

Strain tolerance evolution of EB-PVD TBCs after thermal exposure or CMAS attack

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Abstract The microstructural evolution and Young's modulus evolution of EB-PVD TBCs upon thermal exposure and separately after CaO-MgO-Al₂O₃-SiO₂ (CMAS) attack have been compared and investigated. Moduli measured by four methods all show an increase due to sintering whereas their rates of increase are different. On finer scale (i.e. nano indentation), modulus increases from 87.3 GPa in as-deposited coatings to 198 GPa after sintering at 1400°C for 100 h. While on global scale, the modulus increases from below 10 GPa to 153 GPa after identical exposure. For the CMAS attacked TBCs at 1300°C for 0.5 h, modulus values acquired by different methods are much closer. The effect of sintering and CMAS infiltration on coating's structural integrity is discussed in terms of elastic strain energy available for driving edge delamination. The energy release rate of CMAS attacked TBCs at 1300°C for 0.5 h is ~1200 J/m², which is equivalent to that of TBCs exposed at 1400°C for 250 h (no CMAS).

Keywords: Strain tolerance; Modulus; EB-PVD TBCs; CMAS; Energy release rate

1. Introduction

Thermal barrier coatings (TBCs) made of low-thermal conductivity ceramics are now being used to provide thermal insulation to metallic components from the hot gas stream in gas-turbine engines used for aircraft propulsion [1-4]. A typical electron beam-physical vapour deposited (EB-PVD) TBCs consist of 7-8 wt.% yttria-stabilised zirconia (YSZ) and an aluminium containing bond coat (BC), which has been applied to the underlying superalloy substrate to increase the TBCs adhesion to the substrate and to enhance the oxidation resistance in the demanding environment. The feathery structure, consisting of inter-columnar gaps and intra-

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columnar porosity, leads to superior strain tolerance and improved endurance of EB-PVD TBCs [5, 6].

Driven by the need for increasing fuel efficiency, turbine inlet temperatures have increased, requiring TBCs to endure increasingly high operating temperatures alongside the mechanical demands and chemically aggressive environment [7-9]. At such high service temperatures, the columns of TBCs can sinter together, leading to an increased modulus and degraded strain tolerance. Moreover, as the service temperature exceeds about 1200°C, the ingested silicate e.g. sand, dust, volcanic ash, etc., commonly referred to as CMAS (calcium-magnesium-alumino-silicate), can melt and adhere to TBCs surfaces. If the temperatures are sufficiently high, CMAS can infiltrate into and chemically attack porous TBCs [10-12]. The CMAS infiltration also closes up the pores and leads to an increase in stiffness and thereby decrease of strain tolerance of TBCs, which is undesirable for their lifetime [3, 13, 14].

The measurement of the stiffness of EB-PVD TBCs, including indentation, beam bending, impulse excitation, and compression, has been well developed and reported. The elastic moduli in the reported work vary over a broad distribution, from as low as 5 GPa to over 200 GPa [3, 15-23]. Guo et al. measured the elastic modulus of EB-PVD TBCs by nano indentation [20]. The measured modulus increased from 53 GPa in the as-deposited coating to 108 GPa after sintering at 1400°C for 100 h. A maximum 50 mN load vs displacement of hundreds of nanometers has been used. Therefore, their measurement largely reflects the intrinsic elastic modulus of the YSZ columns which contain fine sub-micron scale pores. The sintering induced modulus thus determined is due to the closure of these fine pores. On the other hand, Wang et al. measured the modulus of EB-PVD TBCs using the beam bending method [15]. Beams of $\sim 2 \text{ mm} \times 12 \text{ mm} \times 0.2 \text{ mm}$ were used in this study. Their measured value for the modulus is only 7.5 GPa after 35 thermal cycles (1 h at 1150°C). Moreover, the increase rate of evolution of the coating's modulus upon thermal exposure using beam bending method is far more significant than that determined by nano indentation [3, 15]. Therefore, it is concluded that the global modulus of the coating is determined by the inter-columnar features and the sintering-induced changes at the inter-columnar regions. The discrepancies in modulus not only come from the different measuring length scales (indentation covers one or a few columns, beam bending spans thousands of columns), but also can be caused by the difference in depositing parameters and consequent microstructure. The direct comparison

of the mentioned modulus of the different measurement methods also involves the influences from the sample difference. While this may be qualitatively correct, it is hard to directly link the measurement results quantitatively. Also, a direct comparison of sintering induced modulus evolution with that caused by CMAS infiltration over different length scales is desired for understanding the detrimental effects of CMAS attack on the coating's strain tolerance and development of lifetime prediction model for EB-PVD TBCs under CMAS attack.

In this study, the nano indentation, micro indentation, three-point bending, and resonant frequency damping analyser (RFDA) techniques have been conducted on the identical EB-PVD TBCs upon thermal exposure and separately after CMAS attack. The moduli evolution of TBCs on identical samples under different thermal stages at different length scales have been compared and investigated. Moreover, the comparison on modulus evolution caused by pure sintering or CMAS infiltration has been studied and the corresponding energy release rate of thermal exposed TBCs or CMAS infiltrated TBCs has also been calculated and compared.

