Thermal diffusivity of TBC: Results of a small Round Robin test and considerations about the effect of the surface preparation and the measuring approach.

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Abstract

Among the techniques used to measure the thermal diffusivity of TBC, the Laser Flash is a standard. Nonetheless, this technique shows two main limitations related to the size and the well-defined geometry of the specimens. Furthermore the most reliable data can be typically obtained only on freestanding coatings. On the contrary, other photothermal and thermographic techniques in reflection configuration (the same side is heated and temperature detected) can overcome these limitations. One aspect, only partially studied in the literature, is common to most of the photothermal and thermographic techniques. It concerns - the effect of the blackening coating used for guaranteeing the absorption of the heating radiation just within a very shallow outer layer and to make opaque the TBC in the sensitivity range of the IR detector/camera.

For this purpose, an inter-laboratory round robin has been promoted for comparing the thermal diffusivity in dependency of the blackening layer deposition technique, the TBC microstructure (in particular porous APS, columnar EBPVD and PS-PVDTM) and the three different experimental set-ups in terms of spectral range and frame rate of the IR cameras, heating source and data reduction.

Keywords: Thermal Barrier Coatings; Thermal diffusivity; Blackening layer; Thermographic technique.

1. Introduction

Thermal barrier coatings (TBCs) are widely applied for protecting hot path components of gas turbines from combustion gases. By this way, the temperature on metallic substrates can be reduced by 30°C to 100°C, depending on the thickness and on the specific properties of the insulating layer [1-2]. The state-of-the-art of these TBCs is represented by yttrium oxide partially stabilized zirconium (YPSZ) oxide (7-8 wt.% $Y_2O_3+ZrO_2$) deposited onto the components either by atmospheric plasma spray (APS) or by electron beam physical vapour deposition (EB-PVD) [1-2].

The thermal insulating ability of the TBC is related to its thermal conductivity and thickness. The thermal conductivity of TBC is the result of the combined effect of the thermal conductivity of the bulk material and its peculiar porous microstructure. As discussed in the literature, the same temperature drop across the TBC thickness could be achieved depositing onto the component either a thin TBC with a very low thermal conductivity or a thicker TBC with higher thermal conductivity [3-5].

In any case, independently from the followed approach, the TBC microstructure should be correctly designed and deposited by properly choosing the deposition parameters to obtain the desired thermal conductivity and elastic modulus, according to the operating conditions of the specific component the TBC will be sprayed onto. Furthermore, it is also important to study the evolution of the TBC microstructure along the operation owing to the sintering phenomena occurring at high temperature. In fact, sintering promotes a significant reduction of both the insulating ability and the strain compliance of the TBC [6-14].

A very wide range of thermal diffusivity values of TBC's are reported in the literature [7,8,11, 14-17] owing to the several microstructures that can be obtained in dependency of powder, production routes, deposition techniques and process parameters.

Possible additional causes of the great variability of the TBC thermal diffusivity reported in the literature, that rarely are taken into account, are related to the experimental testing conditions (not always fully provided in the literature), such as for example the measuring atmosphere (i.e. gas and

pressure), the sample preparation, the measuring technique, the experimental set-up and the algorithm used for parameters estimation. To give an example of this, the thermal diffusivity of a porous APS TBC could be reduced by a factor close to 2, when the measurement is carried out in vacuum instead of in air at atmospheric pressure and room temperature [14,18].

Among the techniques used to measure the thermal diffusivity of TBC, the Laser Flash is a standard [19, 20]; the main limitations are the size and the well-defined geometry (disks or parallelepipeds) of the specimens. Moreover, although this technique can be applied also on two layers samples, the most reliable data can be typically obtained on freestanding coatings.

In the last decades, photothermal¹ techniques in reflection configuration (i.e. the heating and temperature detection confined to the same side of the sample) such as Pulsed Photothermal Technique [21], Time Resolved Infrared Radiometry (TRIR) [22], Thermal Waves Interferometry (TWI) [23] and PopTea [24, 25], have demonstrated their ability to measure the thermal diffusivity on TBC deposited onto substrates without any special requirement on the sample size and geometry. In particular, measurements on real components have been recently reported [25, 26].

In the last fifteen years, the availability of high resolution focal plane array IR cameras with performances comparable to single IR detectors allowed reliable mapping of the thermal diffusivity of TBC deposited onto samples and components [14, 27-30].

