History of Thermal Barrier Coatings for Gas Turbine Engines
Emphasizing NASA’s Role From 1942 to 1990

Robert A. Miller
Glenn Research Center, Cleveland, Ohio
Since its founding, NASA has been dedicated to the advancement of aeronautics and space science. The NASA Scientific and Technical Information (STI) program plays a key part in helping NASA maintain this important role.

The NASA STI Program operates under the auspices of the Agency Chief Information Officer. It collects, organizes, provides for archiving, and disseminates NASA's STI. The NASA STI program provides access to the NASA Aeronautics and Space Database and its public interface, the NASA Technical Reports Server, thus providing one of the largest collections of aeronautical and space science STI in the world. Results are published in both non-NASA channels and by NASA in the NASA STI Report Series, which includes the following report types:

- **TECHNICAL PUBLICATION.** Reports of completed research or a major significant phase of research that present the results of NASA programs and include extensive data or theoretical analysis. Includes compilations of significant scientific and technical data and information deemed to be of continuing reference value. NASA counterpart of peer-reviewed formal professional papers but has less stringent limitations on manuscript length and extent of graphic presentations.

- **TECHNICAL MEMORANDUM.** Scientific and technical findings that are preliminary or of specialized interest, e.g., quick release reports, working papers, and bibliographies that contain minimal annotation. Does not contain extensive analysis.

- **CONTRACTOR REPORT.** Scientific and technical findings by NASA-sponsored contractors and grantees.

- **CONFERENCE PUBLICATION.** Collected papers from scientific and technical conferences, symposia, seminars, or other meetings sponsored or cosponsored by NASA.

- **SPECIAL PUBLICATION.** Scientific, technical, or historical information from NASA programs, projects, and missions, often concerned with subjects having substantial public interest.

- **TECHNICAL TRANSLATION.** English-language translations of foreign scientific and technical material pertinent to NASA's mission.

Specialized services also include creating custom thesauri, building customized databases, organizing and publishing research results.

For more information about the NASA STI program, see the following:

- Access the NASA STI program home page at [http://www.sti.nasa.gov](http://www.sti.nasa.gov)

- E-mail your question via the Internet to help@sti.nasa.gov

- Fax your question to the NASA STI Help Desk at 301–621–0134

- Telephone the NASA STI Help Desk at 301–621–0390

- Write to:
  NASA Center for AeroSpace Information (CASI)
  7115 Standard Drive
  Hanover, MD 21076–1320
History of Thermal Barrier Coatings for Gas Turbine Engines
Emphasizing NASA’s Role From 1942 to 1990

Robert A. Miller
Glenn Research Center, Cleveland, Ohio

Prepared for the
Thermal Barrier Coatings II
sponsored by the Engineering Conferences International
Kloster Irsee, Germany, August 12–17, 2007

National Aeronautics and
Space Administration

Glenn Research Center
Cleveland, Ohio 44135

March 2009
History of Thermal Barrier Coatings for Gas Turbine Engines
Emphasizing NASA’s Role From 1942 to 1990

Robert A. Miller
National Aeronautics and Space Administration
Glenn Research Center
Cleveland, Ohio 44135

Outline
- NBS/NACA role in frit coatings
- Thermal spray coatings for rocket applications
- Stecura-Liebert zirconia-yttria TBCs
- Identification of optimum t'-ZrO₂ composition
- Failure mechanisms and life prediction
- Brief synopsis of post 1990 efforts
NACA's Earliest Turbine Blade-Oriented Ceramic Coatings Research was on NBS Frit Enamel Coatings 1942-1956

Probably the first aero ceramic coatings paper by Harrison & Moore, NBS – published as NACA TN in 1947


The NBS Frit Coating was tested on Turbine Blades in an Engine as Early as 1948

Figure from 1953 engine test (Bartoo & Clure).
Coating on one blade lasted 100 hrs


C.R. Morse, Comparison of National Bureau of Standards ceramic coatings L-7C and A-417 on turbine blades in a turbojet engine, NACA Research Memo E8120, 1948


- Also, frit coating development led by Air Force in the 40s, 50s and 60s

Durability questions followed all ceramic coatings for decades partly due to popular image of enameled kitchenware and possibly from negative Air Force results on engines in the 40s, 50s and 60s.

