A microstructural observation of near-failure thermal barrier coating: a study by photostimulated luminescence spectroscopy and transmission electron microscopy

B.W. Kempshall a,1, Y.H. Sohn a,*, S.K. Jha a,2, S. Laxman a, R.R. Vanfleeta,3, J. Kimmel b

a Advanced Materials Processing and Analysis Center and Department of Mechanical, Materials and Aerospace Engineering, University of Central Florida, P.O. Box 162455, 4000 Central Florida Blvd. Orlando, FL 32816-2455, USA
b Solar Turbines, A Caterpillar Company, 2200 Pacific Highway, P.O. Box 85376, San Diego, CA 92186-5376, USA

Received 23 December 2002; received in revised form 29 January 2004; accepted 20 February 2004

Available online 6 May 2004

Abstract

An intact thermal barrier coating (TBC) specimen, consisting of electron-beam physical vapor deposited (EB-PVD) ZrO2 - 7 wt.%Y2O3 (YSZ) topcoat, thermally grown oxide (TGO), grit-blasted (Ni, Pt)Al bond coat and CMSX-4 single crystalline superalloy, was characterized after 645 thermal cycles. Each thermal cycle was carried out in air, and consisted of 10-min heat-up to 1038 °C, 10-h hold at 1038 °C, and 10-min forced air-quench to ambient temperature. Characteristics of TGO scale were initially examined by photostimulated luminescence spectroscopy (PSLS) and scanning electron microscopy equipped with energy dispersive spectroscopy (EDS). Transmission electron microscopy (TEM) and scanning TEM (STEM) with nano-spot energy dispersive spectroscopy, high-angle annular dark field (HAADF) imaging, selected area diffraction (SAD), convergent beam electron diffraction (CBED), and electron energy loss spectroscopy was carried out for detailed microstructural characterization. A site-specific preparation of TEM specimen for the thermally cycled TBC was successfully carried out using focused ion beam in-situ lift out technique. Photostimulated luminescence corresponding to negligible residual stress in TGO scale was observed for this intact TBC. Microstructural analysis showed undulation of interface between TGO and bond coat, and the corresponding damage near YSZ/TGO interface. Extensive decohesion within TGO (nearly 9 μm thick), near the YSZ/TGO interface, was observed by TEM/STEM, and related to the observation made by PSLS. Microstructure and phase constituents of mixed-oxide zone containing Zr, Y, Ta, Ni, Co, Cr, Ti in Al2O3 matrix and continuous-columnar Al2O3 TGO are presented based on TEM/STEM and related analytical techniques.

© 2004 Elsevier B.V. All rights reserved.

PACS: 81.40.-z; 81.65.Mq

Keywords: Thermal barrier coatings; Luminescence; Oxidation; Microstructure; Transmission electron microscopy

1. Introduction

Thermal barrier coatings (TBCs), consisting of 7–8 wt.%Y2O3 stabilized ZrO2 (YSZ), thermally grown oxide (TGO), metallic bond coat, and superalloy substrate, have been extensively employed to improve the performance of advanced turbine engines [1–5]. Two types of bond coats are widely used: Pt-modified nickel aluminate (Ni, Pt)Al and MCrAlY (M=Ni and/or Co). Upon cooling during cyclic thermal exposure, a large compressive stress within the TGO scale develops as a result of the thermal expansion mismatch between the metallic bond coat and the TGO. This compressive residual stress combined with the stress arising from TGO growth (i.e., growth stress) is believed to be intimately involved with the failure of TBCs. The failure of TBC has been observed to occur near the vicinity of TGO scale, at the TGO/bond coat interface, within TGO and at the YSZ/TGO interface [1–5]. For electron-beam physical vapor deposited (EB-PVD) TBCs with (Ni, Pt)Al bond coats, several mechanisms leading to a TBC failure have been observed, including buckling [4], accelerated grain boundary oxidation after out-of-plane tensile cracking at grain boundary ridges [6,7],
critical TGO thickness [8] and damage due to interfacial instability such as rumpling [9] and racheting [10]. Removal of grain boundary ridges on (Ni,Pt)Al bond coat, by polishing, prior to YSZ deposition has minimized the detrimental effects of ridges [11]. However, TBCs still fail, and the exact mechanism of failure is yet to be established. For example, the concept of critical TGO thickness (5–7 μm) has been proposed and discussed by several authors [8,12,13] and the experimental observations of interface instability, such as rumpling and racheting, are not consistent, while the origins of these phenomena are not clearly understood.