One aspect only partially studied in the literature [31, 32] common to most of the photothermal and thermographic techniques concerns with the effect of the blackening coating used for guaranteeing the absorption of the heating radiation just within a very shallow outer layer and to make opaque the TBC in the sensitivity range of the IR detector/camera.

The most applied coatings consist in thin graphite, Au or Pt layers [33, 34], these latter deposited typically by sputtering. It has been reported that a large difference (>10%) in measured TBC properties may be observed when using different graphite coatings for certain TBCs [35].

¹ Photothermal means that an electromagnetic radiation in visible or near infrared range is used to heat a sample and the related temperature variations are detected to estimate thermo-physical properties of the sample.

For this purpose, an inter-laboratory round robin has been promoted for comparing the thermal diffusivity in dependency of the blackening layer deposition technique, the TBC microstructure (in particular porous APS, columnar EBPVD and PS-PVD™) and the three different experimental set-ups in terms of spectral range and frame rate of the IR cameras, heating source and data reduction. Three laboratories participated to the round robin and they are referred in the following with the acronyms ANL (Argonne National Laboratory, USA), CNR (Consiglio Nazionale delle Ricerche, Italy) and RSE (Ricerca sul Sistema Energetico, Italy).

2. Experimental

2.1 The samples

The experimental activity has been performed on three TBC samples: one standard porous $369 \pm 7 \mu\text{m}$ thick APS (APS163), one $175 \pm 2 \mu\text{m}$ thick EB-PVD (EB-PVD1) and one $140 \pm 3 \mu\text{m}$ thick Plasma Spray - PVD™ (SYS3) TBCs. CMSX4 single crystal Ni-base superalloy was used as substrate (4 mm thickness 25 mm diameter disks), APS TBC has been sprayed onto a $\approx 300 \mu\text{m}$ CoNiCrAlY bondcoat (Amdry 995) deposited by LPPS (Low Pressure Plasma Spray) technique. For both PVD TBCs, the bondcoat was a diffusion Pt-Al coating about $50 \mu\text{m}$ thick. Figure 1 shows the microstructure of all the three TBC systems as seen from the top surface and along the section.

In the following, a short description of each TBC system is given.

2.1.1 APS Standard Porous TBC

The ceramic top coating has been deposited by air plasma spray, using ARTEC SpA F4A type torch and YPSZ commercial powder (Amperit 827.7 produced by H.C. Starck) with a particle size distribution in a range from 45 to 90 μm . The cubic and tetragonal phase content is 98 and 1 wt% respectively; whereas the monoclinic phase content is 1 wt% in the as-received feedstock.

2.1.2 PS- PVD™ TBC

The PS-PVD process is based on the ChamPro™ technology of Sulzer Metco which comprises all those thermal spray processes performing under a defined and controlled atmosphere like LPPS, VPS and LVPS [36]. The PS-PVD™ process operates at lower pressures down to 0.5-2 mbar. Under these conditions, the properties of the plasma jet change substantially [37]. Even though the PS-PVD™ work pressure (~ 1 mbar) is still much higher than the one used in conventional PVD processes ($\sim 10^{-3}$ mbar), the combination of a high energy plasma gun operated at a low pressure environment enables a defined evaporation of the injected powder material. This allows one to produce a controlled deposition out of the vapour phase. In EB-PVD, the transport of the vaporized coating material towards the substrate is done through a diffusion process having a limited throughput and producing coatings at low growth rates. In contrast to that, in the PS-PVD™ process the vaporized coating material is transported in a hot and supersonic gas stream ($2000-4000 \text{ ms}^{-1}$, $6000-10000 \text{ K}$) which is expanding in a 1 mbar atmosphere. This leads to high growth rates and the possibility to coat undercuts and areas which are not in the line-of-sight. More details about the PS-PVD™ deposition technique can be found in the literature [38].

2.1.3. EB-PVD TBC

The topcoat has been deposited via EB-PVD process. The substrate is mounted on a rotating holder positioned perpendicular to the ingot axis and heated in the range $900 - 1000^\circ\text{C}$. The evaporation source material comes from an ingot with standard ZrO_2 7 to 8 wt% Y_2O_3 chemical composition. Evaporation of the ingot is achieved by applying an electron power gun. During deposition the chamber pressure is kept in the 10^{-3} mbar range.