2. Experiments and methods

2.1 Materials

The EB-PVD YSZ coating deposition was conducted by carrying out at Cranfield University in a vacuum chamber equipped with an 8 kW Temescal electron beam gun. Samples were coated at a pressure of 6.5×10^{-3} mbar in an Ar/O₂ atmosphere at 1030 °C for 100 min at a power of 4.1 kW. Substrates were rotated at 8 rpm, ~ 150 mm above a source ingot, 7 wt% yttria stabilised zirconia. Substrates consisted of 97 wt% polycrystalline alumina plates, 60 mm x 25 mm x 1 mm, were for sintering and CMAS trials, and extra sapphire discs 12.7 ± 0.2 mm diameter, 0.6 ± 0.02 mm thick (0001) C-plane $\pm 0.5^\circ$ for CMAS trials (all substrates supplied by Pi-KEM Ltd). Alumina plates and sapphire discs were used as substrates as the melting point of nickel superalloys (~1350 °C) limits isothermal exposures to temperatures up to 1200°C. The alumina plates used in sintering and CMAS trials were coated on one side and these samples were used for indentation and beam bending tests. Some of the alumina plates were coated on both sides to minimise substrate distortion during extended isothermal exposure and these both sides coated samples were only for RFDA testing.

For sintering trials, flat plate as-deposited samples were isothermally heat treated in a calibrated high temperature box furnace (Pyrotherm Furnaces Ltd) for 50 h and 100 h at 1300°C or 1400°C. Samples were placed on an alumino-silicate ceramic brick with the brick being loaded into and removed from the hot furnace at the start and end of the exposure. The exposure time start was determined by the samples achieving 97 % of the desired set point.

For the CMAS trails, the as-deposited samples were dosed with CMAS, C35-A10-M7-S48 denoting mol % constituent oxides, CaO, Al₂O₃, MgO and SiO₂. All powders were supplied by Pi-KEM and at least 99.9% pure. The powders were ball milled for 4 h to ensure mixing and more homogeneous particle size. A CMAS suspension was prepared (roughly 50 vol% CMAS powder in deionised water, in a spray gun attached to a compressed air line. The suspension was constantly missed by a magnetic stirrer during application to 7YSZ coated sapphire discs. Samples were sprayed in short bursts, dried on a hot plate, weighed and the process was repeated to achieve a dose rate of 15±1 mg/cm². CMAS sprayed samples were directly put into pre-heated furnace (1300°C) for 0.5 h and then directly taken out from furnace and cooled in lab air.

2.2 Modulus measurement

The moduli of TBCs in as-deposited, different thermal exposed, or CMAS attacked conditions were measured by nano indentation, micro indentation, RFDA, and there-point bending techniques.

2.2.1 Nano /Micro Indentation

The cross sections of TBCs were mounted, ground, and polished, and then conducted by nano or micro indentation. Nano indentation measurements were performed by MTS Nano indenter XP in a maximum load of ~100 mN, and at least 50 measurements had been made on each condition. Micro indentation test was conducted by CSM Micro indentation in a maximum load of ~3000 mN, and at least 25 measurements on each condition were made. Berkovich indenter tips had been applied in both nano and micro indentation testing rigs. Also, the locations of indent for nano/micro indentation testing were about 20 µm to 80 µm away

from the top coating surface. The modulus values were extracted from the unloading curves, which were widely reported [3, 20].

2.2.2 RFDA

Global composite Young's modulus of double coated beams was measured using an IMCE RFDA. The beam is excited by an impact and its resonant frequency determined from the dissipation of energy within the beam. The resonant frequency depends upon modulus, geometry and density according to ASTM E 1259.

$$E = 0.9465 \cdot \left[\frac{m \cdot f_f^2}{b} \right] \cdot \left[\frac{L^3}{t^3} \right] \cdot T_1 \quad (1)$$

E = (Dynamic) Young's Modulus; m = mass of beam (g); L, b and t = length, width and thickness of beam respectively (mm); f_f = fundamental flexural resonant frequency of the beam (Hz); T_1 is a correction factor for the fundamental flexural mode to account for the finite thickness of the beam, Poisson's ratio, etc.

RFDA measurements were performed on flat plate samples, coated on both sides; each measurement was repeated three times. The resonant frequency is measured to ± 1 Hz. However, the calculation of the modulus is very sensitive to the measurement of the thickness of the beam, $1/t^3$ dependency. The technique returns a value for the composite modulus and the modulus for the coating was extracted using a modified composite beam theory for a two-layer coating.

$$E_{cs} I_{cs} = E_c I_c + E_s I_s \quad (2)$$

Where, I_{cs} , I_c , I_s was related to the corresponding moment of inertial of the whole sample, coating and substrate, respectively. E_{cs} , E_c , E_s were related to the modulus of the whole sample, coating, and substrate, respectively. And these can be calculated by the below equations:

$$I_s = \frac{B_s t_s^3}{12} \quad (3)$$

$$I_c = \frac{B_c t_c t_s^2}{4} + \frac{B_c t_s t_c^2}{2} + \frac{B_c t_c^3}{3} \quad (4)$$

$$I_{cs} = I_s + 2I_c \quad (5)$$

$$E_{RFDA}I_{cs} = 2E_cI_c + E_sI_s \quad (6)$$

$$E_c = E_{RFDA} \left(\frac{I_s}{2I_c} + 1 \right) - E_s \left(\frac{I_s}{2I_c} \right) \quad (7)$$

Where, B_s is the length of substrate, B_c is the length of coating, t_s is the thickness of substrate, t_c is the thickness of one side coating, illustrated in Fig.1.

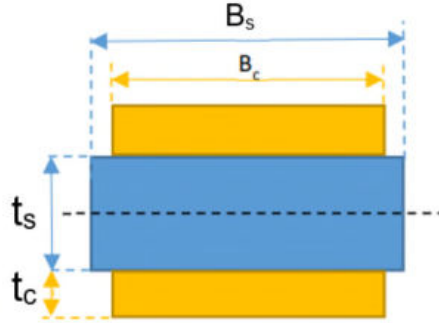


Fig.1 Cross section of sample for RFDA testing.

