Annual Report for Period 8/1/05 to 7/31/06

To

The United States Department of Energy
National Energy Technology Laboratory
c/o Contract Specialist: Richard Dunst

Embedded Optical Sensors for Thermal Barrier Coatings

Award DE-FG26-03NT41794

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Disclaimer

Abstract

The third year of this program on developing embedded optical sensors for thermal barrier coatings has been devoted to two principal topics: (i) continuing the assessment of the long-term, thermal cycle stability of the Eu^{3+} doped 8YSZ temperature sensor coatings, and (ii) improving the fiber-optic based luminescence detector system. Following the earlier, preliminary findings, it has been found that not only is the luminescence from the sensors not affected by prolonged thermal cycling, even after 195 hours at 1425^{o}C, but the variation in luminescence lifetime with temperature remains unchanged. As the temperature of 1425^{o}C is much higher than present engines attain or even planned in the foreseeable future, our findings indicate that the Eu^{3+} doped thermal barrier coating sensors are very robust and have the potential of being stable throughout the life of coatings. Investigation of Eu^{3+} doped coatings prepared by plasma-spraying exhibited the same luminescence characteristics as those prepared by electron-beam evaporation. This is of major significance since thermal barrier coatings can be prepared by both process technologies. A fiber-optic based luminescence system has been constructed in which the hottest section of fiber operates to at least 1250^{o}C.

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1. INTRODUCTION

In the preceding project reports, we have described the successful demonstration of luminescence sensing of thermal barrier coatings based on the solid solution doping of current, and potential, coating materials with rare-earth ions. The key concept being that rare-earth substitutional doping into the crystal structure of the coating material provides an atomic level method of sensing the "health" of thermal barrier coatings. When illuminated with a laser beam, the rare-earth ions luminesce and the luminescence spectra provide information that can be used for sensing. Based on this concept, three types of sensor have been demonstrated; wear sensors, "red-line" sensors and "rainbow" sensors.

In the last two years, research has focused on temperature sensors based on europium doping since experiments indicate that this ion offers the prospect of sensing to the highest temperatures in yttria-stabilized zirconia, the current material used in the majority of thermal barrier coatings. Our studies have utilized the luminescence lifetime of the ${}^5D_o \rightarrow {}^4F_2$ transition of the Eu^{3+} ions, which luminesces at 606 nm, to sense the temperature. The lifetime decays have been found to be the same for both bulk ceramic material as well as coatings deposited by electron-beam evaporation. An example is shown in figure 2, which compares the lifetime decay, following a 10 ns laser pulse, of a 10 micron thick Eu-doped YSZ sensor coating, deposited on a standard YSZ coating, and a bulk ceramic pellet of the same composition. Although, as expected, there is a substantial difference in luminescence intensity, the lifetimes are the same up to the maximum temperature (1100°C) to which we could record spectra with reasonable signal to noise.

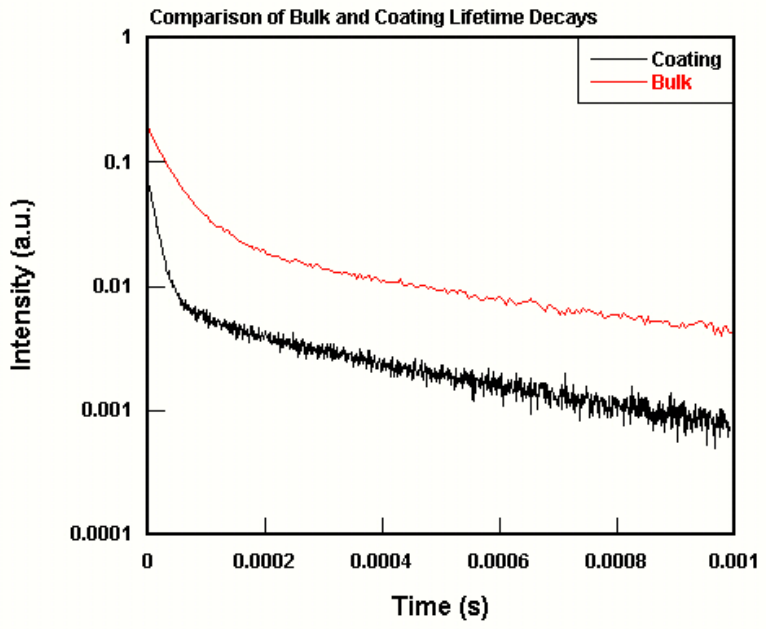

Figure 1. Comparison of the decay in the ${}^5D_o \rightarrow {}^4F_2$ luminescence intensity at 606 nm after a 10 ns laser pulse excitation of a bulk ceramic and a 10 micron thick sensor layer embedded in a standard coating and deposited by electron beam evaporation

