Advanced Thermal Barrier Coatings Produced by SPPS

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Abstract

Advanced thermal barrier coatings (TBCs) are needed to achieve the efficiency goals of the Advanced Turbine System (ATS) Program. Such coatings are intended to allow reduced cooling at current combustion temperatures or increased combustion temperature with current cooling flow while retaining current metal temperature. To achieve such goals, the coatings must provide lower thermal conductivity and oxygen diffusion than yttria-stabilized zirconia. Described in this work is the development of Small-Particle Plasma Spray (SPPS), a patent pending thermal spray process which allows exceptional microstructural controlled coatings with features including controlled porosity (>99% dense to graded porosity), controlled morphology and/or numerous layers (nanometers to microns/layer) which can be produced using conventional thermal spray equipment. Thus, materials with the desired oxygen diffusion coefficients, compliance and thermal expansion and hence, strain tolerance and can be engineered to meet TBC requirements.

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In the current studies, optimization of the SPPS processing parameters has taken place using a statistical design of experiments. Six processing variables, at two levels each, have been studied for a baseline alumina sprayed onto mild steel. Evaluation of the processing parameters is judged by microstructural observation, adhesion strength, hardness measured using nanoindentation, and corrosion resistance.

Microstructural observations using optical, scanning electron and transmission electron microscopies indicated splat layers of approximately 11 μm thick with grain sizes between 0.5 and 1μm. The coating remains adhered to the substrate through the ion beam thinning process, indicative of superior adhesion. The coatings are estimated to be between 85 and 98% dense.

The effect of substrate surface preparation on adhesion strength has been investigated. Mechanical interlocking between the substrate and coating, as seen via optical microscopy, is the key to adhesion of plasma-sprayed coatings. SPPS allows powders with smaller particle sizes (smaller than 10μm) to be deposited. The smaller particles create smaller splats which are better able to conform with the finer features of the substrate surface. Substrates ground and grit-blasted with 220 and 400 grit provide adhesion strength greater than those deposited onto substrates grit-blased with 60 grit. Most of the coatings on substrates grit-blasted with 220 and 400 grit could not be pulled off using conventional adhesion tests. However, the adhesion strengths of all of these coatings are comparable to, if not greater than those reported for conventionally sprayed coatings.

The hardness of these coatings has been measured parallel and perpendicular to the spray direction using a nanoindenter. The corrosion resistance has been measured using both an HCI immersion test and a Prohesion test. These results have been correlated to coating density and to the plasma spray processing parameters.

The future activities of the program will focus in two main areas. First, laminated coatings will be produced to provide lower thermal conductivity through enhanced interfacial resistance and the umklapp process of phonon reversal. Second, graded porosity coatings will be made to enhance or provide the strain tolerance afforded by conventional plasma sprayed coatings. In both sets of experiments, baseline studies will be performed using alumina and yttria stabilized zirconia. Other candidate single component and multi-phase materials will be incorporated in the study as they are identified.

Advanced Thermal Barrier Coatings Produced by Small Particle Plasma Spray

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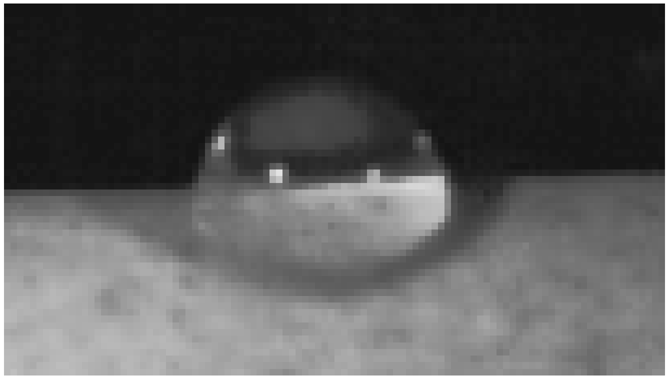
The Small Particle Plasma Spray (SPPS) System:

- Consists of powder feed and injection technology
- Allows powders as small as 200 nm to be thermally sprayed
- Is directly retrofitable to any conventional powder-feed thermal spray system
- Produces >99% dense coatings as thin as 10 μm

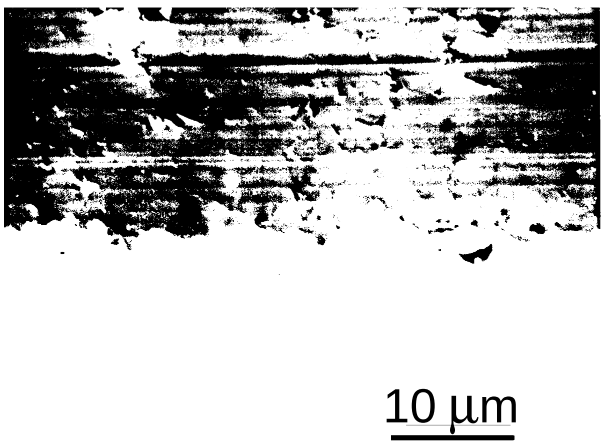


Water bead on a dense SPPS TBC

SPPS vs. Conventional Coatings

SPPS

Al_2O_3

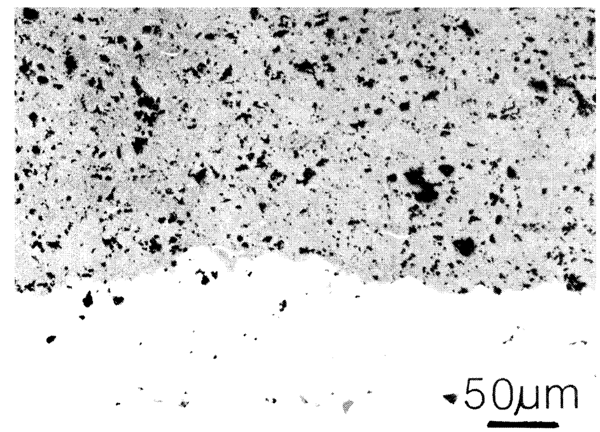


Steel
(blasted
with
400 grit)

- Can have controlled closed porosity: 1% to 40%
- Good adherence with both fine and coarse grit blasting treatments

Conventional Plasma Spray

ZrO_2



- Open porosity typically: > 5%
- Adherence best when substrate blasted with 60 grit

Experimental Plan

Objective:

- To develop and characterize SPPS Al_2O_3 and Al_2O_3-ZrO_2 coatings for thermal barriers and wear applications.