2.2.3 Beam bending

Three-point bending tests were conducted on the sample (one-side coated) with geometry $\sim 25 \times 2.0 \times 1.2$ (thickness) mm, cut from above mentioned alumina big plates, using a loading roller pin and a bend fixture with a span of 20 mm on an Instron universal mechanical machine, as shown in Fig.2. At least 5 testing beams were performed on each condition in a maximum load of 10 N, and the extra bare polycrystalline alumina beams were also measured prior to coated beams testing. The Young's modulus of the bilayer beam was extracted and then the modulus of TBCs was calculated by following equations.

$$\frac{dP}{d\omega}(\text{slope}) = \frac{48E_{bi}I}{L^3} \quad (8) \quad I = \frac{a^3b}{12} \quad (9)$$

$$E_{ysz} = \frac{\frac{E_{bi}(h_{al} + h_{ysz})^3}{4} - E_{al}[(h_{al} + h_{ysz} - h_0)^3 - (h_{ysz} - h_0)^3]}{h_0^3 + (h_{ysz} - h_0)^3} \quad (10)$$

$$h_0 = \frac{E_{al}h_{al}^2 + E_{ysz}h_{ysz}^2 + 2E_{al}h_{al}h_{ysz}}{2E_{al}h_{al} + 2E_{ysz}h_{ysz}} \quad (11)$$

P =applied load at centre, $h=a$ =thickness of double layers, b =width of beam, L = support span, E_{bi} = effective Young's modulus of bilayer, ω =deflection at the center of beam, I is the moment of area, h_0 is the height of neutral axis when the bilayer is loaded, E_{al} is the Young's modulus of alumina (372.1 ± 11.2 GPa), h_{al} is the thickness of alumina, E_{ysz} is the Young's modulus of TBCs, h_{ysz} is the thickness of TBCs layer, the thicknesses measurement of TBCs from multiple locations via scanning electron microscopy.

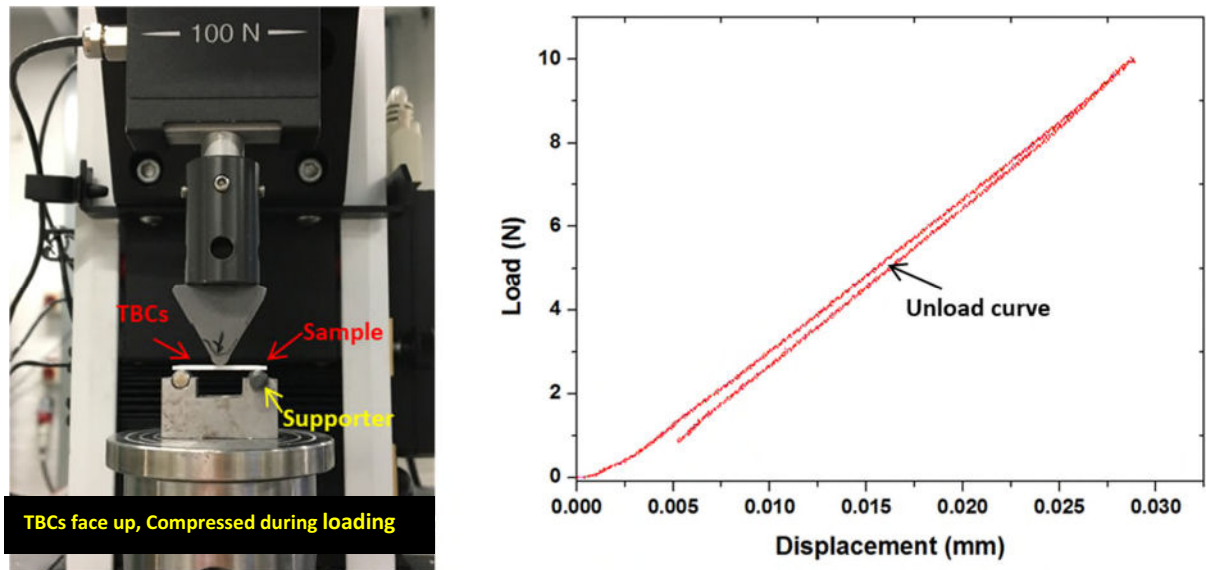


Fig.2 Illustration of the three-point beam test configuration and Load/unloading-displacement curve.

2.3 Microstructural characterisation

The cross-sectional microstructure of the TBCs in the as-deposited state or thermally exposed or CMAS attacked state was observed by a scanning electron microscopy (SEM, FEI, Quanta 650, FEM Magellan 400 XHR), coupled with a focused ion beam (FEI, Helios 660). To study the detailed microstructure and elemental composition of the CMAS attacked samples, thin lamellae were prepared by a FIB via lift-out technique and then observed by a transmission electron microscopy (TEM, FEI, Tecnai T30) fitted with an energy dispersive X-ray spectroscopy (EDS) system. The phase distribution of TBCs after CMSA attack was mapped using a transmission electron backscatter diffraction performed on Magellan microscope.

3. Results

3.1 As-deposited EB-PVD TBCs

Fig.3 shows the cross-sectional SEM images of as-deposited EB-PVD TBCs. The EB-PVD YSZ coatings display a typical feathery structure and the diameters of the columns close to the surface vary from $\sim 5\ \mu\text{m}$ to $10\ \mu\text{m}$. The as-deposited TBC consists of tetragonal YSZ and shows a strong $\{110\}<110>$ fiber texture (not showing XRD here). The $\sim 170\text{--}180\ \mu\text{m}$ thick YSZ coating was deposited on the polycrystalline alumina or sapphire substrate.