From lifetime decay data recorded at different temperatures, the luminescence lifetime as a function of temperature were obtained. An example is shown in figure 2, which again compares the data for a bulk ceramic and an embedded sensor layer only 10 micron thick. Both were the standard 8YSZ composition, used commercially, and doped with 1 m/o $EuO_{1.5}$. In both materials, the luminescence spectra were excited with a frequency-doubled Nd:YAG laser at 532 nm.

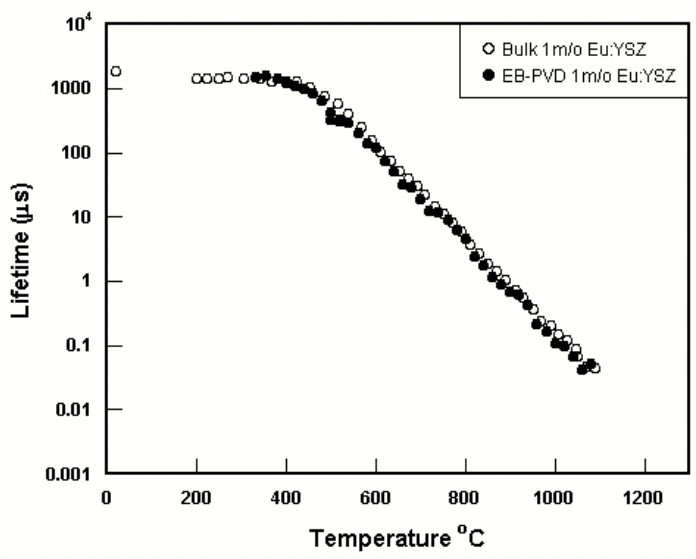

Figure 2. Comparison of the luminescence lifetime decays for a 10 micron thick coating, deposited by electron beam evaporation and a bulk ceramic pellet. The composition of the two materials was 1m/o $EuO_{1.5}$ in standard 8YSZ.

During the current reporting period, the temperature sensor was standardized as a 10 micron thick europium-doped layer deposited by electron beam deposition and embedded in a standard 8YSZ coating of thickness 140 microns.

Towards the end of the preceding year, studies were begun to assess the long-term stability of the europium-based sensors when subject to prolonged, high temperature exposure such as a thermal barrier coating of a gas turbine blade is. Preliminary experiments summarized in the previous report indicated that the luminescence spectra remained essentially unchanged even after isothermal exposure for 195 hours at 1425^{o}C, an exposure far more extreme than current yttria-stabilized zirconia coatings are subject to. During the current reporting period further, more thorough, assessments of the long-term stability were performed with particular reference to the variation of the luminescence lifetime with temperature and the thermal cycle life. These are described in section 2 below. Assessment was made of sensor coatings made by both electron beam deposition and plasma-spraying, the two dominant commercial process technologies used to make thermal barrier coatings. Because of the very long times involved in the aging studies, the number of experiments was, necessarily limited.

In parallel, improvements in developing a fiber-optic based sensor system utilizing the sensor coatings have been made. These are described in section 3 below.

2. LONG TERM, HIGH TEMPERATURE STABILITY

By way of background, current thermal barrier coatings, whether deposited by electron beam evaporation or plasma-spraying, have the metastable tetragonal-prime crystal structure. After extended exposure at very high-temperatures, this metastable phase is known to evolve to a mixture of the tetragonal and cubic phases. On subsequent cooling, the tetragonal phase can transform to the monoclinic phase. This transformation is considered undesirable since it can be accompanied by microcracking and degradation of the coating. To address the question as to whether long-term, high temperature exposure affects the luminescence spectra and lifetimes, electron-beam evaporated coatings of Eu-doped YSZ have been aged for different lengths of time at 1425^{o}C and subsequently aged to produce different concentrations of monoclinic zirconia.

