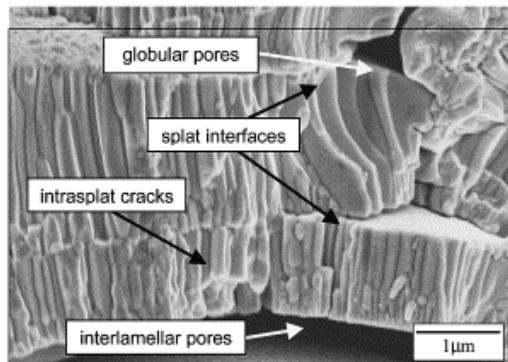
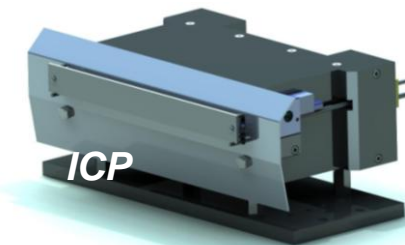
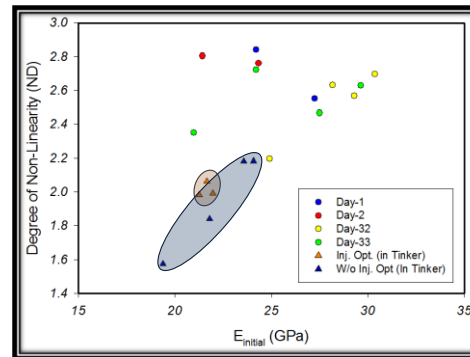
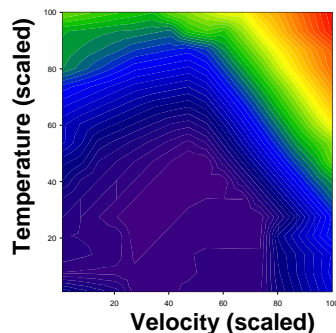


Advanced Thermal Barrier Coatings for Operation in High Hydrogen Content Gas Turbines



Thermal Conductivity



Christopher Weyant, Sanjay Sampath
 Center for Thermal Spray Research, Stony Brook University
 University Turbine Systems Research Workshop
 October 20, 2010

Research supported by:

DOE NETL UTSR

**DOE Office of Fossil Research STTR
 with Plasma Technology Inc.**

AFRL, NSF

Consortium on Thermal Spray Technology

Contributions from faculty colleagues, post-docs, students, national and international collaborators is acknowledged.



Consortium for Thermal Spray Technology

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

Thermal Barrier Coatings in Hydrogen-Fired IGCC Turbines

CHALLENGE: Improved reliability and lifetime of coatings in IGCC gas turbines

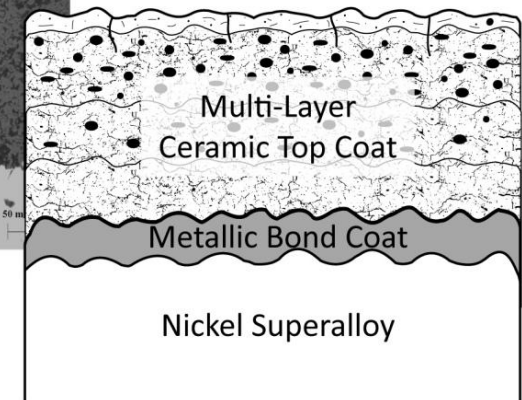
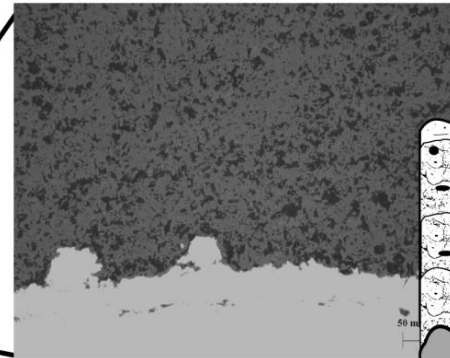
- Increased mass flow of syngas fuel
- Increased heat transfer from water vapor
- Impact of water vapor on oxidation
- Contaminants

APPROACH: Tailored and optimized plasma-sprayed thermal/environmental barrier coating

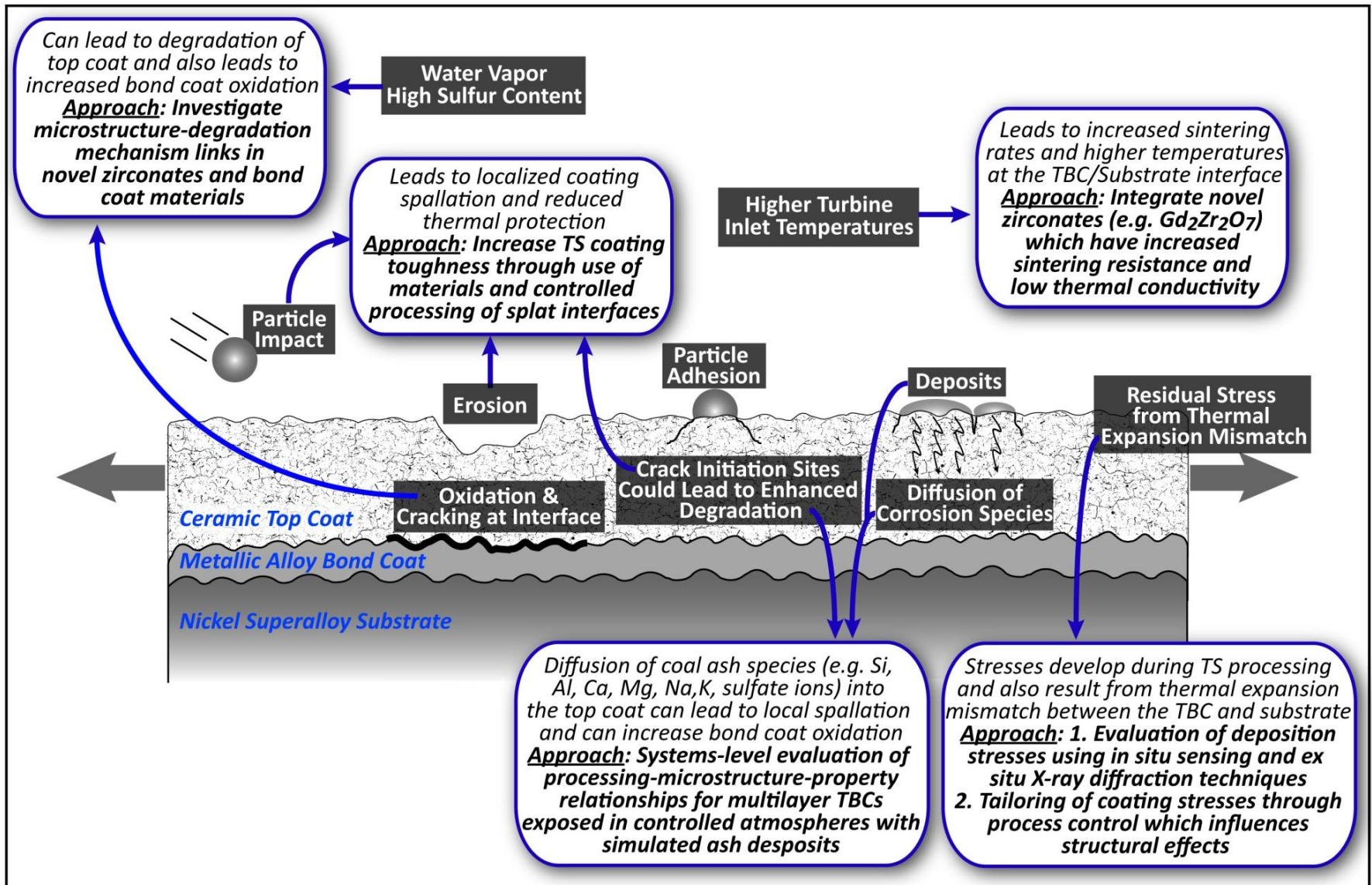
- Material requirements and selection
- Processing impacts on microstructure and properties
- Iterative coating design and testing
- Industry feedback and knowledge transfer



Courtesy of GE



Degradation in IGCC Gas Turbine TBCs



Proposed IGCC Coating Architecture

Development/ Evaluation Plan

Erosion Resistant Top Coat

- Produce dense YSZ and $Gd_2Zr_2O_7$ top coat layers
- Evaluate erosion resistance of dense materials
- Develop density-graded structure for top coat

Thermal Barrier Layers

- Determine $Gd_2Zr_2O_7$ properties (thermal/mechanical) under thermal gradients
- Assess IGCC environmental effects on degradation of zirconates

Bond Coat

- Evaluate processing (HVOF/LPPS + anneal) effects on microstructure and phase composition of MCrAlY (where M = Ni, Co, Si, Hf, and/or La)
- Determine IGCC environmental effects on long-term oxidation of bond coat materials

Performances Attributes

Erosion Resistance

Sinter Resistance
Low Thermal Conductivity

Transition Layer
Mitigates Zirconate/TGO Reactions

Oxidation Protection/Adhesion

Nickel Superalloy
(Rene 80 or CMSX4)

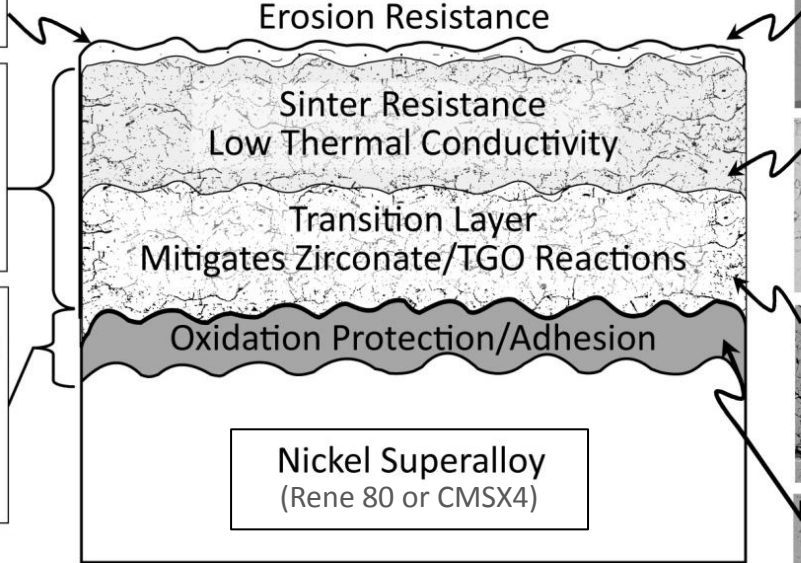
Layer Microstructures

APS Dense $Gd_2Zr_2O_7$

APS $Gd_2Zr_2O_7$

APS YSZ

HVOF/LPPS MCrAlY



Overall UTSR Program Approach

Advanced Thermal Spray TBCs for IGCC Turbine Systems

Bond Coat



Materials: MCrAlY
M = Ni, Co, Si, Hf, La

Processing Effects on
Microstructure
(HVOF/LPPS/Anneal)

Isothermal Exposures in
water vapor

Property Evaluation:
Oxidation behavior in high
temperature water vapor

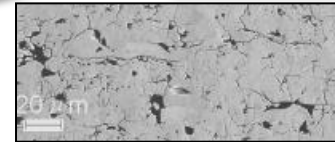
System Level

Rig Testing: Thermal
gradient exposure with
water vapor

Isothermal Exposures with
ash deposits

Property Evaluation: Bond
coat oxidation, through-
thickness residual stress
and composition, erosion

Top Coat



Materials:
YSZ, $Gd_2Zr_2O_7$

Processing Effects on
Microstructure
(APS)

Isothermal Exposures in
water vapor

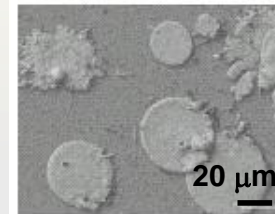
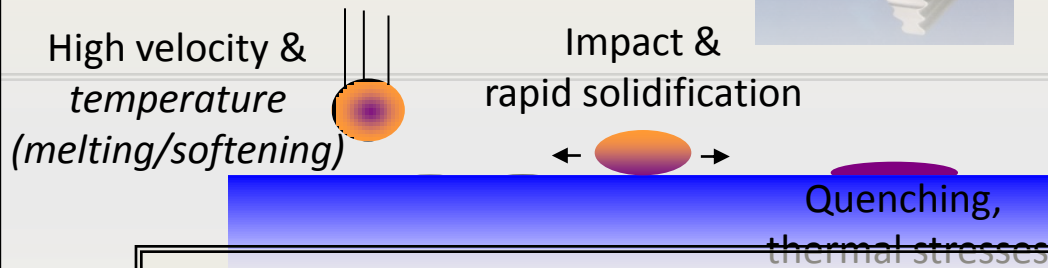
Property Evaluation:
Thermal conductivity,
sintering, compliance,
erosion, thermal
expansion

Thermal spray is a complex process

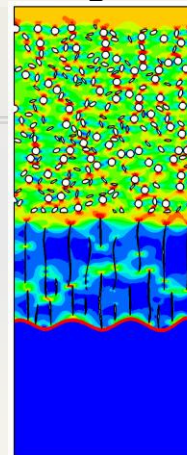
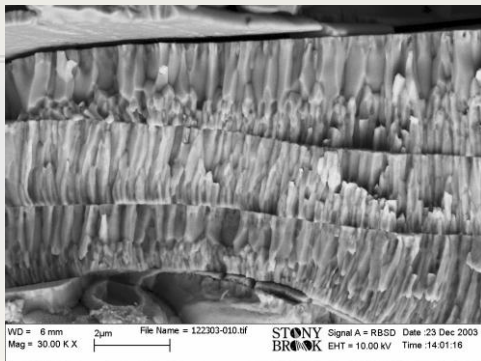
Melting, quenching and consolidation in single process



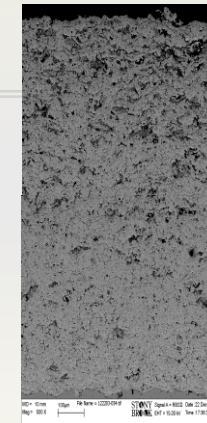
Splat based build-up and state induced properties