Methods:

- Statistical Design of Processing
- Microstructural Characterization by Optical, Scanning Electron, and Transmission Electron Microscopy
- Hardness and Elastic Modulus by Nano-Indentation
- Adhesion by Tensile Tests
- Corrosion Resistance by HCl Immersion

Optimization of SPPS Processing Parameters

Power, P 35, 45 kW	Spray Distance, d 6, 7 cm
Primary Gas Flow, f_p 35, 45 slm Ar	Radial Distance, r 6, 7 mm
Carrier Gas Flow, f_c 5,7 slm H_2	Spray Parameter, s

Test matrix = 2^6 = 64 experiments

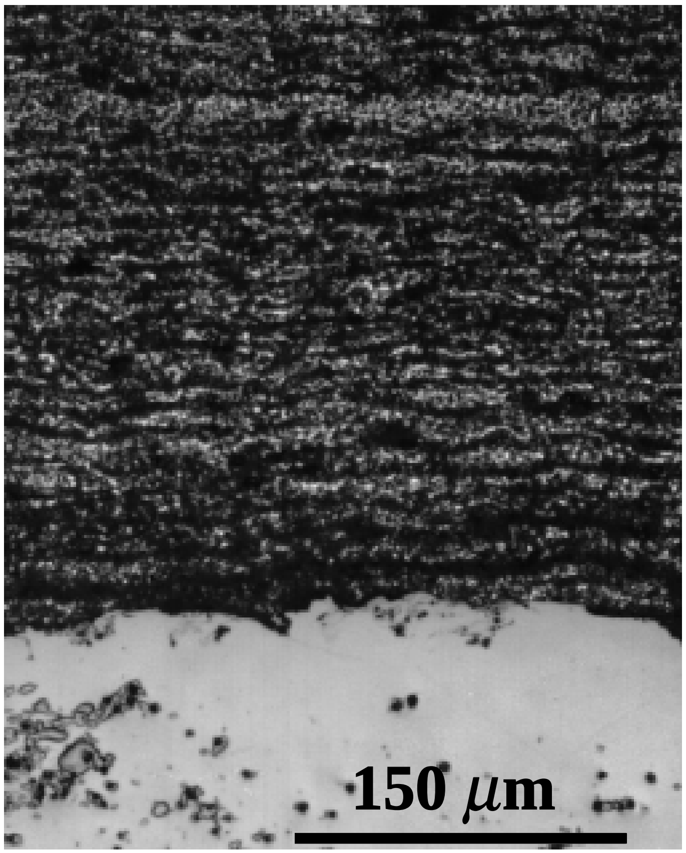
With statistical design of experiments:

Examined 6 variables + 8 two factor interactions (e.g. power/spray distance) with 16 experiments.

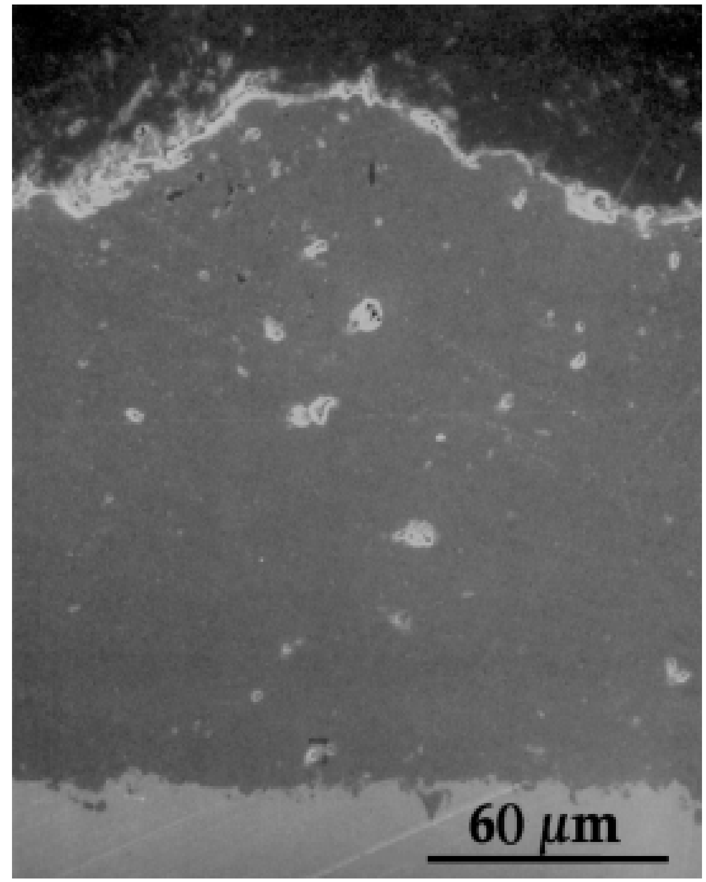
Thickness described by a four degree linear response surface:

