DEVELOPMENT OF NDE METHODS FOR CERAMIC COATINGS AND MEMBRANES

J. G. Sun

Nuclear Engineering Division
Argonne National Laboratory
Argonne, IL 60439

23rd Annual Conference on Fossil Energy Materials
Pittsburgh, PA
May 12-14, 2009

Work supported by U.S. Department of Energy, Office of Fossil Energy, Advanced Research-Materials Program
Outline

- Background

- Thermal imaging methods for TBCs
  - Multilayer thermal modeling method
    - Determine TBC thermal properties (e.g., conductivity)
  - Thermal tomography

- X-ray microCT for ceramic gas-separation membranes

- Summary

- Planned future efforts
**Background**

- Thermal barrier coatings (TBCs) are “prime reliant” material for turbine engine components – evaluation of their conditions by NDE is important.

- NDEs may be used to:
  - Assess TBC process reliability and product quality (specs, defects, etc)
    - *Current TBC processing relies on robust process conditions*
  - Monitor TBC degradation and predict TBC lifetime
    - *As-processed TBC → TBC sintering → TBC degradation (internal cracking) → TBC delamination → TBC spallation (failure)*
  - Detect FOD (foreign object damage)

- NDE detection of delamination is relatively easy: thermal imaging, optical, etc
Few NDEs were reported to monitor TBC condition and predict TBC lifetime
- Mid-IR reflectance (J. Eldridge of NASA)
  - Reflectance increases with damage
- Electrical impedance spectroscopy (P. Xiao of Univ. Manchester)
  - Resistance (cracking), modulus (TGO growth), capacitance (delamination)

Current methods are not quantitative and difficult to be generalized!

A Quantitative Approach for TBC Lifetime Prediction

- Based on NDE measurement of TBC conductivity k
  - TBC conductivity is the most important thermophysical parameter
    - Measured for all coatings
    - Used in component design
  - TBC conductivity evolution has characteristic features (many studies)
    - As-processed TBC: baseline conductivity
    - TBC sintering: conductivity increase
    - TBC degradation (internal cracking): conductivity decrease
    - TBC delamination: significant conductivity drop
    - TBC spallation (failure)
NDE Development for TBCs

- NDE development at ANL is focused on thermal imaging methods
  - For quantitative measurement of TBC thermal properties, e.g., conductivity
    - *TBC conductivity is measured mostly by laser flash method which is a two-sided thermal method and not suitable for NDE of real component*
  - For evaluation of TBC degradation and prediction of TBC lifetime
  - Applicable to TBCs of all types (APS or EBPVD) and conditions (e.g., thickness)

- Multilayer thermal modeling method (2D imaging):
  - TBC thermal conductivity and thickness distribution
    - *Accuracy is most important!*
  - TBC cracking and delamination

- Thermal tomography method:
  - 3D imaging of TBC structure and property distribution
  - Determination of TBC thickness and damage depth
One-Sided Flash Thermal Imaging Setup for Testing of a TBC Coated Turbine Blade

- Image entire surface (100% inspection)
- Fast (a few seconds for testing, up to a few minutes for data processing)
- Data processing is completely automated (no operator adjustment)
**Typical Raw Thermal Imaging Data**

- Flash lamp at left side
- Total time period is ~0.1 s
- APS TBC of 1” diameter
Characteristics of Thermal Imaging Data (1- and 2-layer)

- Thermal imaging data, i.e., surface temperature and its slope at each surface pixel, are significantly different for 1- and 2-layer materials.
- Characteristics in thermal data allow for direct calculation of coating thickness and thermal properties, as well as substrate thickness.
- High detection sensitivity for TBC due to large thermal-property disparity between coating and substrate.
Recent Thermal Imaging NDE Development for TBCs

- 2D multilayer thermal modeling method
  - Two issues identified last year were resolved:
    - (1) nonlinear temperature reading
    - (2) two independent parameters in solution
  - Automated data-processing software was established
    - Speed was not optimized
    - Coating optical property was not yet accounted for
  - Calibration tests are underway for both APS and EBPVD TBCs

- 3D Thermal tomography method
  - Data-processing software was improved
2D Multilayer Thermal Modeling for TBC Systems

**Measured data T(x,y,t):**
Time series of 2D thermal (surface temperature) images

**Surface temperature variation at pixel (x,y)**

**Multilayer TBC model**

Flash heating

- Coating 1:
  
  \[ k, (\rho C_p), (\alpha, \varepsilon, \tau) \]

- Substrate 2:
  
  Fixed properties

**Numerical solution of surface temperature variation**

**Fitting numerical result with exp. data to derive correct TBC parameters:**

- Repeat this process for every pixel
Formulation for Multilayer Thermal Modeling Method