Since the failure of TBCs frequently involves TGO scale, understanding of microstructural development and residual stress within and in the vicinity of TGO is important. In this regard, the photostimulated luminescence spectroscopy (PSLS), pioneered by Clarke [14–16], has provided a method to examine the residual stress within TGO non-destructively without damaging the YSZ topcoat. In this technique, photostimulated luminescence namely R1 and R2 from α-Al2O3 buried underneath the YSZ topcoat, exhibits a systematic shift in their frequency, as a function of residual stress assuming that TGO scale is thin, consists of randomly oriented polycrystalline and biaxially stressed α-Al2O3. PSLs has been developed as a non-destructive evaluation technique for TBCs. Since YSZ topcoat is transparent to these emissions [14–18] have been carried out using PSLS to examine characteristics of TGO and their relations to the failure of TBCs by TGO spallation. Microstructural evaluation of TBCs, especially as a function of thermal cycling has been carried traditionally [19–21] by using X-ray diffraction, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) with specimens prepared by mechanical grinding/polishing. Although these techniques have provided valuable insight to understanding the failure of TBCs, uncertainty remains due to potential specimen damage during preparation and resolution limit of instrumentation.

Transmission electron microscopy (TEM) has been rarely used for the detailed microstructural examination of constituents and interfaces involved in TBCs mainly due to the difficulty in specimen preparation. Chen et al. [22] have employed TEM for distinguishing the nature of ceramic–metal interface using plasma-sprayed thermal barrier coatings in as-sprayed and hot isostatic pressed conditions. Carim et al. [23] also investigated the TGO constituents of as-sprayed and thermally cycled air plasma sprayed TBCs using both SEM and TEM. A few studies have been carried out to examine the microstructure and phase constituents of the YSZ [24], TGO and mixed-oxide zone for as-coated TBCs [25–27] and selected thermally cycled TBCs [26,27]. However, systematic TEM investigations on TBCs are rare, partly due to the difficulty in specimen preparation, since ‘all the layers and interfaces’ at the region of interest must be intact and sufficiently thin.

To that end, focused ion-beam (FIB) techniques have been developed for the preparation of TEM specimens containing fragile interfaces such as TBCs, and other traditionally difficult-to-prepare materials [28–30]. Using the technique, site-specific electron transparent thin (<100 nm) specimens suitable for TEM analysis can be prepared with consistency and efficiency. Ex-situ FIB technique has been previously used with some success in preparing APS TBC specimens with thermal cycling [23]. Recent advances with FIB in-situ lift out (INLO) method [31] now allow consistent and efficient preparation of TBC specimens [32,33] regardless of their thermal cycling history or the extent of damage as long as they are intact as a coating system.

In this investigation, characteristics of TGO scale for an intact EB-PVD TBC with (Ni,Pt)Al bond coat was examined by PSLS, SEM/EDS, TEM and scanning TEM (STEM) after 645, 10-h thermal cycles at 1038 °C (1900 °F). In particular, a successful, yet routine preparation of TEM specimen of this TBC, containing 8–9-μm-thick TGO with extensive decohesion, was achieved using FIB INLO technique. Observations made by PSLS, SEM and TEM/STEM are correlated to facilitate a further understanding regarding the failure mechanisms of TBCs.

