Detection of Micro-Damage Evolution of Air Plasma-Sprayed Y$_2$O$_3$-ZrO$_2$
Thermal Barrier Coating through TGO Stress Measurement

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The micro damage evolution behavior in air plasma-sprayed 8 mass% Y$_2$O$_3$ stabilized ZrO$_2$ thermal barrier coating (APS-TBC) after isothermal heat exposure at 1150°C up to 200 h was observed. Residual stress of thermally-grown-oxide (TGO) layer was measured through the TBC layer using Cr$^{3+}$ luminescence spectroscopy and the measured stress levels were compared with micro damage evolution behavior stored in the TBC system. With heat exposure time of longer than 10 h, microfracture behaviors were noted in the TBC layer. In-plane residual stress of the TGO layer increased for up to 50 h of heat exposure time, and thereafter, diminished with further increase. These behaviors are strongly correlated with the thickness and the residual stress of the TGO layer. This decrease in the TGO stress well contrasts with the evolution of the micro fracture behavior, which is also related to the thickness and undulation of the formed TGO layer. The change of TGO stress, $\sigma_{tgo}$, depending on the average thickness of the TGO layer, $h_{tgo}$, i.e., $d\sigma_{tgo}/dh_{tgo}$ is a useful indicator of the damage evolution in TGO: $d\sigma_{tgo}/dh_{tgo} > 0$: slight damage stage, $d\sigma_{tgo}/dh_{tgo} < 0$: micro fracture evolution stage. The result suggests that Cr$^{3+}$ luminescence spectroscopy is a good indicator for micro damage evolution in the TBC layer and is a useful tool for nondestructive evaluation (NDE) of APS-TBC systems. [doi:10.2320/matertrans.47.2512]

(Received July 24, 2006; Accepted August 31, 2006; Published October 15, 2006)

Keywords: thermal barrier coating (TBC), heat exposure, thermally-grown-oxide (TGO) layer, residual stress, luminescence spectroscopy, damage, crack, nondestructive evaluation (NDE)

1. Introduction

Thermal barrier coatings (TBCs) have been used in gas turbines because they allow 100~200°C higher operating temperature. Among TBCs, studies on air plasma-sprayed (APS) thermal barrier coatings (APS-TBCs) have shown that the damage evolution in an APS-TBC system is strongly affected by the formation of a thermally-grown-oxide (TGO) layer, which results from oxygen diffusion through a ZrO$_2$ TBC layer and diffusion of Al from a bond coat (BC) layer. Therefore, the damage evolution behavior stored in a TBC system has been an important subject of research and many efforts have been devoted to understanding such damage behaviors in APS-TBCs. The formation of a TGO layer causes large ~ GPa order residual stress, and undulation of the TGO layer by this large in-plane compressive stress leads to micro fracture in the TGO layer, in the TBC layer and/or interface delamination between these two layers or the BC layer.

The effect of TGO layer growth and undulation on micro damage evolution in Y$_2$O$_3$ stabilized ZrO$_2$ APS-TBCs with NiCoCrAlY bond coat (BC) has been reported. The reports suggest that large tensile stress of TGO and TBC layers generated by undulation of a formed TGO layer is a major source of crack nucleation and growth of a crack in the TBC layer, and an interface between the TGO and BC layers. The delamination behavior of a TBC layer occurs after growth and linkage of microcracks to a certain crack length. The growth and linkage of micro damage are also undesirable behavior because they lead to delamination of TBC layers from a substrate. In another studies, it is reported that most of these behaviors are strongly related to the residual stress stored in the TGO layer. From typical examples, it is clear that the damage evolution behavior in the APS-TBC system is strongly related to a residual stress of the TGO layer.

To date in the experimental measurement of TGO stress, luminescence spectroscopy from Cr$^{3+}$, which is contained in the formed TGO layer has been applied for various types of thermal barrier coatings. The method seems an attractive tool for nondestructive detection of damage stored in a TBC system. Many studies have been reported on the TGO stress measurement in various kinds of TBC systems. However, the relation between micro damage evolution and residual stress in the TGO layer is not well understood. This relation depends strongly on TBC materials and growth condition of the TGO layer, hence, it is important to obtain detailed information on a candidate TBC system.

The present study focused on the micro structural observation of damage evolution and the change in TGO stress. The use of a measured relationship between TGO stress and micro fracture behavior stored in an APS-TBC system is discussed for application of nondestructive evaluation (NDE).