- Governing heat transfer equation (1D):
  \[ \rho c \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial z^2} \]

- Analytical solution (2 layers, no interface resistance):
  \[
  T(t) = T_\infty \left[ 1 + 2 \frac{x_1 \omega_1 + x_2 \omega_2}{x_1 + x_2} \sum_{K=1}^{\infty} \frac{x_1 \cos(\omega_1 \gamma_K) + x_2 \cos(\omega_2 \gamma_K)}{x_1 \omega_1 \cos(\omega_1 \gamma_K) + x_2 \omega_2 \cos(\omega_2 \gamma_K)} \exp \left( -\frac{\gamma_K^2 t}{\eta_2^2} \right) \right]
  \]

  where \( \gamma_K \) is the \( K \)-th positive root of the following equation,
  \[
  x_1 \sin(\omega_1 \gamma) + x_2 \sin(\omega_2 \gamma) = 0
  \]
  and
  \[
  x_i = e_{12} - (-1)^i \quad e_i = \sqrt{k_i \rho_i c_i} \quad i = 1, 2
  \]
  \[
  \omega_i = \eta_{12} - (-1)^i \quad \eta_i = L_i / \sqrt{\alpha_i} \quad i = 1, 2
  \]
  \[
  e_{12} = e_1 / e_2 \quad \eta_{12} = \eta_1 / \eta_2
  \]

- Two independent parameters for coating: \( e \) (effusivity) and \( \eta = L / \alpha^{1/2} \), which can derive coating conductivity \( k \) and heat capacity \( \rho c \) (or thickness \( L \))

---

Argonne
NATIONAL LABORATORY
For thermal imaging, TBC surface needs to be coated black
- Same requirement as for laser flash, the current standard method for TBC conductivity measurement
- This requirement can be removed if an optical model for TBC is developed

Tested EBPVD TBC sample (black coated)
- 1” diameter, coating thickness = 0.127mm
- Sample curtesy of Dr. A. Feuerstein, Praxair Surface Technologies, Inc.
- Image acquisition rate was at 1068 frames/second
Multilayer Modeling Prediction for TBC Thermal Properties

- Average TBC conductivity: 1.65 W/m-K (1.71)
- Average TBC heat capacity: 3.3 J/cm³-K (high)
  - Higher prediction in heat capacity data is likely due to uncertainty in TBC thickness and other parameters discussed later
Typical Line Plot of Predicted TBC Thermal Conductivity

- Gross conductivity change is likely due to thickness variation
Typical Fitting Results for One Pixel

Temperature vs. time

Temperature slope vs. time

- Good fitting agreement!
Thermal Conductivity Based TBC Lifetime Prediction

- Initial TBC conductivity (baseline)
- Conductivity increase in early life – due to sintering
  - Many studies (NASA, SUNY, DLR, etc); e.g., the increase may be modeled by a Larson-Miller parameter (LMP)
- Conductivity decrease in mid-to-late TBC life – due to micro-cracking
  - NASA, etc
- Significant conductivity decrease in late TBC life – due to delamination

As-processed

Sintering increases conductivity

Degradation and micro-cracking decreases conductivity

Delamination

Conductivity k

TBC life

100 µm

bond coat

substrate

Cracking

Delamination

200 µm
Prediction of TBC Property for Thermally-Cycled Samples

- Based on quantitative measurement of TBC conductivity values
- Sample courtesy of Mr. A. Luz, Imperial College London

Thermal conductivity images

Conductivity k (W/m-K)

TBC life (%)
Thermal Tomography Images of 3D TBC Structure

- Thermal tomography algorithm was improved to enhance image quality
- However, major development is needed to eliminate artifacts
Current Effort: Calibration of Multilayer Modeling Method

- Current computer algorithm is robust with consistent convergence in predicted TBC thermal properties (complete automated prediction)

- Current effort is focused on calibrating predicted TBC results
  - With literature values
  - With laser flash measurements

- Broad collaborations were established with industry and academics
  - Siemens, Praxair, Rolls Royce, DLR, SUNY, NASA, UCSB, etc

- When successful, this new technology may be widely used for both fundamental thermal property measurement and for NDE
  - Only laser flash method is currently available
  - Other reported methods are not expected to be widely adopted
Preliminary Calibration Findings

- For APS TBCs, good agreements in both predicted thermal properties were obtained – work ongoing
  - TBC coatings from 0.2 to ~1mm thickness
  - Different substrates
  - Also for metal coatings (with high conductivity)

- For EBPVD TBCs, predicted thermal properties were higher
  - Possible cause: infiltration of black paint inside feathers and TBC columns
    - *This effect is being assessed*
  - No painting is possible if a long-IR camera is used?