$$\text{Thickness} = 131.3 - 47.9f_p + 20.6d + 16.2P - 13.8s$$

Alumina SPPS Coatings

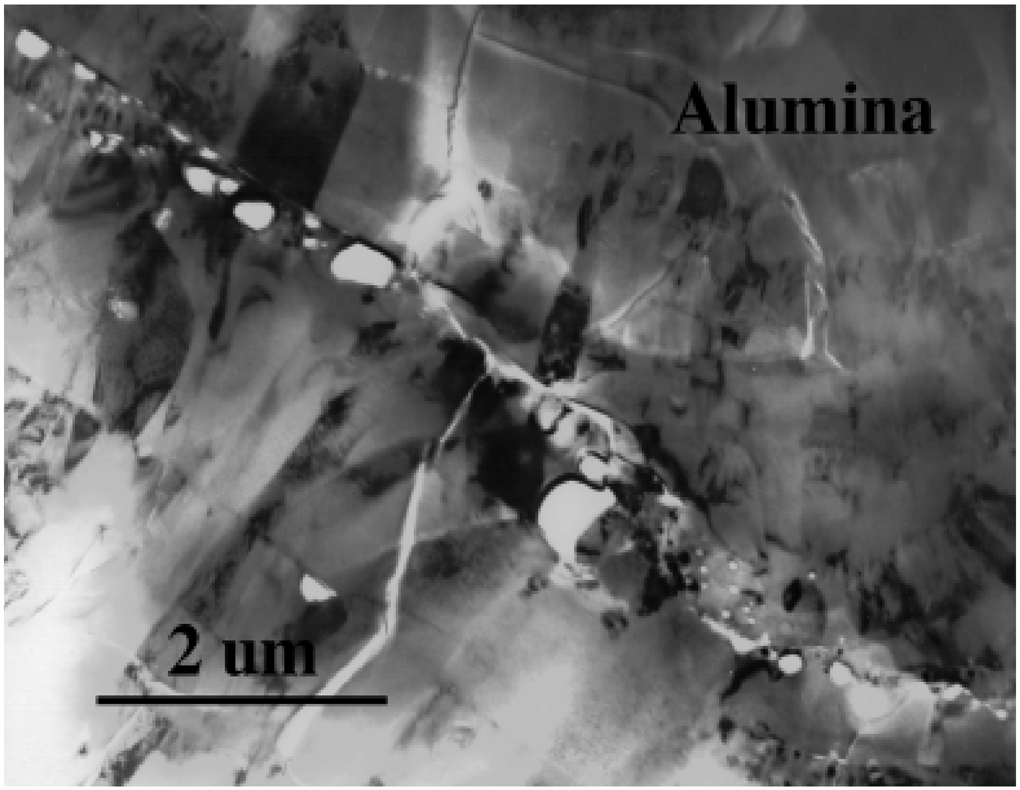


Transmission optical image of a TEM foil

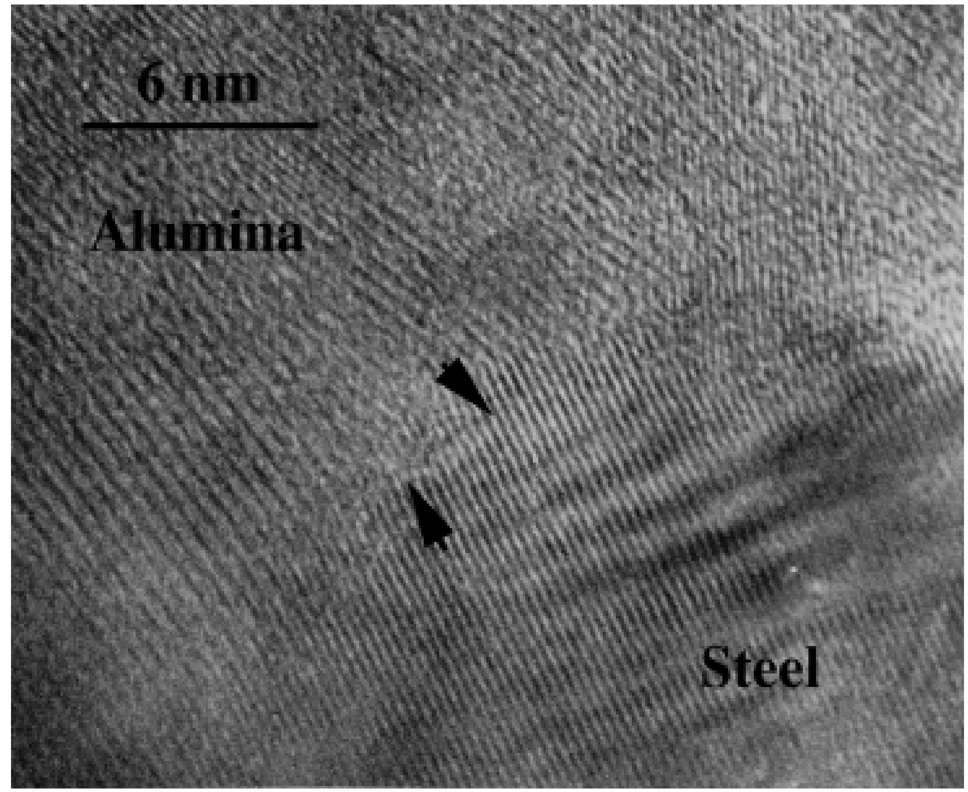


SEM micrograph of a polished cross-section

Alumina SPPS Coatings

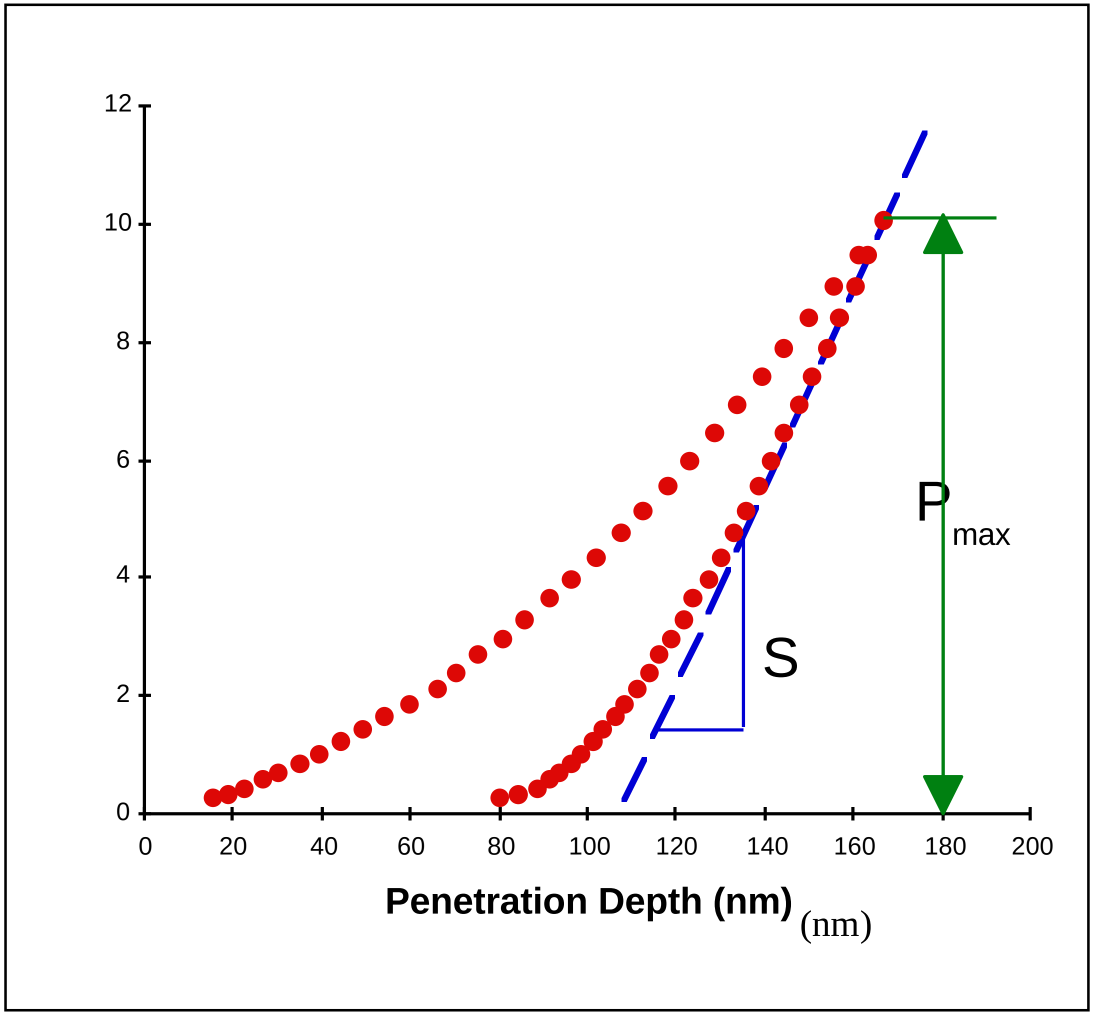


