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Advances in the Development of Silicon Nitride and Other Materials

Environmental Barrier Coatings Workshop

November 6, 2002 - Nashville, TN

Mark van Roode

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Outline

- Ceramics for Gas Turbines
- Evolution of Monolithics
- Critical Technical Issues
- Commercialization Issues
- Summary

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Ceramics For Gas Turbines

VP19990003-09-003

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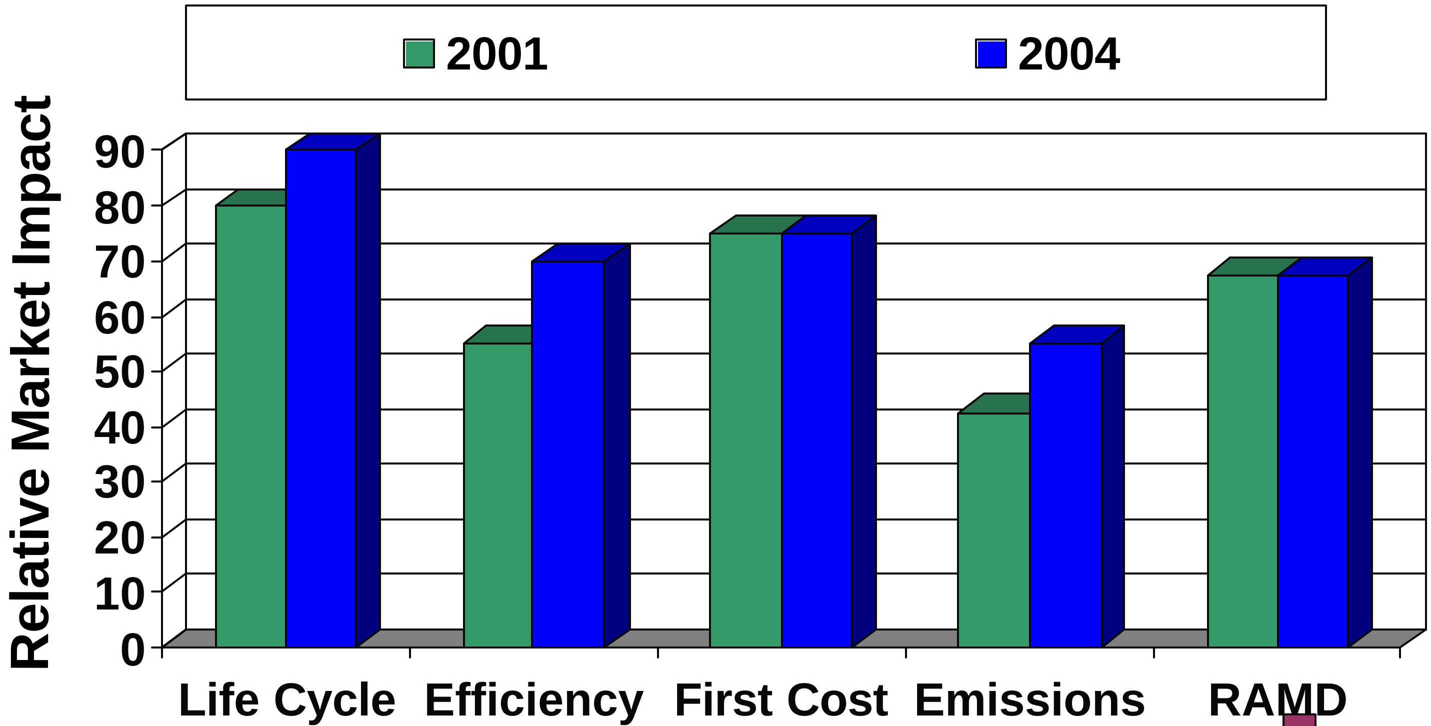
Gas Turbine End User Buying Criteria



Single Digit NOx, CO

- Increase Firing Temperature
- Increase Pressure Ratio
- Reduce Component Cooling
- Extend Component Life

Low Component Cost
- Inexpensive Materials
- Low Cost Processing
- Simple Designs

- 30,000 hrs TBO
- Min. 30,000 hr Component Life
- No unscheduled Shutdowns

Superalloy Components

- Superior Ductility and Thermal Conductivity
- Operating Temperature Limitation: 900°C for Uncooled Components
- Turbine Inlet Temperatures (TITs) are increasing
- Emissions of NOx, CO Need to be Reduced
- Management of Air is Required
  - Sophisticated Cooling Schemes and Coatings for Higher TITs
  - Spatial Limitations to Cooling for Smaller Engines
  - Inconvenience of Steam Cooling for Larger Engines

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Ceramic Components

Good Mechanical Properties up to 1300 - 1400°C

Reduced Cooling Air Requirements

Increase Turbine Inlet Temperatures → Increased Efficiency and Output Power

More Air Available for NOx and CO Emissions Reduction

Light Weight – Important for Transportation Applications

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Ceramic Gas Turbines - Potential Benefits

- Anson et al. , ASME 92-GT-393 (US data)
  - Potential annual fuel savings from more efficient small gas turbines incorporating ceramics:
    - US: 0.2 Quads by 2010 - $ 600M @ $ 3/MBtu Nat.Gas
- Grondahl and Tsuchiya, ASME 98-GT-186
  - MS9001FA Gas Turbine
    - Ceramic transition piece, two stages of buckets, nozzles, shrouds
    - 2-3 Percentage points in combined cycle efficiency improvement compared to current metal engine
- Solar Turbines: Potential component cost savings
  - Silicon nitride blade: 30% of cost of cooled single crystal blade
  - Silicon nitride nozzle: 65% of cost of cooled superalloy nozzle

Monolithics vs. Ceramic Matrix Composite

Monolithics	Ceramic Matrix Composites
Si_3N_4, SiC, Sialons	SiC/SiC, Oxide/Oxide
Superior HT Strength	Lower HT Strength
Lower K_{1C} < ~ 9 MPa.m^{½}	Higher K_{1C} < ~ 25 MPa.m^{½}
Design Stress up to 200-300 MPa	Design Stress < 70-100 MPa
Limited to Small Components	Can Be Used for Larger Components
Lower Cost	Higher Cost
For Smaller Engines	For Larger Engines