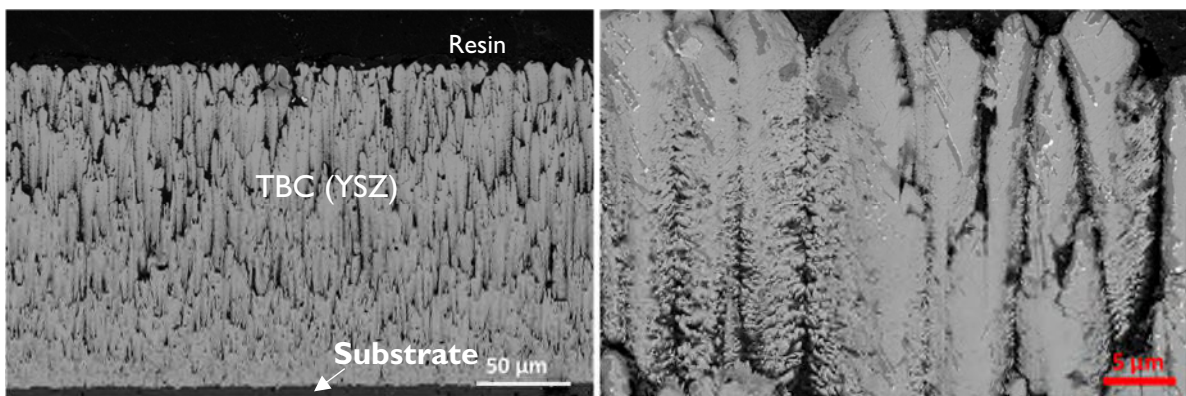


Fig.3 Cross-sectional SEM image of as-deposited EBPVD TBCs

3.2 Young's modulus and microstructural evolutions of TBCs after thermal exposure

The Young's modulus of TBCs upon thermal exposure at different length scales has been measured via nano indentation, micro indentation, beam bending and RFDA methods. The nano indentation and micro indentation focus on a more localised modulus of TBCs while beam bending and RFDA methods reflect the global modulus property. The moduli measured by nano indentation have the highest values for as-deposited or thermal exposed conditions, followed by the moduli via micro indentation, and the beam bending or RFDA method reflects the lowest moduli, as shown in Fig.4. For the as-deposited TBCs, the modulus measured by nano indentation is 87.3 GPa, followed by 67 GPa via micro indentation, while the beam bending method acquires a 6.6 GPa modulus. After thermal exposure, the modulus of TBCs gradually increases, reaching 198 GPa (nano indentation) and 153 GPa (micro indentation) after thermal exposure at 1400°C for 100 h. Noticeably, the increase rates of modulus after

thermal exposure acquired by nano indentation are quite consistent with that by micro indentation. The global modulus of TBCs via beam bending has dramatically increased from as-deposited 6.6 GPa, to 47.2 GPa at 1300°C for 100 h, and 136.6 GPa at 1400°C for 100 h. Moreover, the moduli measured by RFDA agree with the moduli via beam bending to a certain extent.