2.2 The approach

To guarantee the highest level of significance of the results it is essential to design the experimental activity carefully. The main issue to consider in designing the round robin to investigate the effect of the different blackening layers concerns the following alternative choice:

- a) to use the same TBC sample (for each deposition technique, i.e. plasma spray, PS-PVD, EB-PVD) with the consequent needs of removing the old blackening coating before to apply the new one;

b) to coat different TBC samples (even though obtained with the same deposition technique) with the different blackening layers selected for the experimental activity.

In order to answer to this question, the spread of thermal diffusivity values of three sets of TBC (deposited in the frame of the European Project TOPPCOAT) similar to those selected for the experimental activity was considered, as summarized within the probability plot in Figure 2.

It is worth noting that the relative spread of thermal diffusivity (i.e. $(\max - \min) / \max$) ranges from 9% to 18% depending on the TBC set. Since the aim of this experimental activity is to detect small thermal diffusivity variations caused by the blackening layer, it is essential to minimize all the error sources. The results of the probability plot suggest the use of the same sample for each TBC deposition technique to get rid of the variability of thermal diffusivity caused by the small microstructural variations from sample to sample.

This choice requires to consider how removing the blackening layers without significantly altering the sample microstructure, and thus its thermal diffusivity by a significant amount. Since the selected blackening layers are all based on graphite, the candidate solution to remove graphite consists in burning it in a furnace at a temperature slightly higher than the 650°C. Based on previous trials, the suggested heat treatment consists in heating the sample at 700°C for 1 hour.

A preliminary study of the effect of this heat treatment on the TBC thermal diffusivity is thus required.

Since no literature on the effect of heat treatment at 700°C on thermal diffusivity of TBC is available, some considerations have been done starting from data referring to higher temperatures.

Fujii and Takahashi [39] and Diwiddie et al [40] report thermal diffusivity variations at temperatures higher than 950°C and 871°C, respectively.

Moreover, Cernuschi et al report the thermal diffusivity increase after a heat treatment of two hours at temperatures in the range 900°C – 1300°C for standard APS YPSZ TBC [12, 14]. By fitting the relative thermal diffusivity increase as a function of the ageing temperature (see Figure 3), a rough extrapolation of the expected relative thermal diffusivity increase at 700 °C can be carried out. Therefore, the thermal diffusivity increase after 2 hours at 700°C is estimated to range between 0% - 2.5% with an average value of 0.5%. Considering that the typical absolute experimental uncertainty

related to thermal diffusivity is in the range $\pm 3\text{-}5\%$ for Laser flash and the other photothermal techniques, we could conclude that the effect of removing the graphite layer by heat treating the samples does not alter too much their thermal diffusivity, at least for APS TBC.

Moreover, if a sintering code published in the literature [41] and successfully used also in other studies [42] is applied to the present case, no detectable thermal diffusivity increase is expected after heat treating APS TBC for two hours at 700°C .

As concerns EB-PVD samples, there is in the literature only one proceeding paper by U. Schulz et al where a slight increase of the pore surface area for samples aged at 700°C for short times (attributed to a conversion of initially fine-scaled closed porosity within columns into larger size opened porosity) is reported. Unfortunately no data about the associated thermal diffusivity variations, if any, are available [43]. On the other hand, in another work of Ratzer-Scheibe and U. Schulz, thermal diffusivity resulted to be affected only at temperatures higher than 900°C [see Figure 7 in ref. 44], thus it can be supposed that also EBPVD TBC are not affected by the heat treatment for removing the graphite.

2.3 The blackening layers

In the following a short description of deposition process of the three blackening layers considered for this experimental activity is given.

2.3.1. Carbon paint (RSE)

In this case a commercial graphite spray (suggested by a Laser Flash Equipment manufacturer as blackening paint) is mixed with acetone to obtain a diluted graphite paint that can be painted by a brush to obtain a thin gray-black layer on the TBC surface.

2.3.2. Carbon Vacuum Deposition (RSE)

This is the standard technique used to deposit continuous conductive carbon layers on the top of mounted, polished samples to be characterised in a Scanning Electron Microscopy (SEM). A commercial equipment (Carbon Vacuum Deposition, Edwards) has been used to coat the samples.