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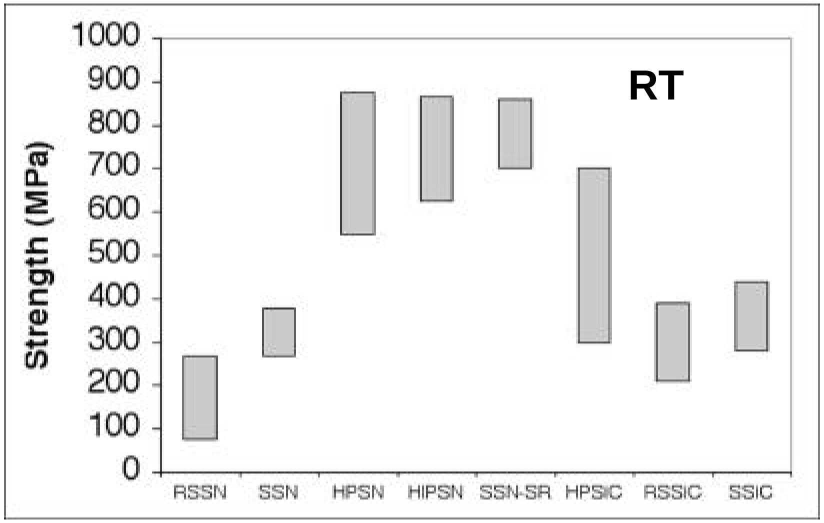
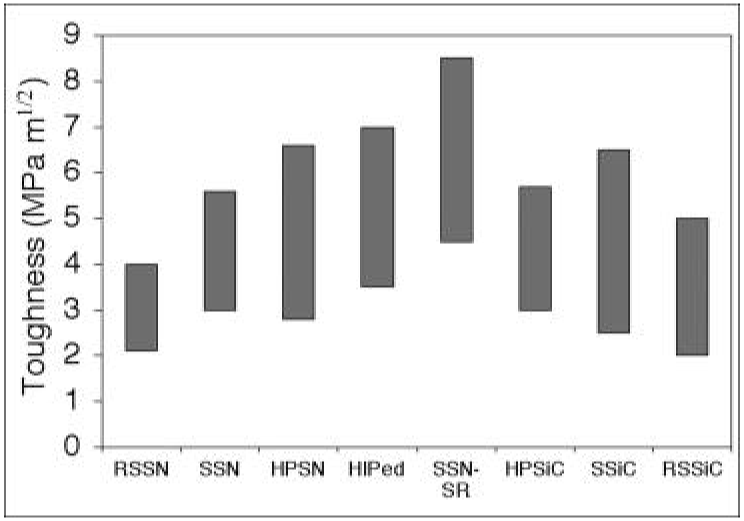
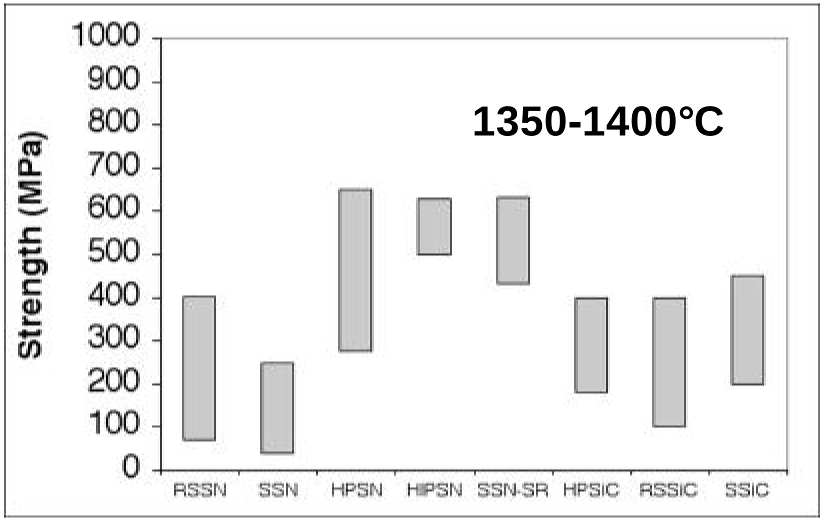
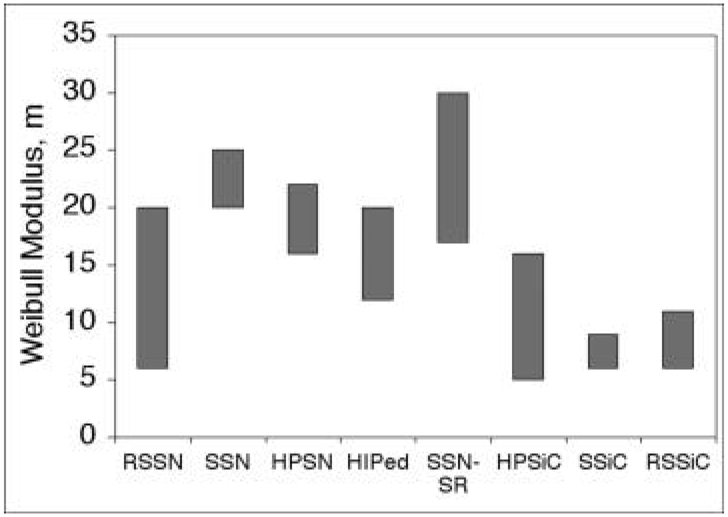
Evolution of Monolithics

Evolution of Monolithics









Courtesy M.K. Ferber, ORNL

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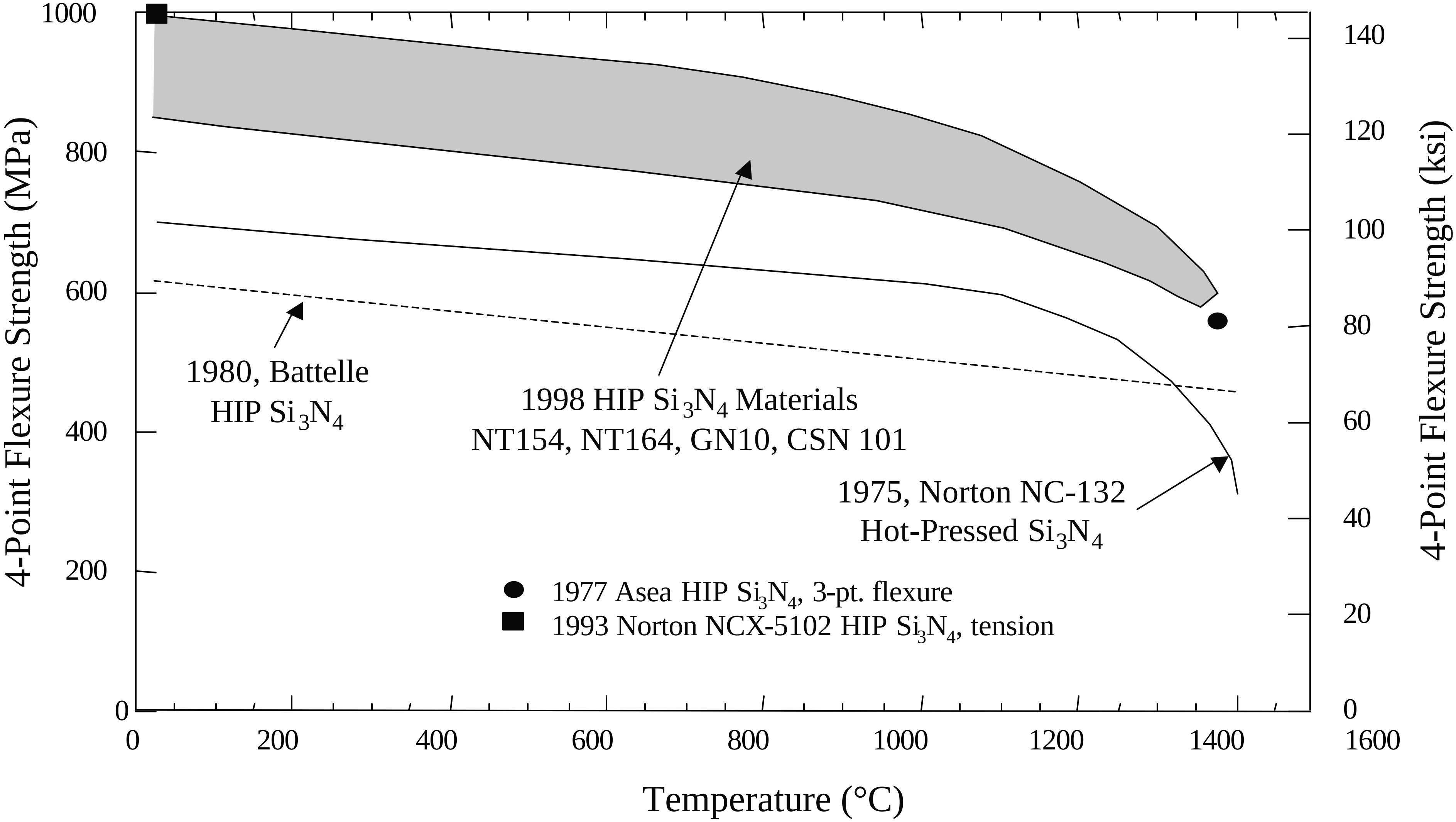
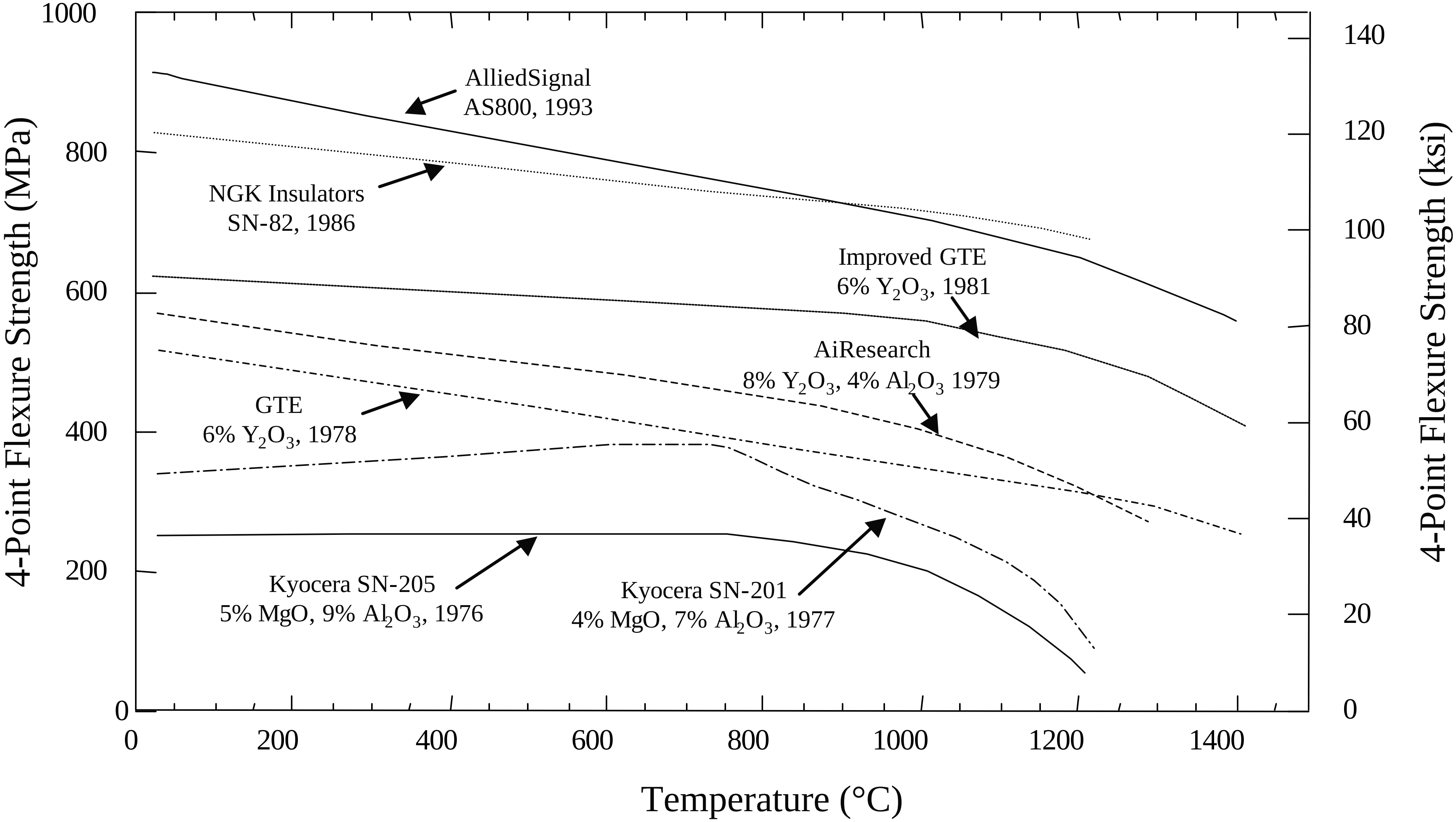
HIP Si_3N_4