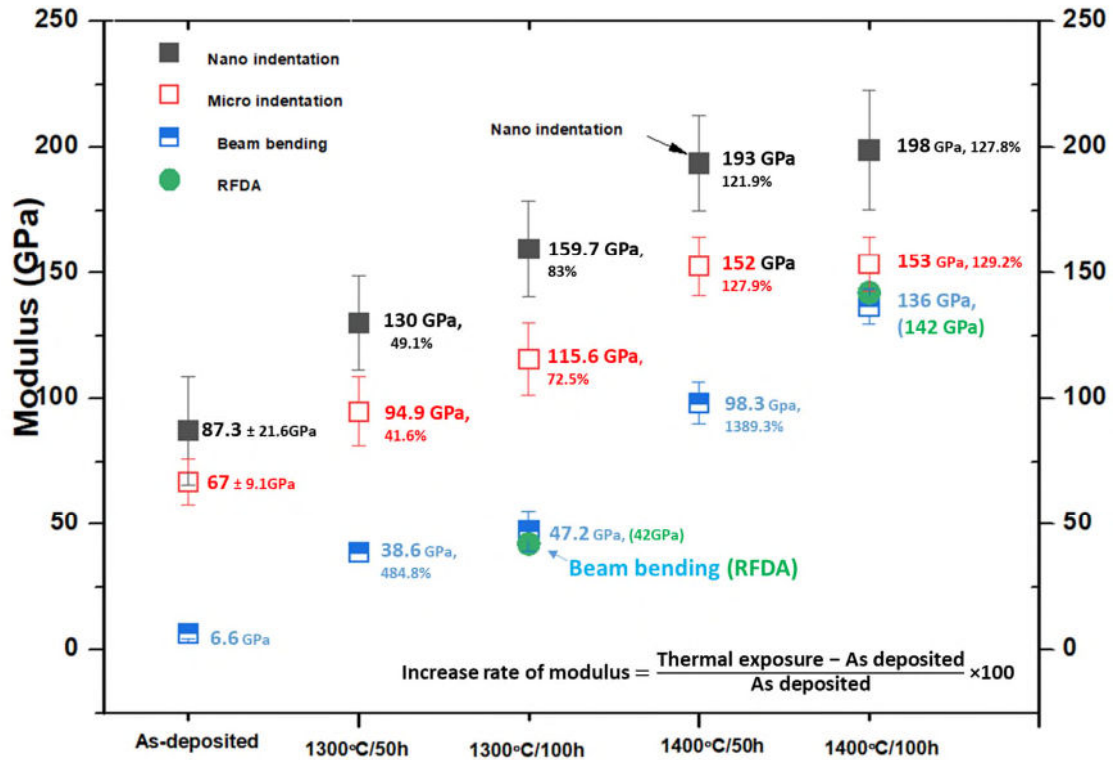


Fig. 4 Young's moduli of TBCs at different length scales upon different thermal exposure. The error bars for those from indentation tests represent the standard deviation of multiple measurements. The error bars for the beam bending tests represent the variations in the results due to uncertainties in the measured TBC thickness.

After thermal exposure, the Young's modulus of TBCs increases, and the corresponding microstructures of TBCs have been observed. Fig.5 shows the cross-sectional SEM images of TBCs upon different thermal exposure conditions. Again, the as-deposited TBCs show a typical feathery-like structure. After thermal exposure at 1300°C for 50 h or 100 h, the feathery-like structure gradually disappears and the surfaces of columns become smooth, and some adjacent columns connect via necks, as shown in Fig.5 b and c. After thermal exposure at 1400°C for 50 h or 100 h, the TBCs become relatively dense and most of the columns sinter together, as shown in Fig. 5 d and e.

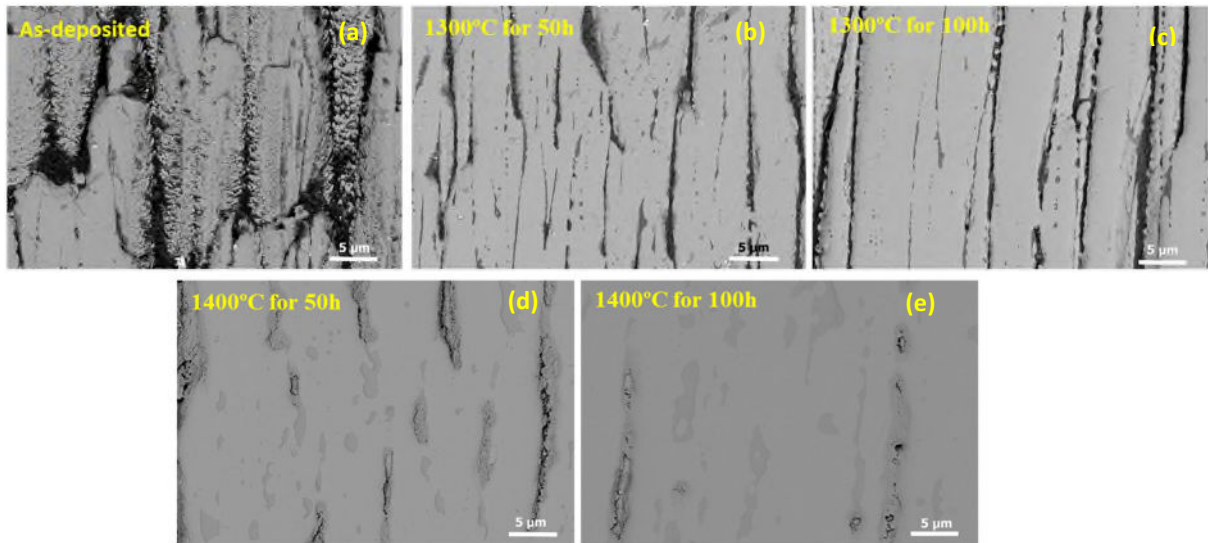


Fig.5 Cross-sectional SEM images of TBCs upon different thermal exposure. (a) as-deposited; (b) 1300°C for 50 h; (b) 1300°C for 50 h; (c) 1300°C for 100 h; (d) 1400°C for 50 h; (e) 1400°C for 100 h.

3.3 Young's modulus and microstructural evolutions of TBCs upon CMAS attack

Fig. 6 shows the Young's moduli of TBCs at different length scales upon CMAS attack at 1300°C for 0.5 h. After CMAS attack, the modulus of CMAS attacked TBCs has dramatically increased, reaching 221 GPa (nano indentation) or 186 GPa (micro indentation), which is close to the modulus of dense YSZ. The indenter locations are 20 μm to 80 μm away from the top coating surface. Fig.7 shows the cross-sectional SEM image and corresponding EDS maps of TBCs upon CMAS attack at 1300°C for 0.5 h. It is obvious that the liquid CMAS has flooded into the columnar gaps, reaching the interface between TBCs and sapphire, confirmed by the EDS maps in Fig. 7. Moreover, the CMAS has been trapped into TBCs columnar gaps, causing a relatively dense microstructure. CMAS has destroyed the feathery structure of TBCs close to the surface and the ~5-7 μm thick zone is named as CMAS attacked zone, as shown in Fig.8 a. The ~5-7 μm thick CMAS attacked zone was also indented by nano indentation and the measured moduli were consistent with the values acquired from locations 20 μm to 80 μm away from the surface, to a certain extent. The tetragonal YSZ phases have undergone a phase transition into monoclinic phases upon CMAS attack, confirmed by the TKD phase map in Fig.8

b. In order to get more details on the CMAS attacked zone, the cross-sectional TEM image and corresponding SAD of CMAS attacked TBCs zone at 1300°C for 0.5 h have been illustrated in Fig.8 c-g. It can be seen that CMAS has infiltrated the pores across TBCs and the SAD in Fig.8 e confirms its amorphous status. The twinned microstructure close to the surface in Fig.8 b and the SAD spots in Fig. 8 f have illustrated the existence of monoclinic phases, which is consistent with the TKD analysis. The morphology and phase change are attributed to the dissolution and re-precipitation of YSZ in molten CMAS, and also Y^{3+} segregation due to different solubility of Zr^{4+} and Y^{3+} in CMAS melt [12].