2.1. Aging Treatment

The samples were aged in air for different lengths of time at 1425^{o}C. This temperature was chosen as it has been used in an earlier study of the phase transformation behavior of YSZ coatings by Raman spectroscopy and X-ray diffraction enabling a direct comparison with the luminescence observations being made in this investigation. As previously reported, phase separation evolution occurs but no transformation to monoclinic occurred even after 195 hours at 1425^{o}C. To produce materials with different concentrations of monoclinic phase, the samples heated for different lengths of time at 1425^{o}C were subsequently aged at 150^{o}C in air for 185 hours. The volume fraction of the monoclinic phase was determined by Raman spectroscopy.

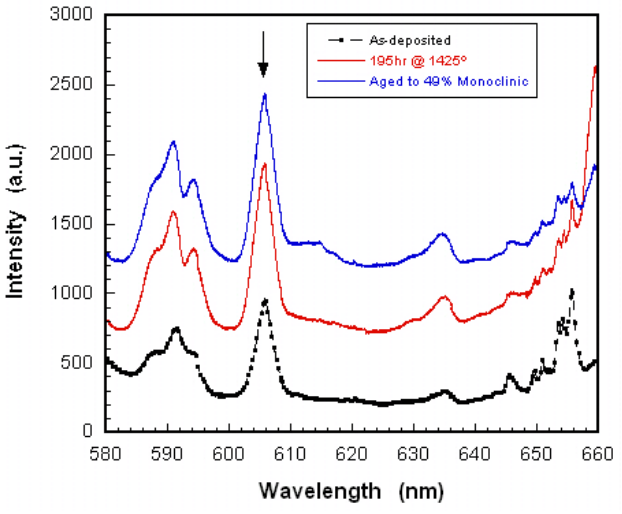

Figure 3. The characteristic luminescence lines of Eu^{3+} from (i) as-deposited EB-PVD coating, (ii) the same coating after annealing for 195 hours at 1425^{o}C, and (iii) after subsequent aging at 150^{o}C for 185 hours, an aging treatment that transforms 49% of the coating to monoclinic zirconia. The luminescence line at 606 nm, used for temperature sensing and arrowed, is unaffected by this aging treatment.

2.2. Effect of Aging on Luminescence Lifetime

Two approaches were taken to investigate the effect of long-term aging on the temperature dependence of the lifetime of the Eu-luminescence at 606 nm. The first was to measure the lifetime-temperature characteristics after successive thermal cycling heat treatments. The second was to accelerate the aging of the coating, as described above through an inter-mediate temperature treatment to produce substantial conversion of the meta-stable tetragonal crystallographic phase to the monoclinic crystallographic phase.

Measurements of the luminescence lifetime at room temperature indicated that any transformation to the monoclinic phase does not alter the bi-exponential luminescence decay, such as illustrated in figure 1, and there are also no additional features in the spectra from other phases. The figure indicates that there is some change in the lifetime-temperature characteristic with transformation to the monoclinic phase but this is within the uncertainty typically seen for room temperature lifetime measurements.

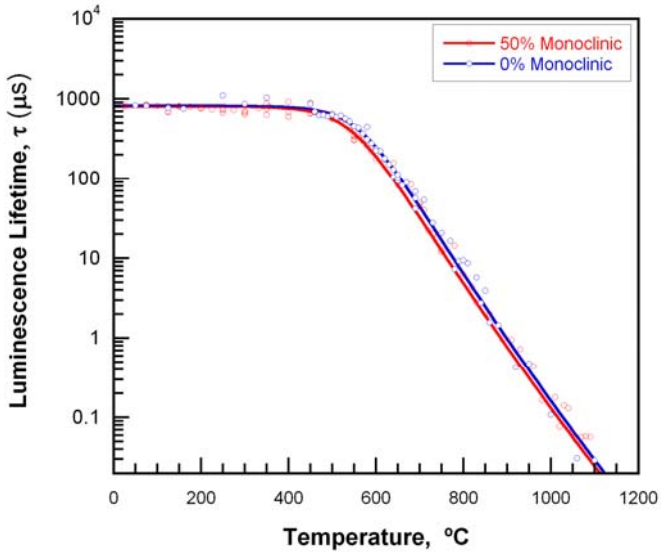

Figure 4. Comparison of the variation of the luminescence lifetime of the $^5D_o \rightarrow {}^4F_2$ *transition at 606 nm as a function of temperature before aging and after prolonged low temperature aging, after 50% of the coating had transformed to the monoclinic phase.*