Flame Sprayed Coatings were Used for Rocket Applications
The first and most visible was the use of Rokide™ Thermal Barrier Coatings on the XLR99 Rocket Engine Nozzles of the X-15, 1960.

<table>
<thead>
<tr>
<th>X-15 Flight in Early 60s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Originally Coated with Rokide Z TBC</td>
</tr>
<tr>
<td>• Zirconia Top Coat/Nickel Chrome Bond Coat</td>
</tr>
<tr>
<td>• Prevents Oxidation of Tube Assembly</td>
</tr>
<tr>
<td>• Prevents Boiling of Liquid Ammonia</td>
</tr>
</tbody>
</table>

Brazed Stainless Steel Tube Structure


**Graded Rokide™ Thermal Barrier Coating Prevented Premature Failure of X-15 Combustion Chamber**

Rokide Z Coating, As Processed

Spalled Region After Test

Graded Coating with Mo “Primer”

Use of Graded Coating Significantly Improved Nozzle Life
- Grading Improved Coating Adhesion
- TiN Outer Layer Prevents Erosion (Chalking)

**TBCs Found Use in LH2/LOX Rocket Engine Development**
- Development by NACA/NASA with Industrial Partners began in 1956

C. Leibert reported to me (personal communication ca. 1984) that TBCs were first used to extend life past one second!

Was a crucial step towards LH2/LOX rocket engine development

NASA in Cleveland had a rocket-TBC group into the 1990s

---

Materials-Oriented Thermal Spray Research in the 60s and Early 70s - Sal Grisaffe

- Sal conducted basic thermal spray research in 60s
- Alumina, Zirconia (Calcia and possibly Yttria stabilized) and Hafnia coatings for nuclear rocket applications in the early 70s
- He founded and headed the first coating’s group in the 60s
  - I joined the coatings group in 1978

Meanwhile TBCs Began finding use in Low Risk Aero Applications especially at P&W

By about 1970, Plasma Sprayed TBC were in use in Commercial Combustors


Mid 70s, Development of “Modern” Thermal Spray Coatings

TBC of zirconia-12%yttria on NiCrAlY survived J-75 engine test

Key Accomplishments

- Use of Yttria as Zirconia Stabilizer
- Use of MCrAlY Type Bond Coat
- First demonstration that Blade TBCs were feasible
- Demonstrated that graded region was not required

Comment from G.W. Goward
-- then of Turbine Components Corp., formerly of Pratt & Whitney

“Although the engine was run at relatively low pressures, the gas turbine engine community was sufficiently impressed to prompt an explosive increase in development funds and programs to attempt to achieve practical utilization of the coatings on turbine airfoils”

S. Stecura, “Two-Layer Thermal Barrier Coating for Turbine Airfoils—Furnace and Burner Rig Test Results,” NASA TM X-3425, National Aeronautics and Space Administration, 1976


The NASA TBC was Tested with Mixed Results in a More Advanced JT9D at P&W, 1977

Sevcik and Stoner/P&W, 1977:
Failure correlated better with regions of high temperature than regions of highest compressive stress.
This suggested that mechanisms associated with high temperature must be occurring

Tom Strangman was involved in the above discussion

Comment from Goward, 1987:
“The results (of the JT9D test of the NASA TBC) indicated that while the coatings had considerable promise, further development would be required”
Stecura Reported Optimum Zirconia-Yttria TBC Composition in 1978 – Still the State-of-the-Art!
- Stecura conducted furnace, natural gas torch, and burner rig tests


Compositions Having Optimum Life Were Correlated With Phase Distribution
(Miller, Smialek, Garlick 1981, 1983)

Stecura optimum from 1978
Xray evidence of tetragonal phase

Phase distribution in early TBC
Tetragonal Correlated with Life

Optimum Phase was t'-ZrO$_2$ Phase First Reported by Scott (Miller, Smialek, Garlick 1981, 1983)

Stecura's Later Work Reported 2X Life for Ytterbia-Stabilized Zirconia on a Yb-Containing Bond Coat

In addition to favoring 6-8YSZ, Stecura also recommended bond coats with lower CTE's.