Courtesy D.W. Richerson



Courtesy D.W. Richerson

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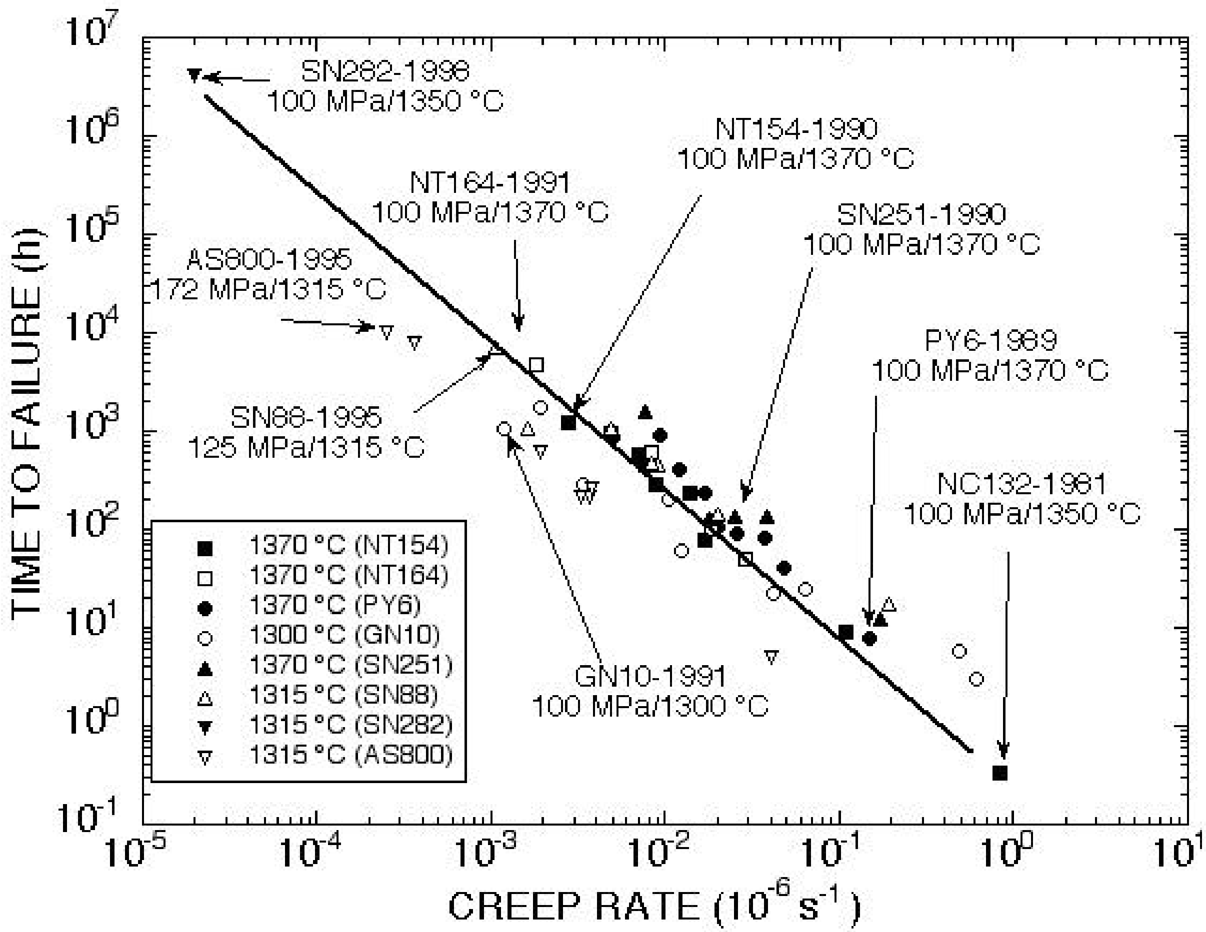
Creep Resistance



Courtesy M.K. Ferber, ORNL

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Critical Technical Issues

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Issue 1. Ceramics vs. Metals