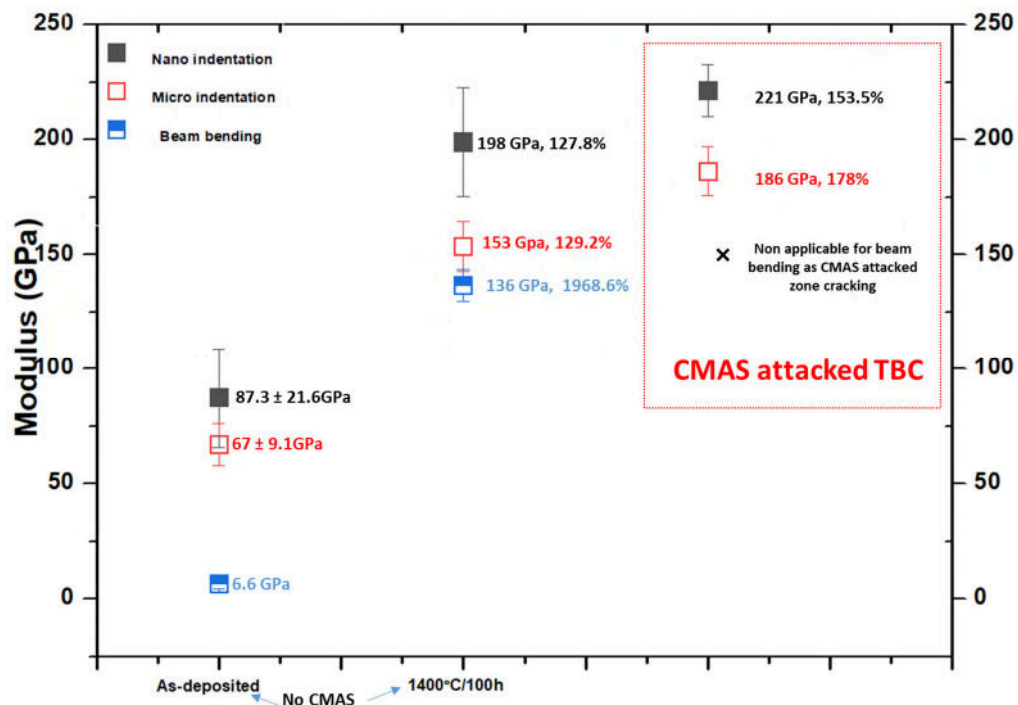


Fig. 6 Young's moduli of TBCs at different length scales upon CMAS attack at 1300°C for 0.5 h; illustrating as-deposited and thermally exposed conditions for comparison.

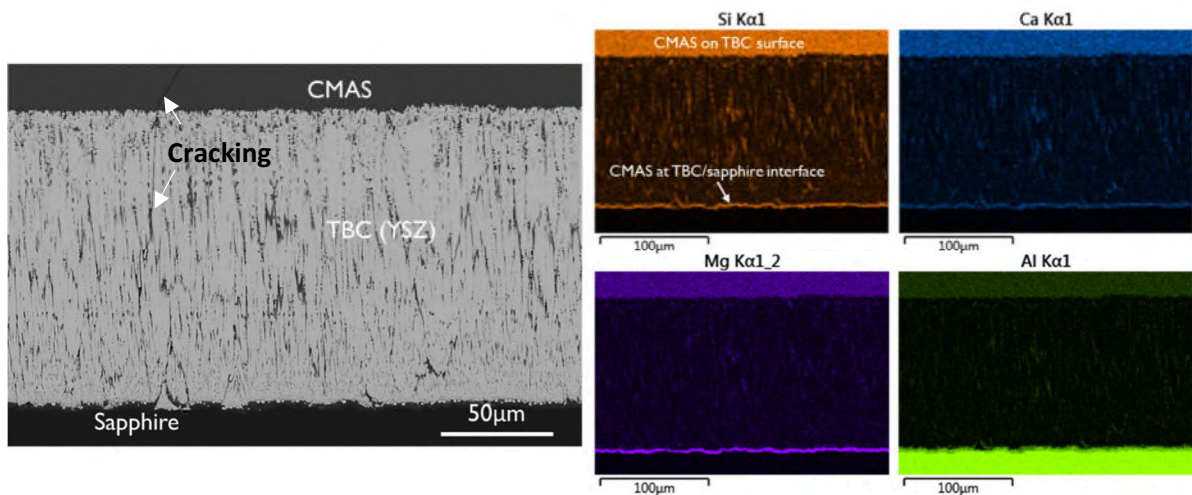


Fig.7 Cross-sectional SEM image and corresponding EDS maps of TBCs upon CMAS attack at 1300°C for 0.5 h.

