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Measurements and Understanding of the Stiffness of an Air Plasma Sprayed Thermal Barrier Coating

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Abstract

In this work, the stiffness of an air plasma sprayed thermal barrier coating (APS TBC) was studied using the three-point bending technique. Various measurements over different time periods were made on detached TBC beams, prepared by acid etching, in both as-deposited states and after heat treatment. Monotonic and cyclic loading were conducted to understand the mechanical behaviour of the TBCs in detail. The TBC beams during bending show nonlinear behaviour, inelastic deformation and hysteresis loops. The derived global in-plane elastic modulus, at first increases and then decreases with thermal exposure, and is of the range 14-18 GPa. This behaviour is a result of competition between sintering and development of microstructural damage. Direct microstructural observations during *In-situ* mechanical testing show that intra-splat opening/closure and inter-splat sliding give rise to the relatively low elastic modulus of the APS TBC.

Keywords: TBC; Elastic Modulus; Bending; Microstructure

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1. Introduction

Air plasma spraying (APS) is one of the most commonly used techniques to manufacture ceramic coatings with desirable functional and mechanical properties [1]. A typical example would be the yttria stabilised zirconia (YSZ) thermal barrier coatings (TBCs) deposited by APS for gas-turbine engine applications [2-5]. The TBCs protect the underlying load-bearing metal components against the hot gases and increase engine durability as well as efficiency. However, TBCs undergo spallation failure after service at high temperatures for a certain period of time. The failure is driven by the residual stress and the associated strain energy stored in the TBCs, induced by the thermal mismatch between the ceramic coating and substrate during cooling from the service temperature. As the stress level is scaled to elastic modulus, quantitative knowledge of the elastic modulus and how it evolves with thermal exposure are essential to understanding and predicting failure of TBCs.

Several techniques, including beam bending [6-14], impulse excitation [15-18], compression [19-22], and indentation [6, 8, 11-14, 23-27], have been developed for measuring the elastic properties of the APS TBCs. The elastic moduli reported in the literature, however, vary over a broad distribution: extending from a value as low as 0.72 GPa to over 150 GPa [6-10, 15-25, 27-29]. While the difference in spraying parameters and consequent microstructure could be partially responsible for these discrepancies, a more important reason is that different techniques produce elastic moduli over different length scales (e.g. macroscale or microscale) [6, 11-14, 29]. For example, the effective volume of the material under the effect of the applied load in beam bending methods generally spans the entire coating cross-section. This can include millimetres even centimetres in the lateral direction, which contains numerous microstructural defects and leads to a significant increase in compliance. While in the indentation methods, especially in case of nanoindentation, the material probed is restricted to a small region (e.g. in the scale of nanometres or micrometres), which is likely to contain far

less defects. Therefore, indentation methods generally give much higher elastic moduli than beam bending methods.

It is generally the global elastic modulus that determines the residual stress levels and the overall driving force (strain energy release rate) for delamination of the TBCs [4, 6].

Furthermore, as the elastic modulus of the TBC is a microstructure dependent property, it evolves with thermal exposure [11-14, 30]. However, inconsistency exists in the literature regarding the variation trend of elastic modulus as a function of thermal treatment. For example, D. Basu et al and Choi et al. have found that elastic modulus increases with thermal exposure [17, 26], but an opposite trend has been reported by Tang and Schoenung [10]. A thorough examination reveals that one of the main discrepancies among these studies is whether the TBC was bonded to or removed from the substrate during thermal exposure.

Thus this determines if the coating undergoes sintering with or without the constraint of the substrate. It has been known that the constraint retards the densification that would occur in a freestanding coating and might also introduce microstructural damage during cooling induced by thermal mismatch stress [11, 31, 32]. During service, the TBC is attached to the substrate and therefore under constraint of the substrate. As a result, the microstructure and properties of the TBC under the constraint of the substrate are expected to be more representative of the real scenarios.

In this study, three-point bending was conducted on APS TBC beams in the as-deposited state and after heat treatment. Monotonic and cyclic loading were conducted to reveal various mechanical behaviours of the TBCs. The global elastic modulus and its evolution with thermal exposure were derived and correlated with microstructure. Following these measurements, we performed direct microstructural observations on the APS TBC during purposely designed mechanical testing to provide experimental evidence for the relatively low global elastic modulus of the APS TBC.

2. Materials and Methods

2.1. Materials

The 8 wt.% YSZ (Amperit 827.873, HC Starck) TBC studied in this work was deposited onto one side of a Hastelloy® X superalloy substrate plate ($55 \times 30 \times 5 \text{ mm}^3$) using APS. The thickness of the as-deposited TBC was $\sim 250 \text{ }\mu\text{m}$. Prior to TBC deposition, a NiCoCrAlY (Amdry 365-2, Sulzer Metco, USA) bond coat with a thickness of $\sim 150 \text{ }\mu\text{m}$ was applied by APS onto the superalloy substrate.