![Painted sample](image)
NDE Investigation for Gas-Separation Membranes

- Gas-separation membranes are being developed for FE applications
  - For example, hydrogen and oxygen membranes

- NDE opportunities are investigated for ceramic membranes
  - For materials
  - For components
Gas-Separation Membranes

Gas-separation membranes are being developed to produce hydrogen

- E.g., ceramic oxygen-transport membrane via water splitting. Hydrogen is produced when the membrane removes oxygen from the water dissociation zone
- Membrane structure: a thin film supported by a porous ceramic substrate

N₂, H₂O = H₂ + 1/2 O₂

N₂, H₂O, H₂

H₂, H₂O, CO, CO₂ etc.

O²⁻

e⁻

Syngas, CO, CO₂, EtOH, H₂*

* Hydrogen is used as a model gas to maintain high pO₂ gradient.
NDE Investigation for Ceramic Membranes

- NDE method: 3D synchrotron microtomography (microCT) at ANL’s Advanced Photon Source (APS)

- NDE possibilities for materials and components:
  - dimension,
  - film/substrate microstructure,
  - defects (leaking)
3D MicroCT System at APS Synchrotron Beamline 2-BM

- X-ray source: monochromatic energy (~25keV),
- Detector: consists of a scintillation plate, a microscope lens (eg, 10X) and a digital camera of size 2048x2048 pixels
Typical Membrane Samples

- Three small membrane samples (~2mm in dimension)
- MicroCT voxel dimension was 1.48 μm/pixel
**Typical Cross-Sectional Slices for Sample 1**

- Pd(60vol%)/CeO$_2$(40vol%) composite thin film on porous alumina (Al$_2$O$_3$) substrate
- CT image shows that the film is porous and at ~22 µm thickness
Typical Cross-Sectional Slices for Sample 2

- SrFeCo$_{0.5}$O$_x$ (CFC2) thin film on porous CFC2 substrate
- CT image shows that the film is dense and between 32-38 µm thickness
**Typical Cross-Sectional Slices for Sample 3**

- **BaCe$_{0.8}$Y$_{0.2}$O$_3$ (BCY) film on BCY/NiO substrate (porous)**
- **CT image** shows that the BCY film is dense and at ~10 µm thickness
- **CT resolution** is not sufficient to determine the pore size distributions

**Image curtsey of Dr. T. Lee, ANL**
MicroCT Imaging of Cracks in Silicon Nitride Subsurface

- MicroCT may detect very thin cracks (@ ~1/10 of the 0.74 µm pixel size)

Image curtsey of Dr. C. Vieillard, SKF
Summary for NDE Developments for TBCs

- Multilayer modeling method was developed for quantitative imaging of TBC parameters
  - Current software is robust to predict TBC thermal properties
  - Capable to predict evolution of TBC conductivity for entire TBC life cycle
    - Conductivity increase due to sintering
    - Conductivity decrease due to cracking/delamination
  - Calibration of predicted thermal properties is ongoing
    - Predicted values for APS TBCs are accurate (comparable to laser flash)
    - Predicted values for EBPVD TBCs are higher
      - Possible effects were identified and being investigated
    - Prediction of conductivity variation along coating depth is being verified

- Thermal tomography method was improved to show enhanced 3D structural image

- Collaborations were established with industry and academics for relevant technology development and potential applications
Synchrotron x-ray microCT was used to study ceramic membrane materials
  – High resolution, fast data acquisition and processing (<20 min each)
  – It can resolve micron-sized volumetric features
    • May determine membrane film and substrate dimension and structure
    – However, not sufficient resolution for fundamental membrane study
    • May detect film defect and leaking
    – Can detect crack-type defect with gap-opening in the order of 1/10 of the voxel dimension (i.e., <0.1 µm)

For NDE of membrane components, other NDE methods may be needed
  – E.g., thermal imaging for leaking and cracking detection
Planned Future Efforts

- Further development of thermal imaging methods for TBCs
  - Continue calibration of predicted TBC properties with laser flash results
  - Apply to wider TBC parameter range: thin/thick, graded/layered, etc
  - For EBPVD TBCs, investigate effects that affect prediction accuracy
  - Develop additional models, such as for 2-layer coating system and coating transparency
  - Establish an accurate and reliable instrumentation for TBC characterization

- Validation of NDE model for TBC lifetime prediction
  - In collaboration with partners, perform TBC life-cycle tests and collect NDE data
  - Correlate TBC parameter change with TBC degradation state
  - Compare with destructive examination results

- Correlation between different NDE methods
  - Work with collaborators who are developing other methods