Ceramics have improved but so

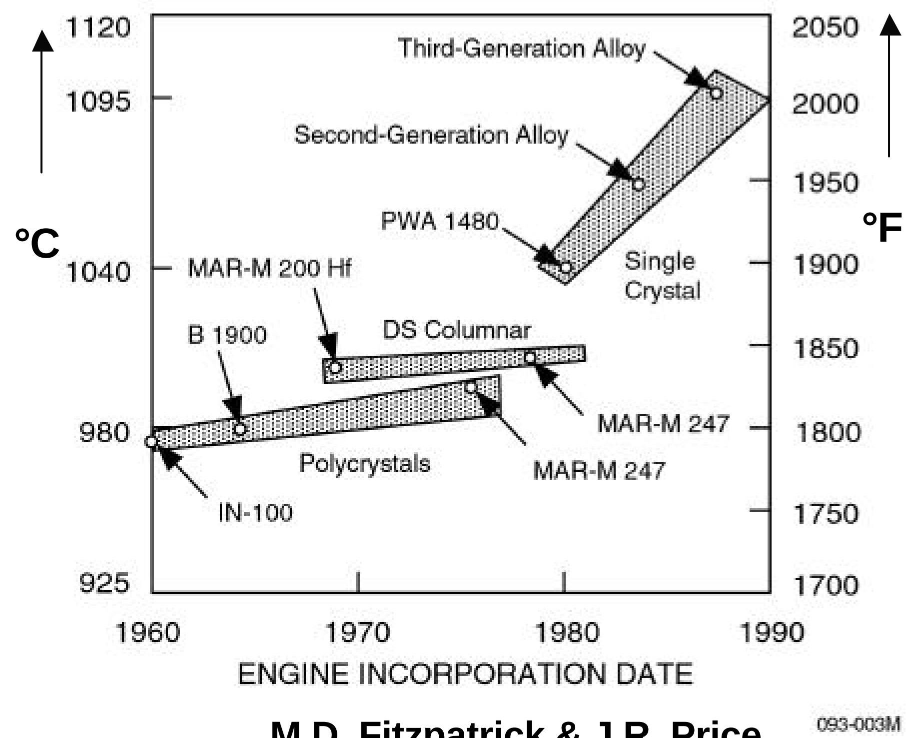
have metals

Metal Design Options up to 1500°C

- **Complex Expensive Cooling Schemes**

Example – TEPCO 20 MW Program

- **Combined Cycle Power Plants**
- **Ceramic Nozzles, Blades, Combustor, Transition Piece**
- **1984: Metal Components - 1100°C Capability**
  - **Ceramic Components for 1300°C Class Gas Turbine**
- **1990: Metal Components - 1300°C Capability**
  - **New Ceramic Target: 1500°C Class Gas Turbine**



M.D. Fitzpatrick & J.R. Price
Solar Turbines Incorporated

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Issue 2. Ceramics Have Insufficient Impact Resistance

- **Critical for Rotor Blades, Integral Rotors (Blisks)**
- **Stresses> 200 MPa – Significant Mechanical Stress Component**
- **Foreign Object Damage (FOD), Domestic Object Damage (DOD)**

- **Rig test at Daimler-Benz**
- **HPSN (NC132) Gasifier Rotor**
- **Survived ~ 57 hrs at T up to 1060°C**
- **Failure at 42,000 rpm and 1000°C**
- **Cause FOD/DOD from piece of combustor metal, melted after overheating**

Hagemeister et al., ASME 83-GT-305, 1983

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Issue 3. Component Surface Condition

- DOE/Solar Ceramic Stationary Gas Turbine (CSGT) Program
- SPSLIFE, NASA CARES/Life: Fast Fracture, Slow Crack Growth
  - SCG: Life Limiting -186 MPa Airfoil Stress -1121ºC TRIT - 30,000 hrs Life Target

Si_3N_4	POS (Blade)	POS (Blade Set)
NT-164 (HIP-SN)	0.96355	0.10004 (GN-10 Similar)
AS-800 (SSN-SR)	0.99999	0.99976
SN-253 (SSN-SR)	0.99993	0.99567
SN-88 (SSN-SR)	0.99998	0.99908

- HIP-SN Materials Have Low POS because of Surface Condition
  - NT-164,GN-10: 1st Gen. Si_3N_4 - Short Term Tests Only
- SSN-SR: AS-800,SN-253/281,SN-88 2nd Gen. Si_3N_4 - Long Term (Engine) Testing

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Issue 4. Ceramics Suffer Contact Stress Damage at Metal Interface

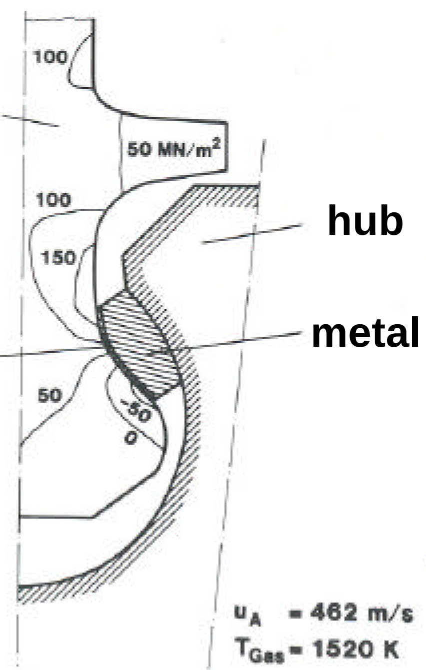
- **Critical for Inserted Rotor Blades**
- **Use Compliant Layer to Mitigate Contact Stresses at Blade Root**
- **Source of Failure in Rotor Blade Tests**
- **Long Term Durability of Compliant Layer Interface Uncertain**