Fig. 1a shows the cross-sectional microstructure of the as-sprayed APS TBC. The architecture of the coating is manifested by an assembly of horizontally-placed YSZ splats stacked along the spraying direction. The splat is around $\sim 1\text{-}4 \text{ }\mu\text{m}$ thick and $\sim 20 \text{ }\mu\text{m}$ in the lateral direction, mainly consisting of through-thickness columnar grains with diameters of $\sim 500 \text{ nm}$. Despite the columnar microstructure, the grains show no crystallographic texture, as determined by electron backscatter diffraction (Fig. 1a) and previous synchrotron X-ray diffraction [28]. The entire coating consists of a network with numerous cracks (horizontal inter-splat and perpendicular intra-splat cracks) and scattered pores. The fractured cross-section of the as-sprayed coating (Fig. 1b) also reveals similar microstructural features described above, including columnar grains in the splats, inter/intra-splat crack networks and pores.

2.2 Sample preparation

The coated Hastelloy® X superalloy plate was sliced to strips of $\sim 12 \text{ mm}$ in length and $\sim 2 \text{ mm}$ in width using a SiC abrasive cutting blade in a precision cut-off machine (Accutom 10, Struers). Some of the strips were then isothermally treated at $1100 \text{ }^\circ\text{C}$ in a Carbolite box furnace in laboratory air for 20, 50 and 100 hours. Spallation was not observed on any of the samples after thermal exposure. Therefore, any microstructural evolution of the TBC should

occur under the constraint of the underlying substrate. Freestanding APS TBC beams ($\sim 12 \times 2 \times 0.25 \text{ mm}^3$) were prepared by soaking the strips in aqua regia, which gradually attacked the interface between the TBC and substrate and led to subsequent debonding of the TBC layer. Before mechanical testing, the width and thickness of each individual TBC beam were measured by a digital Vernier caliper with a maximum measurement error of 0.005 mm. Three sets of measurements were conducted on different parts of each beam in order to obtain a statistical significance for the width and thickness. For a given beam, the variation in the width and thickness is less than 0.02 mm and 0.01 mm, respectively.

2.3 Three-point bending test

Three-point bending tests were performed on freestanding TBC beams using a loading roller pin and a bend fixture with adjustable spans mounted on an Instron universal mechanical testing machine. Our initial tests showed that the beams failed at a relatively low load ($\sim 0.3 - 1\text{N}$), depending on the support span used in the tests. In order to reduce the noise level, a support span of 5 mm (with a measurement precision to $\pm 0.005 \text{ mm}$) was used to maximise the loading force while still maintains a sufficiently large span to thickness ratio (~ 20) to avoid failure caused by shear stress. A loading cell with a capacity of 10 N and a resolution of 0.001 N, and a displacement gauge with a resolution of 1 μm were used during the tests. Prior to testing, the compliance of the machine was calibrated by compressing to the maximum load a tungsten carbide disc placed on the bend fixture. The recorded load-displacement curve was linearly fitted and imported to the computer program. This extension set a baseline and would be subtracted from the total extension (for a given load) recorded by the sensor during subsequent three-point bending tests to obtain the corrected extensions. The loading nose was aligned across the central of the TBC beams and the bending tests were conducted with a constant crosshead speed of 0.1 mm/min in two different modes: monotonic and cyclic loading. In the monotonic loading condition the TBC beams

were simply deflected until rupture occurs, while cyclic loading was performed by consequently loading and unloading the sample either up to the same maximum loading or increasing the maximum load for each cycle.

2.4 Determination of elastic modulus

2.4.1 Elastic modulus of the as-sprayed TBC

The flexural modulus, E_f , for three-point bending within the range of elastic deformation is determined by:

$$E_f = \frac{L^3}{48I} \frac{dP}{d\delta} \quad (1)$$

where L is support span, P is the applied load; δ is the deflection at the centre of the beam;