- His eventual favorite MCrAlY was
  Ni – 35Cr – 6Al – Yb (or Y)

This is a more ductile bond coat due to low aluminum and it has lower expansion due to an \( \alpha \)-Cr

---

**NASA-Sponsored Pratt & Whitney Development Effort Identified Three Optimum 6YSZ TBC Microstructures**

**Task II Optimums:**

1) Conventionally plasma sprayed with fewer fines (55% -325 mesh)*
2) Segmented plasma sprayed structure from 1” stand-off distance
3) EB-PVD

![Graph showing burner rig cycles at 1079°C (1975°F)]

Segmented TBC had thermal conductivity 1.9X conventional optimum
*Note that NASA at that time typically used 15% -325mesh)

---

S. Stecura, Advanced Thermal Barrier System Bond Coatings for Use on Ni-, Co-, and Fe-Base Alloy Substrates, NASA TM 87062, July 1985

Arguments Persisted in early 80s over Role of Heat Flux vs. Thermal Expansion Mismatch and Environmental Effects -- even for Burner Rig Testing

• In the early 1980s some believed that failure occurred due to stresses encountered on heating
  - Those believing heat flux effects caused failure calculated max stress at 2 seconds into heating in burner rig.
• We conducted a series of short- and longer-cycle burner rig experiments and concluded the following:
  - Cracks link up at the interface prior to visible surface cracking or spalling, due primarily to thermal expansion mismatch between ceramic/metal
  - A few cycles after the cracks link up to form a delaminated region (visible as a hot-spot on heating), the rapidly heated unattached portion of the coating spalls on heating
  - Failure is influenced by bond coat plasticity and oxidation at the irregular bond coat/ceramic interface
  - Also, coating life was time and cycle dependent


Paul Siemers of GE CR&D was another researcher to recognize the importance of bond coat oxidation and plasticity

“The durability of thermal barrier coatings is limited by degradation of adhesion by environmental interactions rather than by mechanical stress per se.”

Other NASA Efforts in the 1980s

Abradable seals
P&W, NASA Bob Bill
- First discussion of TBC creep (Firestone, U Illinois)
- This non-textbook use of the term “creep” was controversial!
Later led to thick diesel TBC program

Dirty fuels
- In-house and DOE and EPRI funding
- Many parallels with CMAS
  - For example Sodium Sulfate does not react with Zirconia-Yttria
  - Rather, when the dew point is less than the coating temperature and the melting point is also less, then liquid Sodium Sulfate wicks into the pores and micro-cracks of the coating leading to a loss of strain tolerance
  - Other impurities such as Vanadium salts also react

Other NASA Efforts in the 1980s

Industry trials
- via coatings group and Liebert’s turbine cooling branch
- many different applications

TBCs were in 2 Major NASA projects
- Energy Efficient Engine with GE
- Engine Component Improvement with P&W
- Both contracts involved analytical assessment of the value of TBCs

References:
In 1985 Pratt & Whitney used Zirconia-Yttria TBC to Fix a Vane Platform Endurance Issue
- Application of Thermal Spray TBC Eliminated Distress of Vane Platform
- Extended Service Life to 18,000 hrs

- P&W shared these results with NASA leading to TBC task in Hot Section Technology (HOST) Life Prediction Program


This slide and the next 14 that follow are from a 1987 presentation on progress under the Hot Section Technology (HOST) TBC life prediction program. They are repeated here as history.

HOST TBC LIFE PREDICTION

NASA
C. STEARNS
R. MILLER
J. NESBITT
S. LEVINE
J. MERUTKA

PRATT & WHITNEY
K. SHEFFLER
J. DeMASI (Marcin)
S. MANNING (Meier)
M. ORTIZ
D. NISSLEY*

GARRETT TURBINE
ENGINE CO.
T. STRANGMAN
J. NEUMAN
A. LIU

GE
R. HILLERY
B. PILSNER
R. McKNIGHT

SOUTHWEST RESEARCH
INSTITUTE
T. CRUSE
A. NAGY

CSU
G. CHANG
W. PHUCHAROEN

*Added to acknowledge post 1987 contribution
APPROACH TO TBC LIFE MODEL DEVELOPMENT