Layered and graded architectures through successive splat quenching

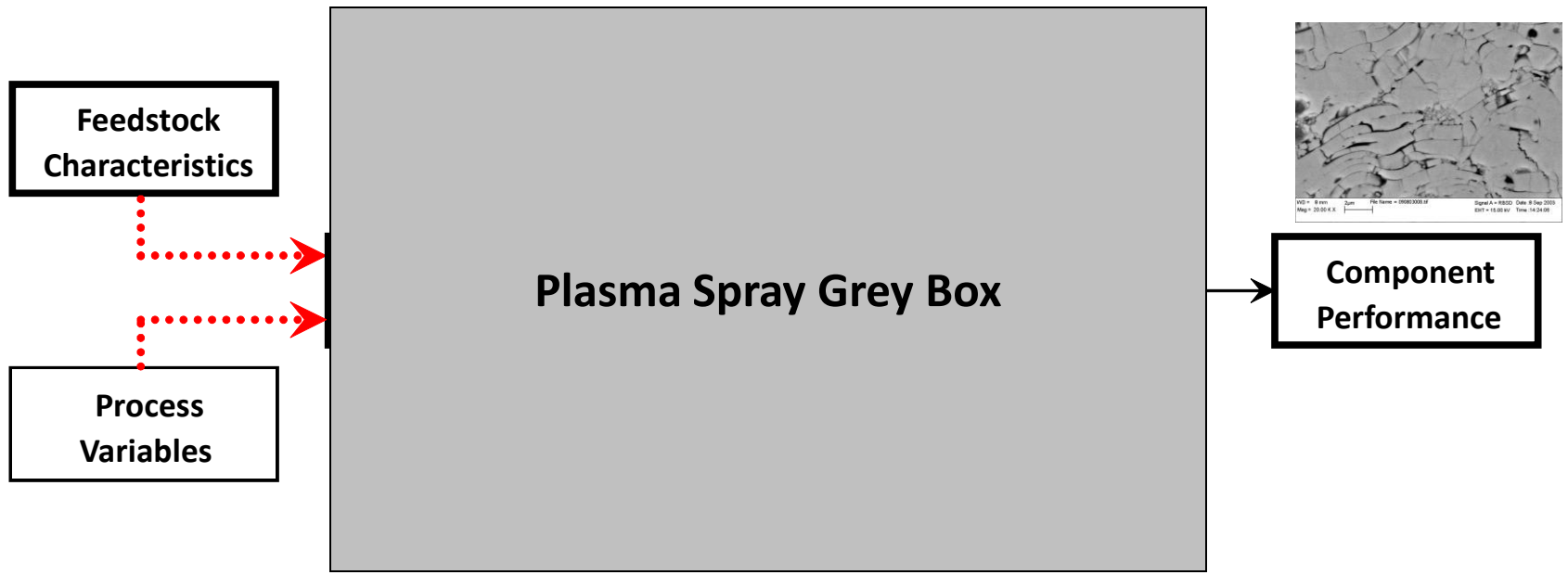


Layered Thick Films

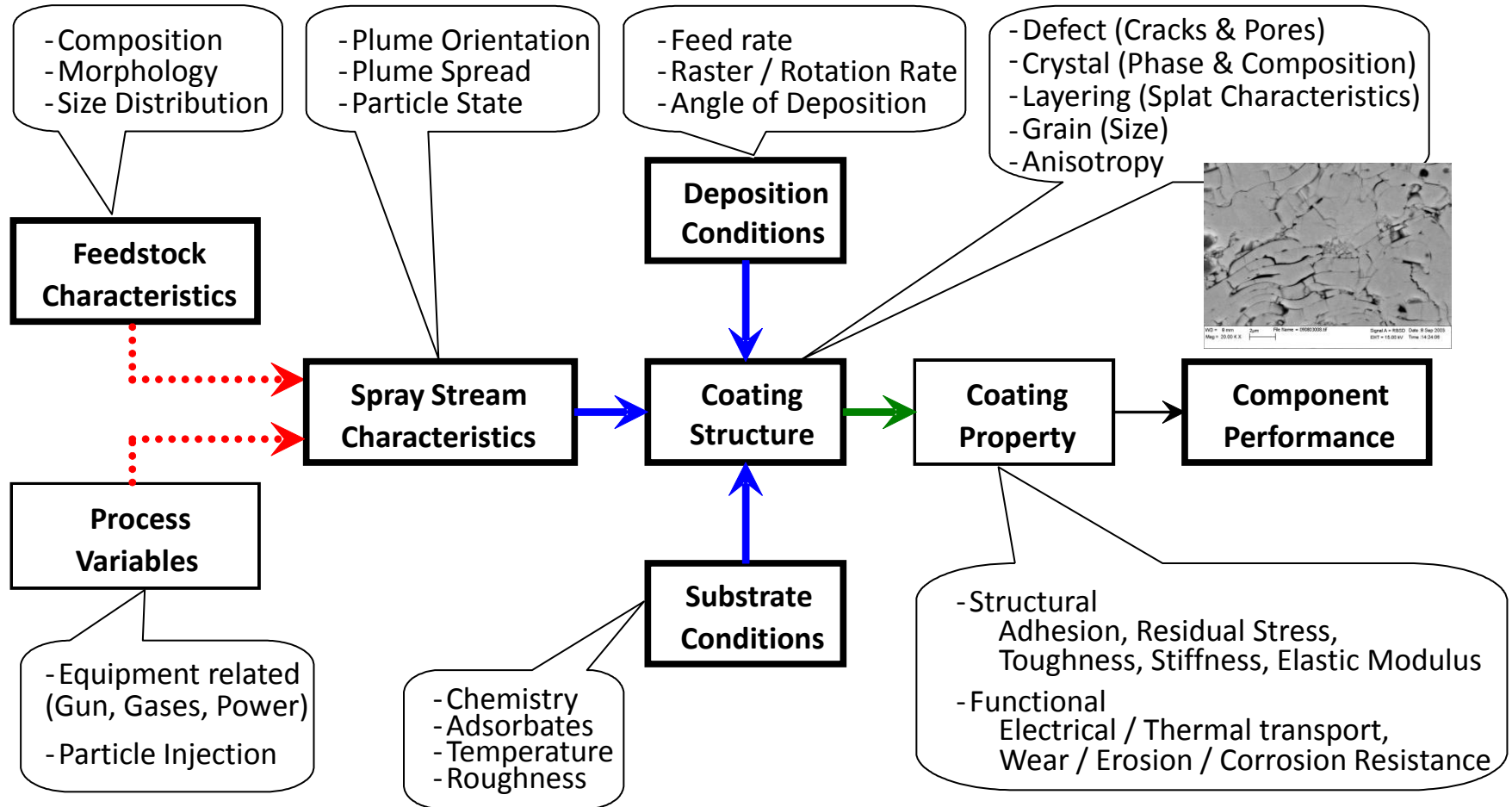


Graded Porosity In ceramics

Common Approach for TBC Manufacturing

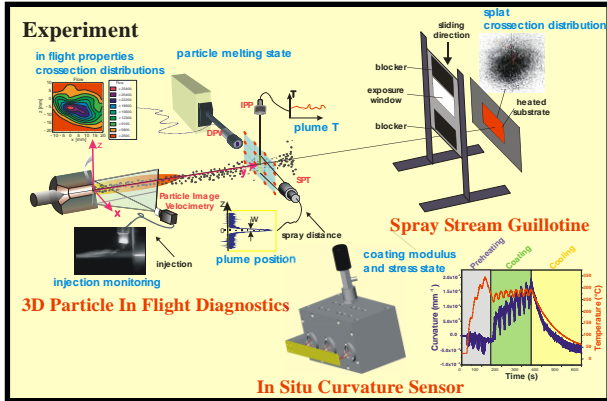


CTSR Approach for TBC Development

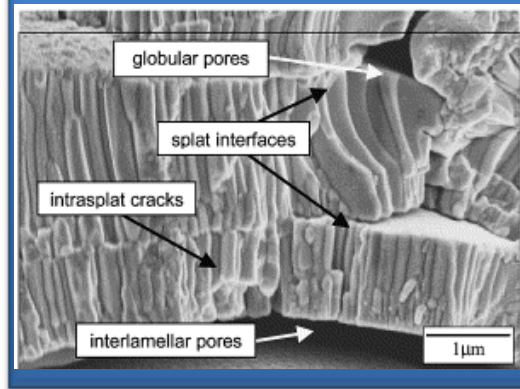


How can modern TS science enhance TBC requirements?

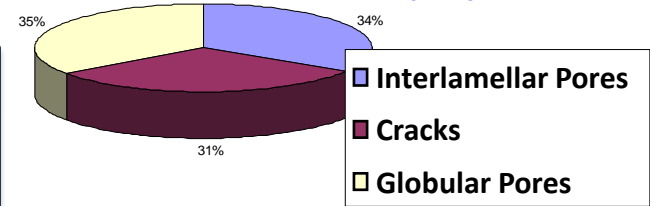
Integrated Process Diagnostics



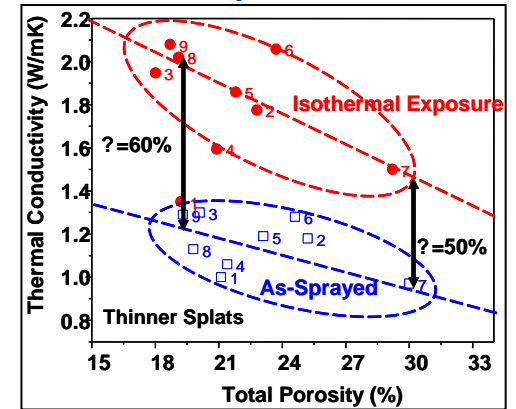
Properties dominated by defects, nanoscale grains, splats interfaces and interphases



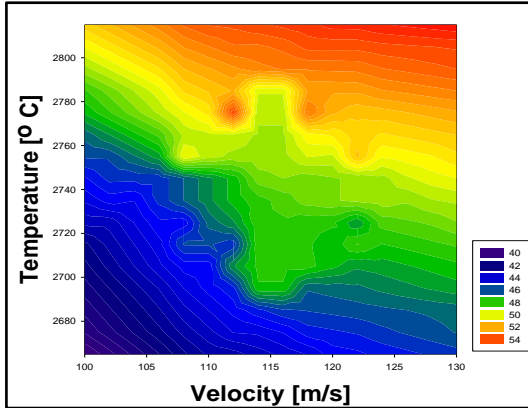
Neutron-based Assessment of Pore Distribution (3D)



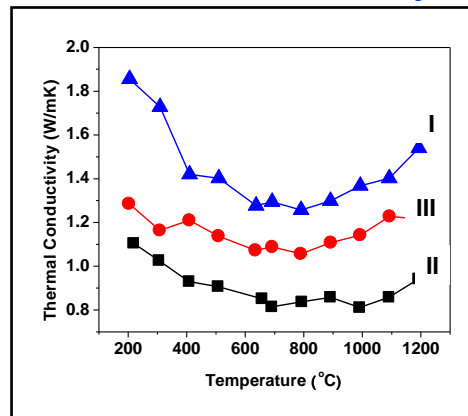
Thermal Aging Effects on Properties



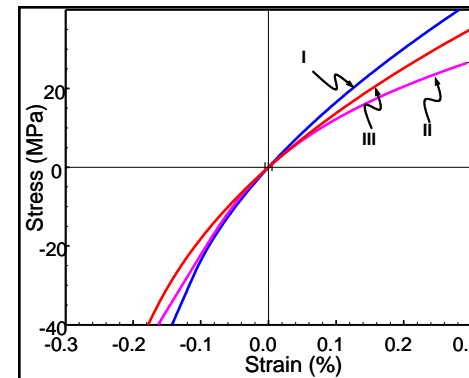
2nd Order Process Map Elastic Modulus Contours



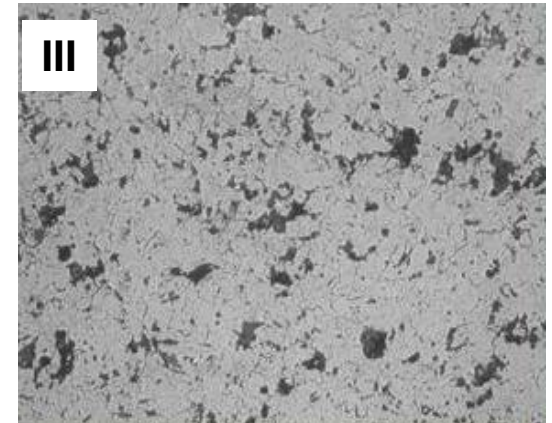
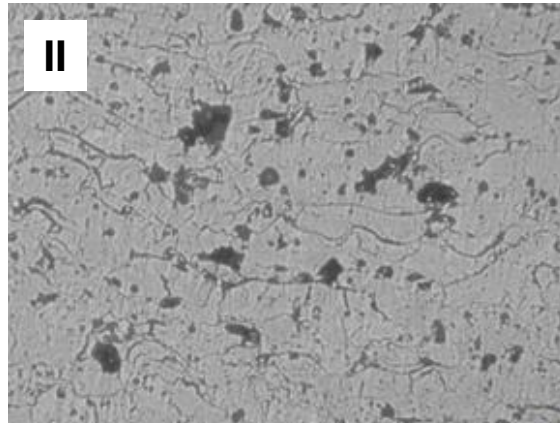
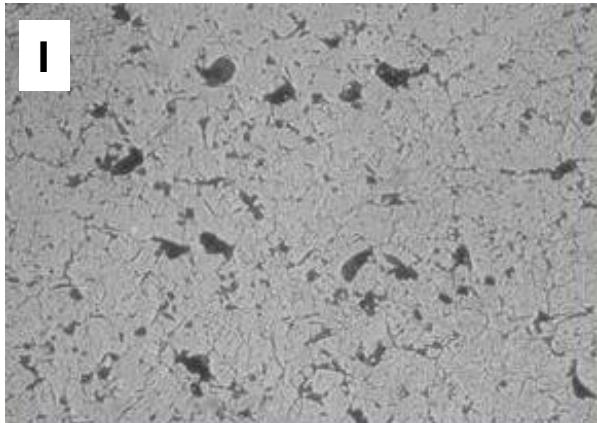
Temperature-Dependent Thermal Conductivity



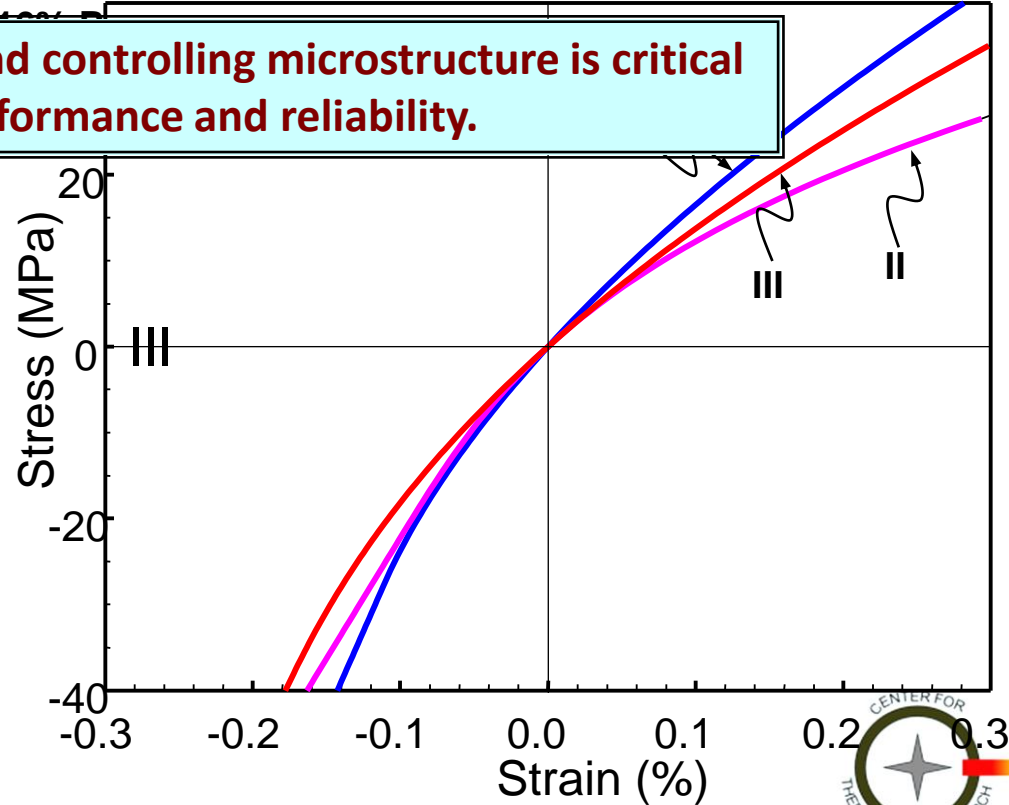
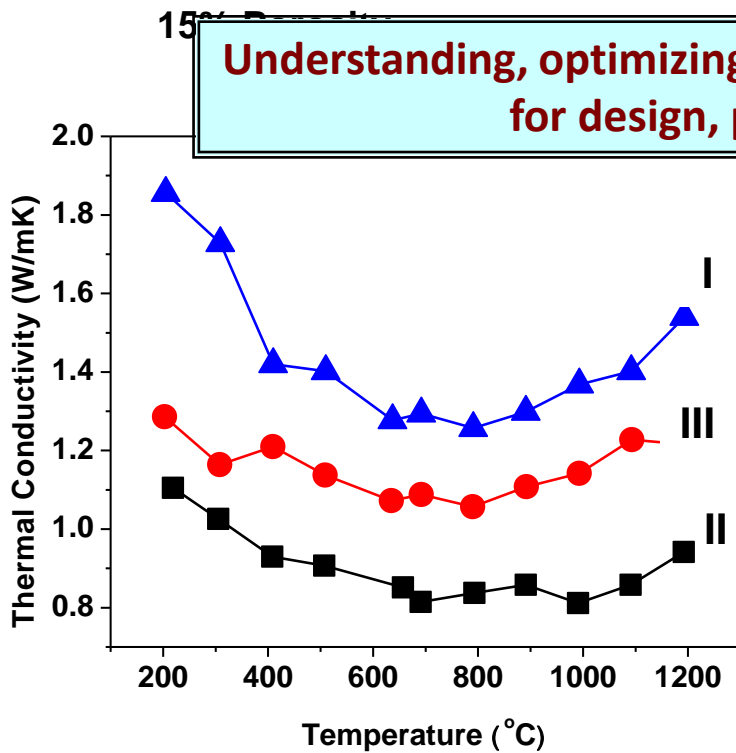
Nonlinear Stress-Strain



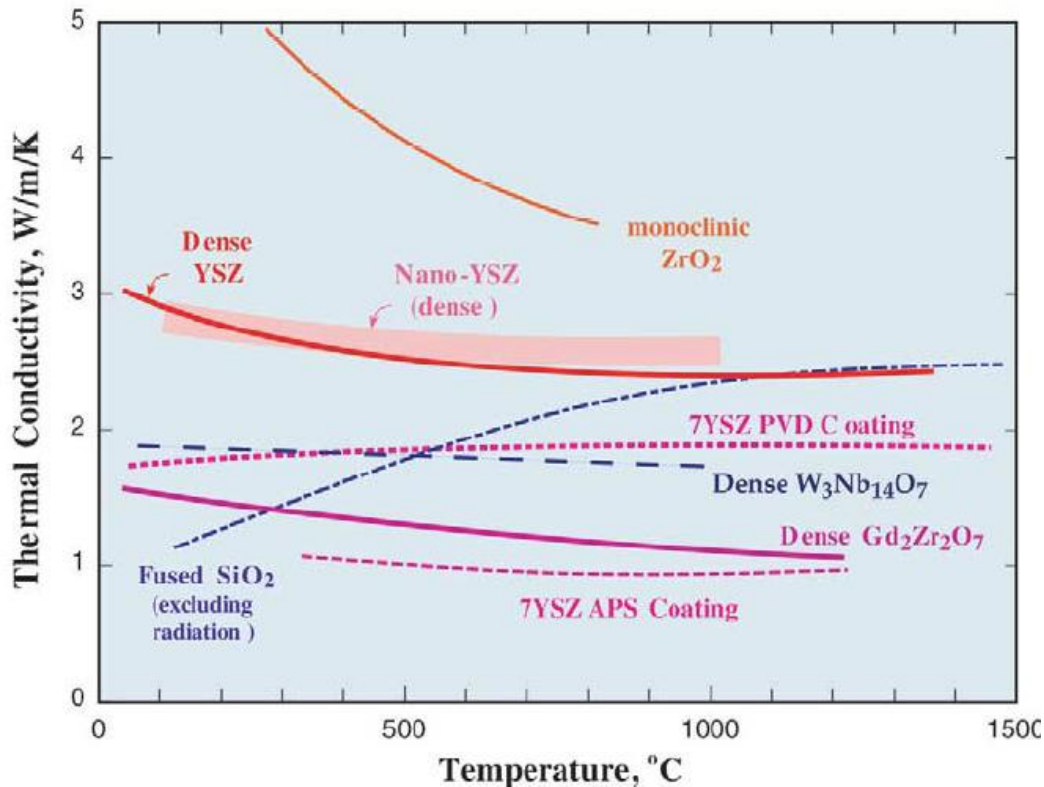
What is the difference in these TBC coatings?



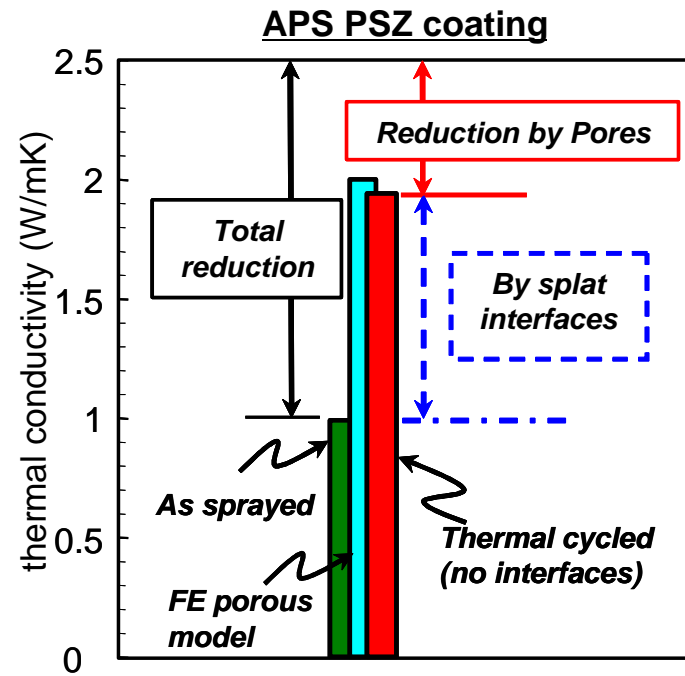
Understanding, optimizing and controlling microstructure is critical for design, performance and reliability.