2. Experimental Procedure

2.1 Air plasma-sprayed TBC system

An air plasma-sprayed thermal barrier coating system processed by Kawasaki Heavy Industries Co., Ltd., Akashi, Japan, was used throughout. The thermal barrier coating (TBC) layer was 8 mass% Y$_2$O$_3$-ZrO$_2$ (hereafter denoted as 8Y-ZrO$_2$). The bond coat (BC) was NiCoCrAlY which had a chemical composition of 22 mass% Co, 17 mass% Cr, 12.5 mass% Al, 0.6 mass% Y and the remainder Ni. The substrate was ≈3 mm thick Inconel 738, and was comprised of a Ni-base superalloy containing 16 mass% Cr, 8.5 mass% Co, 3.5 mass% Al and 3.5 mass% Ti with the remainder Ni. Figure 1 shows a typical polished transverse section of the TBC system observed by optical microscope; two different layers
are clearly distinguished in the section, i.e., TBC layer, BC layer, and substrate. Thickness of the TBC layer was 250 μm and that of the bond coat layer was 150 μm. Hereafter coated material is referred to as the “TBC system.”

2.2 Isothermal heat exposure

Isothermal heat exposure of the TBC system was done in ambient air at a temperature of 1150°C. The TBC specimen with dimensions of 10 by 10 by 3.5 mm thick was placed on an alumina plate and put into an electric furnace. The specimen was heated in ambient air at a rate of 5°C/min until the temperature reached 1150°C, where it was maintained for 10, 50, 100 and 200 h. Different specimens were used for each heat exposure condition. After exposure to the heat for the selected time, the specimen was allowed to furnace cool to room temperature: time required for the cooling was 13.5 ks. As heat-exposed specimens were embedded in an epoxy resin and microstructure on the polished sections perpendicular to through-thickness plane was polished using a standard metallurgical process. These polished sections were observed by optical microscope and scanning electron microscope (SEM). For SEM observation, a thin Au coating was applied to avoid charge-up.

2.3 Stress measurement in TGO layer

Luminescence spectroscopy from Cr³⁺ was used to measure stress in the TGO layer. During the growth of this layer (typically polycrystalline α-Al₂O₃), a very small amount of Cr in a bond coat (BC) layer was trapped within it. The measurement was done at a fully controlled temperature (20°C) in ambient air using a micro-focus laser luminescence spectroscopy system (NRS-1000: Special Version, JASCO Corp., Tokyo, Japan). A green laser (wavelength: 532 nm) with laser power of 100 mW was used as an excitation source and a laser beam was incident perpendicular to the in-plane surface of the TBC layer, i.e., from the outermost surface of specimen. The definitions of x, y, and z coordinates and associated stress components are shown in Fig. 2. Diameter of the incident laser beam at the specimen surface was approximately 4 μm. Resolution of a spectrometer in the spectroscopic wavenumber range used (14363–14449 cm⁻¹) was less than 0.2 cm⁻¹, which gave the measured stress resolution of approximately 40 MPa. Analysis of obtained luminescence spectra was made using built-in software designed by JASCO Corp.

The measured frequency shift from Cr³⁺ luminescence, Δν, was converted to a stress, σ_tgo, using R₂ luminescence peak series assuming the linear relation between Δν and σ_tgo,

\[ \Delta \nu = \Pi \sigma_{tgo} \]  

where Π is the piezo-spectroscopic coefficient for in-plane bi-axial stress condition of the TGO layer. The R₂ peak was chosen because it has been successfully used to evaluate residual stress in this layer. Under this condition, the coefficient Π is given as Π = 5.07 cm⁻¹/GPa.

Assuming plane stress condition in the entire TBC system and neglecting the shear stress component between the layers, measured stress by luminescence spectroscopy of the TGO layer is given by

\[ \sigma_{tgo}^{exp} = \frac{\sigma_x^{tgo} + \sigma_y^{tgo} + \sigma_z^{tgo}}{3} \]  

where \( \sigma_{tgo}^{exp} \) is the measured stress in the layer and \( \sigma_x^{tgo}, \sigma_y^{tgo}, \) and \( \sigma_z^{tgo} \) are the stress components of x, y, and z directions, respectively (cf. Fig. 2). Assuming the plane stress condition of the entire TBC system, the stress component in the TGO layer in through-thickness direction is zero (\( \sigma_z^{tgo} = 0 \)), and then eq. (2) becomes

\[ \sigma_{tgo}^{exp} \approx \frac{2}{3} \sigma_{tgo}^{x} = \frac{2}{3} \sigma_{tgo}^{y} \]  

Here, the stress components \( \sigma_x^{tgo} \) and \( \sigma_y^{tgo} \) are assumed to be the same, i.e., \( \sigma_x^{tgo} = \sigma_y^{tgo} \), because of the in-plane bi-axial stress state in the TGO layer. In the present measurement, the converted stress corresponds to an average value of an in-plane stress (x-y plane) in the TGO layer, \( \sigma_{tgo}^{xy} \). After the onset of undulation in a TGO layer, the stress is no longer uniform but has a distribution and is highly dependent on the morphology of the layer. The large standard deviation of the measured stress in this study incorporates the scattering by undulation of the TGO layer, and is mostly the local stress component of \( \sigma_{tgo}^{xy} \) in eq. (2).

