Depth-Selective Diagnostics of Thermal Barrier Coatings Incorporating Thermographic Phosphors, J.I. Eldridge and T.J. Bencic, NASA Glenn Research Center, Cleveland, OH; S.W. Allison and D.L. Beshears, Oak Ridge National Laboratory, Oak Ridge, TN.

Thermographic phosphors have been previously demonstrated to provide effective non-contact, emissivity-independent surface temperature measurements. Because of the translucent nature of thermal barrier coatings (TBCs), thermographic-phosphor-based temperature measurements can be extended beyond the surface to provide depth-selective temperature measurements by incorporating the thermographic phosphor layer at the depth where the temperature measurement is desired. In this paper, the use of thermographic phosphor ($\text{Y}_2\text{O}_3$:Eu) luminescence decay time measurements is demonstrated for the first time for through-the-thickness temperature readings up to 1000°C with the phosphor placed beneath a 100-µm-thick TBC (plasma-sprayed 8wt% yttria-stabilized zirconia). With an appropriately chosen excitation wavelength and detection configuration, it is shown that sufficient phosphor emission is generated to provide effective temperature measurements, despite the attenuation of both the excitation and emission intensities by the overlying TBC. This depth-selective temperature measurement capability should prove particularly useful for TBC diagnostics, where a large thermal gradient is typically present across the TBC thickness.
Depth-Selective Diagnostics of Thermal Barrier Coatings Incorporating Thermographic Phosphors

J. I. Eldridge and T.J. Bencic
NASA Glenn Research Center
Cleveland, OH

S.W. Allison and D.L. Beshears
Oak Ridge National Laboratory
Oak Ridge, TN

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Thermal Barrier Coatings (TBCs) are Critical to Current and Future Gas Turbine Engine Systems

- Ceramic oxide TBCs can increase engine temperatures, reduce cooling, lower emission, and improve engine efficiency and reliability.

- TBCs provide thermal protection by sustaining a thermal gradient between the TBC surface and underlying metal component.

(a) without TBC  
(b) with current TBC  
(c) with improved TBC
Background

- Accurate measurement of thermal gradients through TBC is critical
  - For evaluation of TBC performance
  - For TBC health monitoring
  - For realistic simulation of engine environment
- Noncontact surface temperature measurements of translucent TBCs in flame environment by IR pyrometry has been problematic.
  - Interference of radiation reflected by TBC.
  - Temperature measurement averages over depth due to TBC translucency.
  - Emittance corrections.
- Two approaches have shown promise in overcoming these difficulties.
  - Long-wavelength (>10 μm) IR pyrometers operate where TBCs are opaque, providing surface temperature measurements and near-zero reflectance. (J.R. Markham, Advanced Fuel Research)
  - Thermographic phosphors applied to TBC surface provide emissivity-independent surface temperature measurements using fluorescence decay times or peak ratios. (S.W. Allison et al., ORNL; J.P. Feist and A.L. Heyes, Imperial College)
Objectives

• Explore potential of achieving depth-probing TBC temperature measurements by placing thermographic phosphor layer at desired depth within translucent TBC.

Strategy

• Select thermographic phosphor that can be excited and emits at wavelengths that can be transmitted through TBC.
  – Severe restriction because most phosphors are best excited by UV wavelengths that do not penetrate TBC.
• Eventually move from distinct phosphor layer to using TBC itself as host for layered doping of luminescent ions. (Feist & Heyes demonstrated doped YSZ can be effective thermographic phosphor.)
Overlap of $\text{Y}_2\text{O}_3$:Eu Excitation and Emission Spectra and TBC Transmittance
Overlap of YSZ:Eu Excitation and Emission Spectra and TBC Transmittance

- 115 micron 8YSZ transmittance
- 195 micron 8YSZ transmittance
- YSZ:Eu emission
- YSZ:Eu excitation

Wavelength (nm)

% Transmittance

Excitation/Emission Intensity

394 466 526 534 590 605
Raman-Spectrometer-Based Luminescence Spectra & Decay Time Measurements

Renishaw 2000 Raman Microscope

- 532 nm edge filter
- Translatable diverting mirror
- Grating
- Prism
- Filter wheel
- PMT
- Focusing objective
- CCD detector
- Digital scope
- 532 nm Nanogreen pulsed laser

Microscope

Linkam hot stage

Specimen

Temperature controller
Raman-Spectrometer-Based Luminescence Spectra & Decay Time Measurements

Microscope + Hot stage

Renishaw 2000 Raman microscope/spectrometer adapted for fluorescence decay time measurements
**Specimen Preparation**

- **Plasma-spray 100 μm 8YSZ**
- **Spray Y₂O₃:Eu (6at% Eu) mixed with water-based binders**
- **800°C heat treatment burns away carbon & sets binder**
- **Freestanding Y₂O₃:Eu/8YSZ**

**Specimen Orientation**

- **Y₂O₃:Eu above TBC**
- **Y₂O₃:Eu below TBC**
Attenuation of 611 nm Emission Signal by 100 μm-thick TBC Overlayer

![Graph showing attenuation of 611 nm Emission Signal by 100 μm-thick TBC Overlayer]
Temperature Dependence of $Y_2O_3$:Eu Emission
Temperature Dependence of 611 nm $Y_2O_3$:Eu Emission

- Emission peak shifts to longer wavelengths with increasing $T$.
- Emission peak broadens with increasing $T$.
Changes in 611 nm Emission Peak with Temperature

