015	2	100HE	2.0-2.75	Fair initial results	100HE itself
Progressive 05/2015	2a	100HE	2.0-2.75	Good, Columnar structure, Vickers Hardness-400	Spray B/C, APS YSZ and SPPS YAG for Thermal Cycling
Metco 09/2015	2a	Sinplex Pro	2.25-2.75	Initial testing with YSZ, Good results	Spray YAG
Praxair 11/2015	2a	F-4	2.0-3.25	Will explore parameters of F-4 gun to deliver acceptable microstructure and hardness	HE1100



Solar Turbines: SPPS YAG Tests



- Solar In-House Thermal Cycle Tests (2100ºF/10 hr) Confirm Thermal Cycle Durability

- 1st Rig Test to 3000ºF In 10 Cycles Showed No Distress

- 2nd Rig Test Showed Temperature Drop For 10 mils of SPPS YAG Comparable to 20 mils of APS YSZ

SOLUTION SPRAY TECHNOLOGIES

Summary & Conclusions-I

- **SPPS YAG TBCs Show Potential For >1500°C Operation Based On Phase Stability, and Sinter Resistance**
- **This Represents >200°C Advantage Over APS YSZ**
- **Durability of SPPS YAG TBCs $\geq$ APS YSZ In Thermal Cycle and Erosion Tests**
- **Thermal Conductivity of of SPPS YAG TBCs with IPBs is 0.7 Watt/m°K at at room temperature extrapolates to 0.58 at 1300 C Measured by Netzsch.**

Summary & Conclusions-II

- Deposition Efficiency increased from 43% up to 70% using a different Precursor and Sinplex Gun.
- *Deposition Rate to part doubled cutting cost in half.
- Standoff distance improved from 1.6 inches to 3 inches Further Improvement sought.
- **More than an order of magnitude improvement in CMAS cyclic life a high doses. Out performs Gadolinium Zirconate so far.
- Has been applied to Engine parts with excellent durability and thermal performance .
- Separate arrangements for Tech Transfer to a fortune [illegible] company.

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Summary & Conclusions-II

- **Engine Manufacturers Show Strong Interest In SPPS YAG TBCs; Are Conducting In-House Testing**
- **Technology Transfer Being Conducted With TBC Coating Suppliers; They Will Conduct Demonstration Trials and Provide Process Economics**
- **SPPS YAG Continues to Show Strong Promise As Higher Temperature (200ºC), Sinter-Resistant, CMAS-Resistant, Low K, Low ρ, Durable TBC**
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SPPS TBC Commercialization

- Solution Spray Technologies (SST) LLC Formed To Further Develop & Commercialize SPPS TBCs
- SST Has Exclusive License to University of Connecticut SPPS TBC Patents
- SST Is Working With Engine OEMs to Qualify SPPS TBCs
- SST is Working With TBC Producers To Optimize & Commercialize SPPS Process

Acknowledgements

- **Dr. Briggs White, DOE Program Manager, UTSR Program on SPPS YSZ with IPBs**

- **Dr. Patcharin Burke, DOE Program Manager, STTR Phase I, II & IIA Programs on SPPS YAG TBCs**

- **Our Industrial Partners for Phase II SPPS YAG TBCs: Solar Turbines, Siemens Energy, Pratt & Whitney, Praxair and Progressive Surface**

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Questions ?