2.3.3. Carbon paint II (ANL)

This is a commercial dry film coating, Aerodag® G, typically used for lubrication applications. It contains highly refined (micron-sized) graphite particles suspended in an isopropyl alcohol with a special thermoplastic resin binder. Aerodag G is supplied in a spray can. It is easy to apply, fast drying

at room temperature, and adheres to many common materials. It usually takes 3-5 light spray passes to make the TBC surface opaque.

Figure 4 shows the three samples before and after the third blackening procedure. As previously discussed, to apply different coatings on the same samples, the previous graphite coating was burned off keeping the sample in a furnace at 700°C for 1 hour.

2.4 Theoretical remarks

The TBC thermal diffusivity α_c of a two-layer sample (the TBC and the metallic substrate²) is estimated by fitting the temperature vs. time $T(t)$ of the front sample surface after being heated by a Dirac pulse (typically a laser pulse). Temperature is measured by an infrared camera at room temperature, being the maximum TBC surface temperature increase just few milliseconds after the flash in the range of 10 – 30 K , depending on TBC features and laser pulse energy.

The analytical one-dimensional two-layer model adopted to fit the experimental data is [45]:

$$T(t) = \frac{Q_0}{\varepsilon_c \sqrt{\pi t}} \left[1 + 2 \sum_{n=1}^{\infty} \Gamma^n e^{-\frac{n^2 l_c^2}{\alpha_c t}} \right] \quad (1)$$

Where Q_0 , $\varepsilon = \sqrt{k\rho C}$, $\Gamma = \frac{\varepsilon_c - \varepsilon_s}{\varepsilon_c + \varepsilon_s}$ and l_c are the absorbed energy density [$J m^{-2}$], the thermal effusivity [$W s^{1/2} K^{-1} m^{-2}$], the reflection coefficient at the interface between coating and substrate and the coating thickness [m], respectively. K , ρ and C_p are the thermal conductivity [$W m^{-1} K^{-1}$], the density [$kg m^{-3}$] and the specific heat [$J kg^{-1} K^{-1}$], respectively. The lowercases c and s refer to coating and substrate, respectively. Eq.(1) is the solution for a semi-infinite substrate. Considering that the duration of the typical experiments is limited to few seconds after the flash, this is a good approximation for thick metallic substrates.

According to the specific experimental set up realised in each Laboratory, a different fitting procedure has been developed, as better explained later.

² For the sake of simplicity and for guaranteeing a higher robustness of the inversion procedure, since the thermal properties of metallic bondcoat and the metallic substrate usually differ negligibly, it is common practice to use a two layers model [14, 21-30].

2.5 The thermographic equipments and processing algorithms

2.5.1 RSE experimental configuration

As heating source, a 1064 nm wavelength Nd:YAG laser (Theta Industries Inc., Port Washington, NY, USA) generating pulses of about 0.5 ms was used. The diameter of the heating shot were fixed roughly equal 10 mm. Typical maximum surface temperature increase few milliseconds after the flash are of the order $\cong 10\text{-}15\text{ }^{\circ}\text{C}$. A detailed discussion of this aspect can be found elsewhere [46].

A snapshot focal plane array IR camera sensitive in the range of 7–10 μm (Jade II LW, FLIR Systems) with a Noise Equivalent Temperature Difference of 30 mK, was used to monitor for 2 s after the pulse the temperature transient of the sample surface at frame rates in the range 500 - 2000 Hz³, depending on the thickness and thermal diffusivity of samples. The length of the IR images sequence is chosen sufficiently long to include the heat propagation in the substrate as well (see for example data at later times in Figure 5)

In this configuration the thermal diffusivity is estimated according to Eq. (1) considering the spatial average of the surface temperature performed on an area almost wide as the whole sample. Typical experimental data and fitting curve are shown in Figure 5. Measurements are repeated at least five times for statistical purposes. More details about this technique can be found in the literature [14].