2. Experimental details

Disk shaped (2.54-cm diameter and 0.32 cm in height) CMSX-4 (nominal composition of Ni−9.6Co−6.4Cr−6.4W−6.6Ta−5.6Al−2.9Re−1.03Ti−0.2Hf in wt.%) coupons were coated with (Ni,Pt)Al bond coat by Pt-electroplating, followed by chemical vapor deposition (CVD) process. The surface of (Pt,Ni)Al bondcoat was grit-blasted prior to the deposition of ZrO2−7wt.%Y2O3 (7YSZ) using EB-PVD process. TBC specimens were thermally cycled for 645 cycles in air, where each cycle consisted of 10-min heat-up to 1038 °C (1900 °F), 10-h hold at 1038 °C and 10-min forced air-quench to ambient temperature. This particular thermal cycling test was employed to best simulate, in an accelerated manner, the environment for the thermal barrier coated first stage blades and vanes of the modern gas turbine engines. The TBC specimen examined in this study was still completely intact, while the other specimens with similar specification have failed after 645 thermal cycles. The intact TBC specimen examined in this study after 645 cycles is assumed to be near-failure.

Photostimulated luminescence spectra from the TBC specimen were collected using a Renishaw™ System 1000B Ramanscope™ equipped with a Leica™ optical microscope. An argon laser with a wavelength of 514 nm, operating at 25 mW was focused on the surface of the specimens with a 5× microscope objective lens. The resulting 693-nm luminescence was collected through the microscope objective, and was separated from the 514 nm by a holographic notch filter. The 693-nm luminescence then went through a diffraction grating and the final spectra were imaged using a CCD array connected to a computer display. The PSLS spectra were systematically collected from 125
locations to perform a detailed mapping of the entire specimen coupon. In each case, the luminescence spectrum was collected and deconvoluted for the calculation of luminescence frequency and intensity. The compressive residual stress in TGO was calculated based on the frequency of $R_2$ luminescence via piezo-spectroscopic coefficients, as described elsewhere [14–16].

For cross-sectional microstructural analysis by SEM with EDS, the TBC specimen was mounted in a transparent cold-setting low-viscosity epoxy resin, followed by cutting using a slow speed saw (Buehler™ Isomet). Cross-sectional specimen was then ground using 600 grit SiC paper, followed by successive polishing using diamond paste with 30-, 6-, 1- and 0.25-μm size particles. Cross-sectional microstructural analysis of TBC was then performed using a JEOL™ 6400F SEM equipped with Noran™ EDS detector.

After the initial characterization by PSLS and SEM/EDS, a TEM specimen containing YSZ, TGO, and bond coat with all the intact interfaces, was prepared by using the FIB INLO technique with a FEI™ 200TEM FIB equipped with an in-situ Omniprobe™. The process of the FIB INLO

![Sequential ion beam images from TEM specimen preparation of TBCs by focused ion beam (FIB) in-situ lift out (INLO) technique](image1.png)

Fig. 1. Sequential ion beam images from TEM specimen preparation of TBCs by focused ion beam (FIB) in-situ lift out (INLO) technique: (a) Pt wire is deposited at a site of specific interest; (b) focused ion milling is carried out to create a wedge-shaped specimen, (c) specimen is welded to a micromanipulator and (d) lifted out. Specimen can now be transferred to TEM grid and thinned further for TEM analysis.

![Macroscopic photographs of the (a) intact and (b) failed EB-PVD TBCs with grit-blasted (Ni,Pt)Al bond coat after 645, 10-h thermal cycles at 1038 °C (1900 °F). Arrows in (b) traces visually observed cracks.](image2.png)

Fig. 2. Macroscopic photographs of the (a) intact and (b) failed EB-PVD TBCs with grit-blasted (Ni,Pt)Al bond coat after 645, 10-h thermal cycles at 1038 °C (1900 °F). Arrows in (b) traces visually observed cracks.
Fig. 3. Residual stress mapping of intact EB-PVD TBC specimen after 645, 10-h thermal cycles at 1038 °C (1900 °F) by the PSLS. Luminescence spectra were collected at an incremental distance of 2 mm both in x- and y-directions. The magnitude of compressive residual stress is reported in GPa.