blade

hub

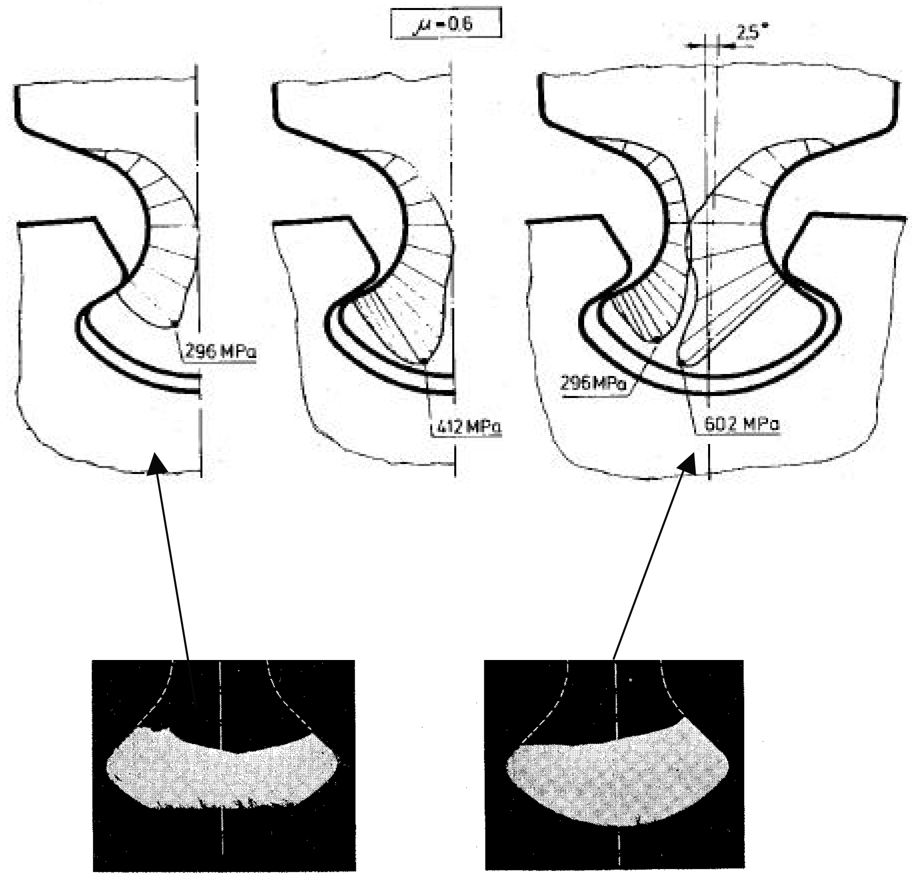
coating

metal pad



Walzer and Langer MTZ Motortech. Zeitschrift, 44[6], 225-228, 1983

Hagemeister et al., ASME 83-GT-305, 1983



Dovetail Blade Failure, Trappman And Rottenkolber, 1978

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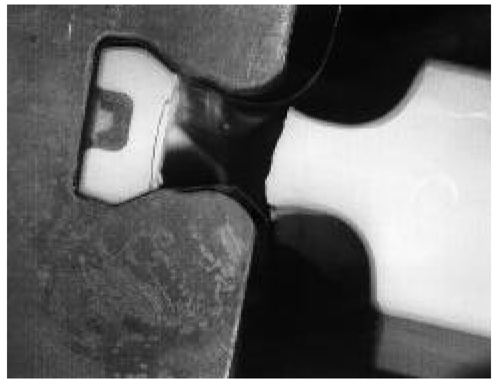
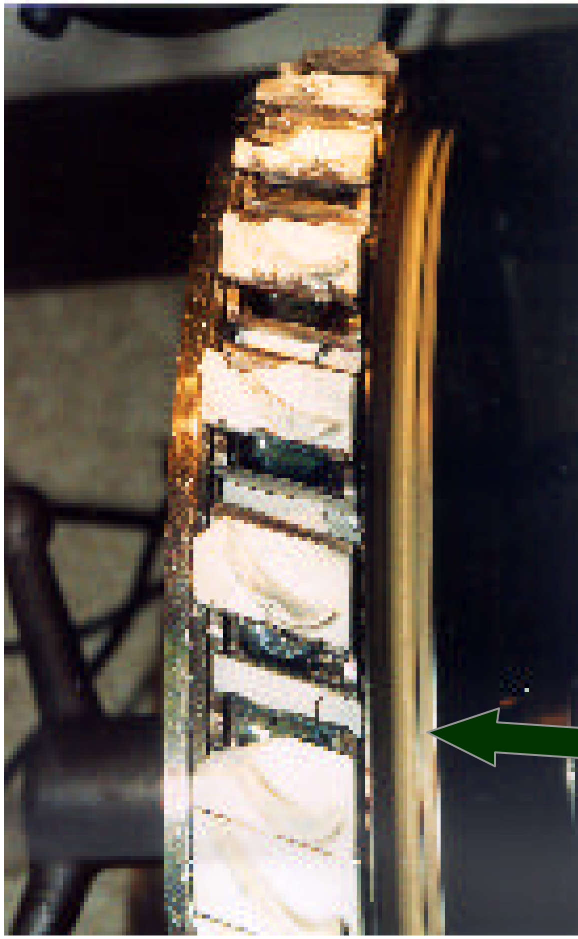
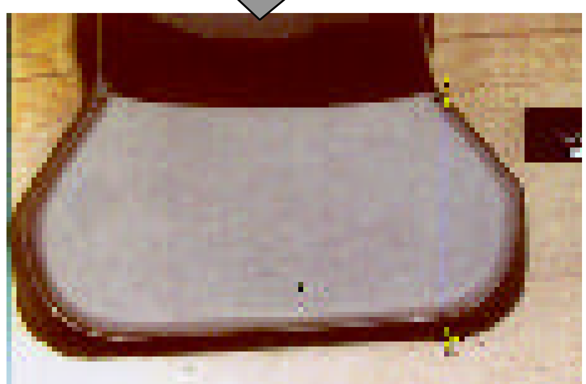
Compliant Layer and Impact Failure

(c) Attachment test failure
Ni-alloy+Pt compliant layer





(a) Rotor with AS-800
blade residues



(b) Failed blade root:
Ni-alloy+Pt compliant layer

- In-house engine test 1996
- 58 hrs at 1010°C TRIT
- AS800 Si_3N_4 Blade – Honeywell Ceramic Components
- Failure initiated as a result of compliant layer Failure
- Ni-alloy/PT CL failed in the root
- Ni-alloy/Pt/BN failed above th platform
- Secondary Impact Failure
- Attachment Test
  - Ni-alloy/Pt CL: 2 cycles
  - N-alloy/Pt/BN: 5000 cycle

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Integral Rotor

- SN252 Si_3N_4 Rotor
- 1000 hr Durability Test
- T > 1427°C
- Blade Tip Rubs
- C Particle Impact
- Molten Superalloy Debris

P.Khandelwal & P. Heitman,
Rolls-Royce, in Ceramic Gas
Turbine Design and Test Experience
ASME Press, 2002

INTEGRAL ROTORS

- No Compliant Layer with Disk
- Attachment Ceramic Rotor to Metal Shaft
- Primarily Small Parts
- Ability to Fabricate Larger Parts Has Improved
- Integral Rotors are Replacing Metal Disks with Inserted Blades

Honeywell Rotor Operating for > 6000 hrs
In Industrial Facility in Utah

Courtesy Honeywell Engines, Systems & Services

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Issue 5. Ceramics Need Rub Tolerance

- Durability to Withstand Rubs: Critical For Optimizing Efficiency Gains
- Rotating Parts: Inserted Blades, Integral Rotors
- Important for Small Engines: Example IHI CGT301 300 kW Program

Clearance	Turbine Efficiency	Cycle Efficiency	TIT	Comments
0.2 mm	87.5%	42%	1350°C	Design Point – Engine Failure
0.8 mm (Cold) 0.5 mm (Hot)	76% 79%	35%	1350°C	Eff. Loss Primarily from Excess Clearance

Data courtesy IHI

- Need Abradable (Rub Tolerant) Tip Shroud for Clearance Control
  - Dense Silicon Nitride Base – Low-Density Surface

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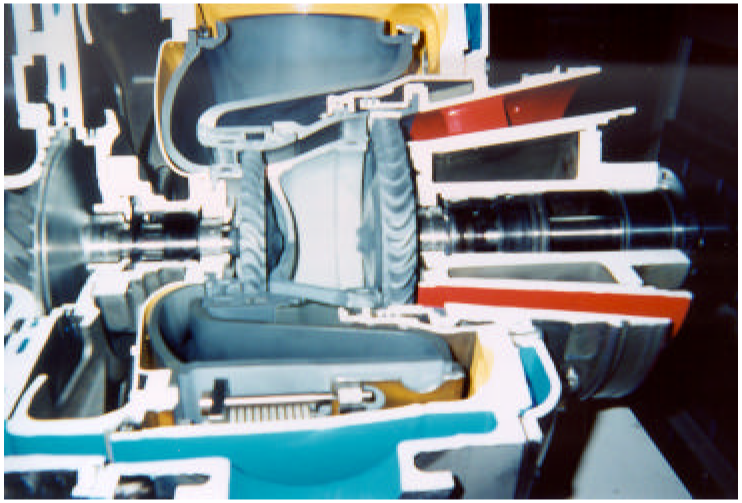
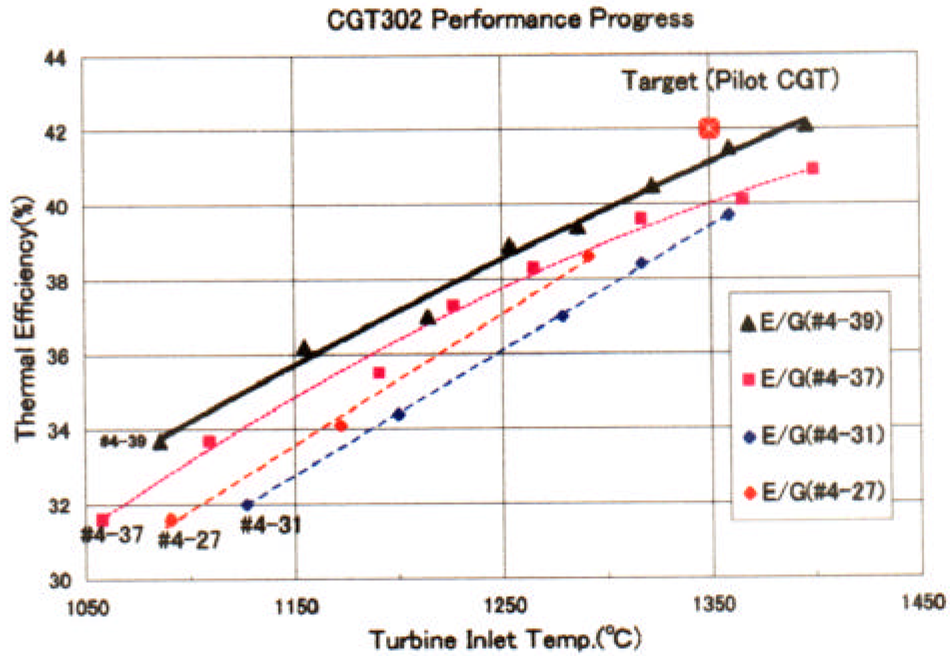
Abradable Shroud Contributes to Efficiency



KHI CGT302 Engine Achieved 42.1% Efficiency and 322 kW Output Power at 1396°C TIT (Courtesy of KHI)



Courtesy of KHI

Abradable Si_3N_4 Power Turbine Shroud
(Fabricated by Kyocera Corp.)