2.3. Thermal Cycle Life

Thermal cycle tests were performed as well to establish whether or not the incorporation of a sensor layer caused a degradation of the thermal cycle life of the coatings. The coatings, deposited on superalloy coupons with PtNiAl bond-coats, were subjected to thermal cycling between room temperature and 1150°C with one hour holds at 1150°C. This is the same thermal cycling exposure used by several groups, including UCSB, to

test the accelerated life behavior of both bond-coat oxidation and thermal barrier coatings. The effect of successive thermal cycling treatments is shown in figure 5 below.

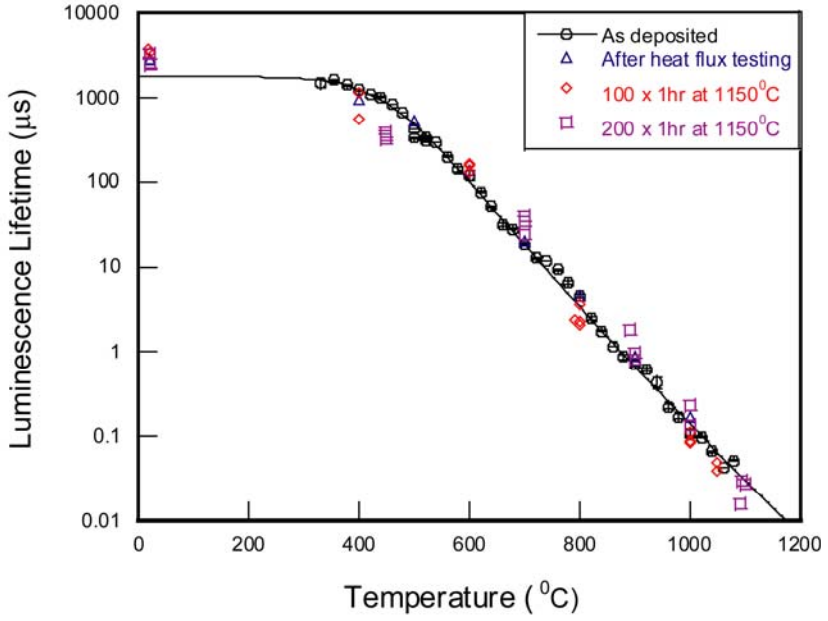

Figure 5. The lifetime-temperature characteristic of Eu-doped YSZ coating in its as-deposited state, after testing in a thermal gradient and after thermal cycling in air at 1150^{o}C for 100 and 200 cycles. There are a few outliers after 200 cycles whose origin is not known. However, overall, all the data after 200 cycles still fits the same fitting function.

The thermal cycle tests performed to date on the electron-beam deposited sensor coatings revealed that the thermal cycle lives were essentially the same as the coatings absent the sensor layer. The lives of the two coatings that had failed by the time of writing were 610 and 590 cycles. Tests of the plasma-sprayed coatings on MCoCrAlY bond-coated alloys are still underway but results obtained to date indicating that the thermal cycle life is at least as long as standard plasma-sprayed 8YSZ coatings on the same bond-coat.

3. FIBER OPTIC BASED LUMINESCENCE DETECTOR SYSTEM

The fiber-optic based luminescence system developed in the preceding period is shown schematically in figure 6. The laser beam from a frequency-doubled Nd:YAG laser, is directed onto the coating or bulk sample situated within the furnace and the luminescence collected with a sapphire fiber whose end is positioned close (within a few centimeters) to the sample. The sapphire fiber is coupled to a standard optical fiber, with an in-line filter to remove any of the laser scattered from the sample, and directly into a

photomultiplier tube (PMT) or an optical spectrometer, depending on the luminescence characterization being performed.