Implications on Properties: Thermal Conductivity



Clarke and Levi, Ann. Rev. Materials, 2003
 Clarke and Phillpot, Materials Today, June 2005



Nakamura et al., Acta Met, 2004

Thermal spray microstructure has significant influence on material properties

Integrated Study of Thermal Spray TBCs

- **Understand and control** the plasma spray process to tailor and optimize the microstructure
- Develop **methodologies** for diagnostics, control, microstructure and property quantification
- Establish **correlations** among process-microstructure-properties so as to affect
 - Microstructure, thermal conductivity and compliance
- Achieve **repeatability** and **reliability** in microstructure and properties
- Assess changes in properties at time and temperature

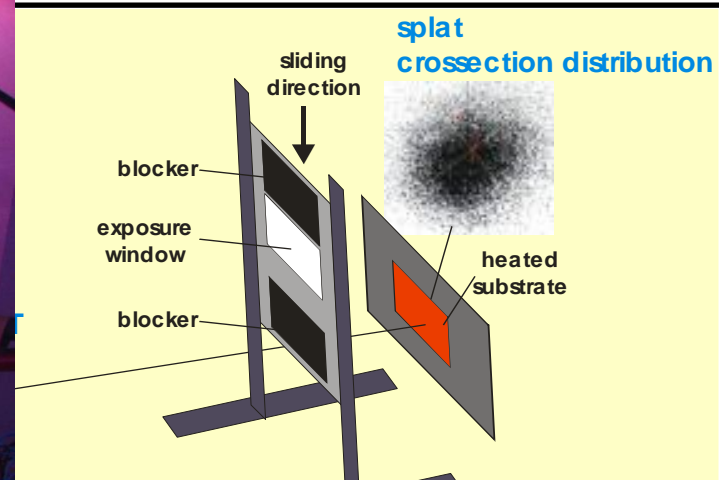
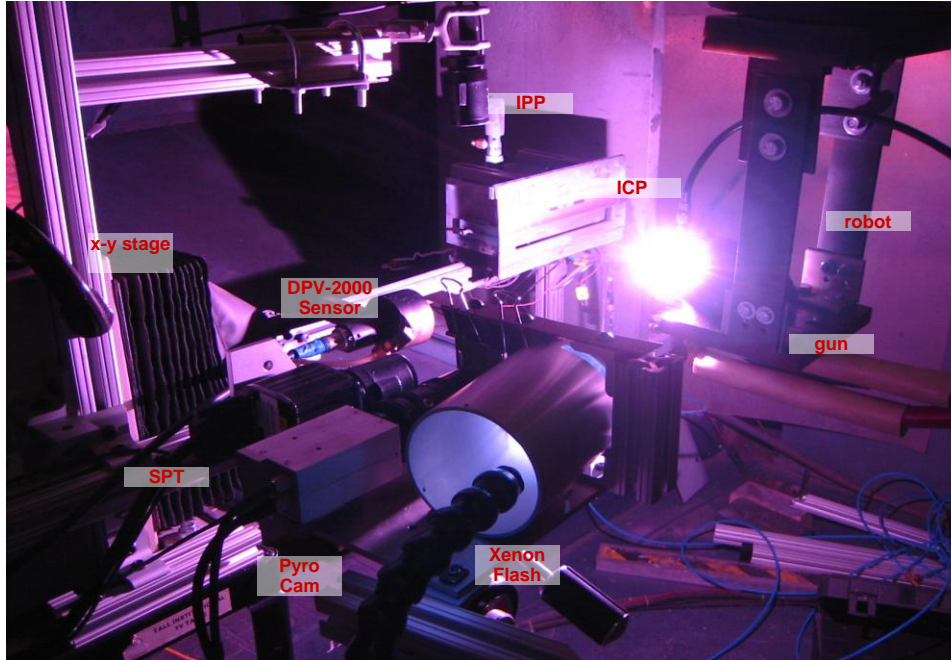
⇒ **Provide input for design**

⇒ **Reduce infant mortality and improve reliability**

⇒ **Quantify microstructure evolution for life prediction**

Integrated Studies of TS Coatings Including TBCs

- Fundamental process science and property evaluation at CTSR



injection monitoring
injection
plume position
spray stream

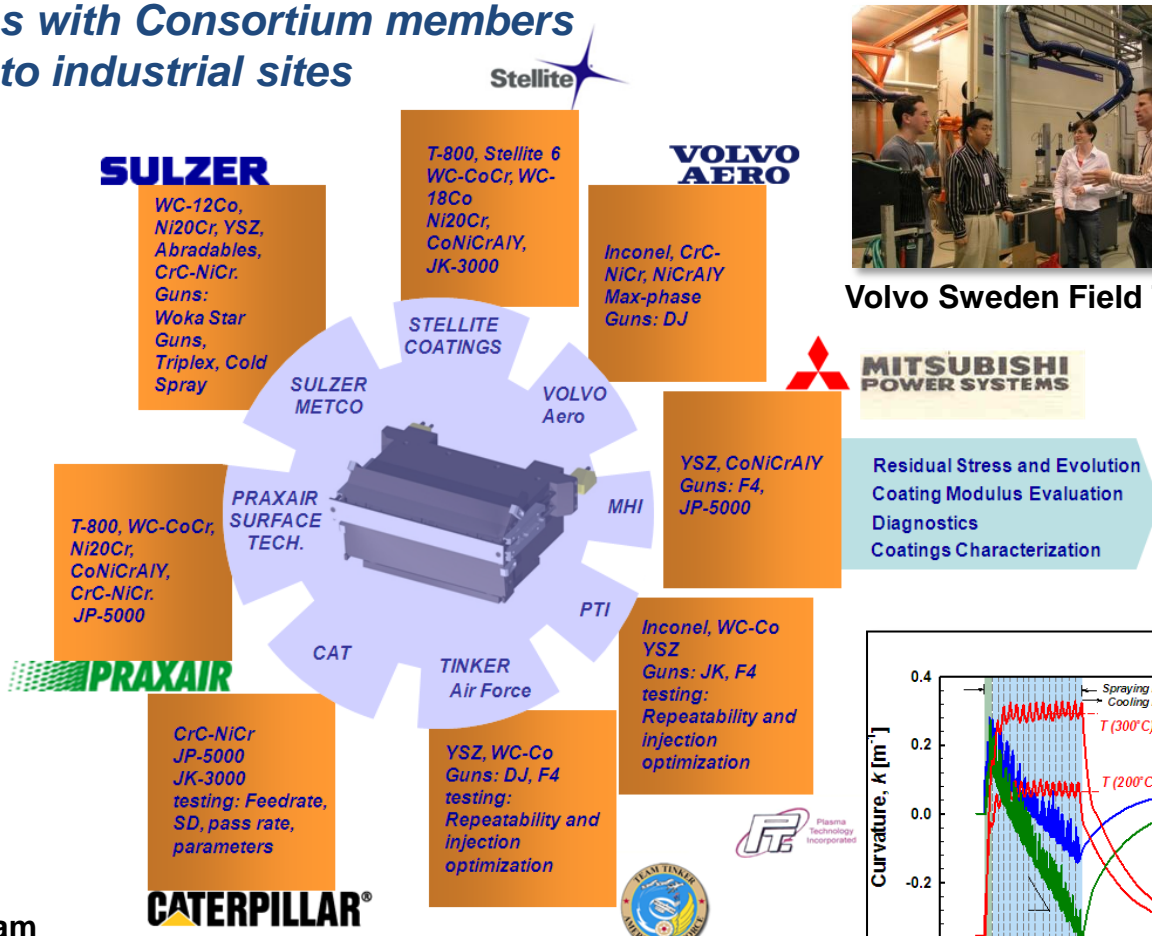
3D Particle In Flight Diagnostics

In Situ C



Integrated Studies of TS Coatings Including TBCs

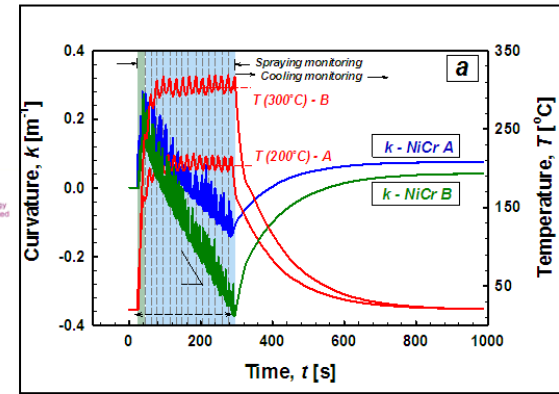
- Fundamental process science and property evaluation at CTSR
- Collaborative studies with Consortium members including field trips to industrial sites



Volvo Sweden Field Trip

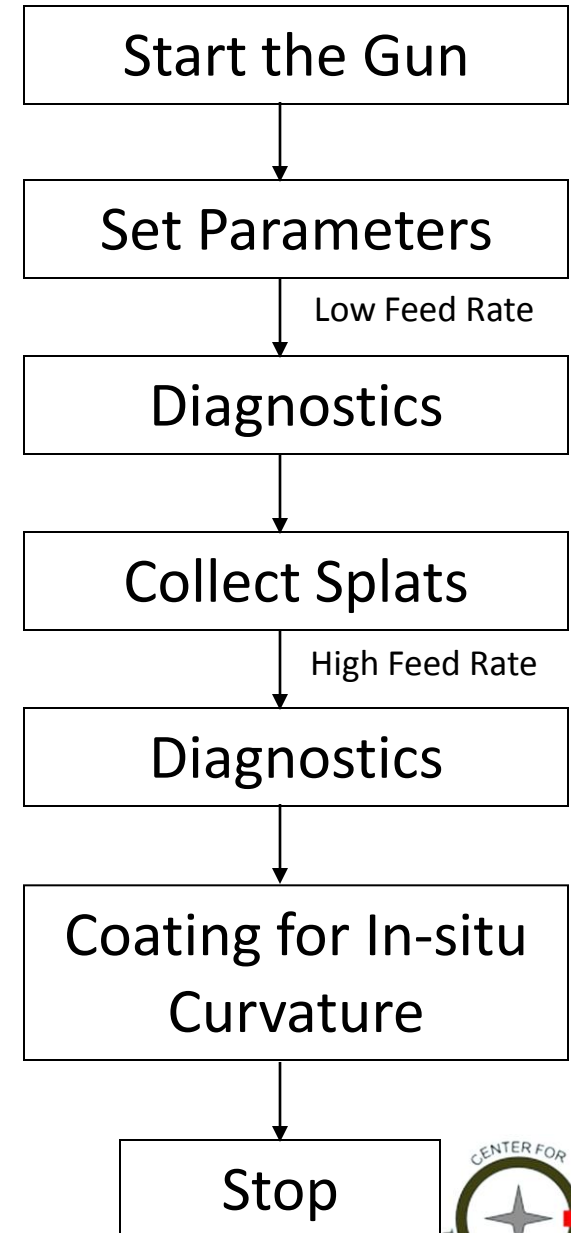


Stony Brook-Caterpillar Team

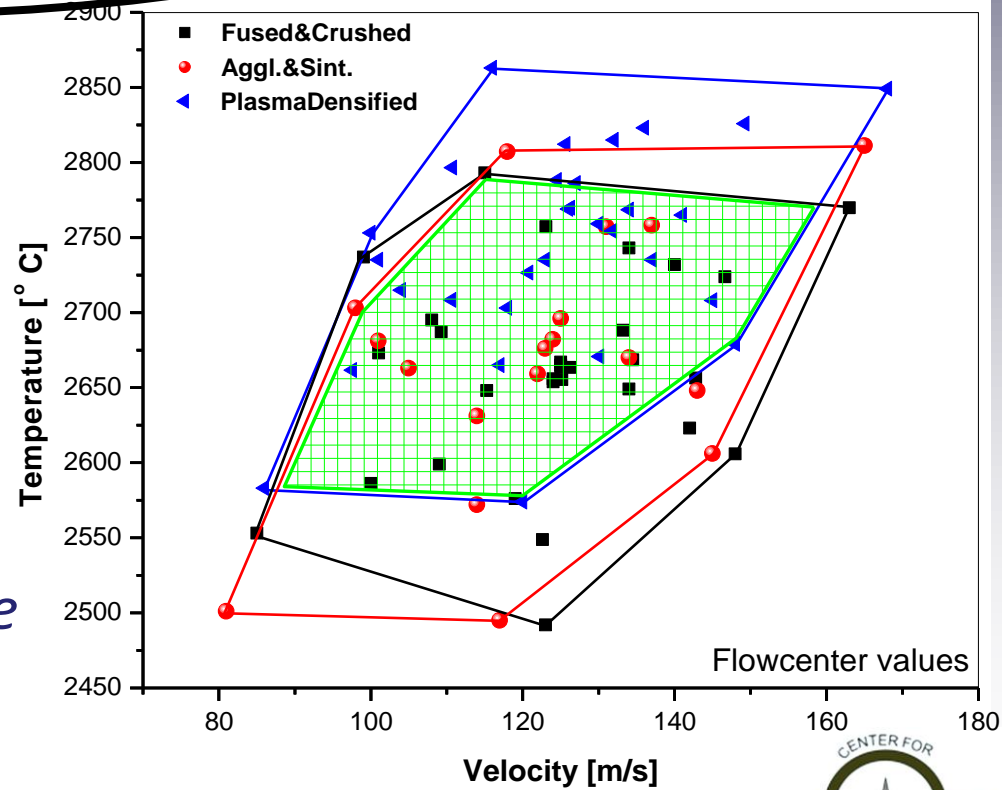
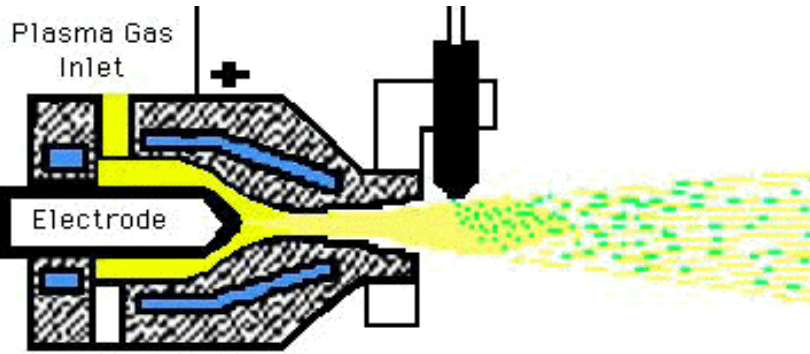
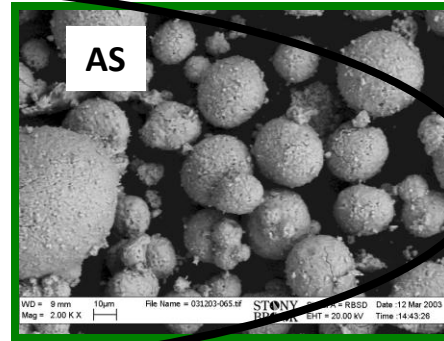
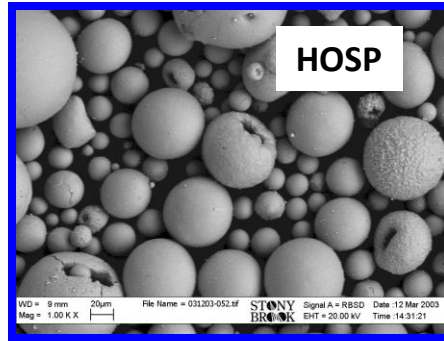
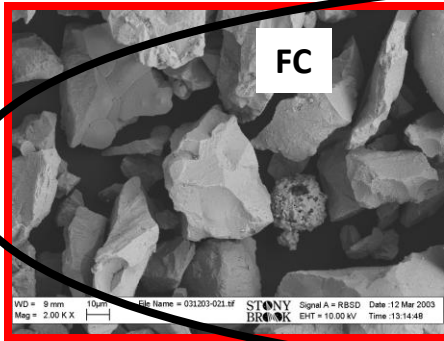


Many parameters can be considered for tailoring a microstructure

- Starting powder morphology
 - Particle size distribution
 - Particle injection
 - Plasma torch, power and gases
 - Substrate temperature
 - Particle flux
 - Robot motion
- + Pore Architecture
Modulus (two orientations)
Indentation
Stress-Strain
Thermal Conductivity
(in-plane and through-thickness)
- Examine process/coating repeatability
 - Examine testing repeatability