2.5.2 CNR experimental configuration

As a heating source, the CNR lab is equipped with an instrumentation that is a twin of that installed at RSE. The IR camera is built around a Quantum Well Infrared Photodetector (QWIP) detector 320 x 240 pixels, sensitive in the range 8-9 μm , with a NETD of 30 mK. The acquisition rate utilized during the test is 750 Hz, the maximum available after windowing the field of view to 320 x 16 pixels. With such a reduced field of view, only part of the spot (1 cm diameter) is visible in the IR image at the minimum focus distance from the specimen. Contrary to the RSE experimental set-up, only the central portion of the heated area is considered in this configuration. In the centre the conduction process is considered 1D along the depth direction, because it is far enough from the heated spot boundary. To improve the signal, a reference area (not affected by the laser spot and located on a massive stone

³ The size of the image varies from 80x60 (2000Hz) up to 160x120 (500 Hz) pixels depending on the frame rate.

block) has been considered and its average temperature has been subtracted to that obtained in the sample area. It improves the Common Mode Noise Rejection that affect the sensor as whole with fluctuations at low frequency (with a period of the order of 1 s). Figure 6(a) illustrates the zone where the signals are sampled, Figure 6(b) shows the temperature on the sample area, the reference area and the difference between the two previous temperature profiles. Measurements are repeated seven times for each specimen. According to Eq. (1), a set of parameters is obtained from an optimization procedure that fit the experimental data according to the least square approximation. The fitting procedure is iterative due to the non-linear appearance of the parameters in Eq. (1). The estimated parameters are:

$$\mathbf{p} = \left\{ \frac{Q_0}{\varepsilon_c \sqrt{\pi}}, \Gamma, \frac{\alpha_c}{l^2}, t_0 \right\} \quad (2)$$

where the first three parameters are obvious from Eq. (1). The forth is the time of laser shooting, that is only approximately known, falling at any time between two successive sampled images. This is because the processes of camera sampling and laser shooting are asynchronous in this experimental configuration. By adjusting the delay t_0 an improvement of the data fitting is obtained. Apart from the standard deviation coming from the repetition of the tests, that allows to evaluate the reproducibility of the measurement process, the scatter plots of different estimated parameters vs. α_c/l^2 are represented in Figure 7. It permits to identify possible correlations among different estimated parameters. By repeating the test it is possible that the energy delivered by the pulse changes or the delay changes but not the α_c/l^2 parameter. Figure 7 shows that the α_c/l^2 parameter changes randomly but it is not correlated to any variation of other estimated parameters that could reveal a weakness of the experimental arrangement or even of the adopted model.

2.5.3 ANL experimental configuration

The experimental system at Argonne consists of a photographic flash lamp (Source 6400; BALCAR, France), an IR filter, and a mid-wavelength (3-5 μ m) IR camera (Phoenix; FLIR, USA). The IR camera

was placed normal to the TBC sample at a distance of ~30cm. The flash lamp is positioned at an oblique angle to the sample, which caused a flash intensity variation on the sample surface that was determined to be negligible [30]. The flash duration [47] for this flash lamp is 1.8ms. The IR filter [48] absorbed all IR radiation emitted by the flash lamp to ensure that the imaged data came only from IR radiation of the TBC surface. The IR camera has a NETD of 25mK. It was operated at 1068Hz with a detector integration time of 0.93ms and an image size of 160x128 pixels. A total 3000 frames were taken for all test samples. Typical maximum surface temperature increase few milliseconds after the flash is ~40°C. A detailed discussion of this aspect can be found elsewhere [30].

A pulsed thermal imaging-multilayer analysis method (PTI-MLA) was used to process the experimental data. It is based on an iterative nonlinear regression algorithm that determines multiple parameters in a multilayer materials model [30]. For two-layer TBC/substrate material with an infinite substrate thickness, the formulation in this method reduces to Eq. (1). The PTI-MLA method also accounts for the flash duration effect that becomes relevant for thin TBC samples. The regression seeks to not only fit the temperature data similar to that in Fig. 5 but also the logarithmic derivative $d(\ln T)/d(\ln t)$ data, and the best fit determines the three parameters Q_0 , ε_c , and α_c/l^2 with known substrate parameters ε_s , α_s , and l_s . This regression process was automated for all individual pixels within the image, so the predicted TBC parameters can be presented in 2D image forms. For the three TBC samples with a thin Aerodag G film, a comparison of the experimental and fitting $d(\ln T)/d(\ln t)$ curves at the center of each sample is shown in Fig. 8. The experimental curves were smoothed by using a moving-window averaging with a window size of $d(\ln t) = 0.5$ where t is in the unit of second. It is seen that the theoretical fitting is generally very good. The flash duration peak at ~4ms was not resolved well in the experimental data because of the low imaging speed (this does not affect the prediction because data fitting was only carried out with $t > 10\text{ms}$). The predicted thermal diffusivity images for these three TBC samples are shown in Fig. 9. Average thermal diffusivity value for each sample was determined from a central rectangular area, as illustrated in the left sample. All samples were normally tested 3 times to derive statistical data as listed below.