3. Experimental Results and Discussion

3.1 TGO growth behavior and morphology

Figure 3 shows examples of the polished transverse section of the entire TBC system after heat exposure, and shows the change of microstructure and formation of a
thermally grown oxide layer. In as-coated condition, many pores and inter-splat cracks are visible (cf. Fig. 1), which are typical of APS-TBCs. After heat exposure for \( t_h = 10 \) and 50 h (Fig. 3(a), (b)), the microstructure of the TBC layer seems essentially the same as that observed in the as-coated one. The major differences are (i) growth of a continuous but irregularly-shaped TGO layer, which is seen between the TBC and the BC layers, and (ii) decrease in the number of small pores and narrow inter-splat boundaries in the TGO layer by the progress of sintering. After heat exposure for \( t_h = 100 \) h, the thickness of this layer is obviously thicker than that observed at \( t_h = 10 \) and 50 h; detailed observation shows that dark gray (D) and light gray (L) regions exist in the layer. Most of the light gray region develops at the convex part of the layer (example is indicated by “L”); the irregularity of light gray TGO tends to increase with the lengthening of heat exposure. The light gray region that formed within the TBC layer next to the TGO layer is spinel with a composition of \((\text{Ni, Co})(\text{Cr, Al})_2\text{O}_4\). The number of transverse cracks in the TBC layer also increases with longer heat exposure, this behavior is explained by a local sintering of TBC layers; i.e., the dense regions and the narrow inter-splat boundaries are likely to sinter and the large inter-splat gap tends to open due to local shrinkage as reported elsewhere.

Plots of average thickness of the TGO layer, \( \bar{h}_{\text{tgo}} \), versus heat exposure time, \( t_h \) are shown in Fig. 4. Here, the average thickness is defined as

\[
\bar{h}_{\text{tgo}} = \frac{\sum_{i=1}^{N} h'_{\text{tgo}}}{N},
\]

where \( h'_{\text{tgo}} \) is the \( i \)-th thickness of the TGO layer and \( N \) is the number of measurements, typically \( N = 100 \) for the same heat exposure condition. The measurement was done drawing 100 equally spaced lines (interval: 7 \( \mu \)m) on an optical microscope photograph (net magnification \( \times 200 \)) of a polished transverse section of a specimen. As clearly shown in Fig. 4, the thickness of the TGO layer increases with longer exposure to heat. It has been reported that the thickness of the layer in APS-TBCs is empirically expressed as

\[
\bar{h}_{\text{tgo}} \approx k(t_h)^m
\]

where \( k \) and \( m \) are the constants which depend on heat exposure conditions. The present experimental result yields \( m \approx 0.3 \), which is nearly the same as the range of reported values (0.3 < \( m < 0.4 \)). This suggests that growth mechanism of the TGO layer is similar to the reported mechanism (\( m \approx 0.5 \)). Figure 5 shows the change of distribution in thickness of the layer with heat exposure time. After exposure for 10 h, most of the thickness in the layer falls between 2 and 18 \( \mu \)m. With increase in exposure, the scattering of thickness obviously increases, e.g., the scattering of the thickness after heat exposure for 200 h becomes 6 to 42 \( \mu \)m with an average of 14 \( \mu \)m. It is reported that a TGO layer formed in the same-processed TBC system after long-term heat exposure (e.g., \( t_h = 100 \) h at 1150°C) is not a single polycrystalline \( \alpha\)-\( \text{Al}_2\text{O}_3 \) phase but that the layer consists of oxides with multiple elements. In addition, YAG (\( \text{Y}_2\text{O}_3\)-\( \text{Al}_2\text{O}_3 \)) phase growth is likely to occur within a polycrystalline \( \alpha\)-\( \text{Al}_2\text{O}_3 \) TGO layer. As shown before, the TGO layer consists of two phases and the light gray phase (L) is considered to be a spinel phase. The measured thickness includes growth of the spinel phase and effect of this phase becomes greater with increase in heat exposure time, because growth of this phase becomes significant after exposure to \( t_h \geq 100 \) h. Consequently, an increase of scattering in the TGO layer thickness with period of heat exposure is largely due to the spinel formation.