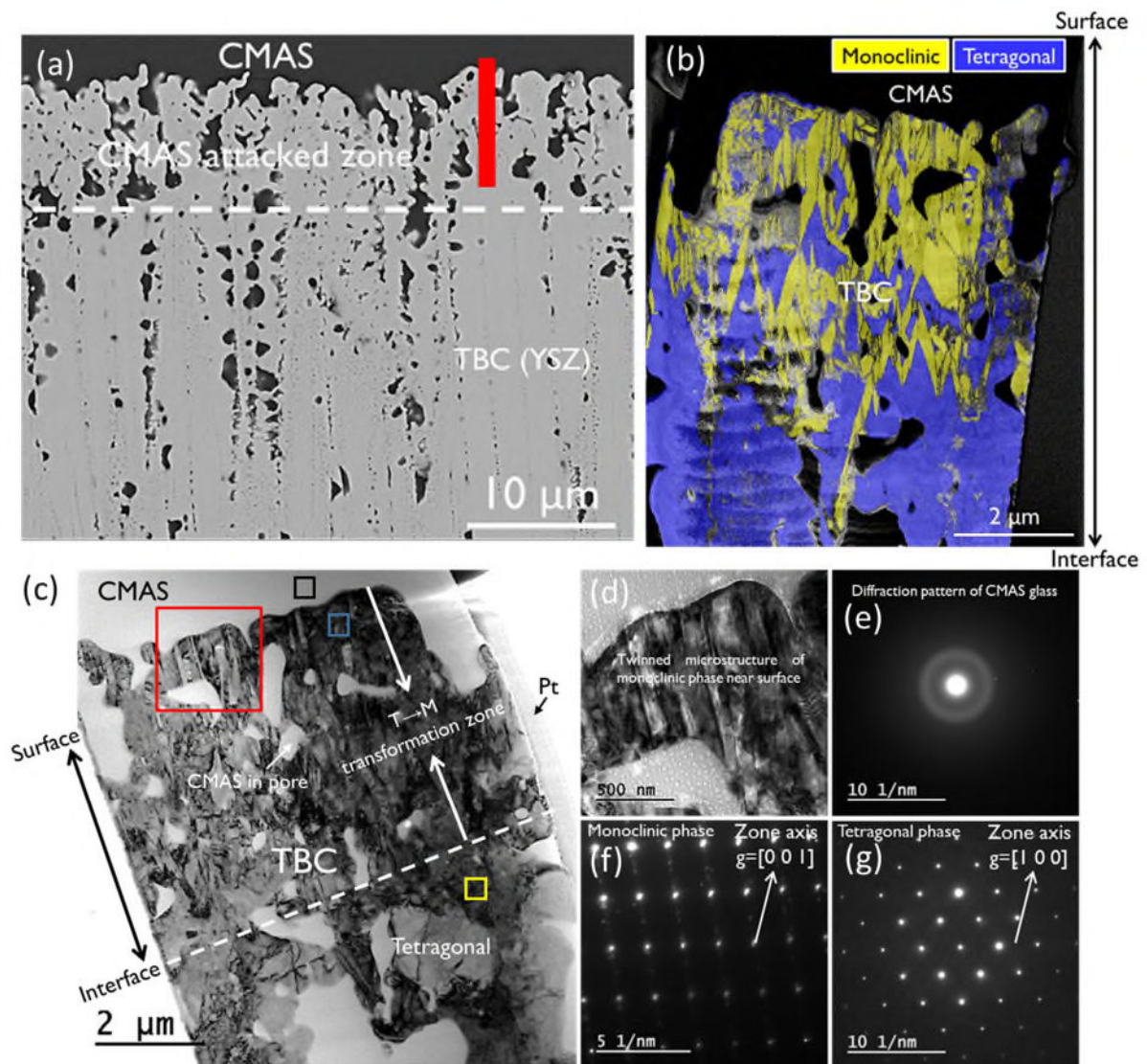


Fig.8 Cross-sectional SEM, TKD and TEM images of CMAS attacked TBCs zone at 1300°C for 0.5 h. (a) SEM image; (b) TKD image, lamellar for TKD and TEM analysis acquiring from the red rectangle in (a); (c)(d) TEM image; (e) Diffraction pattern of CMAS, acquiring from black rectangle box in (c); (f) Diffraction spots of monoclinic YSZ, acquiring from blue rectangle box in (c); (g) Diffraction spots of tetragonal YSZ, acquiring from yellow rectangle box in (c).

4. Discussion

The feathery structure consisting of inter-columnar gaps and intra-columnar porosity enable the TBCs superior strain tolerance upon thermal service [1, 6]. However, the thermal exposure induced sintering or CMAS infiltration induced densification is responsible for the increase of stiffness and decrease of strain tolerance, which is undesirable and lifetime limiting. The sintering process of TBCs caused by thermal exposure has been illustrated by the schematic diagrams in Fig. 9 a-c, which has been well reported [14, 24]. Even though the CMAS exfoliated the ~5 to 7 μm thick feathery structure at the surface of the TBC, as discussed above and displayed in Fig.9 d, the molten CMAS fully infiltrates the TBC and causes densification of the TBC in a very short period. This is detrimental to the coating's strain tolerance.