![Graph showing changes in 611 nm emission peak with temperature. The graph plots peak position and FWHM against temperature.](image-url)
Temperature Measurement from Emission Peak Shift/Widening

- Temperature dependence of emission peak position and width can be used for temperature measurements
  - Both show similar, reproducible, temperature-dependence over full temperature range
    - Close to linear relationship
  - May show undesirable stress dependence (basis of piezospectroscopy)
- Fluorescence decay time measurements are better suited for temperature measurements
  - Higher temperature sensitivity (exponential dependence)
  - Lack of stress dependence
Fitting Fluorescence Decay Curves

611 nm emission from Y$_2$O$_3$:Eu beneath TBC at 700°C

\[ I_{\text{emission}} = \left[ c_1 + c_2 \left[ 1 - e^{-t/\tau_{\text{rise}}} \right] \right] e^{-t/\tau_{\text{decay}}} \]
Energy Levels of Eu$^{3+}$ in Y$_2$O$_3$

- oxygen
- vacancy
- yttrium

$C_2$

$C_{3i}$

$\text{5D}_1$

$\text{5D}_0$

$\text{7F}_2$

$\text{7F}_1$

$\text{7F}_0$

611 nm

587 nm
Temperature Dependence of Decay Curves
$Y_2O_3:Eu$ above vs. below TBC

$Y_2O_3:Eu$ above TBC

$Y_2O_3:Eu$ below TBC
Temperature Dependence of Decay Time

$Y_2O_3$:Eu above vs. below TBC

Wideband bandpass filter (FWHM = 10 nm)
Rise Time vs. Decay Time
$Y_2O_3:Eu$ above TBC

wideband bandpass filter (FWHM = 10 nm)
587 nm vs. 611 nm Fluorescent Decay

$\text{Y}_2\text{O}_3:\text{Eu}$ above 100-mm thick PS-8YSZ
700°C

narrow bandpass filter (FWHM < 1 nm)
587 nm vs. 611 nm Fluorescent Decay
\[ Y_2O_3:Eu \text{ above 100-mm thick PS-8YSZ} \]
\[ 700^\circ C \]

narrow bandpass filter (FWHM < 1 nm)

\[ I_{\text{emission}} = \left[ c_1 + c_2 \left[ 1 - e^{-\frac{t}{\tau_{\text{rise}}}} \right] \right] e^{-\frac{t}{\tau_{\text{decay}}}} \]

\[ I_{\text{emission}} = c_1 e^{-\frac{t}{\tau_{\text{decay}1}}} + c_2 e^{-\frac{t}{\tau_{\text{decay}2}}} \]

\[ \text{Time (\mu sec)} \]

\[ \text{In(Emission Intensity (V))} \]
Comparison of Temperature Dependence of 611 and 587 nm Emission Lines

narrow bandpass filter (FWHM < 1 nm)

\[ \tau_{\text{decay}}^{611} = \tau_{\text{decay}}^{587} \]

\[ \tau_{\text{rise}}^{611} = \tau_{\text{decay}}^{587} \]

- ○ decay time, 611 nm
- △ rise time, 611 nm
- ○ decay time #1, 587 nm
- □ decay time #2, 587 nm

Temperature (°C)

Rise/Decay Time (μsec)
Advantages of Raman Microscope Based Measurements

• Can use same instrument to collect emission spectra and select emission peaks for subsequent fluorescence decay time measurements.
• Microscope-based light collection provides excellent rejection of thermal radiation background that can interfere with high temperature measurements.
  -- Light collection restricted to small region (~1 mm diameter) surrounding laser-excited area (100 μm diameter) of specimen.
  -- Added bonus due to extraneous light rejection:
    • Don’t have to work in the dark!
Summary

• Successful decay-time-based temperature measurements up to 1100°C from Y₂O₃:Eu layer beneath 100-μm-thick TBC.
  – Minor excitation peak at 532 nm produces sufficient emission
  – Sufficient transmission of 532 nm excitation and 611 nm emission through TBC.
  – Close agreement between temperature calibrations for phosphor above/below TBC.
  – Both 611 and 587 nm emission peaks can be used for temperature measurements.
    • 611 nm peak exhibits rise time and decay time.
    • 587 nm peak exhibits two decay times.
    • \( \tau_{611}^{\text{decay}} \) or \( \tau_{587}^{\text{decay}_2} \) for \( T > 600^\circ \text{C} \).
    • \( \tau_{611}^{\text{rise}} \) or \( \tau_{587}^{\text{decay}_1} \) for \( T < 600^\circ \text{C} \).
    • 587 nm emission may be advantageous at higher temperatures due to less interference from thermal radiation.

• Temperature dependence of emission peak position and width can be used for temperature measurements
  – Not as sensitive as decay time measurements
  – May show undesirable stress dependence.
Conclusion

- Strategically selected and located thermographic phosphors show promise for adding depth-selective temperature-sensing functions to TBCs.
Future Work

• Increase detected emission signal to enable higher temperature measurements.
  – Higher power laser
  – Optimize width of bandpass filter

• Replace discrete $\text{Y}_2\text{O}_3$:Eu layer with layered doping of 8YSZ TBC with Eu.
  – Will not affect TBC performance.

• Switch from plasma-sprayed TBCs to electron-beam physical vapor deposition deposited (EB-PVD) TBCs to take advantage of much higher transmittance of excitation/emission wavelengths.
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