TEM micrograph revealing micro-porosity between splats



HR-TEM micrograph of the coating-substrate interface

Nano-Indentation Theory



$$H = \frac{P_{max}}{A_{impression}}$$

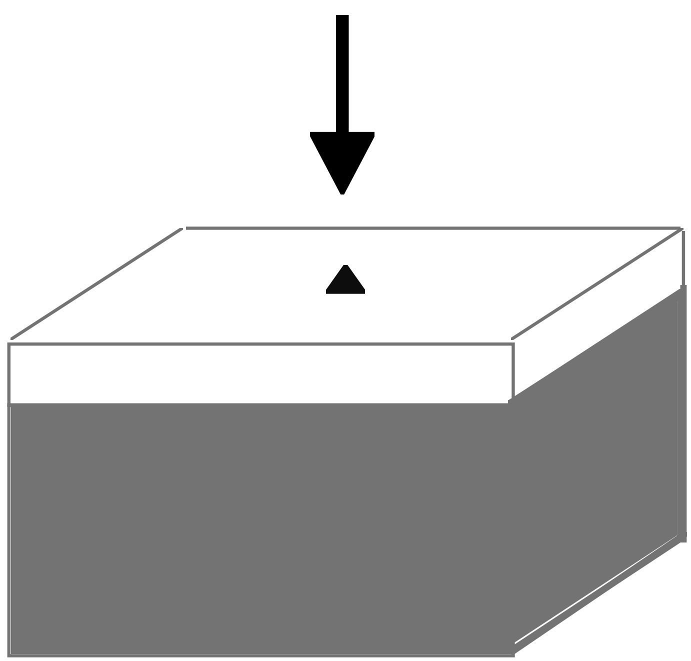
$$\frac{E}{(1-\upsilon^2)} = \left[\frac{1}{E_{reduced}} - \frac{(1-\upsilon_i^2)}{E_i} \right]^{-1}$$