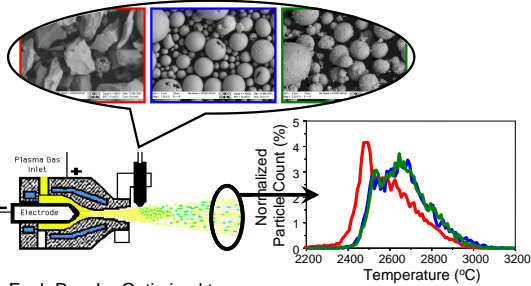


Example 1: Effect of Starting Powder Morphology



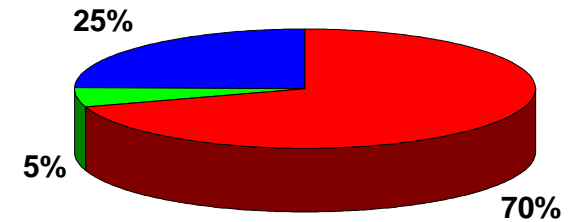
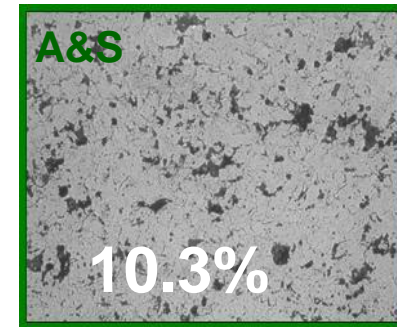
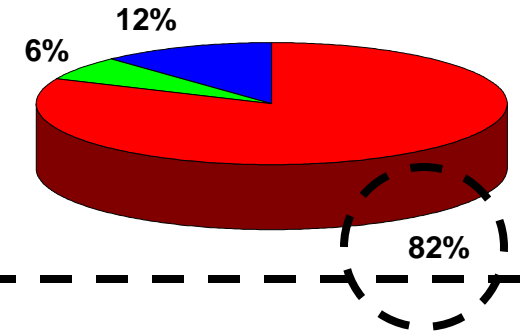
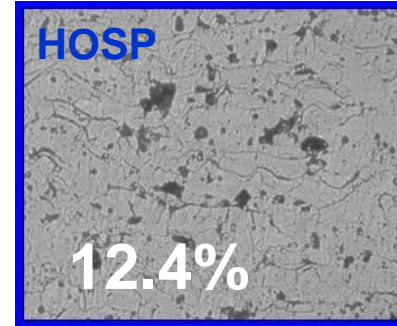
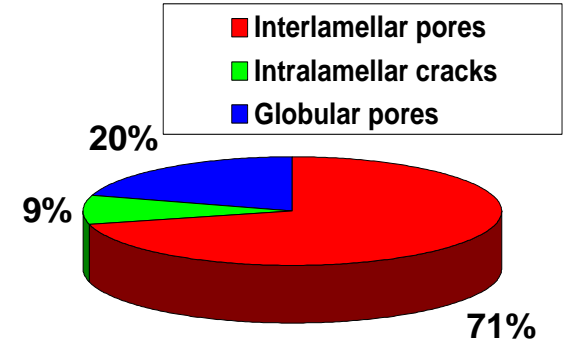
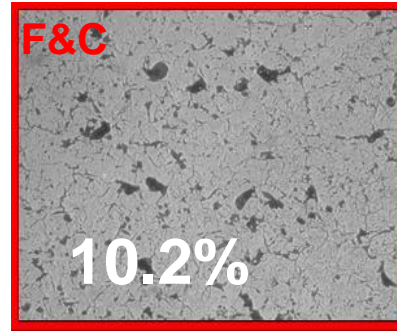
Each Powder Optimized to Produce the Same Average T & V

Example 1: Effect of Starting Powder Morphology

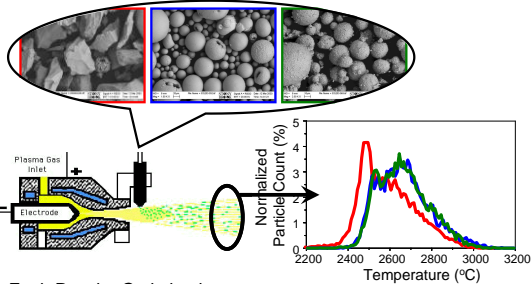


Each Powder Optimized to Produce the Same Average T & V

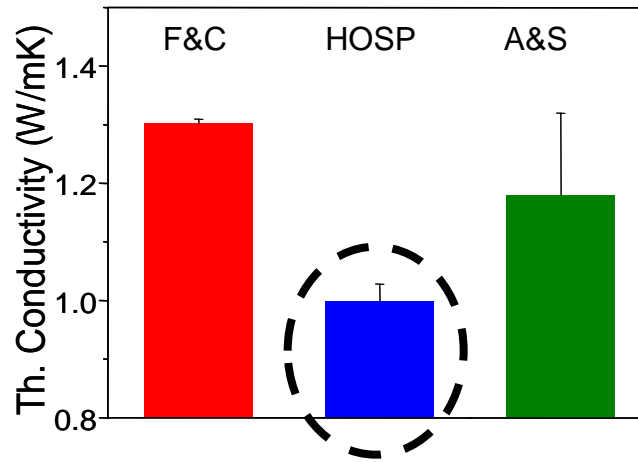
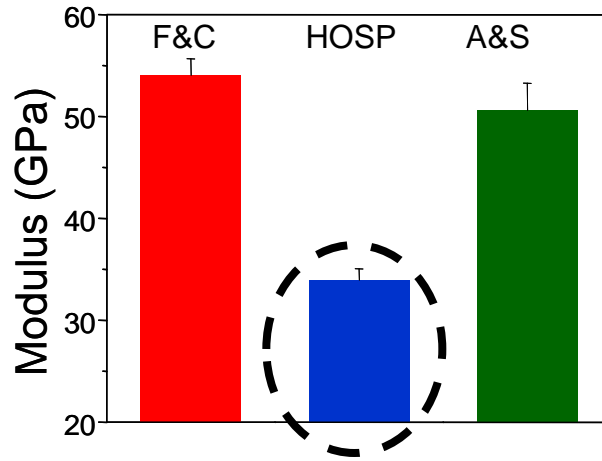
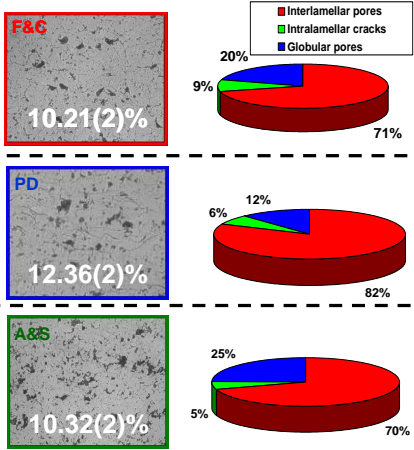
*Similar Total Porosity
and
Higher % ILP*



Example 1: Effect of Starting Powder Morphology

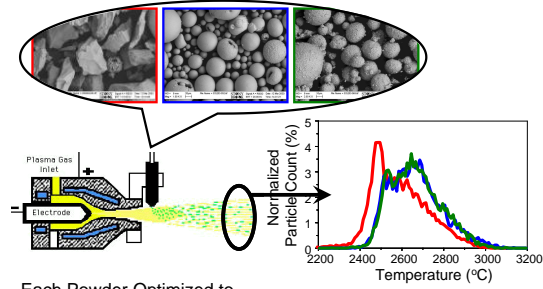


Each Powder Optimized to Produce the Same Average T & V

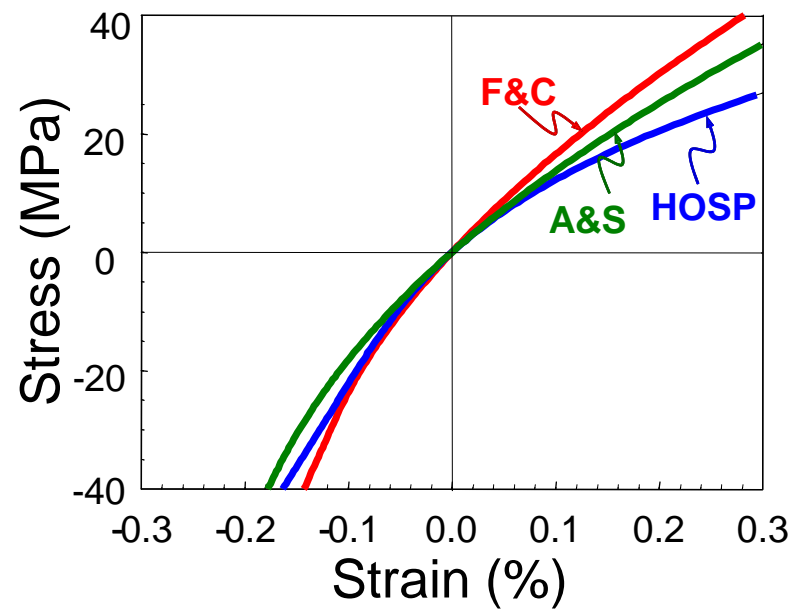
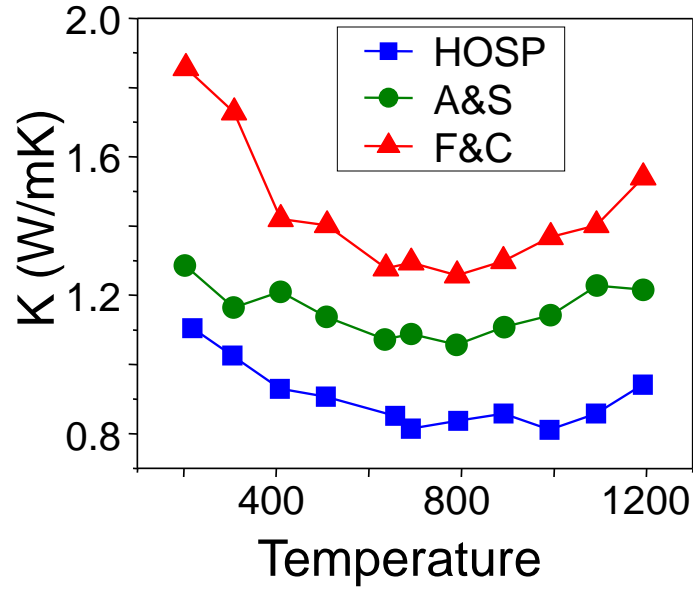
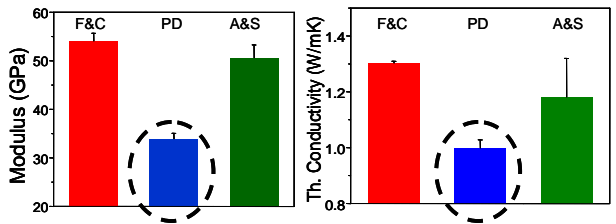
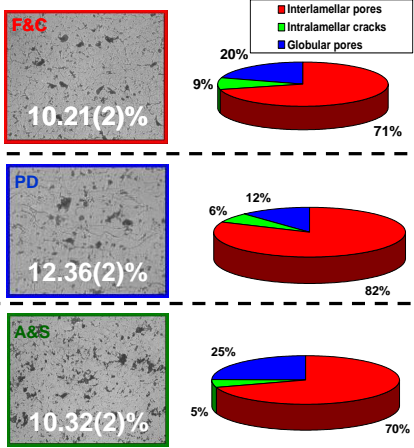


HOSP shows consistently lower E and K

Example 1: Effect of Starting Powder Morphology

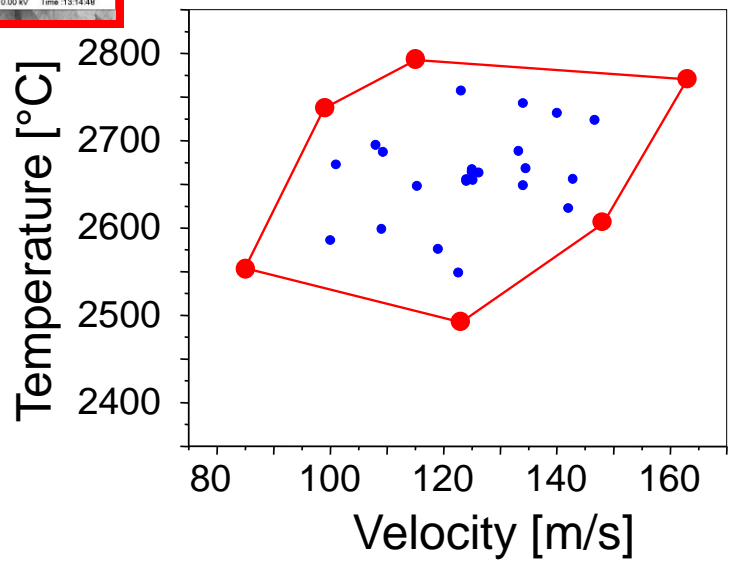
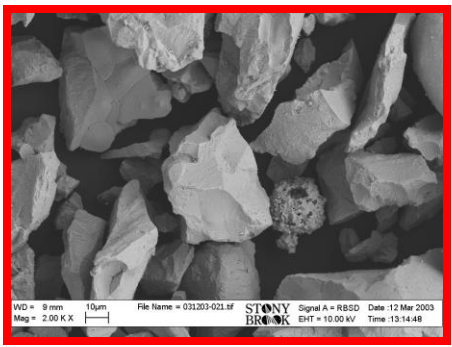


Each Powder Optimized to Produce the Same Average T & V

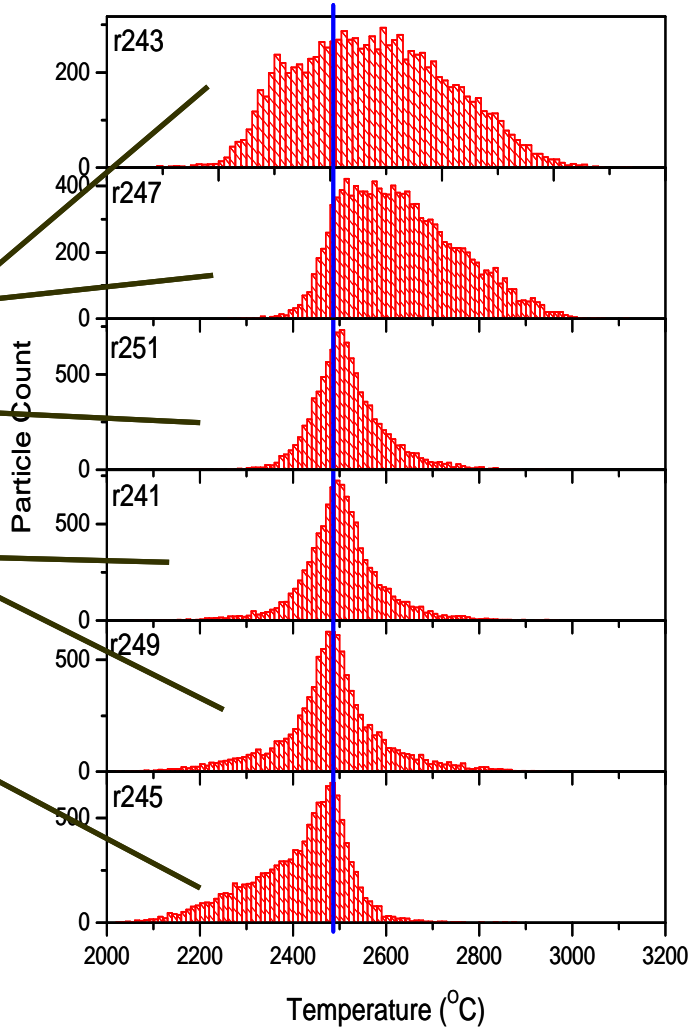
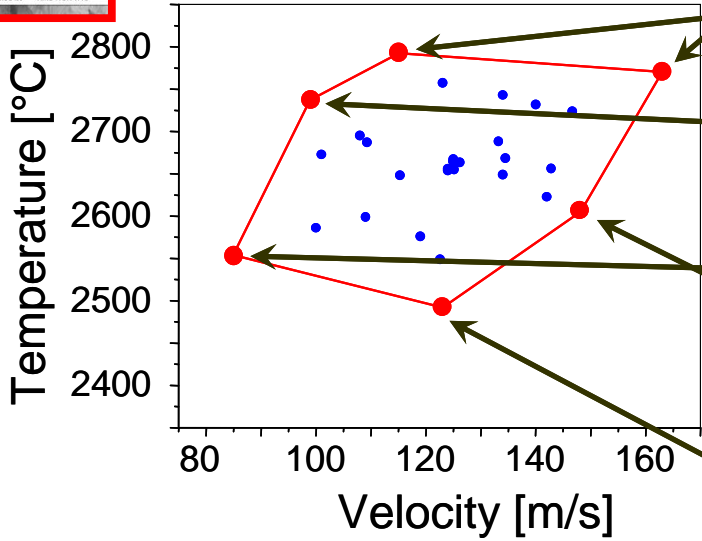
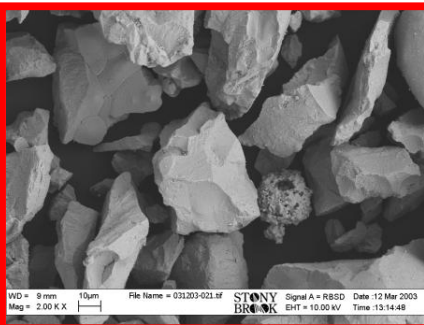


Temperature-dependent K and mechanical behavior differences are observed.