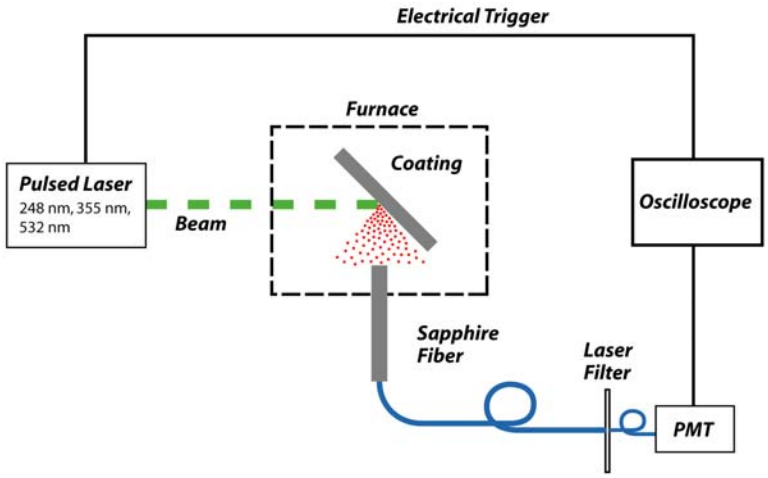

Figure 6. Schematic diagram of the experimental arrangement used to measure the luminescence lifetime of coatings and bulk materials.

For recording the luminescence spectra, the fiber optic is connected to a wavelength dispersive Ocean Optics spectrometer and its output taken straight into a laptop computer for display and recording of the spectra. (In contrast to conventional wavelength spectrometers, the Ocean Optics model has no moving parts). For lifetime measurements, the photomultiplier output is connected to an oscilloscope through a trans-impedance amplifier and the output recorded as a function of time following the trigger pulse sent to trigger the Q-switch of the pulse laser. The oscilloscope output is read directly into a laptop through a GPIB board all under control of Labview^{TM} software.

During the current period, a smaller, air-cooled, solid-state Nd-YAG laser was used in place of the larger, water-cooled Nd:YAG laser. Although somewhat less powerful, the laser pulse length was nominally the same (~ 10 nanosecond). In addition, it was possible to send the laser pulse through a fiber-optic to the sample rather than through free-space, enabling a higher laser flux on the coating. With these improvements, it was possible to implement the system entirely through fiber optics except in the immediate vicinity of the sample itself in the furnace. Not only is this a more efficient system optically but also has obvious safety advantages.

3.1. Use of GaN light emitting diodes

The highest cost as well as the physically largest component in the fiber-optic system developed is the laser. Even though use of the more compact, solid state Nd:YAG reduced both the cost and size of our system, we devoted considerable effort in exploring the use of GaN light emitting diodes (LEDs) as an alternative optical excitation source.

Two commercially available LEDs from Nichia Corporation were evaluated. Their spectral output is shown in figure 7, one peaking at 365 nm and the other at 395 nm. The LEDs were sufficiently intense to stimulate the characteristic $^5D_o \rightarrow {}^4F_2$ luminescence at 606 nm of europium doping. However, these presently available LEDs proved insufficiently intense to make measurements of the luminescence lifetimes at the highest temperatures.