The formed TGO layer is wavy in shape. The origin of this undulation is the lower thermal expansion of the formed TGO layer (polycrystalline \( \alpha\)-\( \text{Al}_2\text{O}_3 \); \( \alpha_{\text{tgo}} \approx 8–9 \times 10^{-6} \text{ K}^{-1} \)) than that of superalloy substrate: \( \alpha_{s} \approx 13–16 \times 10^{-6} \text{ K}^{-1} \). The undulated morphology, e.g., shape and wavelength, of the entire TGO layer in the present study seems to have no significant difference in different heat exposure time although there is increased scattering of the thickness with formation of a spinel phase at the convex region.

The microcrack formation behavior is highly dependent on the thickness and the morphology of a TGO layer as reported elsewhere. Figure 6 shows typical examples of microcrack formation behavior observed in the specimen after heat exposure for \( t_h = 100 \) and 200 h. It is obvious that formation of microcracks occurs near a convex region of the TGO layer. Growth and shrinkage of the formed microcracks become
significant after heat exposure for $t_h = 200\ h$, some of formed cracks grow towards the TBC layer and along and in between the TGO layer and TBC layer. Crack nucleation behavior becomes significant after onset of an increase in population of spinel (light gray region (L)), the time required to reach this condition in the present study was about $t_h = 100\ h$. The linkage and growth of the nucleated microcracks dominated the damage after heat exposure for $t_h = 100\ h$: this condition occurs when formation of a spinel phases extends during the entire TGO layer. The morphology of this layer does not change significantly with heat exposure time, and therefore the microcracking behavior seems strongly correlated with the formation of spinel phases, which occurs under heat exposure for more than 100 h under the present isothermal heat exposure conditions. However, it should be pointed out that these conditions employed in this study (temperature: 1150 °C) are very severe for the formation of a TGO layer because the temperatures of the BC layer and substrate are usually below 1000 °C.28)

### 3.2 Residual stress in TGO layer

Figure 7 shows a typical example of Cr$^{3+}$ luminescence spectra of the specimen exposed to heat for $t_h = 10$ and 200 h. Spectra are measured from through-thickness direction. It is clear that the measurement of Cr$^{3+}$ luminescence signals through relatively thick ($\sim$210μm) air plasma-sprayed coating is possible with quite a high S/N ratio, similar to a case of electron beam-physical vapor-deposited (EB-PVD) TBC.29) In addition, the effect of luminescence signal from the Y$_2$O$_3$ stabilized ZrO$_2$ TBC layer could be neglected in the present case because there was no detection of Cr$^{3+}$ luminescence at the same wavelengths from a polished transverse section of the layer under the same luminescence measurement conditions. The effect of light scattering from a TBC layer usually appears in measured spectra because the latter contains many light scattering sources.14) Thus, the intensity of emitted luminescence from the TGO layer has a low S/N ratio compared to that obtained from direct illumination of the polished transverse section of
the TBC layer and its distribution on an interface between the TBC and TGO layers.

4. Discussion

The present experimental results show that the residual stress in the TGO layer increases after heat exposure time \( t_0 = 10 \) h, then, decreases with further increase in the time. The micro fracture behavior seems to be correlated with the measured stress in the TGO layer. Therefore, the relation between the TGO stress and evolution of the micro fracture behavior observed in the present thermal barrier coating system are discussed.

The residual stress in TGO is known to be highly dependent on the growth stress; thermal mismatch stress, stress associated with its shape, and creep behavior in TBC layer, TGO and BC layer etc.\(^{30}\) These effects are well analyzed in the available literature.\(^{10,30–32}\) Growth strain and thermal mismatch strain are positive effects for the increase, and creep and undulation effects are negative. Figure 9 shows plots of measured average TGO stress, \( \bar{\sigma}_{\text{tgo}}^{\text{exp}} \) versus average TGO layer thickness, \( \bar{h}_{\text{tgo}} \). It is clear that the TGO stress increases to \( \bar{h}_{\text{tgo}} = 9 \) \( \mu \)m, therefore, the slope of the relation is positive \( \frac{d\bar{\sigma}_{\text{tgo}}^{\text{exp}}}{dh_{\text{tgo}}} > 0 \). On the other hand, when the TGO layer thickness exceeds \( \bar{h}_{\text{tgo}} = 9 \) \( \mu \)m, the measured stress decreases, therefore, the slope is negative, \( \frac{d\bar{\sigma}_{\text{tgo}}^{\text{exp}}}{dh_{\text{tgo}}} < 0 \). This result is difficult to explain without considering negative effects for the evolution of TGO stress.