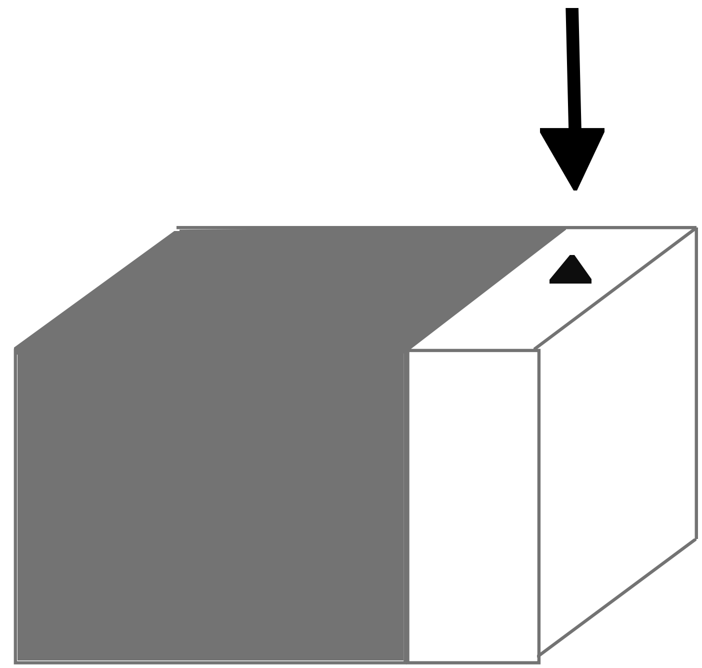
where:

$$E_{reduced} = \frac{S}{2} \left(\frac{\pi}{A_{contact}} \right)^{1/2}$$

Reference: W.C. Oliver & G.M. Pharr, *J. Mater. Res.*, **7** [6] 1564-83 (1992).

Nano-Indentation Results





- Parallel to Spray Direction:

  H = 14 ± 4 GPa

  E = 191 ± 27 GPa

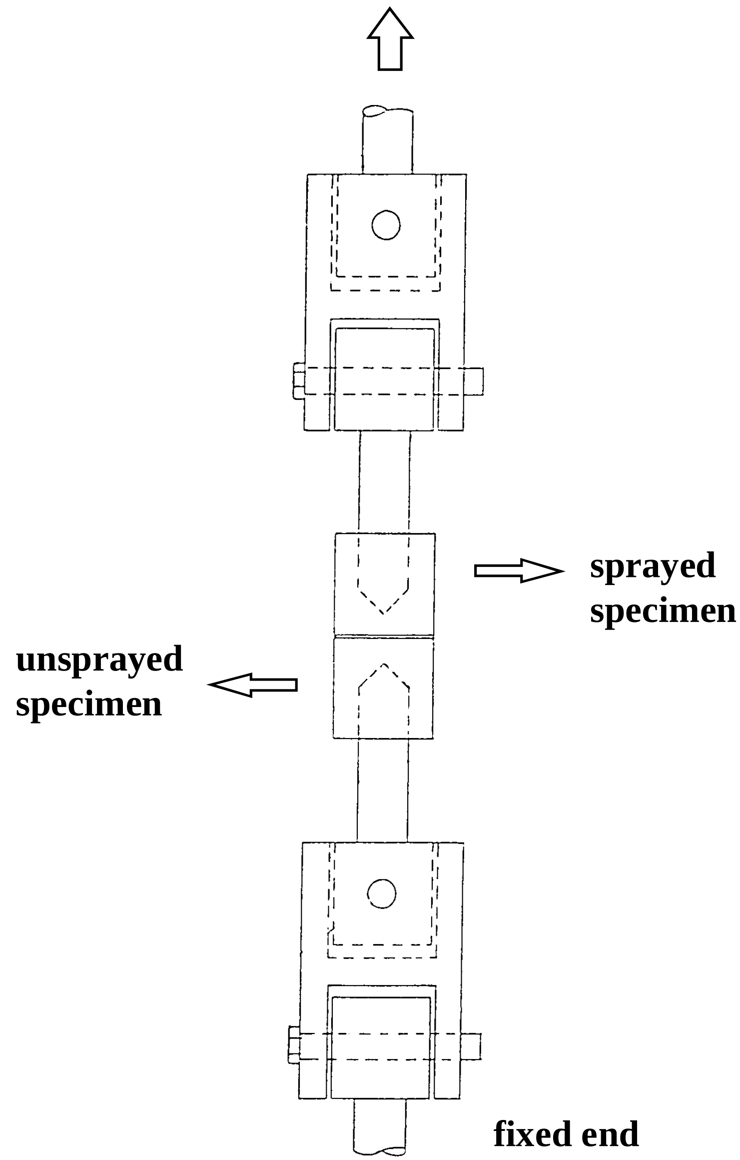
- Perpendicular to Spray Direction:

