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Abstract

Nondestructive and accurate measurement of residual stress in ceramic coatings is challenging, but it is crucial to the assessment of coatings failure and life. In this study, for the first time, the thermal-cycle dependent residual stress in an atmosphere plasma sprayed thermal barrier coating system has been nondestructively and accurately measured using photoluminescence piezo-spectroscopy. Each thermal cycle consists of a 5-minute heating held at 1150 °C and a 3-minute water quenching. The measurement was performed within a crack-susceptible zone in the yttria-stabilized-zirconia (YSZ) top coat (TC) closely above the thermally grown oxide layer. A YSZ:Eu³⁺ sublayer was embedded in TC as a stress sensor. It was found that the initial residual stress was compressive, with a mean value of 240 MPa, which rapidly increased to 395 MPa after 5 thermal cycles (12.5% life) and then increased gradually to the peak of 473 MPa after 25 thermal cycles (62.5% life). After 30 thermal cycles (75% life), the mean stress dropped abruptly to 310 MPa and became highly heterogeneous, with gradual reduction towards final spallation. The heterogeneous stress distribution indicates that many microcracks nucleated at different locations and the spallation occurred due to the coalescence of the microcracks.

Keywords: Thermal barrier coating (TBC), photoluminescence, cracks/cracking, stress, thermal cycling
1. INTRODUCTION

Thermal barrier coating (TBC) has been playing a key role in the development of advanced aircraft engines and energy generators due to its excellent thermal insulation and high durability to protect gas turbine blades\textsuperscript{1-3}. A typical TBC system consists of a ceramic top coat (TC), a thermally grown oxide (TGO, a thin layer formed due to oxidation), a metallic bond coat (BC) and a superalloy substrate\textsuperscript{4}. Each constituent part possesses markedly different thermo-mechanical properties, causing complicated stress field and failure mechanism under thermal cycling\textsuperscript{1}. The main failure mode of TBC systems is the spallation of coatings from the load bearing substrate through cracking in a crack-susceptible zone, which is usually located within TC and close to TC/TGO interface\textsuperscript{5}, as shown in Figure 1a. The thermal cycle induced residual stress in the crack-susceptible zone, which is mainly driven by thermal expansion mismatch, is recognized as the most important cause of the premature spallation of TBC systems\textsuperscript{6}. Therefore, advanced experimental techniques are highly demanded for nondestructive and accurate measurement of the cycling evolution of residual stress, which is crucial for the understanding of failure mechanism, the establishment of life prediction model and the evaluation of structural integrity for TBC systems.

Several types of experimental techniques have been used for the measurement of residual stress in TBC systems. The methods based on curvature change, layer removal and hole drilling are only capable of obtaining average stress, which is insufficient for analysis of microcracks driven by local stress, and moreover, they are either destructive or invasive\textsuperscript{7-10}. The nanoindentation method can be used to measure local stress\textsuperscript{11}, but its intrusiveness of tested sample limits its application.
2D/3D digital image correlation method has the advantages of mapping full-field stress distribution\textsuperscript{12,13}, but it has great uncertainty to define the initial stress state and to process the images. The standard X-ray diffraction (XRD) and the Raman spectroscopy are well-known nondestructive stress measurement methods, but they not suitable to measure under-surface stress in ceramic coatings due to the limitation of their penetration depth\textsuperscript{14,15}. The high energy synchrotron XRD and neutron diffraction methods can overcome the penetration difficulty and achieve relatively high accuracy\textsuperscript{16-19}, but the required facility (e.g. X-ray and neutron sources) is usually difficult and expensive to access, limiting the number of stress measurements that can be made.