$\frac{dP}{d\delta}$ is the gradient of the load-displacement curve and I is the area moment of inertia of the

cross-section, which, for a rectangular beam with width of b and thickness of h , is given by:

$$I = \frac{bh^3}{12} \quad (2)$$

2.4.2 Elastic modulus of the TBC after heat treatment

For the beam after thermal exposure, E_f contains contributions from both TBC and TGO, as the beam has a thin TGO layer (mainly α -Al₂O₃, as shown in Fig.A2) in contact with the underside of the TBC. A further complication associated with the presence of this TGO layer is that it is far from a continuous layer (Fig.A2d). As a result, an analytical solution of the elastic modulus of the TBC, E_{TBC} , for this specific sample configuration was derived based on the elementary beam theory and given by:

$$E_{TBC} = \frac{\frac{L^3}{48} \frac{P}{\delta} - E_{TGO} \left[\frac{h_{TGO}^3}{12} + \left(h_{TBC} + \frac{h_{TGO}}{2} - h_{bilayer}^{NA} \right)^2 h_{TGO} \right] b f_{TGO} \left(\frac{L}{2} \right)}{\left[\frac{h_{TBC}^3}{12} + \left(h_{bilayer}^{NA} - \frac{h_{TBC}}{2} \right)^2 h_{TBC} \right] b f_{TGO} \left(\frac{L}{2} \right) + \frac{bh_{TBC}^3}{12} \left[1 - f_{TGO} \left(\frac{L}{2} \right) \right]} \quad (3)$$

A full derivation of Eq (3) and the physical meanings of the parameters in Eq (3) are given in Appendix.

As the variations of the beam width, thickness and span are orders-of-magnitude smaller than the corresponding dimensions, they have negligible effect on calculation of the elastic modulus. While the variation of the TGO thickness could reach $\frac{1}{6}$ to $\frac{1}{3}$ of the total thickness (Table A1), subsequent calculation shows that the error of the elastic modulus due to this variation is still less than 10%. Therefore, the error bars of the elastic modulus presented in this work represent the variation from sample to sample.

3 Results

3.1 Monotonic loading of as-sprayed TBCs

Fig.2 shows a set of load-displacements curves obtained from five freestanding TBC beams in the as-sprayed condition. All the beams exhibit nonlinear load displacement relationships during bending. In all cases, the slopes of the load-displacement curves (stiffness) gradually decrease with increasing deflection until final failure occurs (the moment when the load slumps). Before complete failure of the beams, the load-displacement curves are generally continuous and smooth. However, small bumps in the curves are occasionally seen, especially when the beams approach to failure, suggesting some local fracture has occurred in the beams. The load did not drop instantly to zero after rupture occurred at the outer surface of the tensile surface because the part of the beam under compression still held the beam until the loading nose was completely withdrawn.

It should be noted that the load-displacement curves of the five APS TBC beams in Fig.2 are slightly different from one to another. This is expected due to the complexity of the APS process. It is known that the APS process consists of a series of sequential events including particle melting, impact, deformation, stacking, cooling, solidification, cracking, etc. Any

variation (e.g. particle size, temperature, residual stress etc.) in the process would cause subsequent change in local microstructure and mechanical properties. The beams were sliced from a relatively large coated plate ($55 \times 30 \times 5 \text{ mm}^3$), which was likely to have spatial variation in microstructure and therefore stiffness over the entire TBC due to the nature of processing.

Because of the nonlinearity of the load-displacement curves, it is difficult to give an elastic modulus simply determined by Eq (1). A simple approach widely adopted in the literature to deal with this problem is to arbitrarily fit a straight line to a fraction of the load-displacement curve that appears linear and use its slope as a measure of the stiffness. A problem associated with this method is that the calculated stiffness depends on how much of the data is used in the fit. Another concern, perhaps more important, preventing this method from being used in this study is that it is not clear at this stage if this nonlinearity results from the intrinsic elastic response of the material or the involvement of the inelastic deformation. Indeed, both nonlinear stress-strain relationship and inelastic deformation has been reported in TBCs during mechanical testing [10, 17, 19, 21]. The application of Eq (1) to calculate the elastic modulus is based on the precondition that deformation is purely elastic. Otherwise, the inelastic deformation would partially relax the stress and lead to an underestimation of the elastic modulus.

While both elastic and inelastic deformation could occur during loading, it is generally believed that for brittle ceramics with limited plasticity, creep and viscosity, only the elastic deformation recovers during unloading at room temperature. Therefore, by implementing bending with cyclic loading, it is expected to gain a better understanding of the deformation of the TBC beams.

3.2 Cyclic loading of as-sprayed TBCs

Fig.3a shows a typical load/unloading-displacement curve of an as-sprayed TBC beam subjected to three cycles to the same maximum load (~ 0.2 N). The unloading curve in the first cycle does not follow the original path of the initial loading curve and ends up with a non-zero remnant displacement after complete unloading. This suggests that inelastic deformation occurs during the initial loading process, which is likely associated with micro-cracking during the loading. The second and third cycles with the same maximum force show reproducible loading/unloading courses without noticeable residual displacement. This suggests that all deformation in these two cycles is purely elastic and therefore fully recoverable. However, the unloading curves in the last two cycles do not follow the original paths of the loading curves, leading to the formation of elastic hysteresis loops. This suggests that although the deformation in these two cycles is purely elastic, energy dissipation occurs (the amount of the energy dissipation is the area of the hysteresis loop), which is likely caused by the internal friction between the planes of numerous micro-cracks.