3. Results

Macroscopic photograph of the thermally cycled (645, 10-h cycles at 1038 °C) TBCs is presented in Fig. 2. The TBC specimen examined in this study was intact (Fig. 2a), covered with a ~1-μm-wide×25-μm-long×1.5-μm-high Pt layer deposited by ion-assisted CVD to prevent spurious sputtering of the top surface of the specimen and to outline the area of interest (Fig. 1a). Then through two milling operations, a wedge-shaped specimen was milled free from the bulk material (Fig. 1b). Next, the in-situ Omniprobe™ was introduced and CVD bonded to the specimen (Fig. 1c), and the specimen was lifted out from the bulk material (Fig. 1d). The specimen was then transferred and CVD bonded to a TEM grid for the subsequent FIB milling to the desired specimen thickness of ~100 nm. Using the FIB INLO process, the specimen can be thinned further to a desired thickness at any time; another distinctive advantage of FIB INLO technique. A FEI™/Tecnai™ F30 TEM/STEM system operating at 300 KeV with analytical techniques such as high-angle annular dark field (HAADF) STEM imaging that gives compositional contrast (i.e., analogous to backscatter electron imaging), selected area diffraction (SAD), convergent beam electron diffraction (CBED), fast-Fourier transformed (FFT) diffractograms, nano-spot energy-dispersive spectroscopy (n-EDS), and electron energy loss spectroscopy (EELS) was employed to characterize this thermally cycled TBC specimen.
except for a few chipped regions on the edge of the coupon. TBCs with similar specification have failed after 645 thermal cycles as seen in Fig. 2b.

3.1. Photostimulated luminescence spectroscopy (PSLS)

Characteristics of TGO buried underneath EB-PVD YSZ coating were examined non-destructively using PSLS at room temperature. Total of 125 photostimulated luminescence spectra were collected as a function of location. The data collection and deconvolution procedure was repeated two times for accurate and objective analysis. Ruby-luminescence from the $\alpha$-Al$_2$O$_3$ scale underneath the intact TBC exhibited negligible magnitude of compressive residual stress as reported in Fig. 3; only 9 out of 125 measurements exhibited tangible magnitude of compressive residual stress with their magnitude above 0.5 GPa. This is a highly unusual observation, considering the fact that the TBC is still intact, and TGO is presumably still adherent to the (Ni,Pt)Al bond coat. Luminescence from metastable Al$_2$O$_3$ phases such as $\theta$ and $\gamma$ [34,35] was not observed.

3.2. Scanning electron microscopy with energy dispersive spectroscopy

Cross-sectional microstructural analysis of this intact TBC specimen was initially carried out using SEM/EDS. Emphasis was given to the microstructures of TGO, and the YSZ/TGO and TGO/BC interfaces. Cross-sectional secondary electron micrograph in Fig. 4 shows a typical microstructure of the intact TBC after 645 thermal cycles. Thick (~ $9 \mu m$) TGO layer, as a result of bond coat oxidation, and undulation of TGO and TGO/bond coat interface, hereafter referred to as “rumpling”, were observed as presented in Fig. 4. Damage at

Fig. 5. Bright field TEM micrograph of intact EB-PVD TBC specimen after 645, 10-h thermal cycles at 1038 °C. Extensive decohesion at or near the YSZ/TGO interface was observed.

Fig. 6. (a) CBED pattern and (b) high resolution BF image of TGO from the intact TBC specimen after 645, 10-h thermal cycles at 1038 °C. The CBED pattern and the fast fourier transformed (FFT) diffractogram (inset in b) demonstrate the presence of $\alpha$-Al$_2$O$_3$ in TGO.
near the center of the TGO, in Fig. 4. Based on the morphology presented by the BF image, this crack is believed to be an artifact from the grinding and polishing process prior to the SEM analysis. Significant decohesion and/or void formation (white region) at the YSZ/TGO interface and within TGO near YSZ/TGO interface was observed. The thickness of TGO ranged from 7 to 8 μm, larger than the critical thickness reported by other investigations [8,12,13]. The crystal structure and phase identification by CBED (Fig. 6a) and FFT diffractogram (Fig. 6b) indicated that the TGO mainly consisted of α-Al2O3. Good interfacial adhesion was observed for the TGO/bond coat interface from this section of the TBC specimen even after 645, 10-h thermal cycling at 1038 °C (1900 °F) as seen by the high resolution TEM (HRTEM) image in Fig. 7. The bond coat crystal structure and phase as identified by the

3.3. Transmission electron microscopy via focused ion beam in-situ lift out technique

A bright field (BF) TEM micrograph of the intact TBC specimen showing the microstructure of the YSZ, TGO, bond coat and interfaces in-between them is presented in Fig. 5. Note that the crack in the TGO observed in the top section of Fig. 5 is the same crack within the TGO, shown and near the YSZ/TGO interface associated with trough of rumpled TGO can be seen in Fig. 4.