• INITIAL LABORATORY MODEL (NASA)
  - UNDERSTAND FAILURE MECHANISMS
  - FORMULATE MECHANISM MATHEMATICALLY
  - COLLECT LABORATORY LIFE DATA
  - FIT MODEL TO LIVES

• ENGINE CAPABLE MODELS (PWA, GTEC, GE CONTRACTS)
  - FURTHER UNDERSTANDING
  - FORMULATE MATHEMATICALLY
  - COLLECT LIFE DATA OVER MANY CONDITIONS ON BOM SYSTEM
  - MEASURE MATERIALS PROPERTIES
  - FIT MODEL TO LIVES
  - EXTRAPOLATE TO ENGINE MISSIONS

• DETAILED FINITE ELEMENT $\sigma$-$\varepsilon$ ANALYSIS (CSU, NASA)

UNDERSTANDING OF FAILURE MECHANISMS
SUFFICIENT TO ALLOW MODELING

FAILURE BY CRACKING/DELAMINATION IN CERAMIC NEAR INTERFACE
  ■ PROGRESSIVE CRACKING OBSERVED
  ■ $\sigma$, $\varepsilon$ MODELED

EMPIRICAL OBSERVATIONS
  CYCLIC COMPONENT TO FAILURE
    ■ THERMAL EXPANSION MISMATCH$^a$
    ■ HEATING TRANSIENTS
  TIME-AT-TEMPERATURE COMPONENT
    ■ OXIDATION$^a$
    ■ PHASE CHANGES
    ■ SINTERING
    ■ DIFFUSION
    ■ CREEP

$^a$KEY FACTORS INCLUDED IN PRELIMINARY NASA MODEL
**DETAILED FINITE ELEMENT STRESS ANALYSIS YIELDS INSIGHTS INTO TBC BEHAVIOR**

700 °C (STRESS FREE) – 600 °C

**HIGH TENSILE RADIAL STRESS IN CERAMIC NEAR INTERFACE**

**LOWER \( \sigma_r \) THROUGH LOWER**
- \( E_{\text{CERAMIC}} \)
- \( \alpha_{\text{CERAMIC}} - \alpha_{\text{BOND COAT}} \)
- YIELD STRENGTH OF CERAMIC
- ROUGHNESS
- OXIDATION

**WEAK EFFECT ON \( \sigma_r \) FROM**
- \( \alpha_{\text{SUBSTRATE}} \)
- \( \rho_{\text{BOND COAT}} \)
- \( E_{\text{BOND COAT}} \)

---

**NASA PRELIMINARY TBC LIFE MODEL**

- ONE COATING SYSTEM
- TIME-AT-TEMPERATURE EFFECT
  - OXIDATION ONLY, \( W_N \)
- CYCLE FREQUENCY EFFECT
  - SLOW CRACK GROWTH (MICROCRACK LINK UP IN CERAMIC)

\[
d\alpha = A c^b a^c \\
\frac{cN}{cN}
\]

(FATIGUE/MINER'S LAW APPROACH ALSO NOTED)

- ASSUMED RELATIONSHIP BETWEEN WEIGHT GAIN AND STRAIN

\[
\epsilon_c = (\epsilon_f - \epsilon_s) (W_N/W_C)^m + \epsilon_f
\]

---


NASA PRELIMINARY TBC LIFE MODEL CONTINUED

**RESULTING MODEL**

\[ \sum_{N=1}^{N_f} \left[ (1 - \epsilon_f/\epsilon_{fr}) (W_N/W_C)^m + \epsilon_f/\epsilon_{fr} \right]^b \]

**ALTERNATIVE ASSUMPTION OF STRENGTH DEGRADATION FROM \( \epsilon_{f0} \) TO \( \epsilon_r \)**

\[ \epsilon_f/\epsilon_r = (1 - \epsilon_{f0}/\epsilon_{fr}) (W_N/W_C)^m + \epsilon_{f0}/\epsilon_{fr} \]

**RESULTING ALTERNATIVE MODEL**

\[ \sum_{N=1}^{N_f} \left[ (1 - \epsilon_{f0}/\epsilon_{fr}) (W_N/W_C)^m + \epsilon_{f0}/\epsilon_{fr} \right]^{-b} = 1 \]