Apart from the loading/unloading cycles with the same maximum force, another cyclic loading regime with incremental maximum load in subsequent cycles was also conducted. Fig.3b shows a series of load-displacement curves of an as-sprayed TBC beam subjected to this type of loading cycles. The unloading curve in each cycle was highlighted with a red colour to facilitate presentation. It is found that an unrecoverable displacement is produced in each cycle after complete unloading. This suggests that inelastic deformation consistently develops in the beam when the maximum force in a subsequent loading/unloading cycle exceeds that in the previous one.

The persistent development of the inelastic deformation during loading makes the determination of elastic modulus using loading curves obtained by monoclinic loading conditions less useful. However, the elastic nature of the unloading curves load could be used

to calculate the elastic modulus. To achieve this, the initial portions of the unloading curves are linearly fitted and the quality of the fitting is evaluated by a factor named adjusted R square, R_{adj}^2 , described by the equation:

$$R_{adj}^2 = 1 - \frac{\frac{1}{n-p-1} \sum_{i=1}^n (P_i - P_{i,exp})^2}{\frac{1}{n-1} \sum_{i=1}^n (P_i - \bar{P})^2} \quad (4)$$

Where P_i is the calculated load for a given displacement; $P_{i,exp}$ is the measured load at this displacement and $\bar{P}$ is the mean value of P_i . n is the number of the data points and p is the number of covariates. To achieve successful fitting while incorporating as many data points as possible, a threshold of $R_{adj}^2 = 0.99$ (mathematically, $R_{adj}^2 = 1$ means a perfect fitting) is imposed.

Fig.4 gives the elastic moduli calculated based on unloading curves of 7 TBC beams. It is seen that the calculations based on different curves, in this case, reloading to 0.1, 0.2, 0.3 N and 0.4 N, produce slightly different elastic moduli, decreasing with the increasing bending force. This is probably due to the development of microstructural damage with increasing load. Extrapolating all the data to a zero displacement based on a power law function yields a modulus of 14.59 ± 1.12 GPa.

3.3 Effect of thermal exposure on mechanical behaviour and elastic modulus of TBCs

Both monotonic and cyclic loading were conducted on TBC beams after thermal exposure to examine the effect of heat treatment on deformation behaviour and elastic modulus. It is found that the load-displacement curves of these beams exhibit almost the same features as those of the as-sprayed ones, such as non-linear behaviour, development of inelastic deformation during loading, cyclic loading/unloading hysteresis loop, etc. Quantitative

examination on the hysteresis loops of the as-sprayed and heat-treated beams, however, shows that for a given loading force the area of the loop significantly decreases after 20 hours thermal exposure (Fig.5), which suggests that the associated energy dissipation is substantially decreased. Further heat treatment shows limited effect on the areas of the loops (Fig.5c).

Combining the methodology used in Section 3.2 with Eq (3), the elastic unloading curves were used and fitted to calculate the elastic moduli of the TBC layers, which are then plotted as a function of thermal exposure time (Fig.6). It is found that the modulus of the TBC layer, however, does not monotonically increase with thermal exposure time. Instead, it first increases with the exposure time up to 20 hours and then decreases with the exposure time.

4. Discussion

4.1 Direction observations of the microstructural evolution during deformation of TBCs

The elastic moduli measured in this work is generally in agreement with the those of the APS TBCs obtained by beam bending reported in the literature, but significantly lower than the moduli measured by micro/nano-indentation [6-10, 14]. This is expected as the characteristic size of the material that undergoes deformation during micro/nano-indentation is only at microscale or nanoscale, which contains far less microstructural defects than the macroscale TBC beams used for the three-point bending. On the other hand, It has been suggested that the low global elastic modulus of the APS TBC is attributed to its highly-flawed microstructure, in which opening/closure of numerous intra-splat cracks and inter-splat sliding could occur upon deformation to accommodate the applied strain [6, 14]. However, unambiguous experimental evidence, especially direct observation of these mechanisms in the APS TBC, is sparse.