Example 2: Changing T-V process space via torch parameters

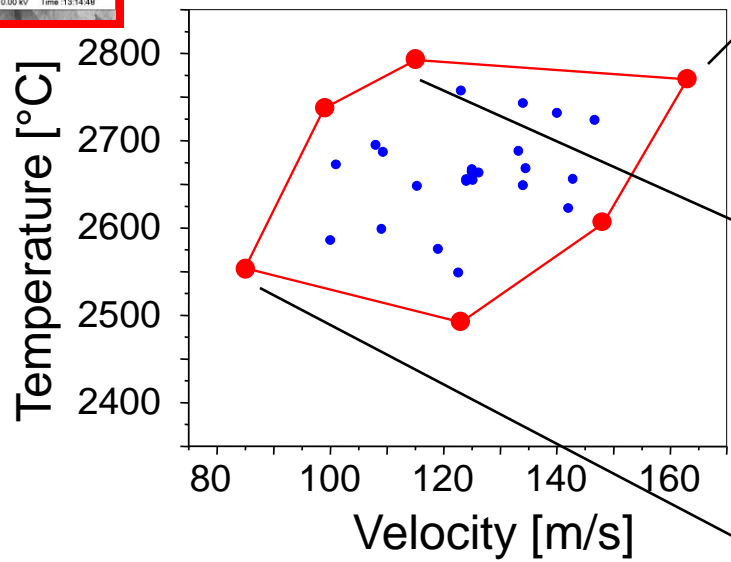
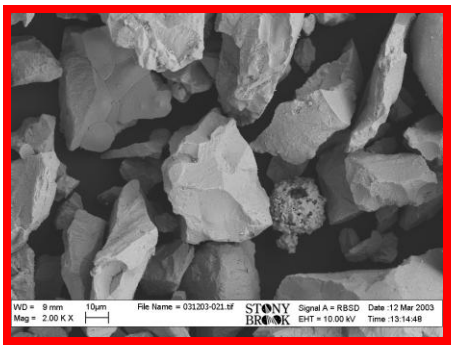


Example 2: Changing T-V process space via torch parameters

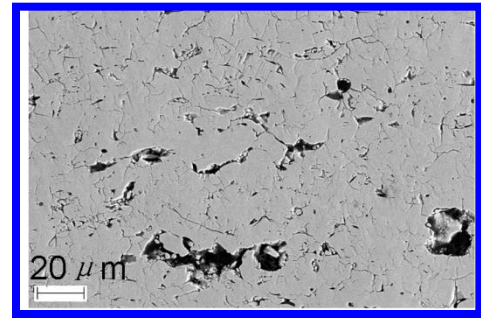


Changing torch parameters effects particle temperature distribution

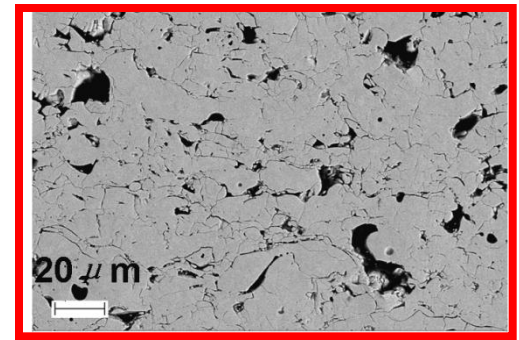
Example 2: Changing T-V process space via torch parameters



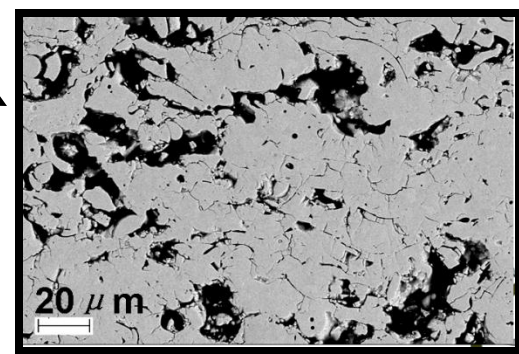
67 GPa 1.3 W/mK



51 GPa 1.13 W/mK

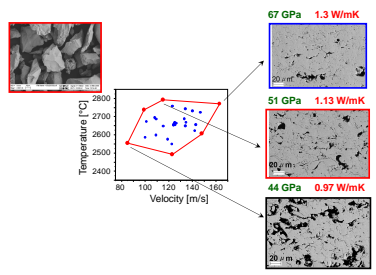


44 GPa 0.97 W/mK

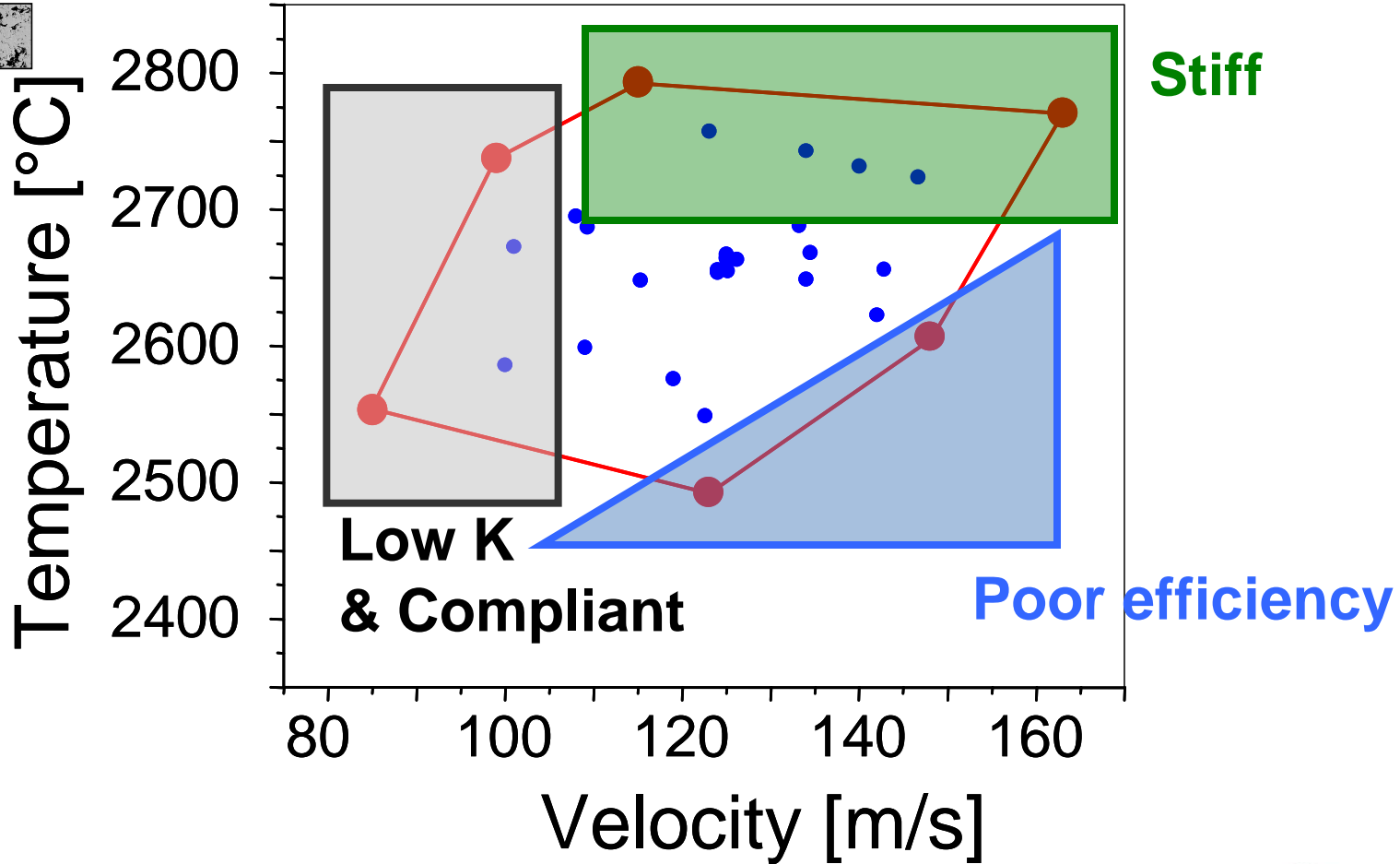


Changing torch parameters effects microstructure, elastic modulus and thermal conductivity.

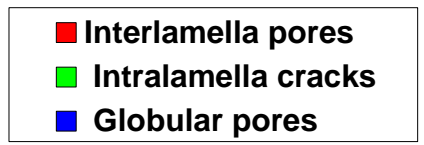
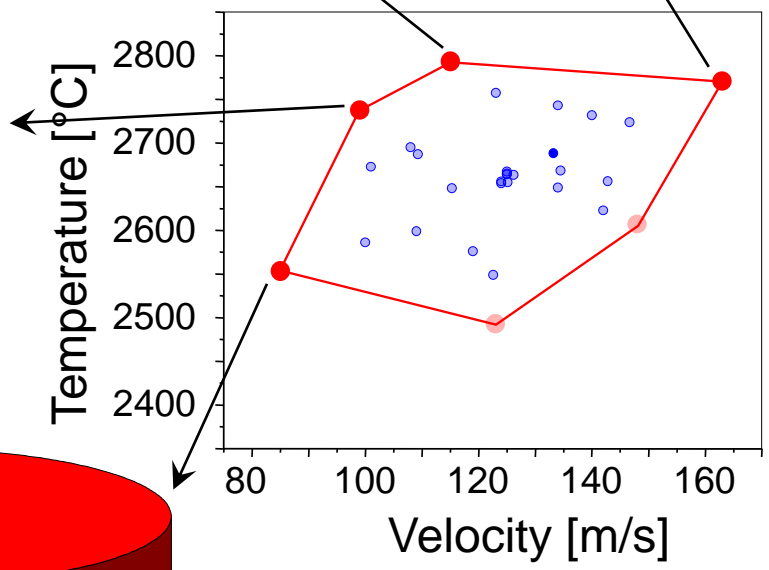
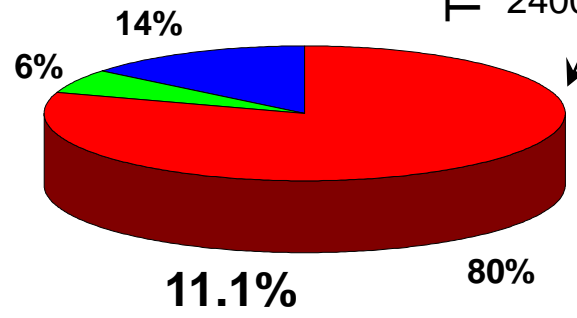
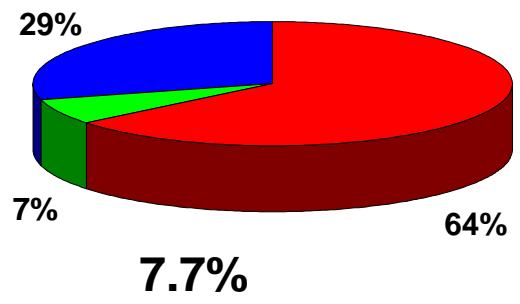
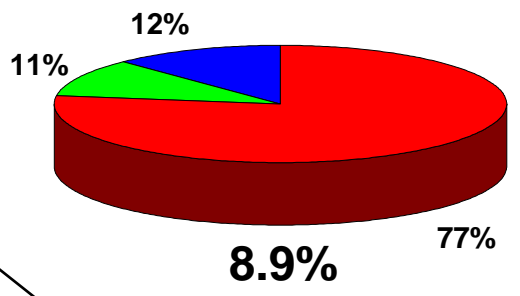
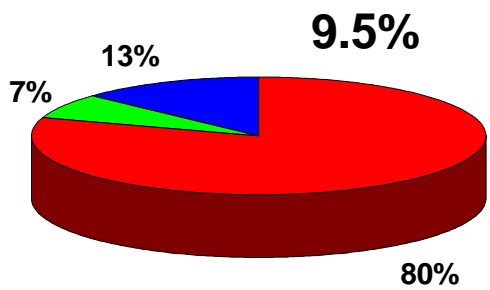
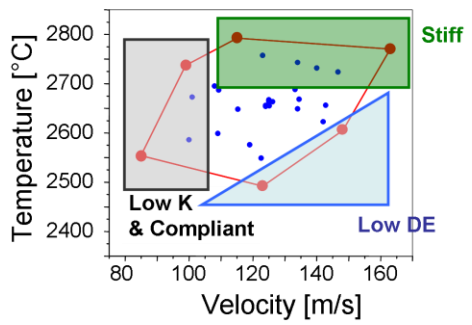
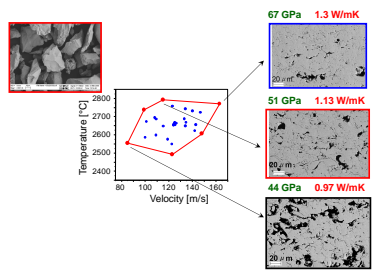
Example 2: Changing T-V process space via torch parameters



2nd Order Process Map

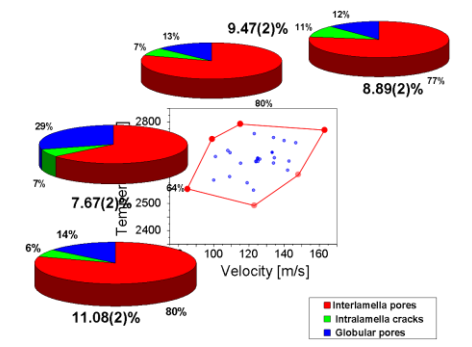
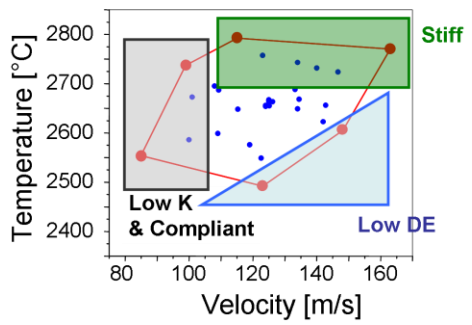
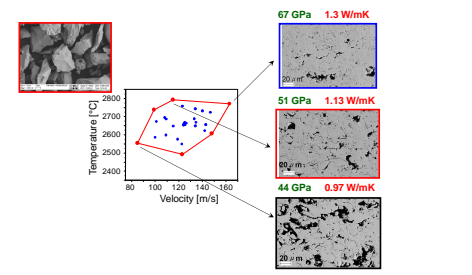


Example 2: Changing T-V process space via torch parameters

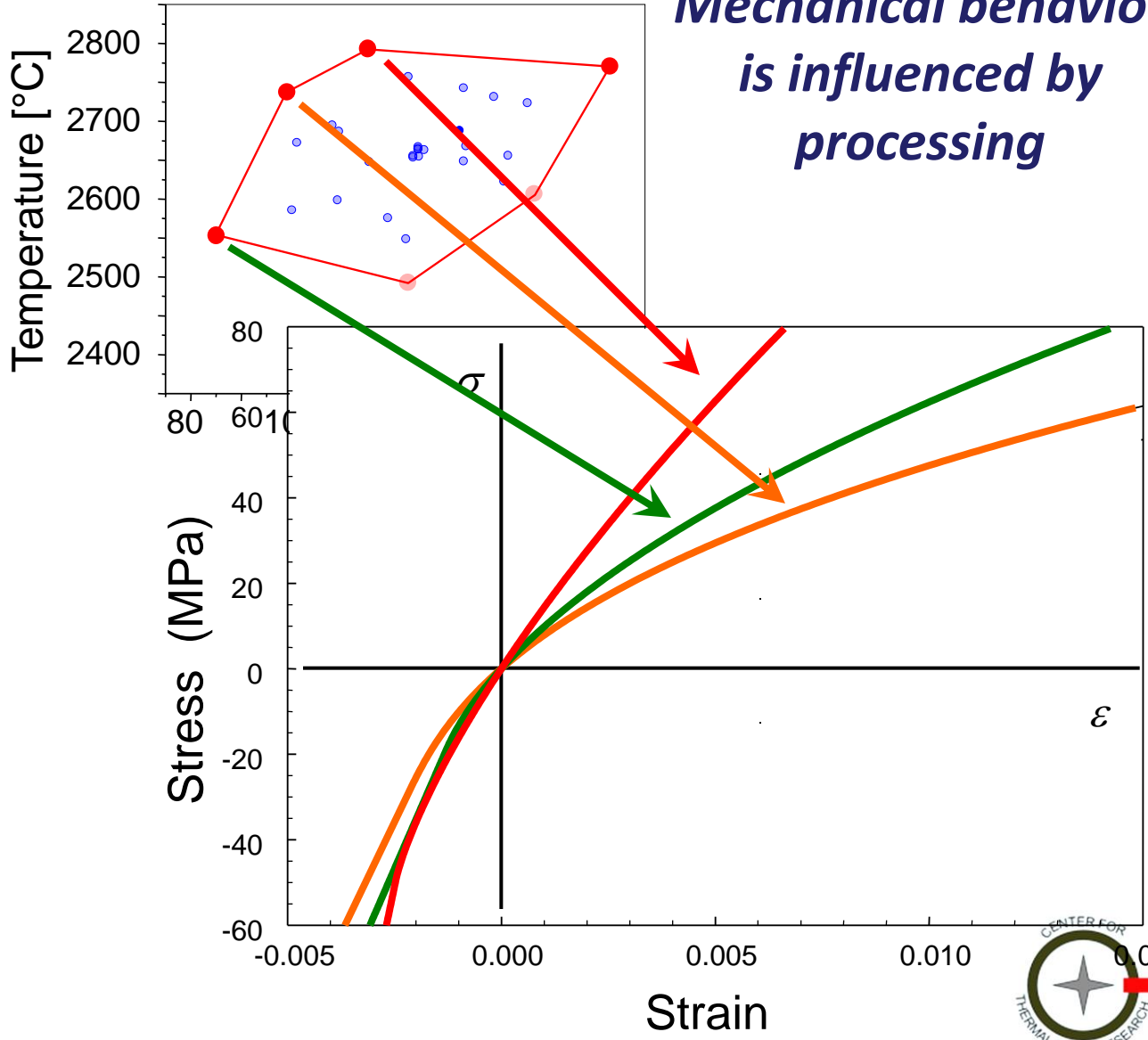


Total amount and type of porosity can be controlled

Example 2: Changing T-V process space via torch parameters



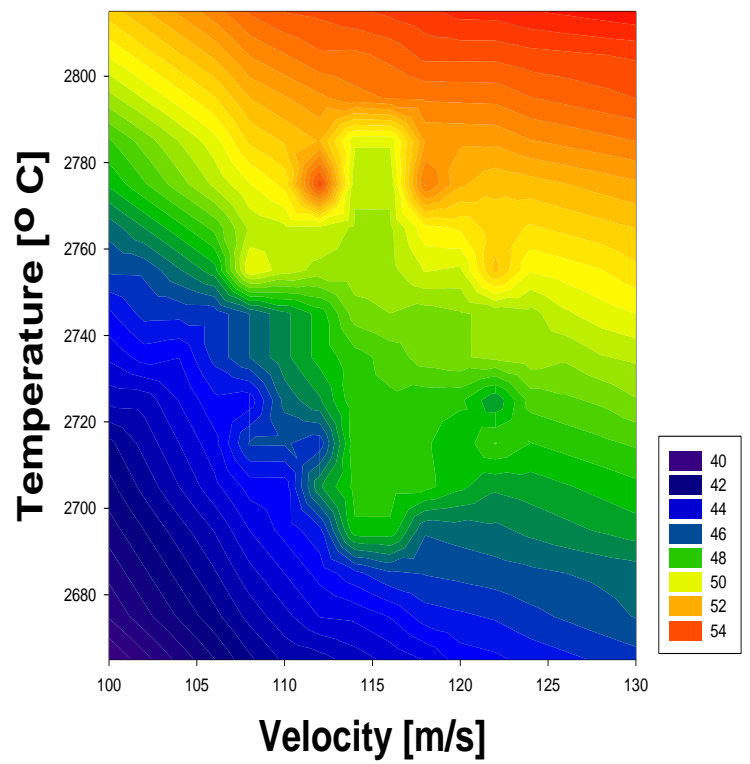
Mechanical behavior is influenced by processing