---

PRELIMINARY MODEL YIELDS GOOD AGREEMENT BETWEEN EXPERIMENTAL AND CALCULATED TBC LIVES

MODEL:

\[ \sum_{N=1}^{N_f} \left[ \left( 1 - \frac{\epsilon_f}{\epsilon_{fr}} \right) \left( \frac{W_N}{W_C} \right)^m + \frac{\epsilon_f}{\epsilon_{fr}} \right]^b = 1 \]

- \( b = 17.00 \)
- \( m = 1.00 \)
- \( W_C = 2.4 \text{ MG/CM}^2 \)
- \( \frac{\epsilon_f}{\epsilon_{fr}} = 0.38 \)

**Cycles to Failure**

- Open symbols denote measured
- Closed symbols denote modeled
P&W HOST ACCOMPLISHMENTS
DEGRADATION MODES IDENTIFIED

• Mechanical (major mode)
  - Near interfacial ceramic cracking
  - Apparent near-interface ceramic weakening

• Oxidation (major mode)
  - Oxidation effect phenomenologically characterized
  - Complex oxide scale characterized
  - Interaction mechanism not understood

• Hot corrosion (minor mode)
  - Not observed in flight service
  - Threshold corrodant level identified in lab

• Erosion (minor mode)
  - Isolated occurrence in flight service
  - Limited lab characterization needed

• F/BMOD (minor model)
  - Not identified in flight service
  - Experimental engines exhibit high –resistance

P&W HOST ACCOMPLISHMENTS
MAJOR MODE CORRELATIVE LIFE
MODEL PROPOSED

• Fatigue based model
• Reversed ceramic plastic strain is primary driving force
• Oxidation acts to "weaken" ceramic
• Preliminary correlation coefficient 0.89
  (90 experimental data points)
• Upgraded analysis in progress
• Incorporates improved ceramic behavior model
• Oxidation contribution improved by use of NASA data

Thermal Barrier Coating Life Prediction Model Development: Phase I-Final Report, NASA CR 182230
J.T. DeMasi, K.D. Sheffler, M. Ortiz - National Aeronautics and Space Administration, Washington DC, 1989
Thermal barrier coating life prediction model development—phase II
PWA/SwRI TBC LIFE MODEL

- BILL-OF-MATERIAL COATING SYSTEM
- TIME-AT-TEMPERATURE EFFECT
- OXIDATION ONLY, $\delta$
- ARRHENIUS LAW
- CYCLE FREQUENCY EFFECT
- INELASTIC FATIGUE MODEL

$$N_i = \left(\frac{\Delta\sigma_i}{\Delta\sigma_0}\right)^b$$
$$\Delta\sigma_i = \Delta\sigma_0 - \Delta T + \Delta r_T + \Delta r_c - 2S_y^s$$

ASSUMED STRENGTH DEGRADATION DUE TO OXIDATION

$$\Delta\sigma_i = \Delta\sigma_{i0} (1 - \delta\sigma_C)^{1/c} + \Delta\sigma_i (\delta\sigma_C)^{1/d}$$

- MINERS RULE

$$\sum_{i=1}^{N} \frac{1}{N} < 1$$

CORRELATION BETWEEN MEASURED AND MODELED LIVES
(PRELIMINARY PRATT & WHITNEY DATA)

Experimental cycles, thousands

Predicted cycles, thousands

$R^2 = 0.842$

$\delta = 0.000327$

$\Delta\sigma_{i0} = 0.01222$

$b = 30.985$
GARRETT TBC LIFE MODELING APPROACH

\[ TBC \text{ DEGRADATION RATE} = \frac{F_1 (\text{MECHANICAL}) + F_2 (\text{OXIDATION})}{F_2 (\text{OXIDATION})} \]

- COATING STRESSES
- TEMPERATURE
- MATERIAL SYSTEM
  - \( K_C \)
  - FLAW SIZE
  - ELASTIC MODULUS
  - SPALLING STRAIN

+ \( F_3 \) (SALT DEPOSITION)
- ALTITUDE (SALT INGESTION)
- TURBINE PRESSURE
- SALT EVAPORATION
- SALT SOLIDIFICATION
- TEMPERATURE
- GAS VELOCITY
- AIRCRAFT LOCATION
- MATERIALS SYSTEM