In order to provide experimental evidence for the argument above, we performed detailed microstructural observations on TBC beams upon being deformed via a combination of a self-built miniaturised 4-point bending rig with SEM (Figs.7 and 8). Specifically, an APS TBC beam was bonded to the centre of a rectangular PMMA strip ($70 \times 15 \times 2 \text{ mm}^3$) surface using cyanoacrylate adhesive, which was then deflected in the bending rig and observed by an SEM. The glue is strong and adhesive enough to prevent the beam from debonding throughout the experiment. The long axis of the TBC beam was aligned parallel to the length of the PMMA strip. The whole set-up was then coated with a thin layer of gold to avoid charging. A resistance strain gauge was attached to the centre of the PMMA slide (next to the TBC beam) to measure the strain imposed by bending. As the PMMA glass is an order-of-magnitude thicker than the TBC beam, the surface strain measured by the strain gauge is taken as the strain on the coating beam surface. The testing takes the advantage of the uniform bending moment and strain between the supporting rods, which results in a uniform strain within the inner span and facilitates the observations of the microstructural evolution of the TBCs. The beam was deflected stepwise and the microstructure of the identical areas at each deformation step was tracked. The bending configuration was set up so the TBC beam was either in tension or compression by gluing the beam either on the upper (tension) or bottom surface (compression) of the PMMA slide. Due to the restriction of the design, the beam subjected to compression cannot be observed from surface. Therefore, the cross-section of the beam was imaged during the test. The recorded images of the TBC beams before deformation were correlated with the images acquired at different deformation stages using digital image correlation software (DIC, DaVis 8, LaVision). The DIC analysis produced full-field in-plane displacement and strain distribution over the areas of interest. Shift and rotation corrections were conducted on the images for each deformation step to align the central features before strain vector analysis.

Fig.7b and c shows the morphology of an area on the tensile surface in the undeformed state and upon being deformed to a strain of 0.2%, respectively. Quantitative strain (ϵ_{xx}) mapping extracted from DIC analysis is also overlapped in Fig.7c. The distribution of the ϵ_{xx} is found to be highly heterogeneous, with significantly larger local strain ($> 2\%$) over some of the cracks (a few locations with such high strain are highlighted with black circles in Fig.7c). This high strain, in principle, could either be induced by stress concentrations associated with the presence of the micro-cracks or opening of the cracks during tension. However, the former explanation is unlikely for a couple of reasons. First, in theory significant stress concentration is generally constricted to the tips of the cracks, while the areas of the high local strain locations in Fig.7c are much larger and almost cover the whole cracks. Second, if the high strain over the cracks were purely associated with stress concentration, the corresponding stress would be too high and result in fracture. For instance, if the bulk modulus of the YSZ is taken as 200 GPa, a local tensile strain of 2% would produce a tensile stress of ~ 4 GPa, which would be way above its fracture stress and cause fracture. Nevertheless, no fracture was identified over the entire imaging area. As a result, the high strain over the micro-cracks is believed to relate to crack opening. It should be noted that during DIC analysis, in order to make sure the same area with the same orientation was analysed, image shift and rotation corrections were made prior to strain calculation. These actions are likely to cause some artefacts during the image analysis, especially in the edge regions of the images. The large compressive strain in Fig.7c (the deep blue colour around the edges) is likely due to this reason.

In contrast to crack opening in tension, crack closure is expected in compression. As the APS TBC is intrinsically stronger in compression than in tension, much larger compressive strain could be applied to facilitate our observations. In this case, the closure of the cracks could be even directly identified without the assistance of the DIC analysis, which is illustrated by the

SEM observations shown in Fig.8. The three images in Fig.8b-d correspond to applied strain of 0, 1% and 2%, respectively. It is seen that an intra-splat crack undergoes a substantial closure upon incremental compressive strain: the gap of the crack decreases from 261 to 202 nm when a compressive strain of 1% is applied and further decreases to 137 nm when the compressive strain is increased to 2%. A closer examination on a junction (framed by the red circles in Fig.8b-d) between the intra-splat crack and an inter-splat crack shows progressive inter-splat sliding during compression. It should be noted that opening or closure of the intra-splat cracks and inter-splat shear may not be independent as both movements may involve lateral displacement of the splats. Nevertheless, intra-splat opening/closure and inter-splat sliding in the macroscale APS TBC beam provide various mechanisms for the increase of compliance, leading to the corresponding low elastic modulus.

4.2 Effect of heat treatment on microstructure

The study shows that the global in-plane elastic modulus obtained from the three-point bending first increases and then decreases with thermal exposure time. The increase of the elastic modulus with thermal exposure is expected as the TBC undergoes sintering and subsequent stiffening at high temperature [11, 14, 30]. The decrease of elastic modulus, however, suggests introduction of microstructural damage into the coating after the long-term thermal exposure. Observations of the coating microstructure before and after thermal exposure provide some direct evidence of sintering as well as microstructural damage induced by thermal exposure.

Fig.9 shows the fractured cross-section of two splats exposed after failure of the TBC beam during bending. Compared with the morphology of the as-sprayed coating (Fig.1b), the columnar through-splat grains show spheroidising and thermal grooving, which are typical indications of surface diffusion. Although surface diffusion itself does not lead to overall densification of the coating, the roughening of splat surface associated with thermal grooving

is expected to create more bridging areas between asperities on the splats. An example illustrating this argument is highlighted in the red circle in Fig.9 where the asperities in the adjacent splats are brought into contact. These contact locations provide diffusion paths for other diffusion mechanisms (e.g. lattice and grain boundary diffusion) that contribute to densification and subsequent stiffening of the coating [11, 30].