Abradable Si_3N_4 Shroud Fabricated By Technologhia (Russia)

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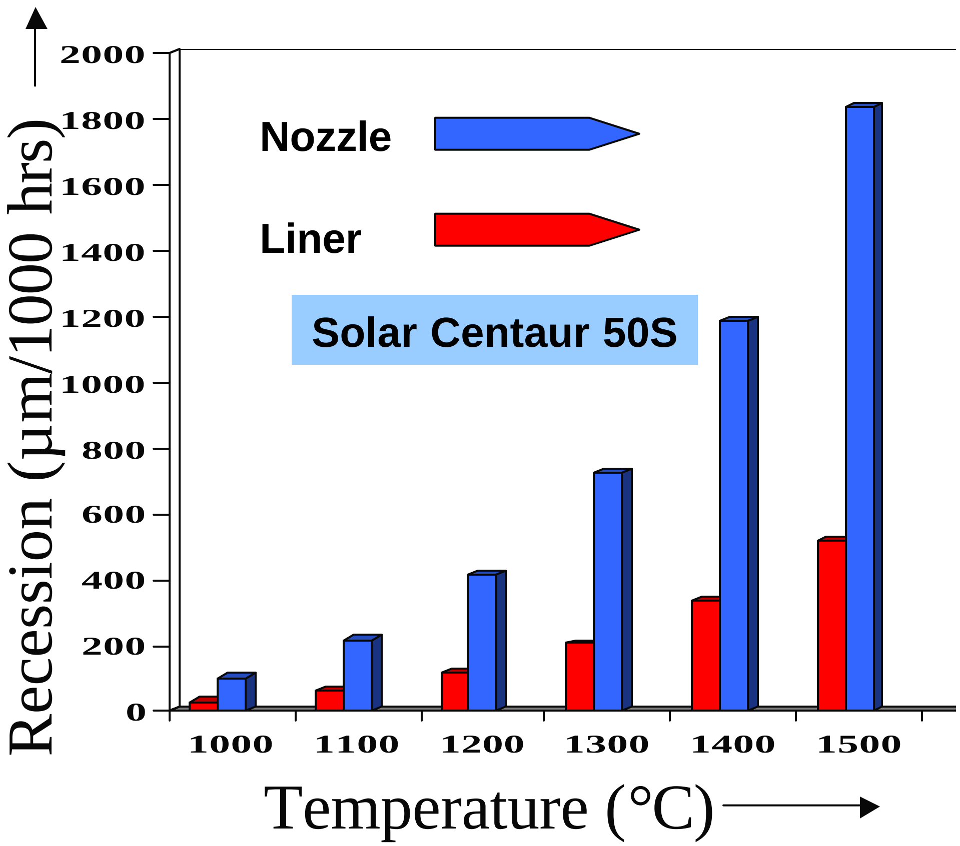
Issue 6. Environmental Degradation

- **Silicon-Based Ceramics Degrade in the Gas Turbine Environment**
- **Solar CSGT Centaur 50S Surface Recession (30,000 hrs)**
  - **TRIT = 1121°C**
  - **Nozzle**
    - **Hot Spot - 1300°C: 24 mm**
    - **Nominal - 1150°C: 12 mm**
  - **Combustor Liner**
    - **Hot Spot - 1250°C: 5 mm**
    - **Cold Spot - 1000°C: 1 mm**



NASA Formula (SiC):

k(lean) = 2.04 exp (-108,000/RT) $P^{1.5}$ $v^{0.5}$

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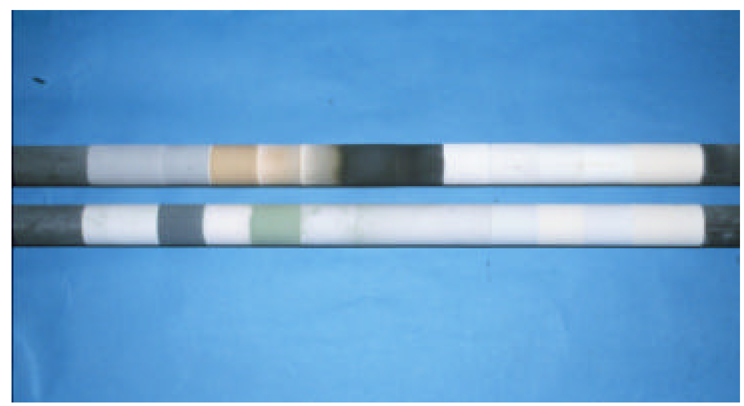
Solar's Early "EBC" Experience

- Corrosion Resistant Coatings for Ceramic Heat Exchanger Tubes (GRI Contract to Solar)
  - M. van Roode et al. ASME 91-GT-38
- Aluminum Remelt Processing – Corrosive Attack by Alkali Chlorides, Cryolite on Heat Exchanger Tubes
- Ceramic Oxide-Based Coatings (0.5 – 1.3 mm thick)
  - Mullite, Zircon, Hafnia, Alumina, Zirconia, mullite-alumina-zirconia
  - Single-Layer, Multi-Layer, Graded
  - a-SiC (Hexoloy SA, Si-SiC (Coors SCRB 210), Nextel/SiC (Syconex), SiC/alumina Substrates
  - Coatings Applied by Air Plasma Spray
  - Alkali Etch to Roughen Substrate Surface

Tubes Exposed for 4000+ hrs In Aluminum Remelt Heat Exchanger Test, Reynolds Aluminum, Mussel Shoals, AL



Early “EBC” Durability

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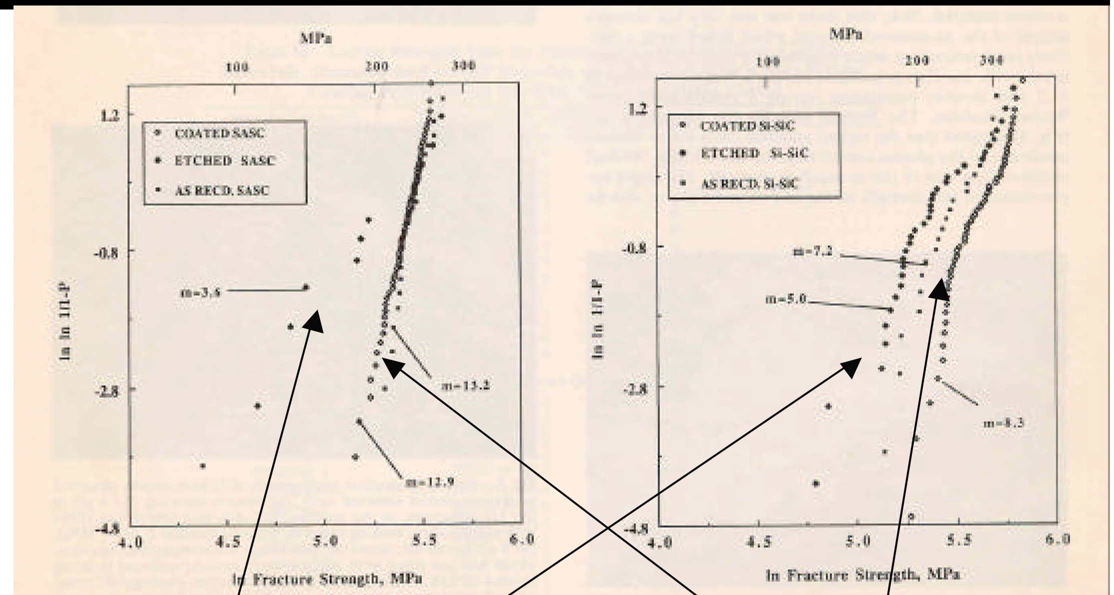
Chemical compatibility, Expansion Match with Substrate, Low Modulus