2.6 The experimental results and discussion

The results of the Round Robin test are reported in Table I. Basically, the technique adopted by the three laboratories is the same, but differences in the equipment like the heating system (e.g. pulse duration, area of heating, uniformity, energy density, etc.) and the IR camera (e.g. frame rate, spatial resolution, Noise Equivalent Temperature Difference (NETD), wavelength sensitivity range, etc.) can lead to different results in so far some experimental details could not meet the hypothesis adopted in the heat diffusion model presented in 2.4. As an example, a problem due to the limited frame rate of CNR equipment arose during the measurement of the PS-PVDTM sample, that being quite thin and with a higher diffusivity than APS (connected with a microstructure being essentially columnar) does not allow to CNR camera to grab enough data for a reliable estimation. As a rule of thumb, the heat pulse released on one face reaches the back side of the slab at a Fourier number $F_0 = \alpha t / L^2 \cong 1/\pi$. Assuming the diffusivity of PS-PVDTM equal to $\alpha = 8.6 \cdot 10^{-7} \text{ m}^2 \text{ s}^{-1}$ and its thickness equal to $L = 140 \cdot 10^{-6} \text{ m}$, the time of reaching the back side is around 7.3 ms and to grab at least 10 samples in the first interval of the thermal process a camera with around 1400 Hz is needed.

Considering the fitting algorithms, it exists a certain degree of arbitrariness in the choice of the data. It is mainly related to the choice of the interval of samples to consider in the fit. It is quite common to reject some data at the beginning of the process, immediately after the pulse, to avoid departures from the ideal model due to possible absorption of light in the depth of the material, or nonlinearities connected with consistent exchange phenomena with the ambient. Furthermore, data collected far from the heating pulse, when the temperature is approaching again the ambient value, are affected by random fluctuations of the environment (e.g. convective air movement) and should be rejected. The effect of the arbitrary choice of the window of the data to consider for the estimation of the diffusivity can be observed in the Table I for the results of CNR. CNR follows its own criteria (column 2) in one case and criteria similar to the RSE lab (column 3) leading to differences greater than 8 % for EB-PVD sample. A part from the above, that could bring to systematic differences between the results of different labs, the other sources of uncertainties are connected to random phenomena and possibly minimized by suitable repetition of the test.

Table I shows that the results of the different labs are globally within 10 % of uncertainty, demonstrating the intrinsic robustness of the technique and that the departures from the model shown

in 2.4 are maintained low. These promising results could be considered as a preliminary step paving the way towards the standardization of this technique for measuring the thermal diffusivity of TBC coating directly deposited onto a substrate, as is the case of real gas turbine components.

Considering the effect of the different blackening coatings it appears that they do not affect the TBC thermal diffusivity of APS. EB-PVD and PS-PVDTM are slightly more affected by the blackening layer. Both paint I and II can penetrate more easily inside the pores and especially in columnar microstructures like the ones characterizing EB-PVD and PS-PVDTM. The more the penetration depth, and therefore the filling of the feathery pores of the columns, the greater the increase of the effective thermal diffusivity. For APS microstructure this is a less severe problem because only the vertical crack-like pores open on the surface can be partially filled by the paint. In fact the effect on through the thickness thermal diffusivity of vertical pores is the least important. In the case of CVD the blackening layer should deposit just on the top of the TBC without filling any secondary porosity along each single column. The main concern about this coating is to have a thickness thick enough to avoid the transmission of laser light through the column. By looking at Figure 10 it appears that CVD is the coating that guarantees the greater agreement among the results of the three labs.

From table I and Figure 10 it is possible to recognize that the variations in thermal diffusivity results of APS is greater among the labs (for the same blackening technique) than among the blackening techniques (for the same lab). For EB-PVD differences between lab and blackening techniques are of the same order of magnitude, while for PS-PVDTM it seems that the effect of blackening affects more one lab than the other, being the differences between the labs (at the same blackening technique) much less affected.