Fig.10 presents two images acquired from an identical region near the TBC/bond coat interface of the cross-section before and after thermal exposure at 1100 °C for 100 hours. A direct comparison of the two images reveals complete or partial healing of some thin, narrow micro-cracks (the areas marked by the black circles in Fig.10a) after thermal exposure. Relatively large pores or wide cracks do not show any noticeable sign of healing. This suggests that the effective diffusion distance after thermal exposure at 1100 °C for 100 hours is limited, comparable to the typical gap of the micro-cracks. New cracks running through several splats and opening of the pre-existing cracks (the areas marked by the red circles in Fig.10a), however, are also generated in accompany with thermal exposure. The development of these cracks could be the reason for the decrease of the elastic modulus after long-term thermal exposure.

The healing of the inter/intra-splat cracks during sintering is also helpful to explain the reduction of the area of load-displacement hysteresis loop after thermal exposure (Fig.5). Energy dissipation (associated with the formation of the hysteresis loop) during cyclic loading is generally attributed to the internal friction of the material and subsequent release of heat [33, 34] , in case of the APS TBC studied in this work, the internal friction between the planes of numerous micro-cracks embedded in the coating. As thermal exposure heals some of the micro-cracks, the ability of the coating to absorb the energy decreases and leads to a decrease of the areas of the hysteresis loops.

5. Conclusions

Freestanding APS TBC beams during three-point bending exhibit non-linear load-displacement relationships, inelastic deformation and load-displacement hysteresis loops. The global in-plane modulus of the TBC first increases with thermal exposure at 1100 °C up to 20 hours, then decreases for longer exposure time and is in the range of 14 – 18 GPa. This variation trend is a result of the net contribution from sintering and development of microstructural damage. Direct experimental observations confirm that the intra-splat opening/closure and inter-splat sliding are responsible for the low global elastic modulus of the TBC.

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Appendix

We consider a cross-section of the beam at a given horizontal position x ($0 \leq x \leq \frac{L}{2}$) (Fig.A1). The cross-section consists of a thick, continuous TBC layer with thin, scattered TGO patches bonded to the underside of the TBC layer, as depicted in Fig.A1. The TGO patches have a thickness h_{TGO} and the TBC has a thickness h_{TBC} . The elastic modulus of the TBC and the TGO is denoted as E_{TBC} and E_{TGO} , respectively. The cross-section can be treated as a combination of numerous TBC/TGO bilayer rectangles and TBC single layer rectangles.

The bending moment of the i^{th} TBC/TGO bilayer rectangle **abgh** with respect to its neutral axis is given by [35]:

$$M_{bilayer}^i = \frac{d^2y}{dx^2} (E_{TGO} I_{TGO}^i + E_{TBC} I_{TBC}^i) \quad (A1)$$

Where y is the displacement of the beam at the position x ; I_{TGO}^i and I_{TBC}^i are the area moment of inertia of the TGO and TBC with respect to the neutral axis of the bilayer, respectively, and can be calculated using parallel axis theorem [36]:

$$I_{TGO}^i = \frac{w_{bilayer}^i h_{TGO}^3}{12} + \left(h_{TBC} + \frac{h_{TGO}}{2} - h_{bilayer}^{NA} \right)^2 w_{bilayer}^i h_{TGO} \quad (A2)$$

$$I_{TBC}^i = \frac{w_{bilayer}^i h_{TBC}^3}{12} + \left(h_{bilayer}^{NA} - \frac{h_{TBC}}{2} \right)^2 w_{bilayer}^i h_{TBC} \quad (A3)$$

Where $w_{bilayer}^i$ is the width of the rectangle **abgh** and $h_{bilayer}^{NA}$ is the position of the neutral axis of the bilayer (the distance from the neutral plane to the TBC surface), which can be derived from force balance over the entire cross section and given by [37]:

$$h_{bilayer}^{NA} = \frac{E_{TGO} h_{TGO}^2 + E_{TBC} h_{TBC}^2 + 2E_{TGO} h_{TGO} h_{TBC}}{2(E_{TGO} h_{TGO} + E_{TBC} h_{TBC})} \quad (A4)$$