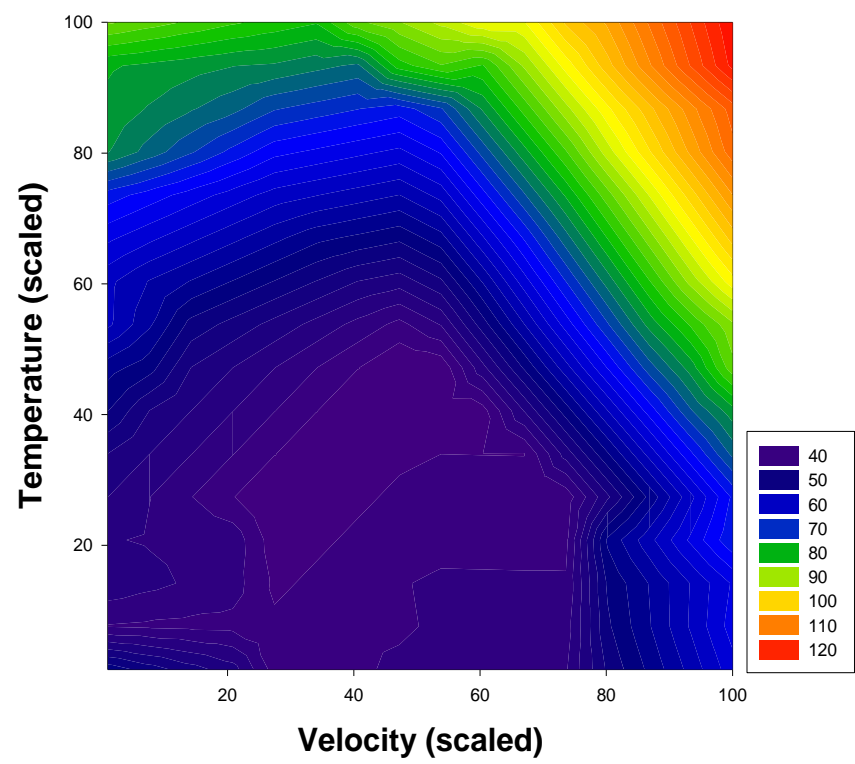
Example 2: Changing T-V process space via torch parameters

Detailed process maps can be created for use by process and design engineers

Elastic Modulus Map



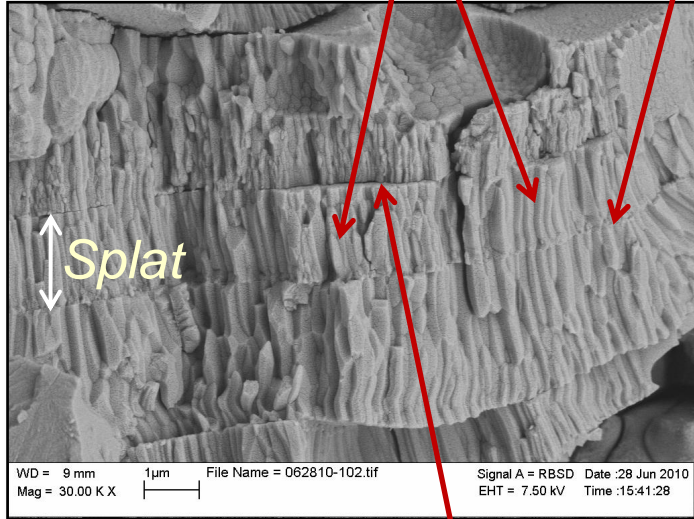
Thermal Conductivity Map



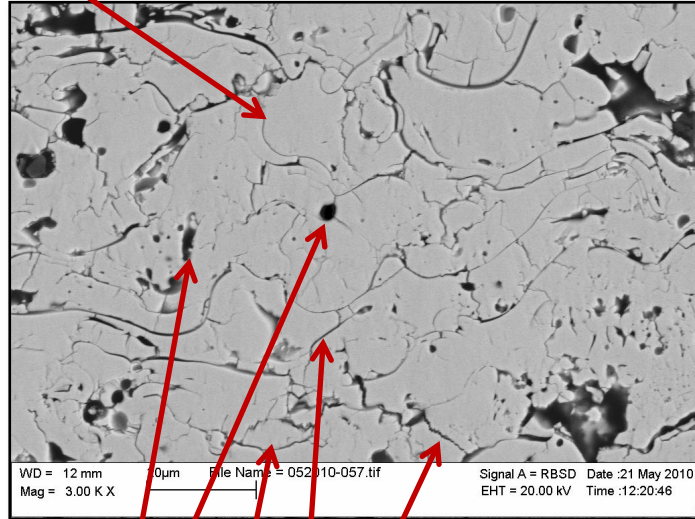
Microstructural Effects on Mechanical Behavior

Intra-splat columnar grains
Inter-splat interfaces

Splat



Fractured Surface
Cross-section APS-YSZ

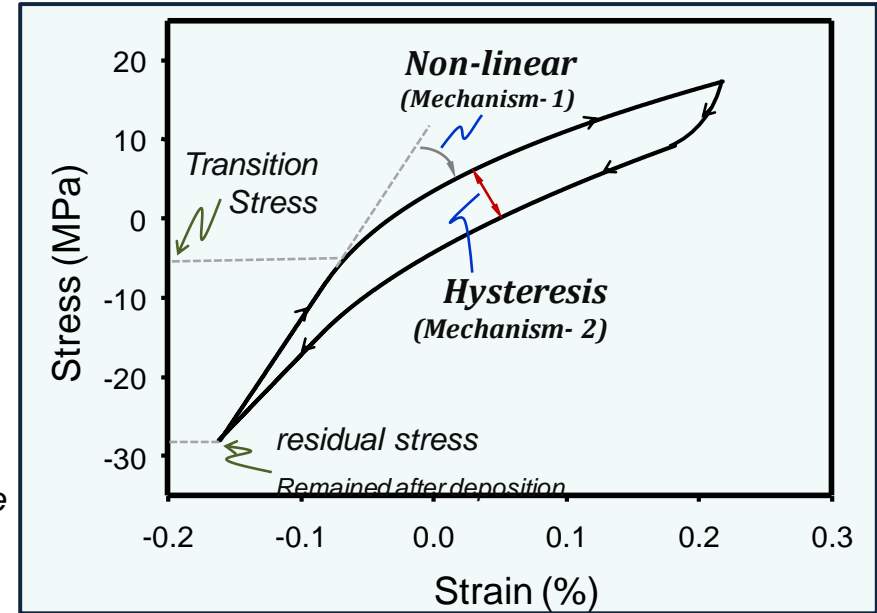
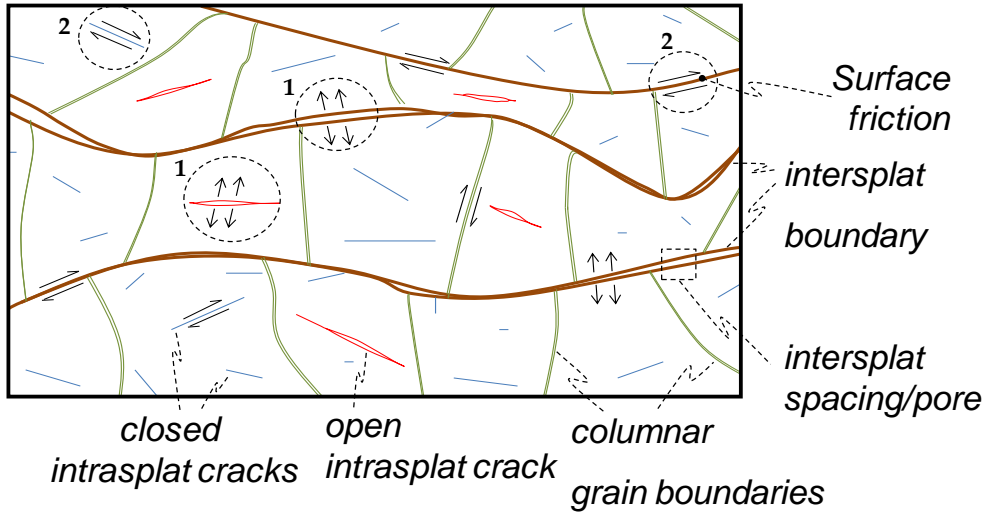


Polished Surface
Cross-section APS-YSZ

Globular Pores
Inter-splat Spacing
Cracks within a splat
Cracks between the splats

Microstructural Effects on Mechanical Behavior

Upon Mechanical Loading

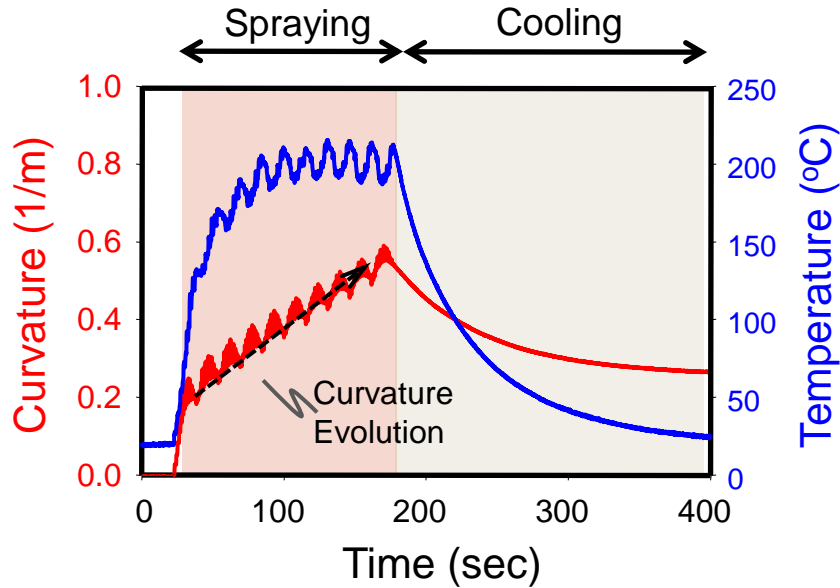


- **Mechanism 1:** Opening/closure of pores or spacings, the source of Non-linearity
- **Mechanism 2:** Sliding of defect surfaces causes frictional energy loss, Hysteresis behavior

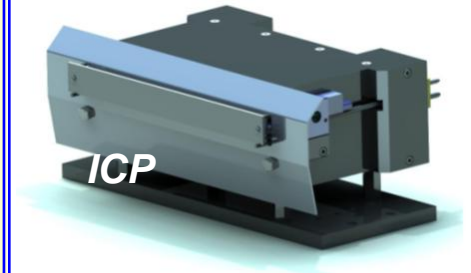
Non-linearity of the coating represents the compliance present in it

Microstructural Effects on Mechanical Behavior

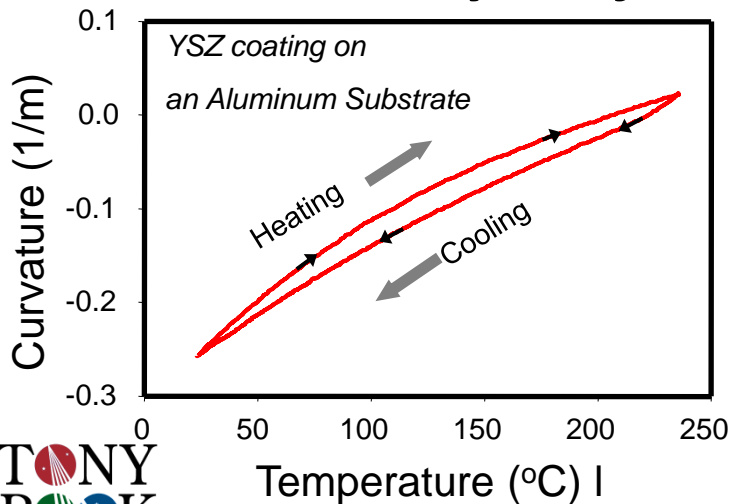
In-situ: Curvature Monitoring



Measurement tells the evolution history of a deposited coating. Each local peak corresponds to a pass (deposition of one layer). The slope of the curvature evolution is referred as "Evolving stress"



Ex-situ: Thermal Cycle of the Coated Specimen

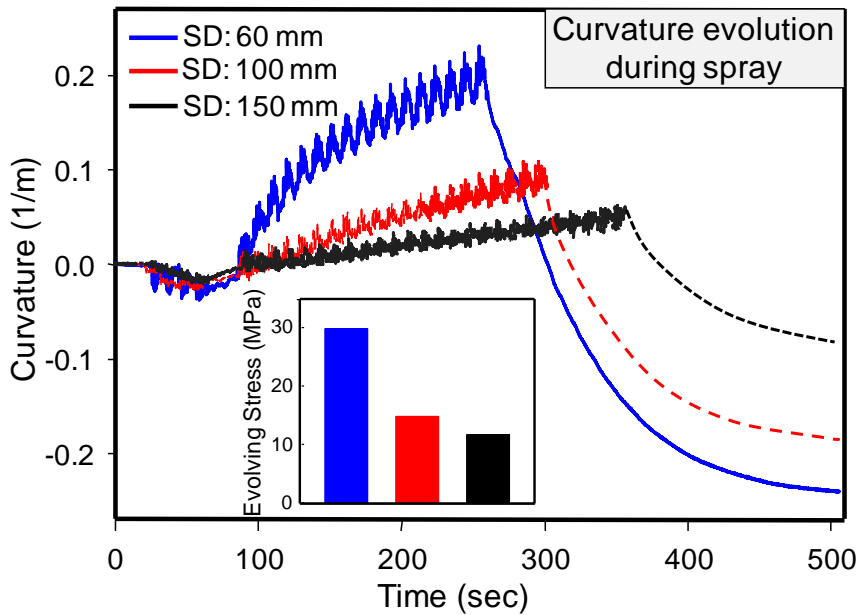


After spraying, the coating (with substrate) is heated inside a furnace. The temperature change induces mismatch strain, and the curvature of coating changes. The continuous recording of one thermal cycle provides an ANELASTIC curv-temp plot, which is then converted to a stress strain curve to quantify the coating compliance.

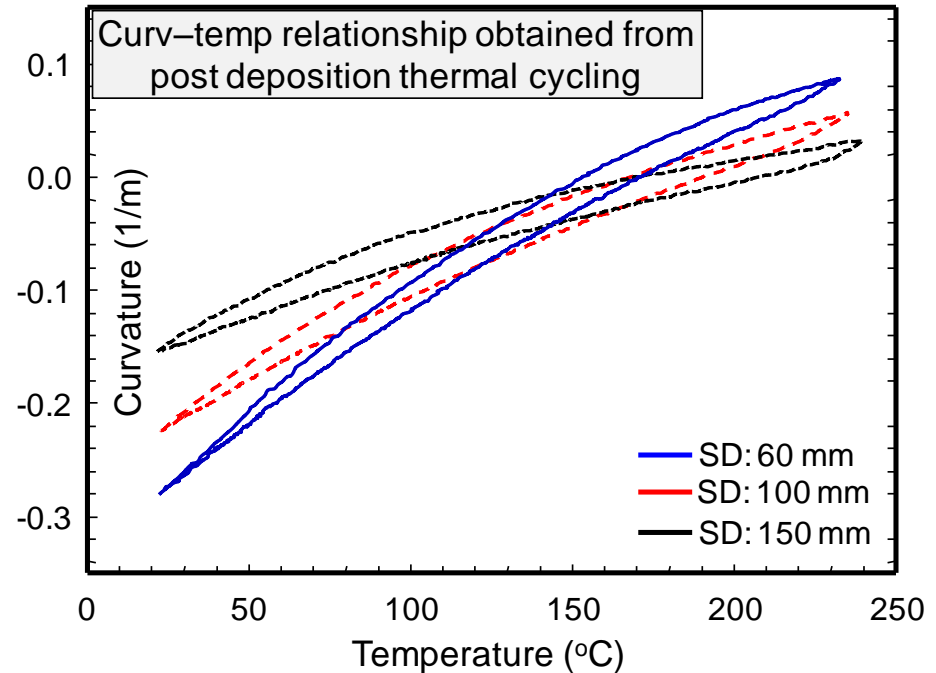
Microstructural Effects on Mechanical Behavior

Case study: three coatings deposited at three different spray distances

In-situ

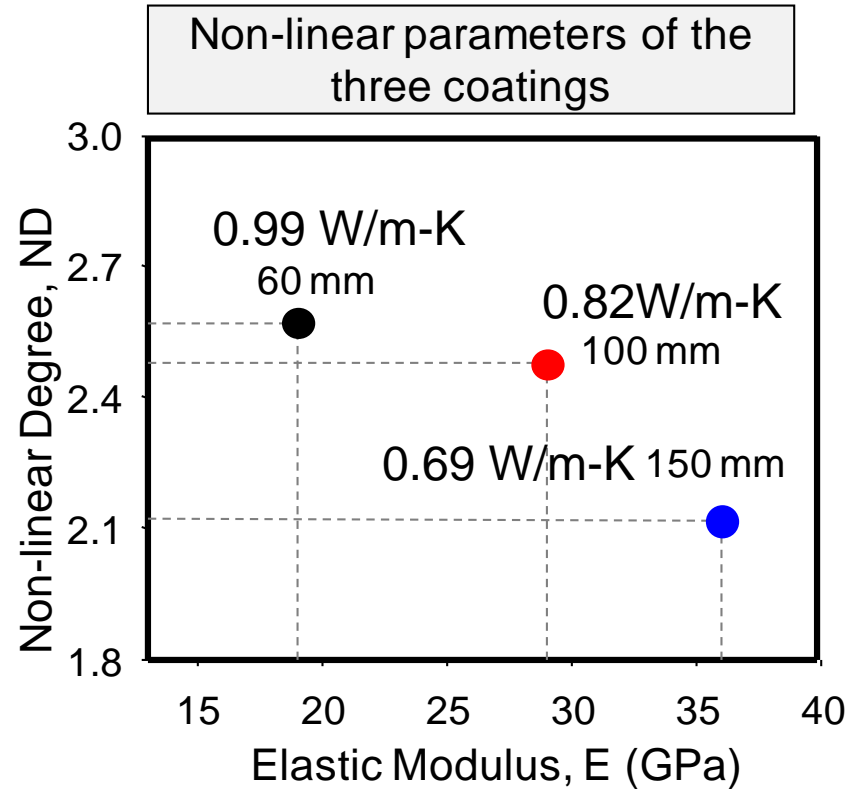
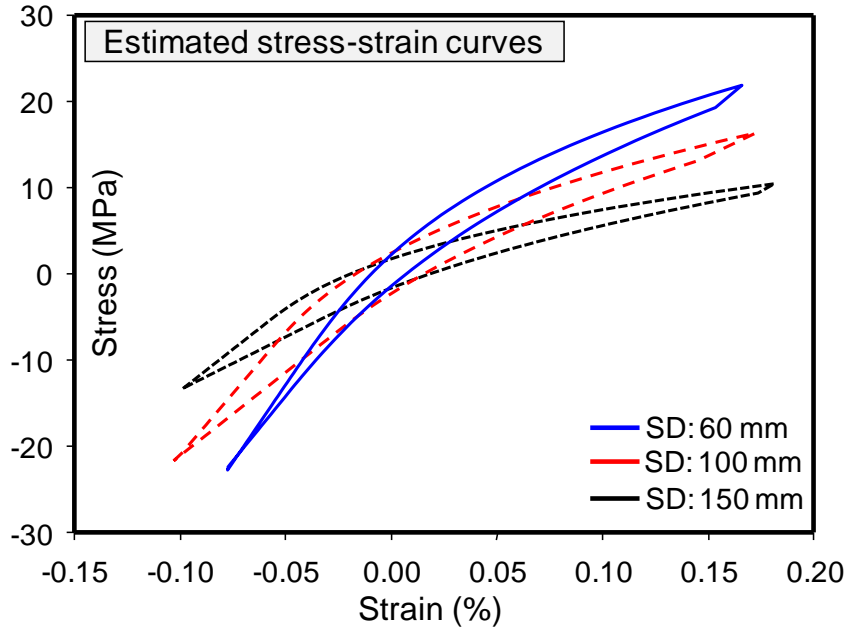