---

GARRETT TBC LIFE MODEL HAS THREE DEGRADATION MODES

\[
\text{TBC LIFE} = \frac{1}{(\text{HEATING CYCLE LENGTH FACTOR})^{-1}} + \left[ \frac{1}{(\text{OXIDATION LIFE})^{-1}} + \frac{1}{(\text{ZIRCONIA DENSIFICATION PLUS OXIDATION LIFE})^{-1}} \right]^{-1} + \left[ \frac{1}{(\text{SALT FILM DAMAGE LIFE})^{-1}} \right]^{-1}
\]

- SALT SOLIDIFICATION
- SALT EVAPORATION
- BOND COATING OXIDATION
- ZIRCONIA TOUGHNESS REDUCTION
- MOLTEN SALT FILM DAMAGE

---

GARRET TBC MODEL FIT THROUGH MINIMUM LIVES

GENERAL ELECTRIC TBC LIFE MODELING APPROACH

- ANALYSIS—PREDICTS $\sigma_e$ UNDER VARIOUS TIME, TEMPERATURE CONDITIONS
- TESTING—DEFINES EFFECTS OF SPECIMEN HISTORY, LOADING, $\sigma$, AND TIME ON TIME TO FAILURE
- EMPIRICALLY RELATED ANALYSIS AND TEST—INFECTION
- GREATER NUMBER OF TEST CONDITIONS GIVES INCREASED INFECTION AND CONFIDENCE CAPABILITY
- VERIFY AND MODIFY BY ADDITIONAL TESTS

\[ \Delta R_Z + 0.4 \Delta R = 0.084 N_t^{-1.445} \]

WHERE
- $\Delta R_Z$ SHEAR STRAIN RANGE
- $\Delta R$ NORMAL STRAIN RANGE
- $N_t$ CYCLES TO FAILURE

By 1989 an Infant Mortality Issue had been Overcome and EB-PVD TBCs Were Introduced onto Turbine Blades in Engines in Revenue Service

• First Introduced on South African Airways B747
• High Altitude Airport, High Mean Ambient Temperature Resulted in Unexpected Airfoil Distress


EB-PVD TBCs Remain the Coating of Choice for 1st Blade

This and previous slide and slides 6,7, and 10 based on slides from M. Malony N. Ullen and R.A. Miller, Irsee 2003 Presentation
Concluding Remarks --
NASA had Substantial Involvement in Early TBC Research and TBC Research Continued through the 90s and 00s …

1990s:
- Thick Diesel
  - With the Army Research Lab at NASA and Caterpillar
  - Built on thick shroud work
  - Dongming Zhu joined NASA team

- EBCs
  - Built on initial Solar Turbines Research

- High Speed Research
  - NASA/GE/P&W
  - Began a period of strong interaction with industry
    - A useful reality check!

2000s:
- Ultra Efficient Engine Technology
  - Low k TBC / High heat flux laser rig testing
  - EBCs


Concluding Remarks --
... and TBC Research Continues Today

Fundamental Aeronautics Program
- Erosion
  - Rotorcraft oriented; first blade EB-PVD
  - Burner rig has been modified for particle injection

- Damping
  - High force/high frequency/high temperature capability

- TBC Lifting
  - Small program aimed at Supersonic mission

- EBCs
  - Current task is also aimed at Supersonics
History of Thermal Barrier Coatings for Gas Turbine Engines
Emphasizing NASA's Role From 1942 to 1990

NASA has played a central role in the development of thermal barrier coatings (TBCs) for gas turbine applications. This report discuses the history of TBCs emphasizing the role NASA has played beginning with (1) frit coatings in the 1940s and 1950s; (2) thermally sprayed coatings for rocket application in the 1960s and early 1970s; (3) the beginnings of the modern era of turbine section coatings in the mid 1970s; and (4) failure mechanism and life prediction studies in the 1980s and 1990s. More recent efforts are also briefly discussed.