The bending moment of the i^{th} TBC rectangle **bcef**, with respect to its neutral axis is given by:

$$M_{TBC}^i = \frac{d^2 y}{dx^2} E_{TBC} I_{TBC}^i \quad (A5)$$

Where I_{TBC}^i is the area moment of inertia the TBC relative to its neutral axis, given by:

$$I_{TBC}^i = \frac{w_{TBC}^i h_{TBC}^3}{12} \quad (A6)$$

The sum of the bending moment, $M(x)$, over the entire cross-section is:

$$M(x) = \sum_{i=1}^n M_{bilayer}^i + \sum_{i=1}^n M_{TBC}^i \quad (A7)$$

Combine Eqs (A1-A7)

$$M(x) = \frac{d^2 y}{dx^2} \left\{ \left[E_{TGO} \left[\frac{h_{TGO}^3}{12} + \left(h_{TBC} + \frac{h_{TGO}}{2} - h_{bilayer}^{NA} \right)^2 h_{TGO} \right] + E_{TBC} \left[\frac{h_{TBC}^3}{12} + \left(h_{bilayer}^{NA} - \frac{h_{TBC}}{2} \right)^2 h_{TBC} \right] \right] \sum_{i=1}^n w_{bilayer}^i + E_{TBC} \frac{h_{TBC}^3}{12} \sum_{i=1}^n w_{TBC}^i \right\} \quad (A8)$$

On the other hand,

$$\sum_{i=1}^n w_{bilayer}^i = b f_{TGO}(x) \quad (A9)$$

$$\sum_{i=1}^n w_{TBC}^i = b [1 - f_{TGO}(x)] \quad (A10)$$

Where $f_{TGO}(x)$ is the fraction of the TGO along the width of the beam, b , at position x . Insert Eqs (A9) and (A10) into Eq (A8), we have:

$$M(x) = \frac{d^2 y}{dx^2} \left\{ \left[E_{TGO} \left[\frac{h_{TGO}^3}{12} + \left(h_{TBC} + \frac{h_{TGO}}{2} - h_{bilayer}^{NA} \right)^2 h_{TGO} \right] + E_{TBC} \left[\frac{h_{TBC}^3}{12} + \left(h_{bilayer}^{NA} - \frac{h_{TBC}}{2} \right)^2 h_{TBC} \right] \right] b f_{TGO}(x) + E_{TBC} \frac{h_{TBC}^3}{12} b [1 - f_{TGO}(x)] \right\} \quad (A11)$$

On the other hand, the bending moment, $M(x)$, at a given position, x ($0 \leq x \leq \frac{L}{2}$), of the beam for three-point bending is given by:

$$M(x) = -\frac{1}{2}Px \quad (\text{A12})$$

Combine Eqs (A11) and (A12):

$$-\frac{1}{2}Px = \frac{d^2y}{dx^2} \left\{ \left[E_{TGO} \left[\frac{h_{TGO}^3}{12} + \left(h_{TBC} + \frac{h_{TGO}}{2} - h_{bilayer}^{NA} \right)^2 h_{TGO} \right] + E_{TBC} \left[\frac{h_{TBC}^3}{12} + \left(h_{bilayer}^{NA} - \frac{h_{TBC}}{2} \right)^2 h_{TBC} \right] \right] b f_{TGO}(x) + E_{TBC} \frac{h_{TBC}^3}{12} b [1 - f_{TGO}(x)] \right\} \quad (\text{A13})$$

Integrate Eq (A13) under boundary conditions: at $x = 0, y = 0$ and at $x = \frac{L}{2}, \frac{dy}{dx} = 0$, and after reorganisation we have:

$$E_{TBC} = \frac{\frac{Px}{48y} (3L^2 - 4x^2) - E_{TGO} \left[\frac{h_{TGO}^3}{12} + \left(h_{TBC} + \frac{h_{TGO}}{2} - h_{bilayer}^{NA} \right)^2 h_{TGO} \right] b f_{TGO}(x)}{\left[\frac{h_{TBC}^3}{12} + \left(h_{bilayer}^{NA} - \frac{h_{TBC}}{2} \right)^2 h_{TBC} \right] b f_{TGO}(x) + \frac{b h_{TBC}^3}{12} [1 - f_{TGO}(x)]} \quad (\text{A14})$$

Eq (A14) is reduced to Eq (3) at the centre of the beam ($x = \frac{L}{2}, y = \delta$) where final fracture takes place.

All the parameters on the right hand side of Eq (3) are either known or can be experimental determined: E_{TGO} is taken as 380 GPa [38] as the TGO is predominantly $\alpha\text{-Al}_2\text{O}_3$; h_{TGO} is experimentally measured by examining the polished cross-section of the TBCs after thermal exposure using a scanning electron microscope (SEM, Magellan 400 XHR, FEI), as shown in Fig.A2a-c and Table A1; to determine $f_{TGO}(\frac{L}{2})$, the fracture area on the underside of the beam was imaged using the SEM under the backscattered electron (BSE) mode (Fig.A2d). $f_{TGO}(\frac{L}{2})$ was then quantified using Image J software which takes advantage of the significant difference in contrast between the TGO and TBC under the BSE mode. To improve

resolution while still cover the entire width of the beam, several consecutive images with partial overlaps were taken along the crack and these images were then stitched together to give the distribution of TGO along the crack.