Ex-situ



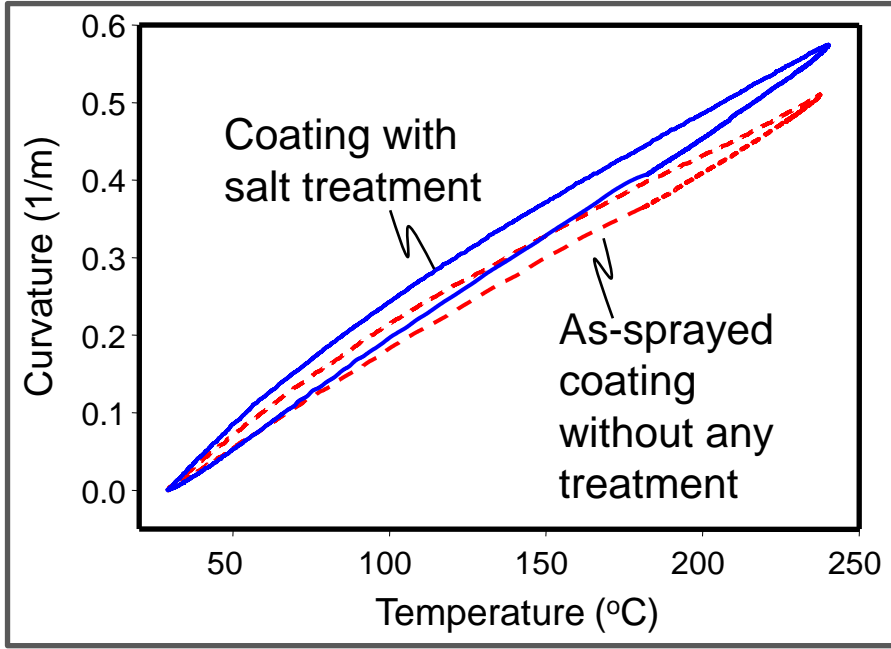
Microstructural Effects on Mechanical Behavior

Case study: three coatings deposited at three different spray distances

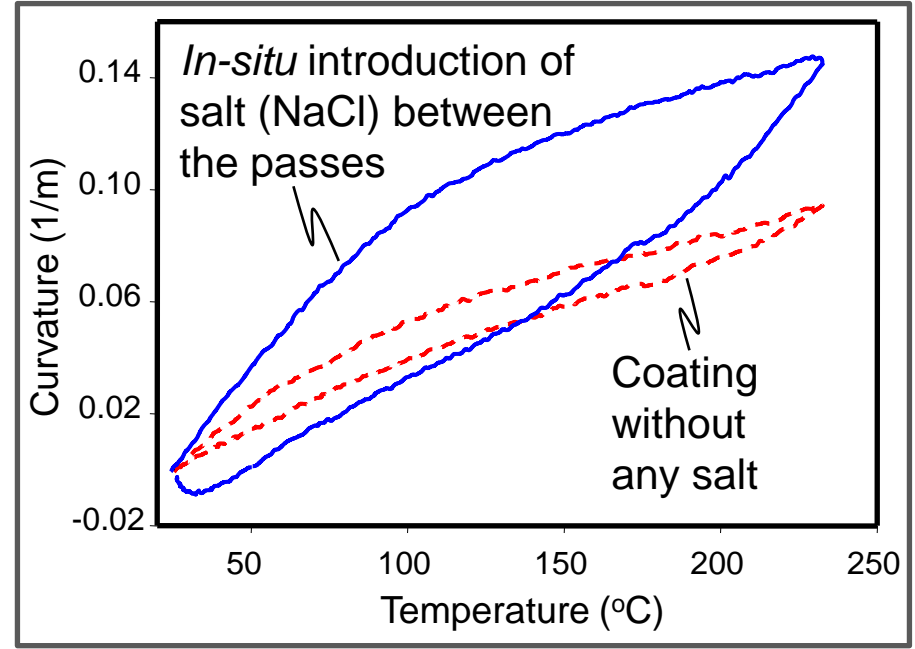


Microstructural Effects on Mechanical Behavior

How could deposits impact mechanical behavior?



Coating with salt solution treatment was 30% stiffer than as sprayed one. It also showed more hysteresis in it.

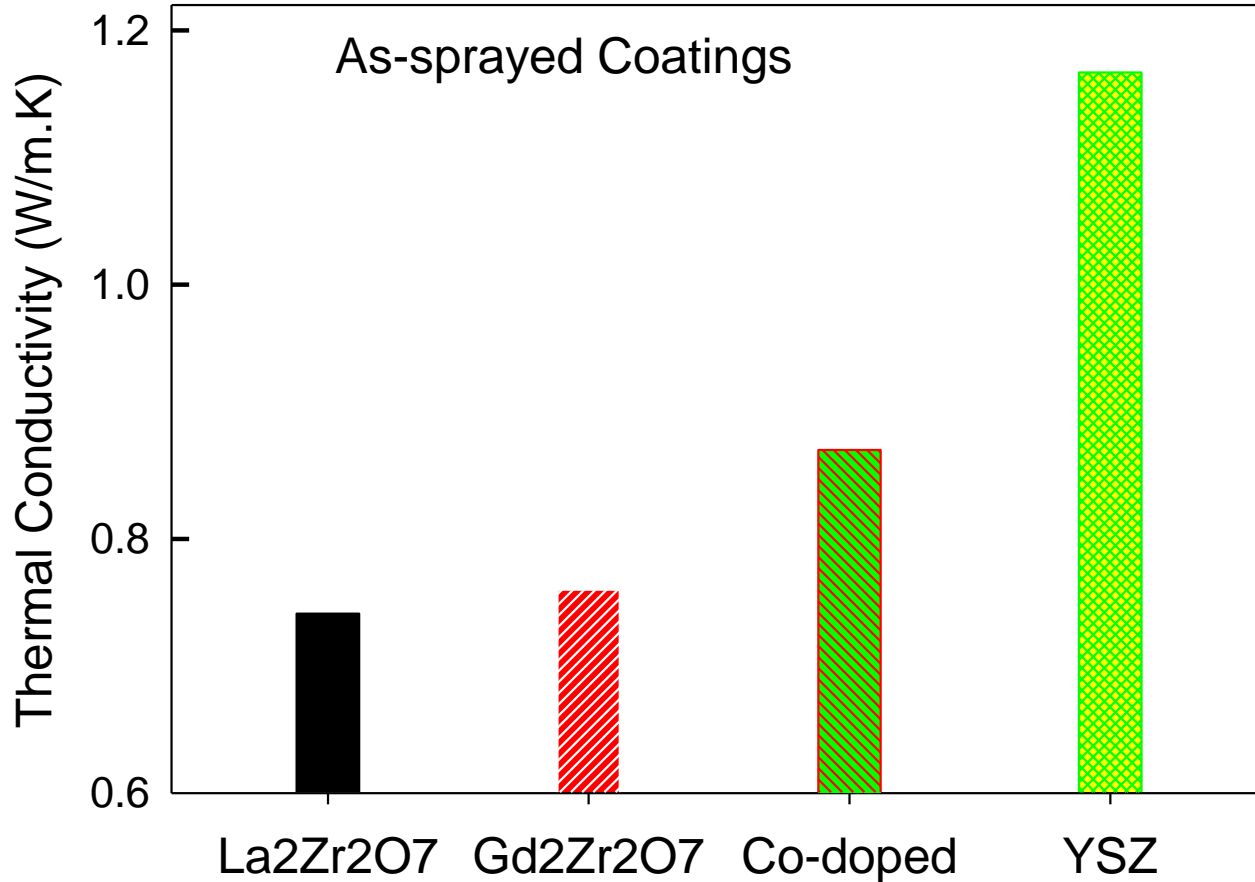


Salt mist was introduced between some selective passes during coating deposition.

The presence of salt at defect surfaces made the coating stiffer, with increased non-linearity and hysteresis.

IGCC Turbine Coating Properties: Material Effects

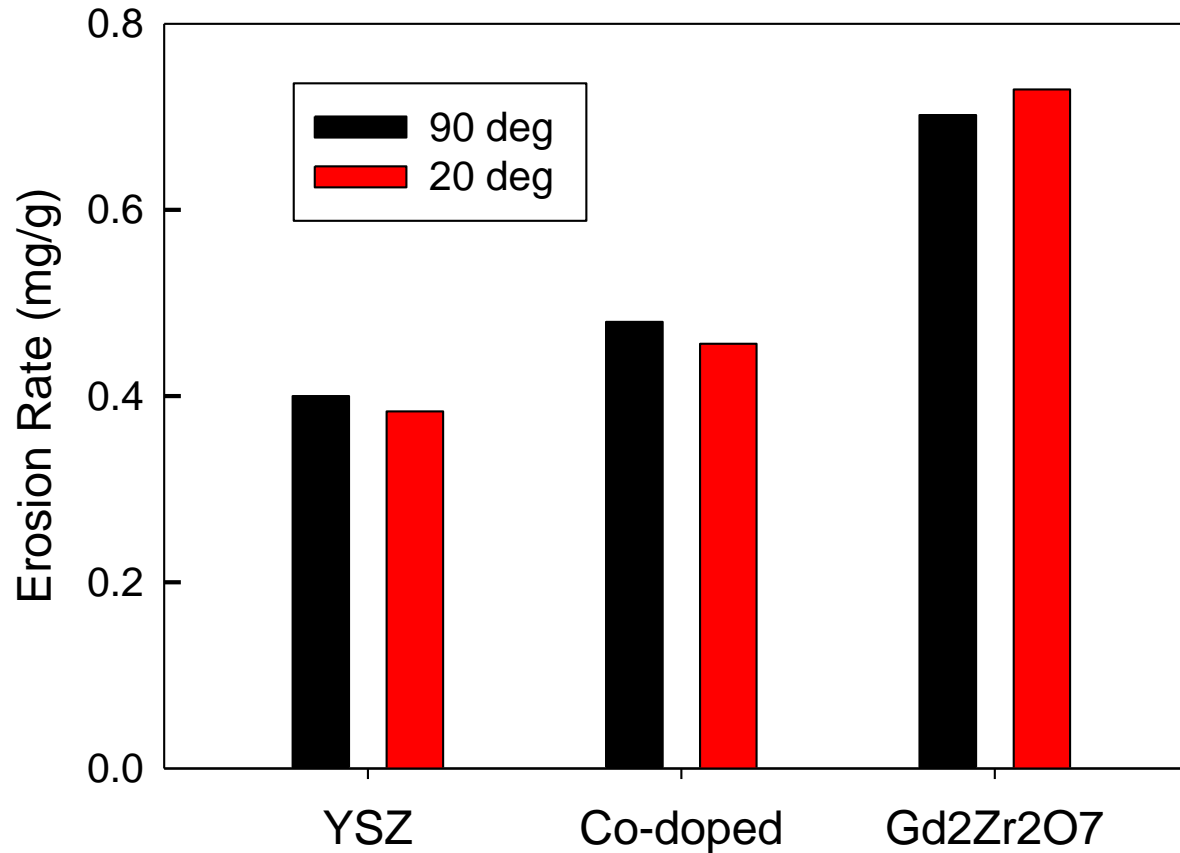
Thermal Conductivity of As-Sprayed Coatings



Material choice influences thermal properties

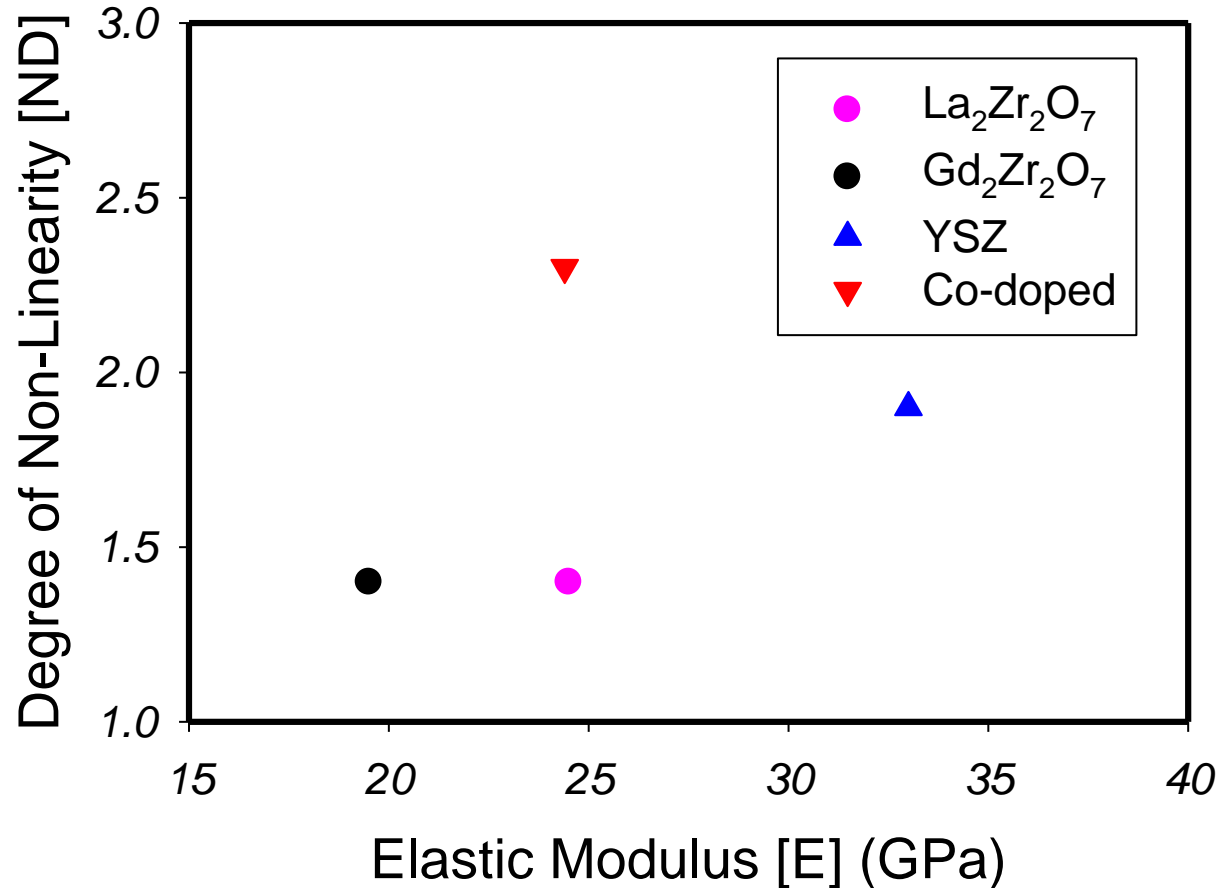
IGCC Turbine Coating Properties: Material Effects

Erosion of As-Sprayed Coatings



Material choice influences erosion properties with $Gd_2Zr_2O_7$ having high erosion rates.