Fig. 7. High resolution BF image of the interface between TGO and (Ni,Pt)Al bond coat for the intact EB-PVD TBC specimen after 645, 10-h thermal cycles at 1038 °C. The FFT diffractogram (inset) from the bond coat corresponds to that of γ-Ni3Al solid solution phase.

Fig. 8. High-angle annular dark field (HAADF) scanning transmission electron microscope (STEM) image of intact TBC specimen after 645, 10-h thermal cycles at 1038 °C showing diffraction/composition contrast of corresponding image in Fig. 5.

Fig. 9. High magnification HAADF STEM images of (a) decohesion within TGO near the YSZ/TGO interface and (b) TGO in intact TBC specimen after 645, 10-h thermal cycles at 1038 °C. (a) n-EDS elemental mapping revealed the presence of some Zr, Ta, Ti, Ni and Co on either side of the decohesion. (b) Zr, Ta, Ti, and Cr were also found along the grain boundaries of α-Al2O3 TGO.
inset diffractogram of Fig. 7 is consistent with the cubic L12 crystal structure of the γ’-Ni3Al solid solution phase.

The YSZ, TGO, and bond coat with all the interfaces in-between them were further examined using HAADF imaging in STEM mode to obtain the diffraction/composition contrast images of the various phases, followed by n-EDS analysis. HAADF micrographs from the cross-section of the TBC are presented in Fig. 8. Several types of oxide particles containing Zr, Ta, Ti, Cr and Ni were identified within the TGO near the YSZ/TGO interface on both sides of the decohesion as presented in Fig. 9a. Ta-, Ti- and Cr-containing oxide particles were frequently observed at the α-Al2O3 grain boundaries as seen in Fig. 9b. An interesting observation is the presence of Pt-containing particles (white particles in YSZ) extending up to about 5 μm in the YSZ as seen from HAADF image presented in Fig. 8. Analysis by EELS indicated that Pt particles observed were metallic as presented in Fig. 10. The presence of Pt particles in the YSZ coating is unknown at this time. Potential sources of Pt include CVD Pt during FIB, thermocouples used during EB-PVD process and during deposition of bond coat.

4. Discussion

The observation of photostimulated luminescence from α-Al2O3 corresponding to negligible compressive residual stress in TGO is highly unusual for intact TBCs. In general for intact TBCs, TGO bonded to metallic bond coat is expected to have a significant amount of compressive residual stress (~2–4 GPa) due to coefficient of thermal expansion (CTE) mismatch between the TGO and the metal substrate upon cooling. Local observation of negligible or near-zero magnitude in compressive residual stress has been generally associated with subcritical and localized spallation TGO from the bond coat, which causes the significant stress-relief [16,18].

Observation of mostly (116 out of 125 spots) stress-free or negligibly stressed TGO on intact TBC can be explained based on the microstructural features observed from this specimen. Figs. 5 and 8 illustrate extensive decohesion within TGO near and at the YSZ/TGO interface, particularly at troughs associated with rumpling of TGO/bond coat interface. The magnitude of residual stress in TGO adhered only to the YSZ coating may be negligible. Thus, results from PSLS and microstructural analysis can be correlated if the luminescence originates mainly from the TGO, debonded from the (Ni,Pt)Al bond coat, but still attached to the YSZ coating. This type of damage thus can be monitored by PSLS, if it progresses with thermal cycling.