  H = 10 ± 2 GPa

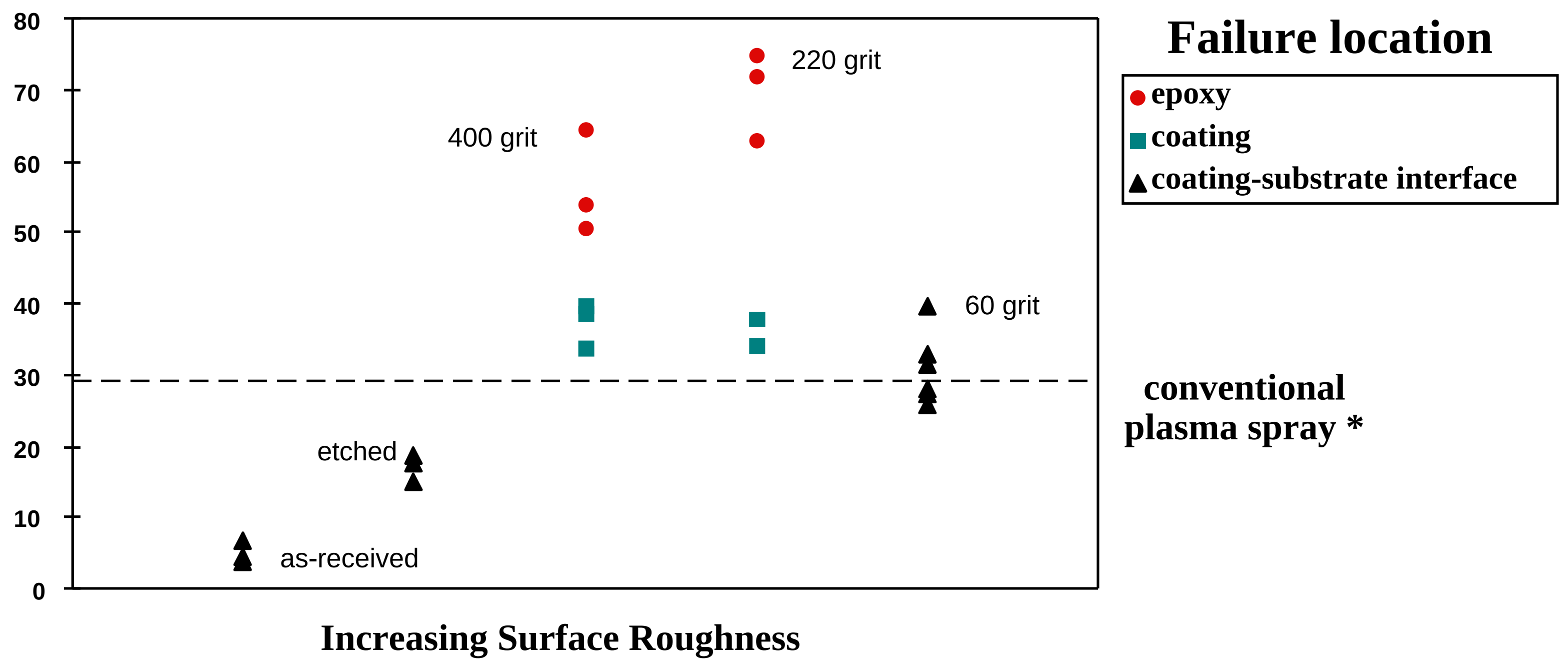
  E = 150 ± 30 GPa

Adhesion Pull Test

- Investigate effects of surface treatment on adhesion strength
- ASTM C633-79 standard for flame-sprayed coatings
- Epoxy: EC-2214 by 3M
- Apply tension until rupture
- Adhesion strength = maximum load /cross-sectional area

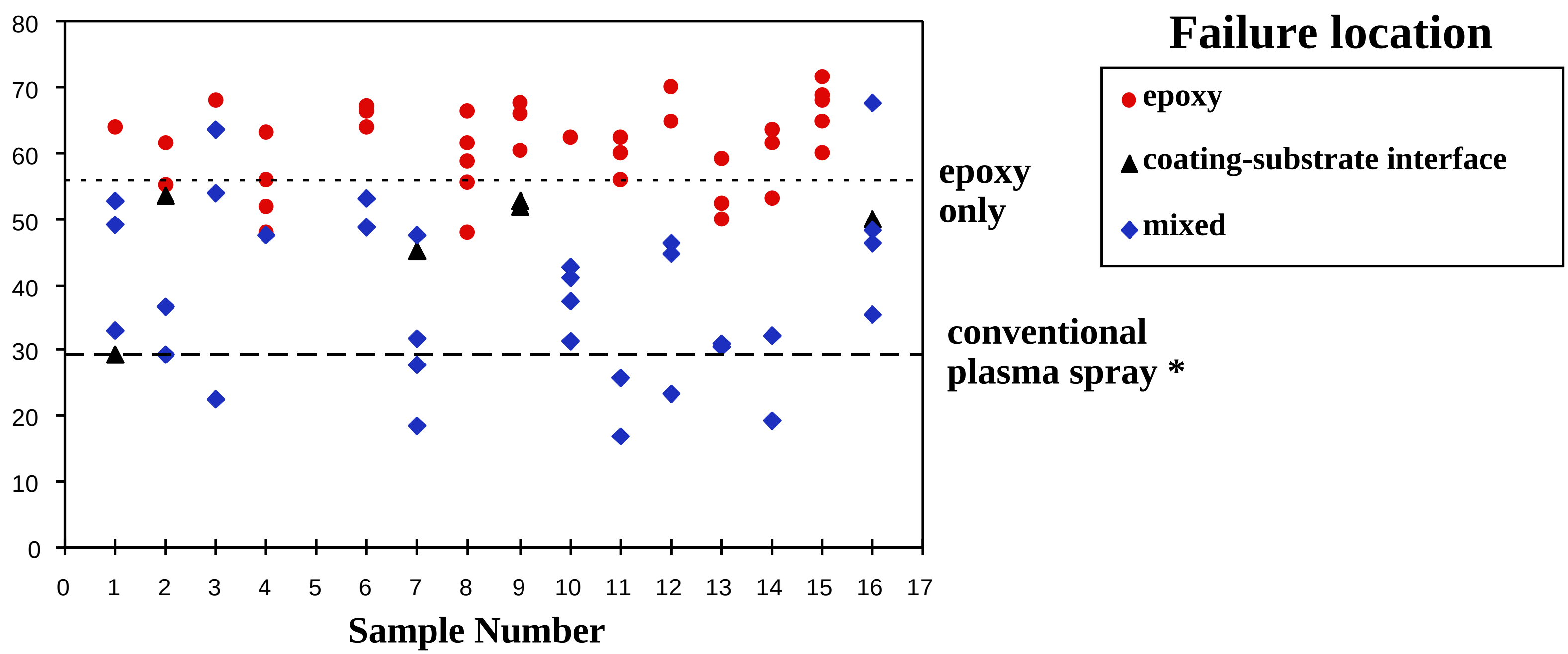


Adhesion Strength vs. Surface Roughness



* W. Han, E. R. Rybicki, and J. R. Shadley, *Proceedings of the National Thermal Spray Conferencce*, 1993, Anaheim, CA.