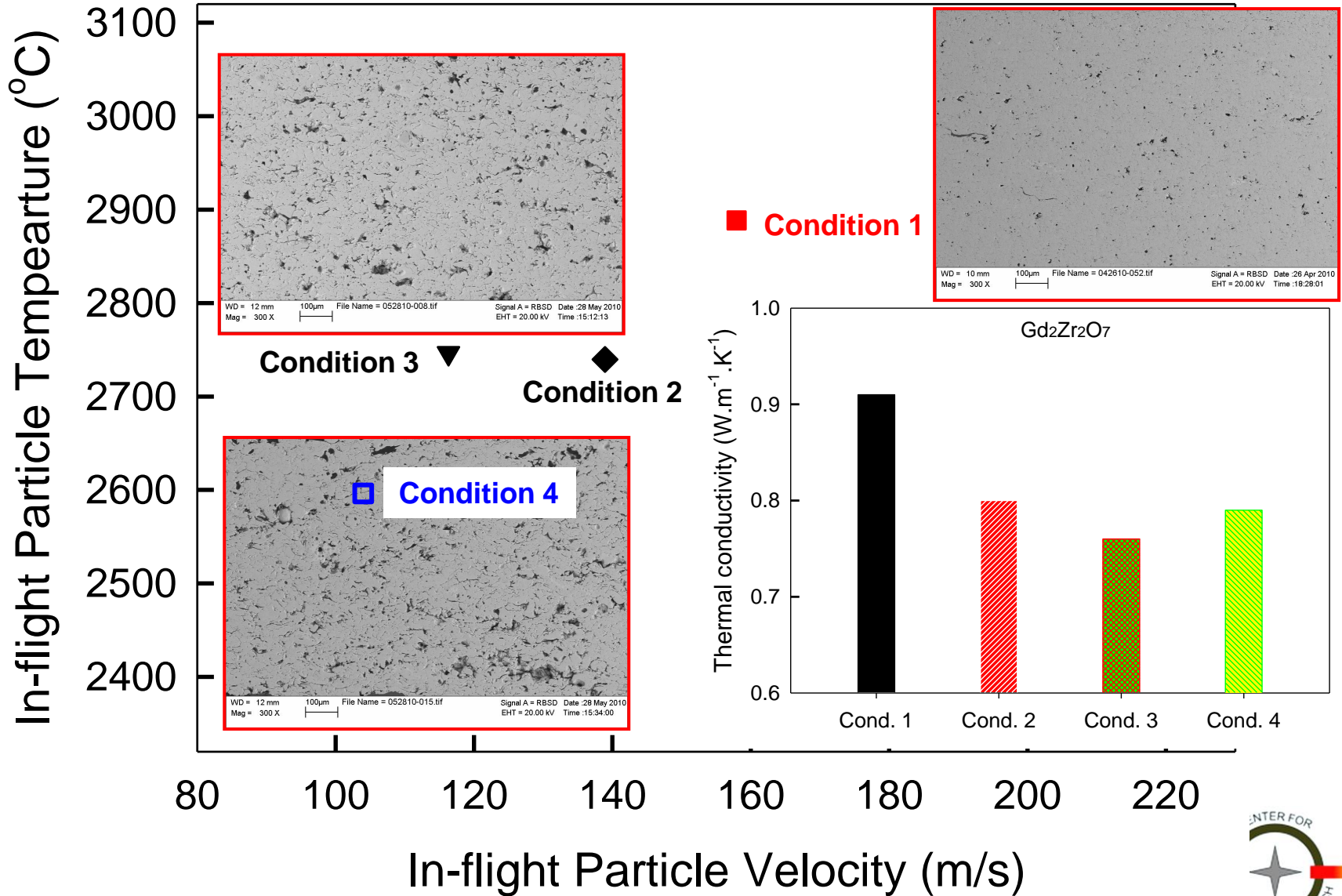
Mechanical Behavior of As-Sprayed Coatings



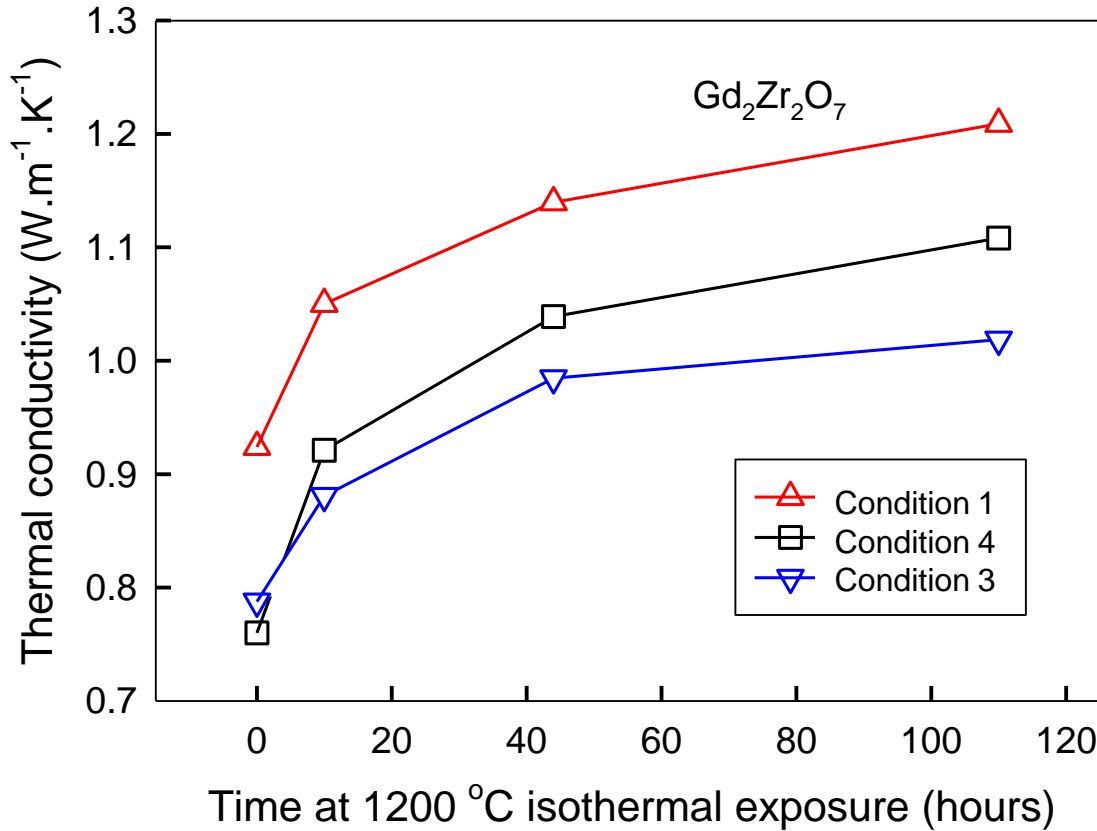
Material choice influences mechanical properties.

IGCC Turbine Coating Properties: Processing Effects

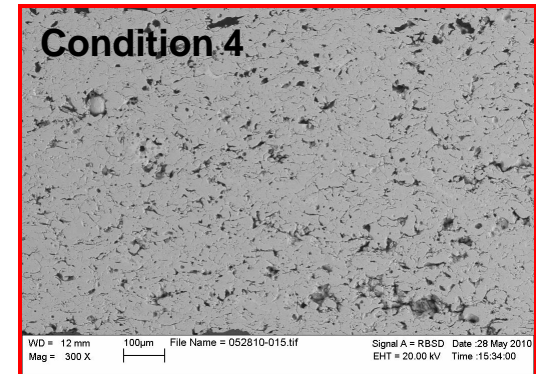
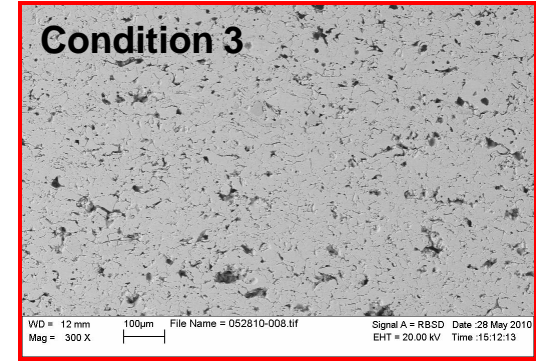
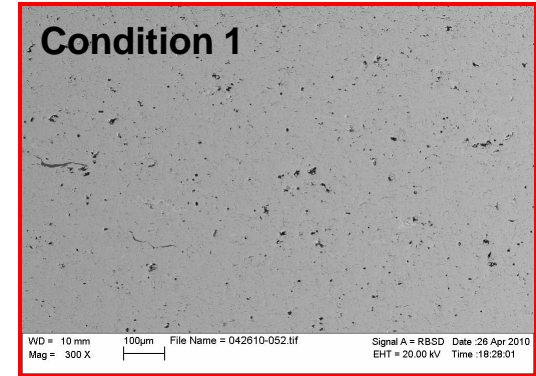
Gadolinium Zirconate $Gd_2Zr_2O_7$



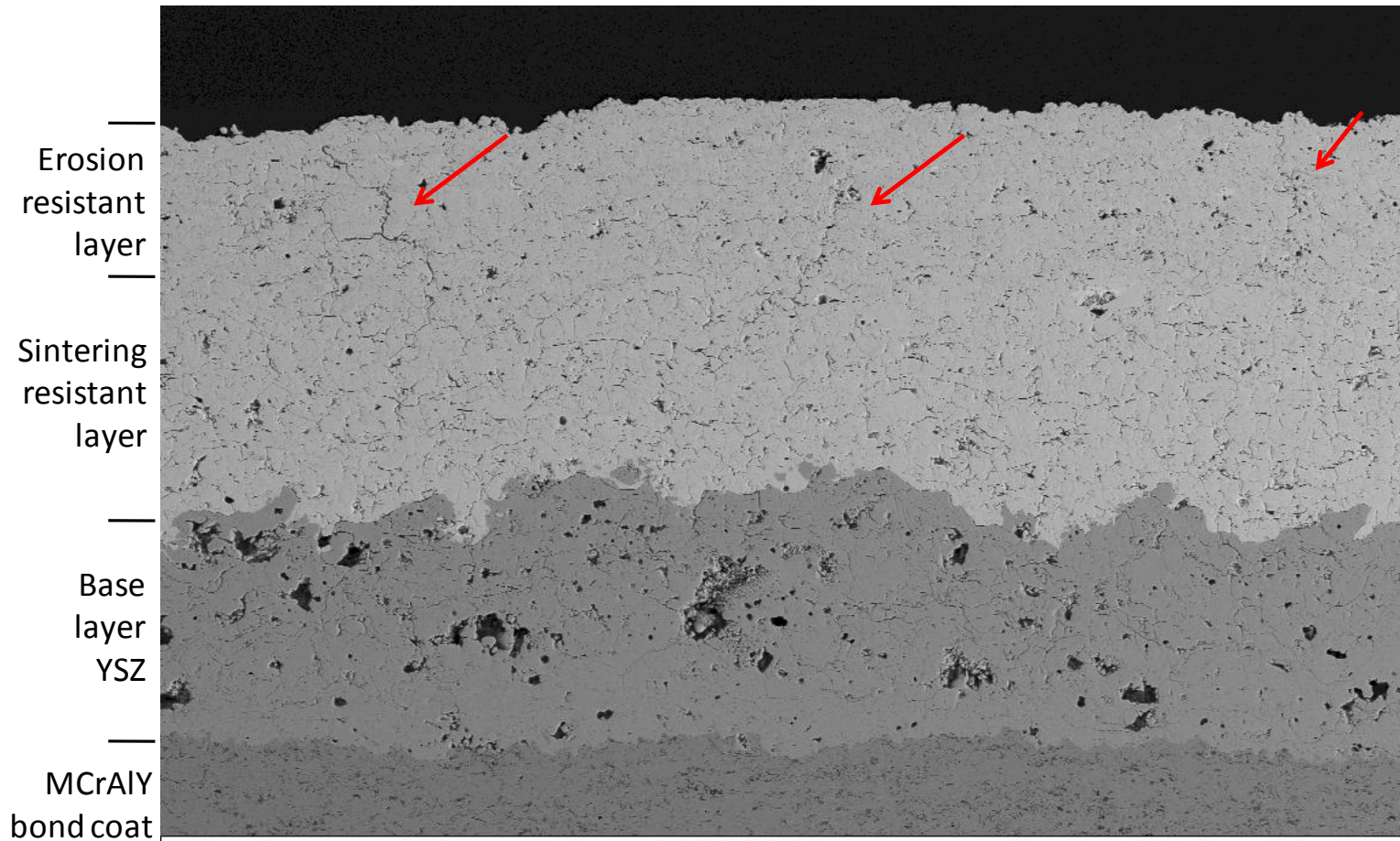
IGCC Turbine Coating Properties: Processing Effects



Microstructure influences thermal properties

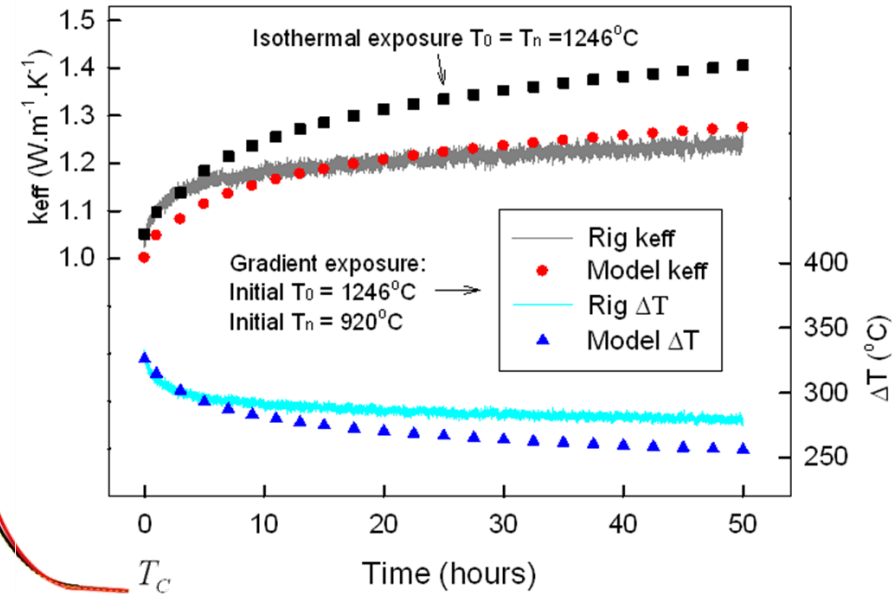
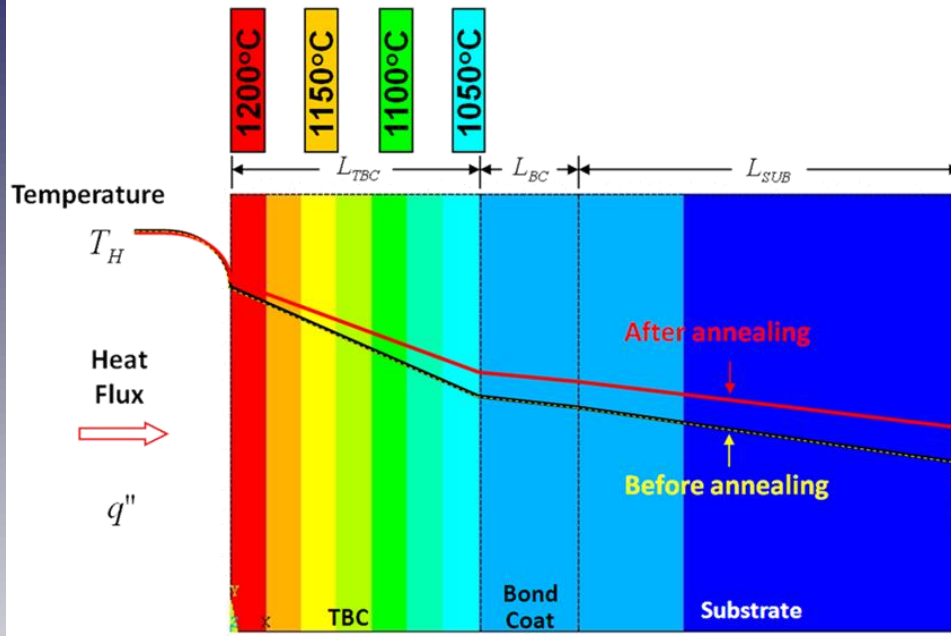


Thermally Sprayed Multilayer TBC



Multilayer coating demonstration

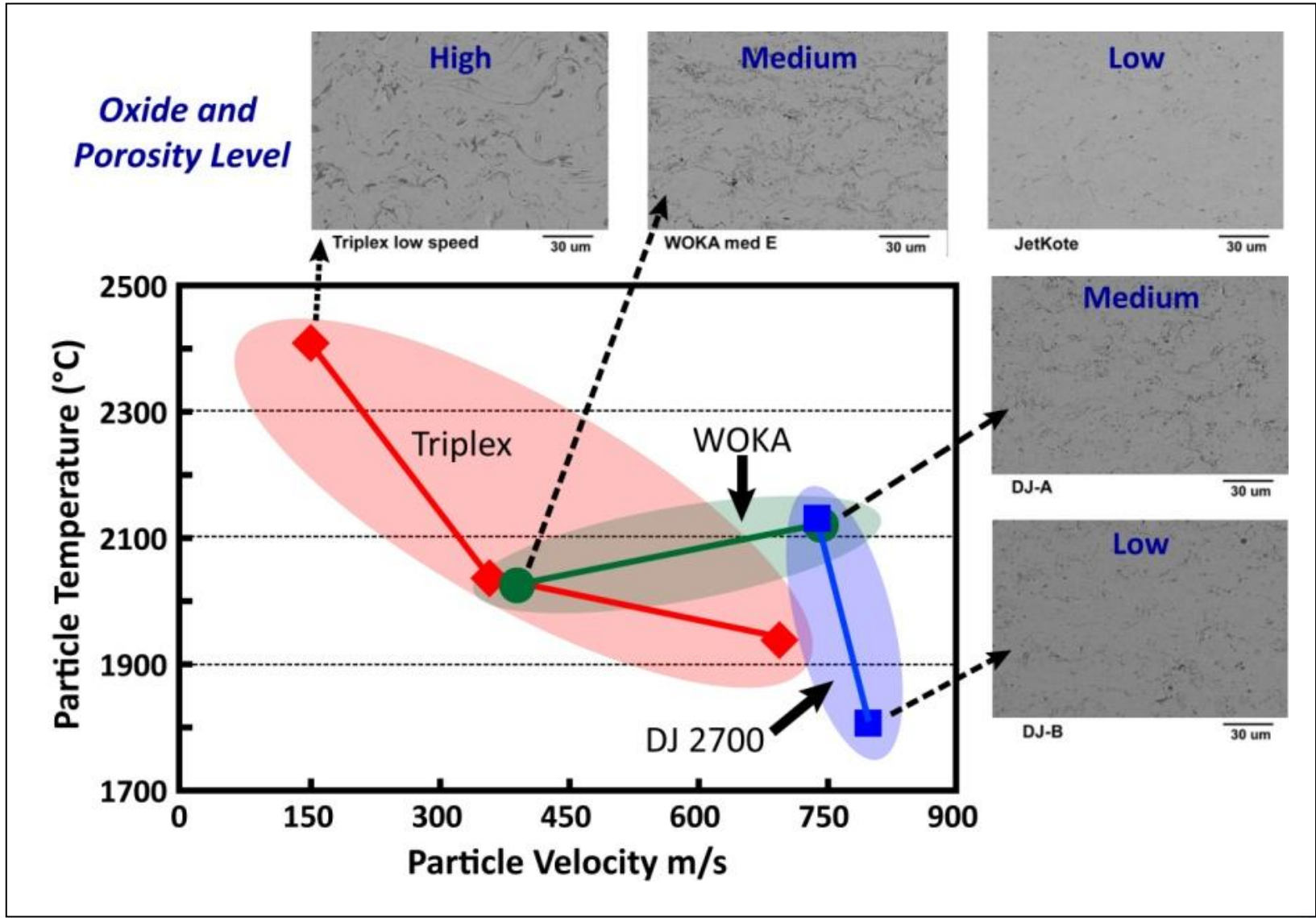
Modeling of Thermal Conductivity Evolution in a Gradient



Schematic of the model used to predict temperature gradients in TBCs from thermal conductivity values determined isothermally.

Comparison of isothermal and thermal gradient models with rig test thermal conductivity and temperature change across the TBC data showing good agreement

Processing Effects on HVOF Bond Coats



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