ORNL: Thermal Cycling in Air (50 cycles/300-1300°C/2 hrs) – Coatings showed no degradation

Corrosion Rig: 1000–3000 hrs

- **Coatings Were Protective**
- **Long Term: Cracking Debonding**



Etched Substrate Strength Loss

Coating Restored Strength

C-Ring Testing at Penn State CAM
D. P. Butt et al. J.Am.Ceram.Soc., 73[9],2690-6(1990)

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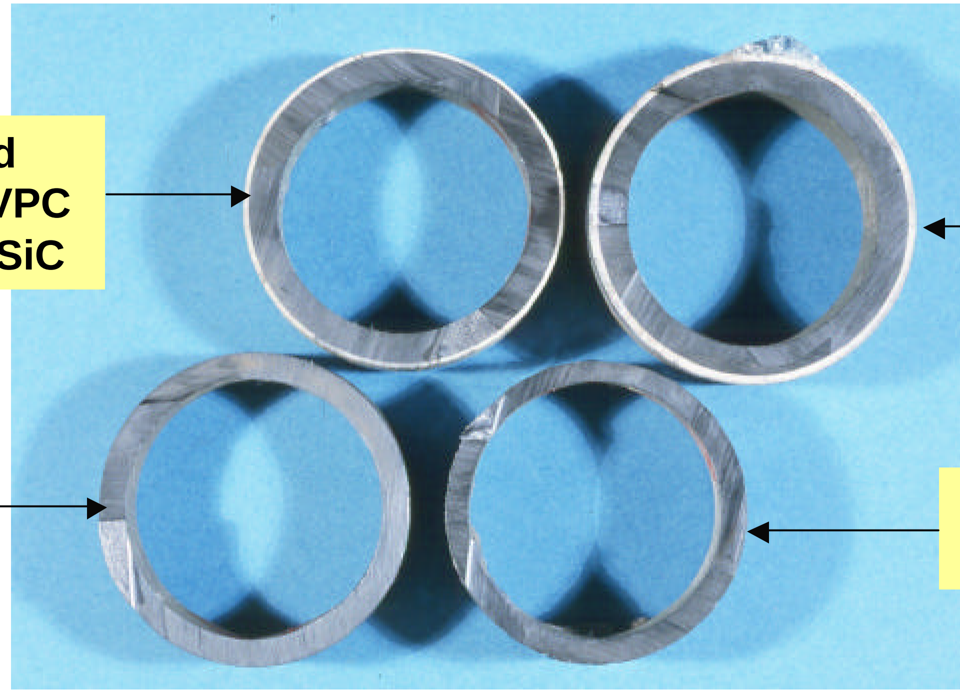
Early "EBC" Durability

Coors SCRB 210Tube Sections after 2000 hrs Exposure at 871°C

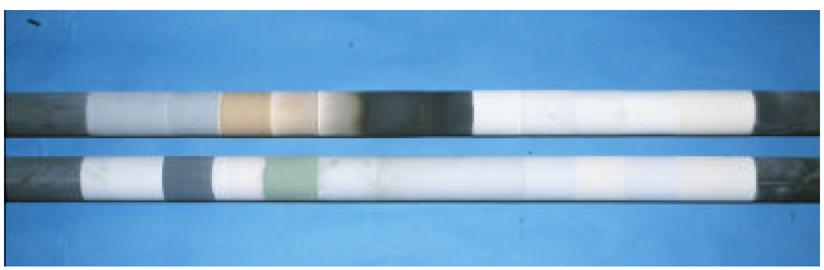


Exposed Mullite/VPC Coated SiC

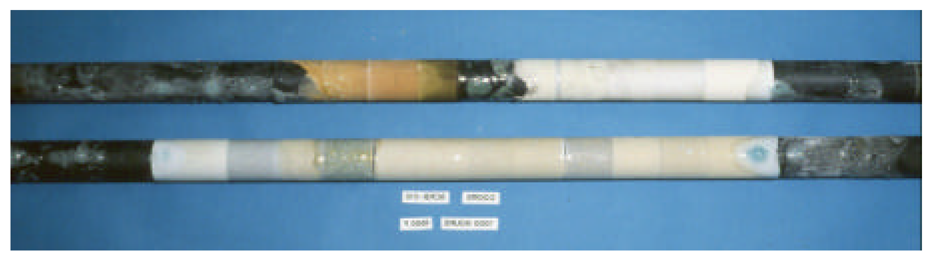
Exposed Mullite Coated SiC

Unexposed Uncoated SiC

Exposed Uncoated SiC



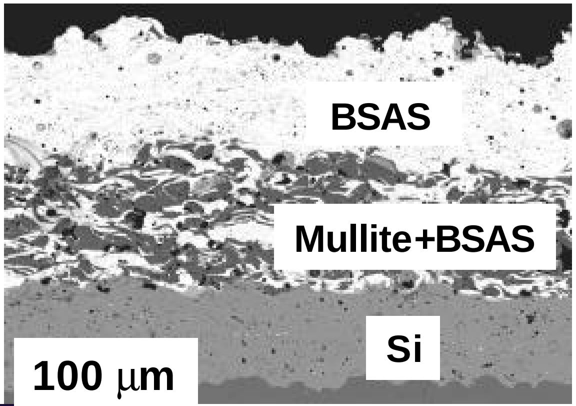
As Coated Coors SCRB 210Tubes



After 1000 hrs Exposure at 871°C

CMC/EBC Combustor Liners

- DOE/Solar CSGT and Advanced Materials Contracts – 1996 – Current
- SiC/SiC CMCs (DuPont Lanxide/AS-ACI/HACI/PSC and Goodrich Corp.)
- GC, Hi-Nicalon, Tyranno ZM Fibers – CVI and MI Matrices - Multi-Layer EBC (UTC)
- 50,000 hrs of Engine Testing – 13,937 Hrs and 15,144 Hrs
- EBC Extends Life of CMC 2-3 Fold