Adhesion Strength vs. Sample Number

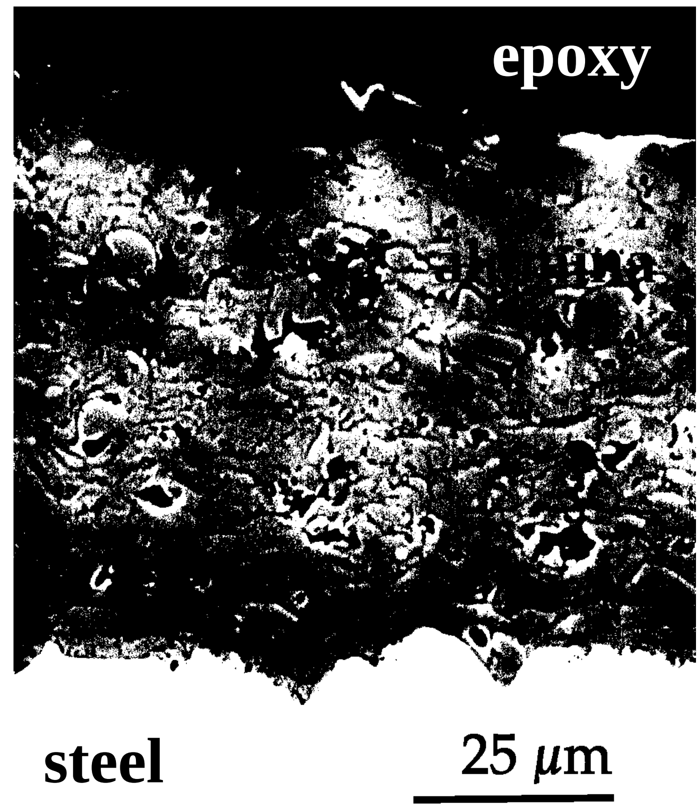


*** W. Han, E. R. Rybicki, and J. R. Shadley, *Proceedings of the National Thermal Spray Conferencce*, 1993, Anaheim, CA.**

- Al_2O_3 coatings on 220 grit-blasted steel substrates

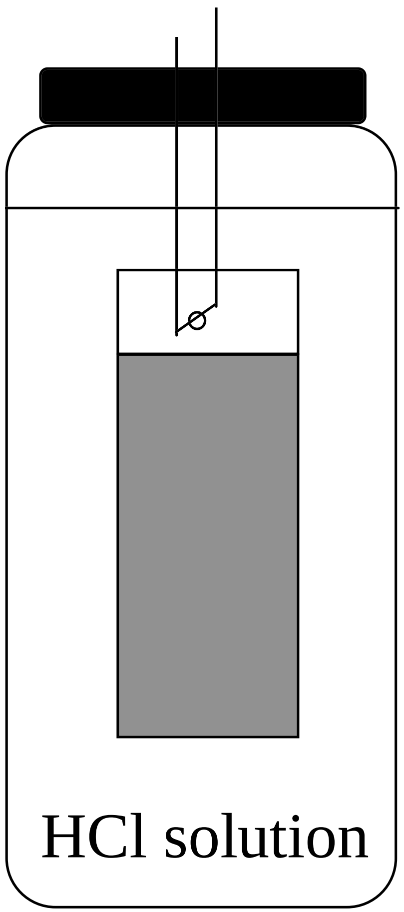
Adhesion Pull Test Results

- 45% of the samples failed in the epoxy
- Epoxy did not penetrate into the coating
- Coating adhesion strength is higher than epoxy strength
- Minimum coating strength = 62 MPa



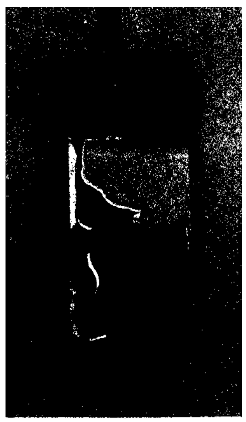
Corrosion Test Procedure

- Immersed specimen in 0.03 M HCl solution
- Observed damage by visual inspection
- Recorded coating lifetime (i.e. time initial cracking was observed)



Corrosion Test Results

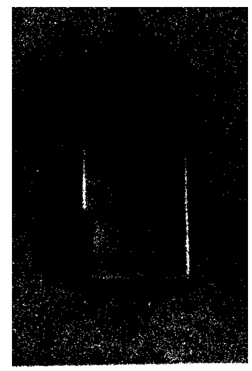
24 h



#12

#14

121 h



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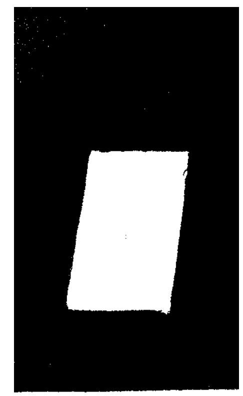


#10

- Coating lifetime ranged from 24 - 121 hours
- Lifetime does not systematically vary with thickness