It is reasonable to assume that both undulation of TGO layer and microcrack evolution in TBC and/or TGO layers reduce net residual stress in the TGO layer because the cracking releases this. Observations of the polished transverse sections show no clear difference in the shape of the TGO layer. Therefore, the major change of the TGO stress seems reasonable and originates from a location dependent on TGO stress. To understand the scattering behavior more clearly, additional experiments are needed including a scattering effect of incident laser beam in the same TBC system using the same measurement system.\(^{23}\) The change of light scattering does not affect the peak shift of the \( \text{Cr}^{3+} \) luminescence. Therefore, the effect of scattering is not considered here.

The change in average TGO layer stress, \( \bar{\sigma}_{\text{tgo}} \), with heat exposure time is shown in Fig. 8. The measurements were done randomly selected 10 points. Approximately, the stress is in bi-axial in-plane compression state with a level of few GPa. The orders of the measured stress value agree quite well with the similar experimental results\(^{41}\) and the numerically calculated values.\(^{20}\) At the beginning of heat exposure, the measured TGO stress slightly increases and then gradually decreases with increasing time. This stress increase occurs after heat exposure of \( \bar{h} = 50 \) h and when the compressive stress reaches \( \sim 2.2 \) GPa. However, after heat exposure for \( \bar{h} = 100 \) h, the measured stress in the TGO layer obviously decreases with an increase in the period of exposure. Stress in the TGO layer is not uniform but has a scattering, which is associated with the morphology.\(^{23,29}\) Therefore, the scattering of the present stress seems reasonable and originates from a location dependent on TGO stress. To understand the scattering behavior more clearly, additional experiments are needed including a scattering effect of incident laser beam in
the TBC layer also introduces cracking in the TBC layers, most of which are located perpendicular to the transverse direction of the TBC layer.25) This crack formation contributes to the decrease of the effective in-plane Young's modulus of the TBC layer. The origin of this type of cracking behavior is reported to be local shrinkage of the APS-TBC layer, which depends on the uniquelamella structure of this layer.25) When the average TGO layer thickness exceeds \( h_{\text{tgo}} = 9 \text{\mu m} \), many microcracks both in the TGO and in TBC layers are evident. Microcracking in the TBC layer near the adjacent TGO layer also releases stress in the TGO layer, although it is difficult to explain quantitative analysis within the present study.

Summarizing the results, it is clear that stress in the TGO layer is closely related to micro fracture evolution in APS-TBC systems. The measurement of a TGO stress by Cr layer is closely related to micro fracture evolution in APS-TBC systems. However, the relationship between TGO stress and micro damage behavior should be clearly understood prior to the application of the present procedure for NDE of a TBC system.

5. Conclusions

The change of residual stress in an air plasma-sprayed thermal barrier coating (APS-TBC) system after heat exposure in ambient air has been studied. The evolution of residual stress in a TGO layer depends on the micro damage evolution in TBC and TGO layers. The major sources of microcracks in TBC and TGO layers, respectively, are local densification and spinel formation, which occur after shortage of Al in the BC layer. The measured in-plane TGO stress is well correlated to the micro fracture evolution in the TBC layer. The change of TGO stress with its thickness, i.e., \( \sigma_{\text{tgo}}/d_{\text{tgo}} \), is a useful indicator of damage evolution in a TBC system. When the rate is \( \sigma_{\text{tgo}}/d_{\text{tgo}} > 0 \), damage introduced in the TBC layer is small, while when the rate is \( \sigma_{\text{tgo}}/d_{\text{tgo}} < 0 \), a micro fracture evolution has occurred in the layer.

The stress in TGO is detectable through the TBC layer and therefore the stress change, \( \sigma_{\text{tgo}}/d_{\text{tgo}} \), is an effective indicator to estimate the existence of micro damage evolution in an APS-TBC system. This change could be detected through the TBC layer, and therefore no need for cutting the TBC system. However, the micro damage evolution behavior is highly dependent on the APS-TBC system and heat exposure conditions. Engineering application of the present method for non-destructive evaluation (NDE) needs more extensive experimental work including more realistic thermal cycling conditions and a wider variety of temperatures and holding times.

Acknowledgement

This work was performed as a part of the Nano-Coating Project carried out by the New Energy and Industrial Technology Development Organization.

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