Considering the small effect of the blackening layer on TBC thermal diffusivity test and that since the typical scatter of the TBC thermal diffusivity from sample to sample is greater or similar to that promoted by the blackening layer, performing tests on the same set of samples for all the blackening layers was mandatory to observe their effect on thermal diffusivity, as discussed in 2.2. Furthermore, the results summarised in Table I confirm that the heat treatment needed to remove the graphite layers does not affect significantly the thermal diffusivity of all the three samples (the blackening sequence was paint 1, paint 2 and last CVD), or, at least, thermal diffusivity variations ascribable to the heat

treatments appear to be smaller than (or of the same order of magnitude of) the experimental uncertainty. The fact that no monotonic trend of the thermal diffusivity as a function of the painting sequence have been noticed, can be considered as an indirect confirmation of the previous statements. The other point that has to be investigated is related to the systematic error induced when the presence of the black paint is not taken into account in estimating the TBC thermal diffusivity⁴. To address this problem, the following approaches have been considered: a) weighting a rectangular shaped freestanding APS TBC sample both before and after the black coating has been painted on it; b) estimating the thickness of this coating from graphite density. In particular, depending on the assumed porosity of the coating, the thickness estimates ranges between 2 μm and 4 μm and 0.1 μm , for RSE paint and CVD, respectively. Concerning ANL paint, its thickness resulted not detectable with a micrometer before and after painting the TBC sample; furthermore under an optical microscope looking at a fresh-break TBC cross section, the paint thickness was also not clearly visible under adequate lighting and at 1000X magnification. Therefore, these outcomes suggest that the thickness should be in 1 – 2 μm range.

According to previous results reported in the literature [31], the effect of porosity on thermal conductivity of graphite coating has been estimated by using a simple in parallel model for APS TBC. Assuming a porosity content of about 40% (probably significantly overestimated) the black coating thickness resulted about 4 μm with a thermal conductivity of about 48 W/m K. The resulting thermal conductivity of the two-in-series layers (graphite coating and TBC) differs from that of the TBC alone less than 1%. Since α/L^2 is the fitting parameter from which TBC thermal diffusivity is estimated multiplying it by the thickness L, to evaluate the error caused by neglecting the black coating, the difference between the ‘true’ thermal diffusivity and that estimated multiplying α/L^2 (as computed for the two layer system black paint+TBC) by the TBC thickness (neglecting the paint thickness) has been evaluated. In all the simulations the difference between the ‘true’ and the estimated thermal diffusivity resulted smaller than 1%, always smaller than (or comparable to) the intra-lab and inter-laboratory experimental uncertainty. These results are in good agreement with those reported by A . Mendioroz and co-authors [32].

⁴ The topic is limited to APS TBC where the effect of the paint in modifying the thermal conductivity of the TBC can be considered negligible, as also previously discussed.

As concern the experimental configurations the main difference in using flash lamps or pulsed laser it is that in the first case the whole sample surface is heated while in the latter case only a portion of the surface is heated by the laser. Moreover the laser pulse is single wavelength radiation out of the sensitivity range of IR cameras and no parasitic radiation it is expected to be emitted after the flash. On the contrary if flash lamps are used MW IR camera could become blind for some images after the flash because of the partial overlapping of the emission and detection ranges. Furthermore, parasitic radiation emitted by the flash lamps has to be filtered as previously explained in the text.

3 Conclusions

A round robin among three laboratories has been carried out to assess the robustness of the technique and the effect of different blackening paints for measuring the thermal diffusivity by pulsed thermographic techniques.

The main outcomes are resumed below:

- The experimental results provide an indirect confirmation that the approach selected to carry out this inter-Laboratory Round Robin, in terms of choice of single or multiple samples and blackening layer removal performed by heat treating the samples at 700°C for 1 hour, was able to minimize the parasitic effects affecting the thermal diffusivity not ascribable to the blackening layers.
- Results of thermal diffusivity as measured at the different labs are globally within 10 % of uncertainty, demonstrating the intrinsic robustness of the technique and providing preliminary data for a possible standardisation of the thermographic technique for estimating the thermal diffusivity of TBC deposited onto substrate, as the case of real gas turbine hot path components.
- Considering the effect of the different blackening coatings it appears that they do affect equivalently the TBC thermal diffusivity of APS owing to its specific

microstructure. The estimation of the effect of the blackening coating for APS TBC gives indications of errors always smaller than 1% in thermal diffusivity.