It is also worth mentioning that the TGO patches attached to the underside the TBC are almost stress free (Fig.A2e), as confirmed by the measurements using photoluminescence piezospectroscopy (PLPS) according to the methodology described in the literature [39, 40]. Therefore, it is expected that the mismatch strain at the TGO/TBC interface has negligible effect on the bending and subsequent determination of the elastic modulus.

Figure Captions

Fig.1 Microstructure of the as-sprayed APS TBC (a): electron backscatter diffraction (EBSD) map showing the crack network, grain morphology, grain size and crystallographic orientation with respect to the interface normal; (b) fractured cross-section of the as-sprayed APS TBC

Fig.2 Load-displacement curves of the as-sprayed freestanding TBC beams for the three-point bending test conducted under the monotonic loading mode. The inset is a photo of a TBC beam being bended.

Fig.3 Load/unloading-displacement curves of the as-sprayed freestanding TBC beams for the three-point bending test conducted under the cyclic loading mode: (a) same maximum load (~ 0.2 N) and (b) incremental maximum load in subsequent cycles. The TBC beams show inelastic deformation and load-displacement hysteresis loops.

Fig.4 Elastic modulus of the as-sprayed freestanding TBC beams calculated based on reloading curves with different maximum loads. All error bars represent the stand deviations of the measurement results of 7 beams.

Fig.5 Comparison of load-displacement hysteresis loops between the as-sprayed and thermally-treated TBC beams: (a) hysteresis loops of the as-sprayed TBC beam upon cyclic loading to different maximum loads; (b) hysteresis loops of the TBC beam after 20 hours exposure at 1100°C upon cyclic loading to different maximum loads (c) quantitative comparison of the area of the hysteresis loops before and after thermal exposure.

Fig.6 Elastic modulus of the TBC as a function of thermal exposure time. All error bars represent the stand deviations of the measurement results of 7 beams.

Fig.7 *in-situ* mechanical testing with the TBC beam under tension: (a) schematic illustration of the test configuration. The TBC beam is attached to the upper surface of the PMMA glass and under tension. (b) surface morphology of an area before deformation and (c) quantitative lateral

strain (ϵ_{xx}) map of the area in (b) upon being deformed to a strain of 0.2%. Much larger strain is seen over a few cracks (the areas highlighted by the black circles).

Fig.8 *in-situ* mechanical testing with the TBC beam under compression: (a) schematic illustration of the test configuration. The dash lines mean that the TBC beam is attached to the lower surface of the PMMA glass and under comparison. In this scenario, the TBC beam is imaged from cross-section as the surface of the beam is blocked by the PMMA glass. (b-c) morphological evolution of an area upon compressive strain of 0, 1% and 2%, respectively, showing gradual closure of an intra-splat crack and inter-splat sliding (the area within the red circle).

Fig.9 Fractured cross-section of a TBC beam after exposure at 1100 °C for 100 hours, showing spheroidising, thermal grooving and bridging of splat asperities. The area within the red circle shows an example where the columnar grains from two adjacent splats are in contact.

Fig.10 Comparison of an identical area on the TBC cross-section (a) before and (b) after exposure at 1100 °C for 100 hours, showing healing of pre-existing micro-cracks (highlighted by the black circles) and generation of new cracks (highlighted by the red circles).

Fig.A1 Schematic illustration of the cross-section of a TBC beam at a given position, x , after heat treatment. The cross-section consists of a thick, continuous TBC layer with thin, scattered TGO patches bonded to its underside. The cross-section can be treated as a combination of numerous TBC/TGO bilayer rectangles and TBC single layer rectangles.

Fig.A2 Cross-sectional microstructure of the TGO after thermal exposure for (a) 20 hours, (b) 50 hours and (c) 100 hours. (d) the underside of a detached TBC beam after heat treatment for 100 hours. The beam has been subject to three-point bending and the failure crack path through the width is indicated. (e) typical PLPS spectra of the attached TGO patches and stress-free sapphire

Fig.1 Microstructure of the as-sprayed APS TBC (a): electron backscatter diffraction (EBSD) map showing the crack network, grain morphology, grain size and crystallographic orientation with respect to the interface normal; (b) fractured cross-section of the as-sprayed APS TBC

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Table. A1 TGO thickness as a function of oxidation time at 1100 °C

Oxidation time (hours)	20	50	100
TGO thickness (μm)	2.02 ± 0.63	2.79 ± 0.62	3.81 ± 0.67