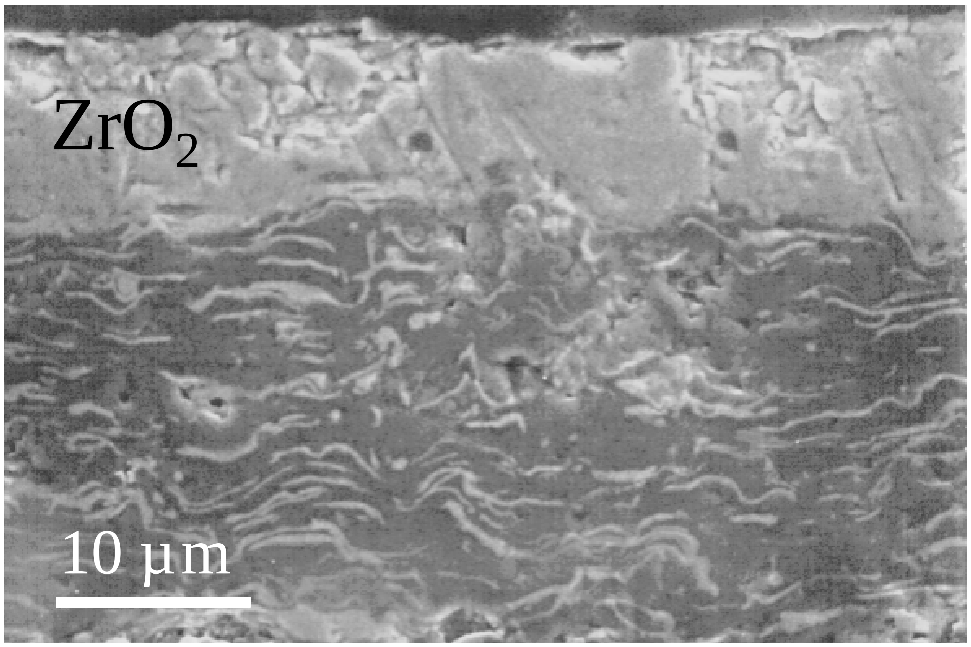
Summary: Al_2O_3 SPPS Coatings

- Small Particle Plasma Spray has been demonstrated to produce dense, micron-sized coatings.
- Through statistical design of experiments, a model to describe coating thickness as a function of processing variables has been developed.
- There is no statistical difference in hardness or modulus as a function of processing conditions.
- Adhesion strength of the SPPS coatings surpasses tensile strength of epoxy.
- Coatings retain their mechanical integrity for up to 120 hours in HCl.

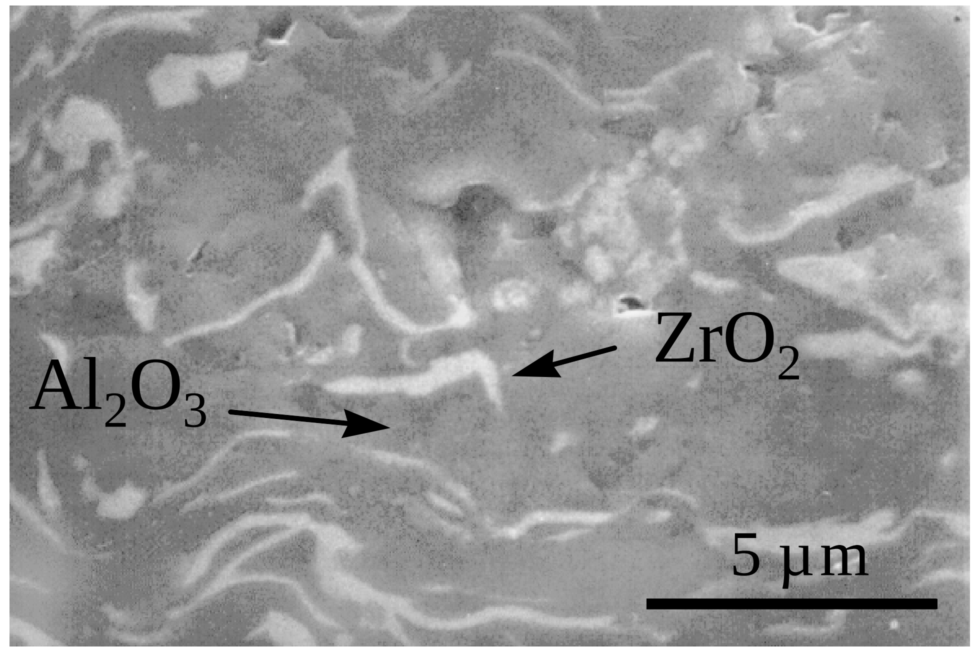
Al_2O_3-ZrO_2 Coatings

- Mechanically blended powders of 50% Al_2O_3 and 50% ZrO_2 (yttria-stabilized).
- Sprayed with standard conditions for YSZ coatings.
- Al_2O_3 and ZrO_2 splats are well mixed, but remain distinct.
- Implications for a variety of composite coatings: multiphase, laminates, and coated powders.

Al_2O_3-ZrO_2 Coatings



SEM micrograph revealing a relatively uniform top layer of ZrO_2



Deposition of alternating layers of the two materials is possible

Planned Studies

AGTSR

Northwestern/ACTG

Technical steering committee: ORNL, GE, AlliedSignal, Allison, NASA-LeRC, and P&W

Multi-Layer

- micrometer thick layers
- enhanced toughness from delamination
- lower thermal conductivity from interfaces

Graded Porosity

- more pores near the TBC surface
- creates desired elastic modulus anisotropy
- lower thermal conductivity from pores

Materials Engineering

- coated powders
- control grain growth and sintering

Acknowledgments

- Work on thermal barriers supported by the U. S. Department of Energy's Fossil Energy Technology Center, under Cooperative Agreement DE-FC21-092MC29061 with the South Carolina Energy Research and Development Center, under subcontract No. 96-01-SR047 (Daniel B. Fant, Technical Representative for AGTSR) for the period June 13, 1997 through June 12, 1998

- Work on hard coatings supported by the Defense Advanced Research Projects Agency, through Hard Chrome Alternative Technology Program, Hugh DeLong, Contract Monitor