To date, photoluminescence piezo-spectroscopy (PLPS) method is the most successful nondestructive technique for measuring residual stress in TBC systems\textsuperscript{20-22}. The PLPS method is based on the linear relationship between stress and peak shift of Cr\textsuperscript{3+} luminescence at 690 nm, which can penetrate through the ceramic coating and is advantageous due to low cost, high efficiency and sufficient accuracy. However, the standard Cr\textsuperscript{3+} PLPS method is only suitable to measure residual stress in TGO. The residual stress within the crack-susceptible zone in TC, which is directly responsible for the coatings spallation, requires more sophisticated measurement technique. Zhao et al.\textsuperscript{23} developed a new experimental technique based on Eu\textsuperscript{3+} PLPS to overcome the aforementioned limitation. However, they used YSZ:Eu\textsuperscript{3+} powder to obtain the relationship between stress and luminescence peak shift, while the actual microstructure of TC is a plasma-sprayed porous ceramic coating.
In present work, we have improved the Eu$^{3+}$ PLPS method to measure the residual stress within the crack-susceptible zone in a 250-μm thick TC of an atmosphere plasma sprayed TBC system. Furthermore, we have obtained the residual stress in an identical TBC sample at room temperature after different thermal cycles, showing the stress evolution as a function of thermal cycle number. The implication of the residual stress is also analyzed and discussed.

2. EXPERIMENTAL PROCEDURE

2.1 Sample preparation

Three plasma-sprayed free-standing YSZ:Eu$^{3+}$ bulk material specimens were produced and used to obtain the relationship between uniaxial stress and Eu$^{3+}$ luminescence peak shift. The specimens in a thickness of 1 mm were prepared onto a graphite substrate (20 mm × 20 mm × 5 mm) using atmosphere plasma-spray (APS) method and then stripped off from the substrate. Eventually, the specimens were cut and polished into 2 mm × 2 mm × 1 mm pieces.

Three normal TBC specimens and one TBC specimen with a YSZ:Eu$^{3+}$ sublayer embedded closely above the TC/TGO interface were fabricated. The three normal specimens were used to identify the thermal-cycle life of the TBC system and hence guide the strategy of measuring the thermal-cycle dependent residual stress. The substrate was nickel-based superalloy Hastelloy X (20 mm × 20 mm × 5 mm). For the TBC specimen with YSZ:Eu$^{3+}$ stress sensor, a 20-μm thick YSZ:Eu$^{3+}$ sublayer was sprayed onto a 150-μm thick BC, followed by the deposition of a 230-μm thick TC composed of YSZ,
all using APS method. The TBC specimens were finally cut into a rectangular shape (2.5 mm × 3.5 mm) and the cross-section is schematically shown in Figure 1b. Detailed parameters used in thermal spraying can be found in a previous study\(^{24}\).

### 2.2 Calibration test

A micro-loading system (Microtest 2000, Deben, UK) with a load capacity of 2000 N was integrated into a spectroscopy equipment (HR 800, Horiba, France) for the calibration test, as shown in Figure 2a. A 532-nm laser was used to excite the Eu\(^{3+}\) ions in the YSZ:Eu\(^{3+}\) lattice. The spectral resolution was set as 0.3 cm\(^{-1}\) with 1800 g/mm grating. The objective magnitude was chosen to be 10× to ensure a much larger laser beam spot size than the grain size of TBC\(^{20}\). The acquisition time was 15 s at 10% laser power. The luminescence spectrum of plasma-sprayed free-standing YSZ:Eu\(^{3+}\) specimens were recorded at different uniaxial compressive stresses at the same location with a load interval of 50 MPa up to 350 MPa. The Lorentz curve method was selected to fit the spectrum and determine the peak position of \(^{5}D_0^{-7}D_2\)\(^{23}\). Three specimens were tested to obtain the average result.

The relationship between uniaxial stress, \(\sigma_U\), and the luminescence peak shift, \(\Delta \nu\), can be expressed as\(^{15}\)

\[
\Delta \nu = \Pi_U \sigma_U, \tag{1}
\]

where \(\Pi_U\) is piezo-spectroscopic coefficient (PSC) under uniaxial stress state, and

\[
\Delta \nu = \nu_s - \nu_0, \tag{2}
\]