- EB-PVD and PS-PVDTM are slightly more affected by the blackening layer. This is especially true for both paint I and II which can penetrate more easily inside the columnar microstructures. Thus, for columnar TBC, CVD coating is the most recommended blackening layer because it minimises the infiltration of feathery structure porosity of each single column.

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Table I Summary of thermal diffusivity measurements as carried out at the three Labs on the three samples coated by three different black layers.

		ANL	CNR	CNR according to RSE approach	RSE
		$\alpha [10^{-7} \text{ m}^2/\text{s}]$			
APS 163	paint I	2.24±0.04	2.29±0.04	2.12 – 2.21	2.4±0.1
	CVD	2.25±0.05	2.29±0.06	-	2.4±0.1
	paint II	2.25±0.007	2.15 – 2.17	-	2.4±0.1
EBPVD1	paint I	7.51±0.03	7.11±0.21	7.66 – 7.72	7.9±0.1
	CVD	7.37±0.05	7.44±0.15	-	7.4±0.1
	paint II	7.70±0.04	7.51 – 7.56	-	8.1±0.1
SYS3	paint I	8.63±0.05	n.a.	n.a.	8.9±0.1
	CVD	8.61±0.05	n.a.	n.a.	8.5±0.4
	paint II	8.58±0.05	n.a.	n.a.	8.7±0.2

Figure Captions

Figure 1. Scanning electron images (SEI) of a the top surface and the section of (a-b) Porous APS, (c-d) EB-PVD and (e-f) PS-PVD™, TBC systems.

Figure 2. Probability plot of the thermal diffusivity for three sets of TBC deposited by APS, PS-PVD and EB-PVD technique, respectively. Measurements were performed at RSE Laboratory using the blackening layer later named paint1.

Figure 3. Relative thermal diffusivity increase vs. ageing temperature for APS TBC from [12, 14]. The continuous line represent the fitting of the experimental data (full square). The discontinuous lines represent the confidence interval (95%) and the significance of extrapolation, respectively.

Figure 4. Pictures of the three samples (a) before and (b) after the painting with the carbon paint Aerodag® G coating.

Figure 5. Experimental average surface temperature as a function of time and the corresponding non-linear fitting curve according to Eq.(1). Axes are represented in logarithmic scale. The maximum temperature increase is smaller than that stated in the text because these data refer to the temperature averaged along the sample surface.

Figure 6 (a) 1) Due to the windowing, necessary to reach the maximum available sampling frequency, it was not possible to sample an area containing all the heated zone; therefore a small area in the centre of the laser spot was considered. The temperature has been averaged in this area for each sampled image. 2) To improve the signal, a reference area (not affected by the laser spot and located on a massive stone block) has been considered and its average temperature has been subtracted to that obtained in the sample area. It improves the Common Mode Noise Rejection that affects the sensor as whole, with fluctuations at low frequency (with a period of the order of 1 s). To appreciate the improvement, the signal is visualized far from the pulse time, when the temperature dynamic is comparable to the noise. 4.(b) 1) The top figure shows the temperature on the sample area. 2) The

middle figure shows the temperature on the reference area. 3) The bottom figure shows the difference between the two previous temperature profiles with a monotonic decaying behaviour.

Figure 7. Four scatter plots of the fitting parameters vs α_c/l^2 are represented: delay = $t_{max}-t_0$ where t_{max} is the time of maximum temperature; the maximum of temperature reached after the laser shot is also considered.

Figure 8. Comparison of measured and fitted logarithmic surface-temperature slope data for a typical pixel in each of three TBC samples.

Figure 9. Thermal diffusivity mapping of three TBC samples as estimated by ANL approach.

Figure 10. The results of the Round-Robin test are resumed here. Three plots (one for each TBC) report the different values obtained by the three labs for the three different paints that have been considered.

Fig 1a

Fig 1b

Fig 1 c

Fig. 1d

Fig 1 e

Fig 1f

Fig 2

Fig 3

Fig 4a

Fig 4b

Fig 5

Fig6a

Fig6b

Fig 7

Fig 8

Fig 9

Fig 10