ChevronTexaco
Bakersfield, CA

Malden Mills
Lawrence, MA

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Si_3N_4 Nozzle EBC

Initial EBC Coating Trials with Solar Centaur 50S Nozzle (SN88) Promising

No Spallation Observed

As-Coated

After Thermal Cycling and Burner Rig Testing

UTRC Development Work

- Solar SN88 nozzle coated with 3 layer EPM/DOE EBC

* Thermal cycled 50X RT to 1300°C in air, 1 hour cycles

- 457 $m.s^{-1}$/1250°C burner rig testing 5 hrs/5 cycles

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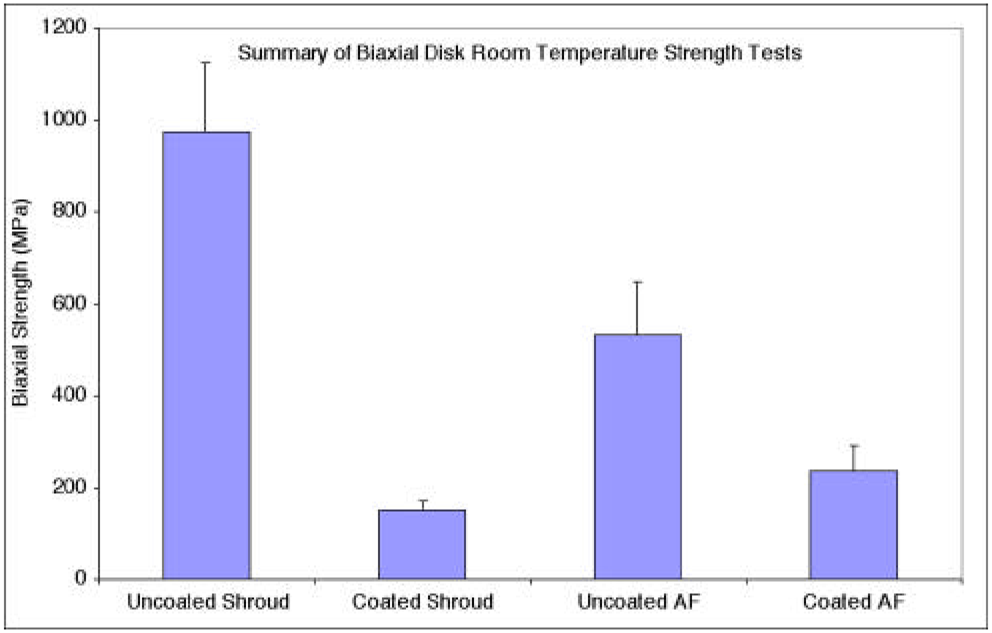
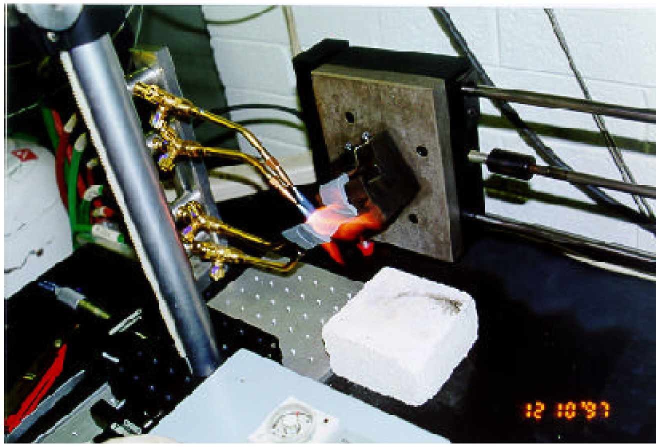
Si_3N_4 Nozzle EBC

- Limited Study for CSGT Program
- One SN88 and two SN282 Si_3N_4 Nozzles
- Test in Gradient Temperature Rig
  - RT-> 1190ºC in 18s
  - 113% of Max. SS Stress
- Nozzles that Had Passed the Proof Test were Coated with UTRC EBC



Data Courtesy M.K. Ferber, ORNL



SN88/EBC Nozzle Survived Intact
2 SN282/EBC Nozzles Failed
1 SN282/EBC Nozzle Not Tested

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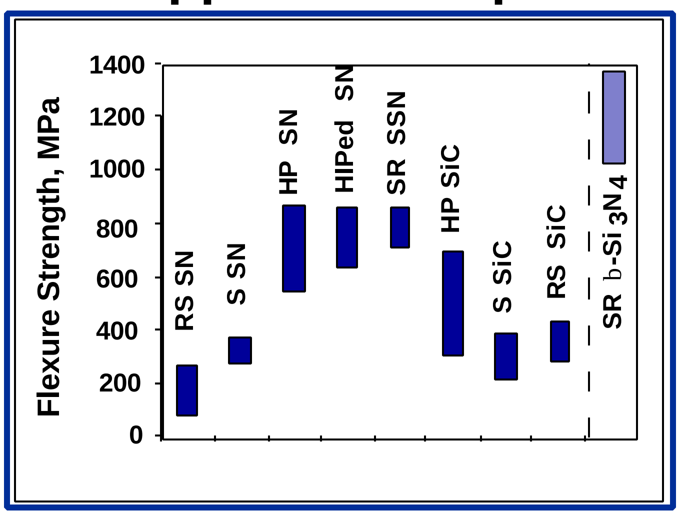
Commercialization Issues

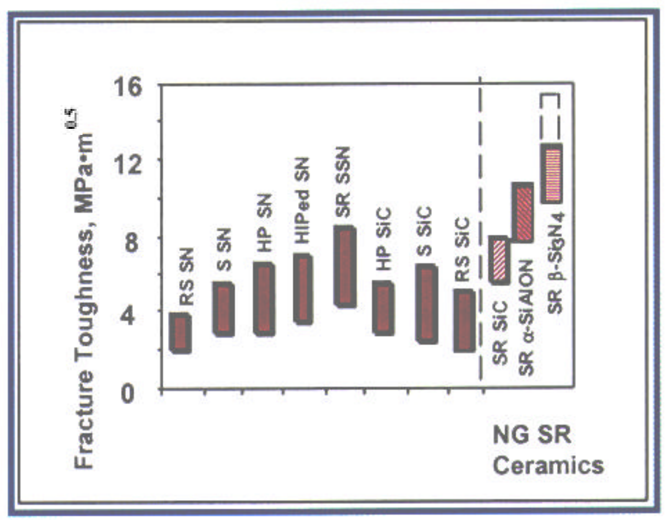
Barriers to Commercialization

- Gas Turbine Applications are a Small Niche Market for Ceramics
- Large Scale Applications Have Not Materialized To-Date
- Insufficient Durability in Industrial Gas Turbine Environment
  - Impact Resistance, Environmental Degradation
- Component Cost Needs to be Competitive with Cost of Metal Parts
  - CMC Components: Cost Substantially Greater
  - Volume Cost of Monolithic Parts is Competitive
- Need a Strong Supplier Base
  - Suppliers Have Exited the Gas Turbine Component Arena
  - Suppliers Have Reduced Development Efforts
  - Suppliers Have Restricted Sale of Materials
- Less Funding for Ceramic R&D Programs

Development Strategie

- Next Generation of Monolithics
  - Further Improvements in Strength and Toughness
    - Improved Impact Resistance
  - Fundamental Research in Processing
    - Highly Aligned Elongated Reinforcing Grains (Seeding of Powders)
    - Tailoring of Sintering Additives
    - NG SR Ceramics: ß-Silicon Nitrides, a-Sialons, SiC
  - Supplier Participation





W.D. Carruthers et al., ASME GT-2002-30504

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EBC Development for Si_3N_4

- Less Mature than SiC/SiC EBCs
- Chemical Stability/Inhibit Oxidation in Gas Turbine Environment
- Adherence to Substrate
- Thermal Expansion Match with Substrate
  - EBC on Si_3N_4 EBC Lower CTE than EBC on SiC/SiC CMC
- Not Adversely Affect Mechanical Properties of Substrate
- Minimize Surface Damage During Application
- Combine Environmental and Impact Resistance
- Thinner EBC (compared to CMC EBC) to Retain Favorable Aerodynamics
- Mechanical Property and Oxidation/Recession Testing
- NDE Methodology to Establish EBC Integrity
- EBC Life Prediction Methodology

Summary

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Summary

- Ceramics are Enabling Materials for Improving Performance and Emissions Reduction in Gas Turbines
- Properties and Processing of Monolithic Ceramics and CMCs Have Significantly Improved over the Past 40 Years
- Ceramic Components Have Been Demonstrated for Thousands of Hours in Test Rigs and Gas Turbines - Need 30,000+ Hrs of Life
- Critical Issues for Monolithics to be Competitive with Metals
  - Impact Resistance, Surface Condition, Contact Stress Resistance (Slow Crack Growth Resistance), Rub Tolerance, Environmental Resistance
- Durable High Performance Component Designs
- Develop EBCs for Long Service Life
- Cost Goal: Competitive with Cost of Metal Components
- Fundamental Research to Resolve Barriers to Commercialization