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with \( v_o \) being the peak position for the stress-free state and \( v_s \) being the peak position for the stressed state. The PSC value, \( \Pi_U \), can be obtained from the slope by linear fitting the experimental data of \( \sigma_U \) and \( \Delta v \). The stress state in the YSZ:Eu\(^{3+}\) sublayer in the TBC specimen is assumed to be biaxial (i.e. \( \sigma_{xx} = \sigma_{yy}, \sigma_{zz} = 0 \)), and the biaxial residual stress can be rewritten as\(^{15}\)

\[
\frac{\sigma_{xx} = \sigma_{yy}}{\sigma_{zz}} = \frac{\Delta v}{2 \Pi_U}.
\]

Therefore, the biaxial residual stress in the crack-susceptible zone can be determined when the Eu\(^{3+}\) luminescence peak shift in the YSZ:Eu\(^{3+}\) sublayer is measured.

### 2.3 Thermal-cycle dependent residual stress measurement

For the TBC specimen with YSZ:Eu\(^{3+}\) stress sensor, a mineral oil impregnated approach was adopted to alleviate Eu\(^{3+}\) luminescence attenuation by pores and microcracks, which enhances the PLPS signal for detection during the stress measurement\(^{25}\). The entire TBC specimen was vacuum-impregnated with mineral oil (Johnson & Johnson, New Brunswick, NJ) for 60 min before stress measurement. The spectroscopy equipment was used to record the Eu\(^{3+}\) luminescence spectrum of the YSZ:Eu\(^{3+}\) sublayer inside the TBC specimen. The evolution of residual stress within the crack-susceptible zone of one identical specimen was determined at room temperature after different number of thermal cycles. Each thermal cycle consisted of a 5-minute holding at 1150 °C and a 3-minute water quenching to 20 °C, as shown in Figure 2b. The thermal cycling life of the TBC system was defined to be the thermal cycle number when approximately 20% coating surface was damaged. The excitation laser, the spectral resolution, and the objective magnitude were set same as those used in the calibration test. The acquisition time was set to be 60 s at 100% laser power. An
in-plane area of 2.5 mm × 3.5 mm was measured point by point with moving the focused laser beam, and 10 vertical rows and 14 horizontal columns were scanned. Each data point corresponds to an approximately 250 μm spatial resolution.

3. RESULTS AND DISCUSSION

Figure 3a illustrates the characteristic peak of $^5D_0-^7D_2$ obtained from YSZ:Eu$^{3+}$ luminescence spectra and the peak shift due to compressive stress. Figure 3b presents the relationship between uniaxial compressive stress and Eu$^{3+}$ luminescence peak shift for the plasma-sprayed free-standing YSZ:Eu$^{3+}$ specimen. The peak shift was obtained at the same location independent of applied stress. This procedure is effective to reduce scattering associated with the location of the measured area$^{15}$. The observed luminescence peak (main peak of $^5D_0-^7F_2$ transition) shifts linearly with stress. The linear relation can be described and fitted by

$$v_s - v_0 = \Pi_U \sigma_U,$$

where $v_0$ is 16508.49 cm$^{-1}$ and $\Pi_U$ is 4.32 cm$^{-1}$/GPa, with a Pearson correlation coefficient of 0.9897.

Figure 4 shows the measured distributions of the biaxial residual stresses in the crack-susceptible zone after different number of thermal cycles. The average thermal cycling life of the TBC system is determined to be 40 cycles under water-quenching condition. The residual stress
(positive in compression) is color-coded and the stress-scale is adjusted to optimize the colour contrast. It is clearly seen that the residual stress was compressive and the initial stress value was 220–260 MPa, and then it increased to 400–450 MPa after 10 thermal cycles (25% of TBC life), and to 450–550 MPa after 20 thermal cycles (50% of TBC life). Afterwards, the residual stress dropped abruptly and exhibited a significantly inhomogeneous distribution, for which the low-stress areas correspond to the presence of cracks while the high-stress areas are mainly composed of intact ceramic materials. The high heterogeneity in residual stress indicates that the damage occurred not through the initiation and growth of single major crack, but rather many microcracks nucleated at different locations and the final spallation was caused by the coalescence of these microcracks.