Rumpling was frequently observed at the TGO/bond coat interface as presented in Fig. 4. Although the origin of rumpling at the TGO/bond coat interface can be attributed to several phenomena [9], geometrical incompatibility with the TBC clearly can initiate the damage by causing local decohesion of the TBC at or near the YSZ/TGO interface. Microstructural analysis of this specimen by TEM clearly indicates that decohesion associated with rumpling occurs at the YSZ/TGO interface and within the TGO just below the YSZ/TGO interface where “mixed-oxide” zone exists as seen in Figs. 8 and 9.

HAADF images in STEM mode and n-EDS analysis revealed a distinct mixed-oxide zone between YSZ and TGO with substantial presence of Zr, Y, Ni, Co, Cr and Ta. The formation of mixed-oxide zone [25] has been reported...
both in as-deposited condition and after high temperature exposure in air. The formation of the mixed-oxide zone as observed in this case can occur as both Zr and Y fills the irregularities in the TGO morphology during EB-PVD processing. The presence of Ni, Co, Cr and Ta in the mixed-oxide zone can be attributed to the outward diffusion of these elements from the (Ni,Pt)Al bond coat and the superalloy substrate through the TGO. In Fig. 9b, there is evidence of these elements in the grain boundaries of the $\alpha$-Al$_2$O$_3$.

The microstructural observation in this study suggests that a significant damage of the TBC near and at the YSZ/TGO interface can exist although failure of TBC has not occurred. However, this type of damage near and at the YSZ/TGO interface may have a significant effect on the thermo-mechanical behavior, and thus the failure mechanism of EB-PVD TBCs. Intuitively, a significant accumulation of decohesion at or near the YSZ/TGO interface will lead to failure of TBCs at or near the YSZ/TGO interface. However, more importantly, Tolpygo and Clarke [36,37] have clearly demonstrated that the presence of YSZ coating on top of TGO clearly suppresses rumpling [9], and furthermore that the rumpling-induced decohesion at or near the YSZ/TGO interface leads to accelerated rumpling with further thermal cycling. Increase in out-of-plane tensile stress at the geometrical irregularities [6,38] of rumpled interface can lead to decohesion at the TGO/bond coat interface. Clearly, the adherence of the YSZ coating to the TGO influences the overall thermo-mechanical behavior of TBCs during thermal cycling. Such an influence may extend to phenomena related to other failure mechanisms such as buckling [4] and ratcheting [4,10]. Due to the decohesion at the YSZ/TGO interface, effective thickness against buckling (i.e., critical defect size at TGO/bond coat interface) and ratcheting may be reduced from the combined thickness of YSZ+TGO to TGO only, although the thickness of TGO is increased.

5. Conclusions

An intact thermal barrier coating (TBC) specimen, consisting of electron-beam physical vapor deposited (EB-PVD) ZrO$_2$–7 wt.%Y$_2$O$_3$ (YSZ) topcoat, thermally grown oxide (TGO), grit-blasted (Ni,Pt)Al bond coat and CMSX-4 single crystalline superalloy, was characterized after 645 h thermal cycling test in air at 1038 °C. Critical characteristics of YSZ/TGO and TGO/bond coat interfaces and TGO scale were examined by PSLM, SEM with EDS, TEM/STEM with n-EDS, SAD, CBED, HAADF, and EELS. FIB INLO technique was successfully employed for the preparation of thin and intact TEM specimen containing YSZ, TGO, bond coat and interfaces in-between from the thermally cycled TBC. Extensive decohesion near and at the YSZ/TGO interface associated with rumpling was observed. This type of damage near and at the YSZ/TGO interface may have a significant effect on the overall thermo-mechanical behavior, and thus the failure mechanism of EB-PVD TBCs. Negligible compressive residual stress within the TGO for intact, near-failure TBC was observed by PSLM. This highly unusual stress evolution in the TGO after the thermal cycling was related to decohesion within TGO near the YSZ/TGO interface.

Acknowledgements

Financial support from the National Energy Technology Laboratory (NETL) of the U.S. Department of Energy (DOE), through University Turbine Systems Research (UTSR) program administered by South Carolina Institute for Energy Studies (SCIES) is sincerely appreciated (No. 02-01-SR103). Acknowledgement for this investigation also extends to Solar Turbines, San Diego, CA for the additional financial support and technical collaboration.

References