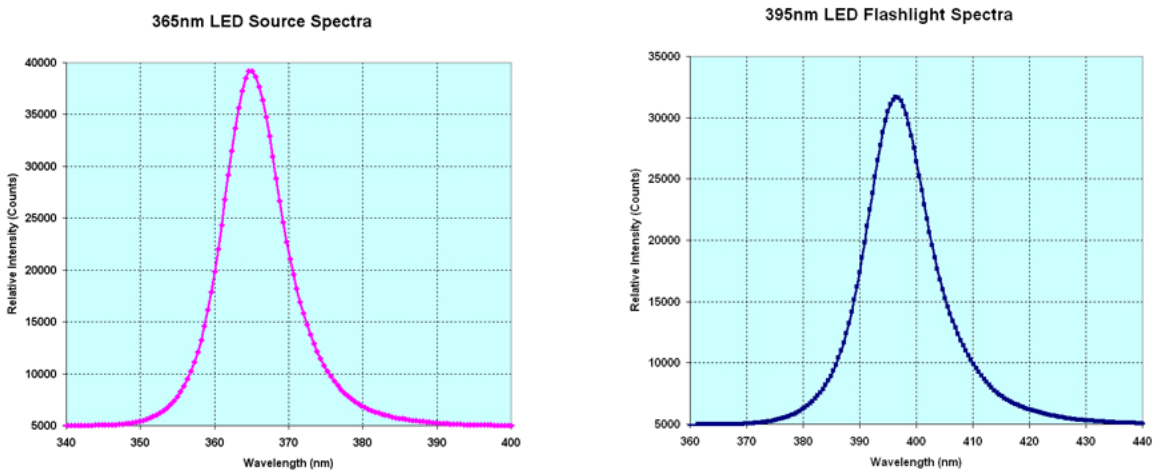

Figure 7. Output spectrum of two Nichia blue LEDs considered for our fiber-optic based temperature sensor system.

Part of the explanation is probably that currently available LEDs emit at non-optimum wavelengths, wavelengths at which the excitation of the europium ions $^5D_o \rightarrow {}^4F_2$ at 606 nm is rather inefficient. The importance of the excitation wavelength is illustrated by the excitation spectra shown in figure 8, reproduced from the previous annual report. As indicated, the wavelengths of 365 and 395 nm correspond to almost the lowest excitation efficiencies. Almost an order of magnitude greater efficiency is possible with excitation at ~ 300 nm and above ~ 520 nm, the wavelength that the frequency-doubled Nd:YAG laser operates.

It is also possible that the relatively low power of current LEDs and the difficulty in focusing the LED emission onto the coatings contributed to the inability to produce sufficiently strong spectra at the highest temperatures for lifetime measurements to be made.

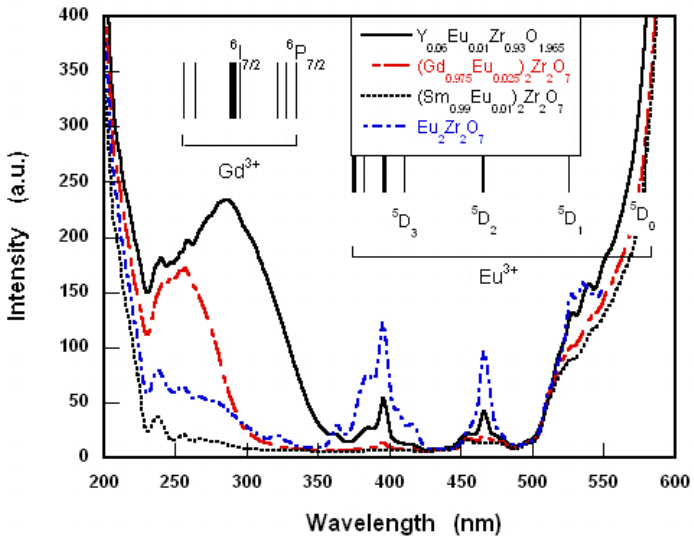

Figure 8. Wavelength spectra of Eu-doped YSZ, $Eu_2Zr_2O_7$ and Eu-doped $Sm_2Zr_2O_7$ and $Gd_2Zr_2O_7$ for excitation of the Eu^{3+} luminescence line at 606 nm. The principal electronic levels of the Gd^{3+} and the Eu^{3+} ions are also shown.

4. SUMMARY

Europium-doped sensor coatings for measuring the temperature of thermal barrier coatings have proved to be stable for at least 195 hours at 1425°C, an exposure far in excess of that yttria-stabilized zirconia coatings are subject to in current gas turbine engines. The variation of luminescence lifetime with temperature, the basis for non-contact, *in-situ* sensing of temperature, remains unchanged even after these extreme conditions and also after almost half the meta-stable tetragonal-prime phase had converted to the monoclinic crystal phase. Furthermore, although an insufficient number of tests have been performed to assure statistical significance, the thermal cycle life of the sensor coatings appears to be indistinguishable from that of the same coatings without the incorporated europium sensor layer.

On the system side, currently available LEDs do not yet have sufficient emissive power to replace the larger, and more costly, Nd:YAG lasers used in the sensor system. However, given the extraordinary developments in GaN LEDs and lasers, it is likely that this situation will change in the next couple of years and a much cheaper, more compact thermal barrier coating temperature sensor will be possible.