Figure 5 shows the evolution of the mean and standard deviation of the biaxial compressive residual stress in the crack-susceptible zone, as a function of thermal cycle number. The whole evolution of residual stress can be divided into two stages, i.e. the stress development and relaxation stages. In the stress development stage (0–25 thermal cycles, 0%–62.5% of TBC life), the stress accumulated due to the thermal expansion mismatch after heating and cooling. The stress firstly rose rapidly from a mean value of about 240 MPa to 395 MPa after 5 thermal cycles (12.5% of TBC life), and then increased gradually until reaching a mean value of about 473 MPa after 25 thermal cycles (62.5% of TBC life). The initial residual stress measured here is consistent with Zhu et al.’s measurement\textsuperscript{26}, i.e. ~200 MPa near crack-susceptible zone in the TBC system, while the revealed feature of residual stress evolution until spallation has not been reported before. The measured spallation stress in this study is close to that reported by Zhao et al.\textsuperscript{11}, who found a compressive failure stress of 500 MPa near TC/TGO interface using a nanoindentation method. In
the stress relaxation stage (25–40 thermal cycles, 62.5%–100% of TBC life), the stress dropped rapidly after peak stress but decreased slowly afterward, indicating that most damages occurred quickly at a critical moment. The decrease in residual stress is mainly due to the nucleation and coalescence of microcracks in the crack-susceptible zone, as inferred from Figure 4. The standard deviation (60–75 MPa) of residual stress in the relaxation stage is much larger than that (15–25 MPa) in the stress development stage. This further confirms that the microcracks nucleate at different locations and their coalescence leads to the spallation. This cracking behavior can be mainly attributed to the highly heterogeneous microstructure of the APS coatings.

4. SUMMARY

We have developed an improved Eu$^{3+}$ PLPS method to nondestructively and accurately measure the residual stress within the crack-susceptible zone in a 250-μm thick TC of a TBC system. The residual stress was obtained as a function of thermal cycle number. The relationship between uniaxial residual stress and luminescence peak shift in the YSZ:Eu$^{3+}$ sublayer (i.e. stress sensor) embedded in TC was directly determined by a calibration test using a micro-loading device integrated into a spectroscopy equipment for plasma sprayed YSZ:Eu$^{3+}$ bulk material, which provides a solid basis of accurate stress measurement. The biaxial compressive residual stress increased rapidly from 240 MPa to 395 MPa after 5 thermal cycles (12.5% of TBC life) and then gradually increased until reached a peak value of 473 MPa after 25 thermal cycles (62.5% of TBC life). After 30 thermal cycles (75% of TBC life), the stress dropped drastically to around 310 MPa and became highly heterogeneous, followed by a gradual reduction in mean stress after 40 thermal cycles (100%
of TBC life) wherein 20% coatings damage developed. The highly heterogeneous stress distribution 
after the critical stress value indicates that the spallation occurred due to the nucleation and 
coalescence of many microcracks at different locations. The accurate measurement results of 
residual stress within the crack-susceptible zone, as presented in Figures 4 and 5, can be further 
used to examine TBC failure theory and validate TBC life prediction model.

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Captions:

FIGURE 1. (a) Typical failure of a TBC system due to TC cracking in a crack-susceptible zone located close to TC/TGO interface; (b) schematic of a TBC system with a 20-μm thick YSZ:Eu$^{3+}$ sublayer (i.e. stress sensor) embedded in the crack-susceptible zone.
FIGURE 2. (a) A micro-loading system integrated into a spectroscopy equipment for the calibration test; (b) the temperature changes of the TBC specimen during thermal cycling.

FIGURE 3. (a) Schematic plot of luminescence peak shift for YSZ:Eu$^{3+}$ under compressive stress. (b) The variation of peak position, i.e. luminescence peak shift, of plasma-sprayed YSZ:Eu$^{3+}$ bulk material with uniaxial compressive stress.

FIGURE 4. Biaxial compressive residual stress distribution within the crack-susceptible zone in the TBC system after different number of thermal cycles.

FIGURE 5. The mean and standard deviation of the thermal-cycle dependent biaxial compressive residual stress within the crack-susceptible zone in the TBC system.
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