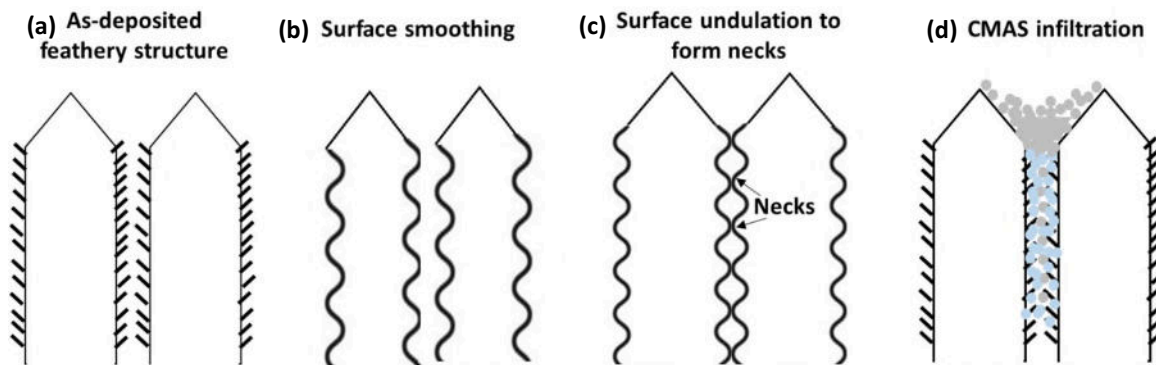


Fig.9 Microstructural evolution of TBCs upon thermal exposure and CMAS attack. (a) to (c) Feathery structure evolution of TBCs as function of increasing temperature and duration; (d) CMAS infiltration of adjacent columnar gaps.

The stiffening process of TBCs, caused by thermal exposure or CMAS infiltration, has been evaluated through Young's modulus via nano indentation, micro indentation, beam bending and RFDA at different length scales. These four methods span from approximately a single column, a few columns (and inter-columnar regions), thousands of columns, to the coated whole plate, respectively, as illustrated by Fig.10. The modulus via nano indentation in as-

deposited TBCs increases by 87% from 87.3 GPa to 159.7 GPa in the TBCs after sintering at 1300°C for 100 h, and it can be expected that nano indentation detects the elastic response on a small length scale, which can represent the local sintering processing, e.g. the closure of fine pores inside YSZ columns, surface smoothing or partially necking, as shown in Fig.5 a-c and illustrated by diagrams in Fig.9 a-b. However, a six-fold increase in coatings' modulus evolution from as-deposited condition to sintering condition at 1300°C for 100 h via beam bending has been observed. This global modulus of coating reflects the effect of the inter-columnar features and the sintering-induced changes at the inter-columnar regions, which determines the lifetime of the coating system. Compared with typical feathery and disconnected columns in as-deposited TBCs, sintering in TBCs results in the partial healing of the gaps between columns and reduction in porosity, as shown in Fig.5 and illustrated in Fig.8, which can explain the dramatic increase in modulus. The global in-plane moduli of thermal exposed coatings (without CMAS) measured by beam bending have been used and fitted as a linear function of the Larson–Miller parameter (LMP), as shown in Fig.11.

$$E = \max(6.6, 48.436 * LMP - 1130.9) \quad (12)$$

Notice that the function is bounded by the modulus of the as-deposited coating i.e. 6.6 GPa since sintering can only lead to an increase in the modulus as shown by the measurements. The effects of sintering temperature and sintering time are included into the LMP. Also, notice that Equation 12 has been obtained by fitting measurements on TBCs that have been sintered while constrained by the alumina substrate. In practice, a compressive stress will develop within the YSZ TBC upon reaching the sintering temperature as the YSZ has a larger coefficient of thermal expansion (CTE) than the alumina substrate and its expansion will be constrained by the alumina substrate. Making use of the simple analysis by Fleck et al. [25], the in-plane stress relaxes with a relaxation time constant of $3\eta_c / E$. Using an in-plane modulus of 6.6 GPa determined from the as-deposited sample and a uniaxial viscosity of 2.5×10^6 Mapas at 1300°C gives a time constant for stress relaxation of 1136s, which is much shorter than the sintering time in our experiments. Therefore, Equation 12 can be used to describe the general modulus evolution during sintering under constraint.

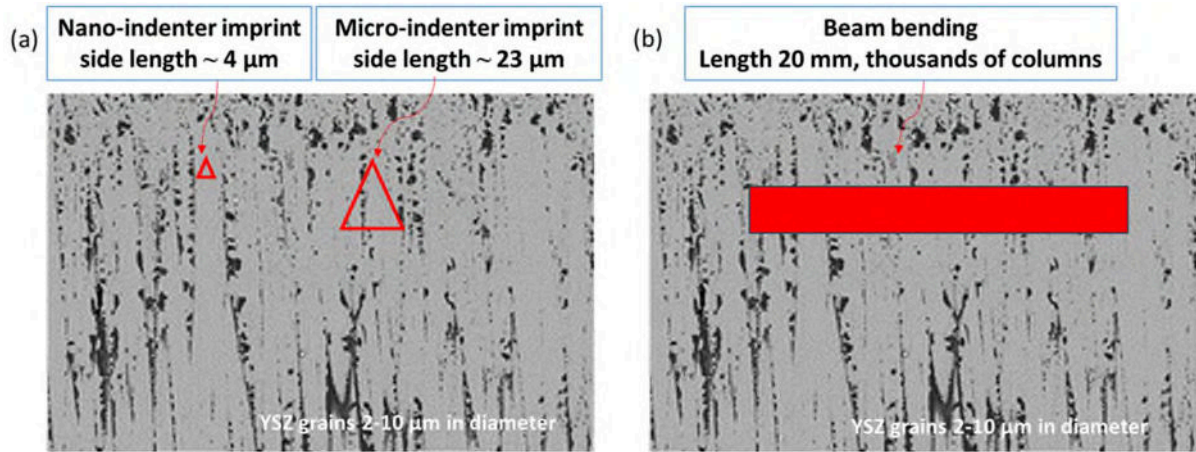


Fig.10 Schematic diagrams of measuring length scales of nano indentation, micro indentation (a) and beam bending methods (b).

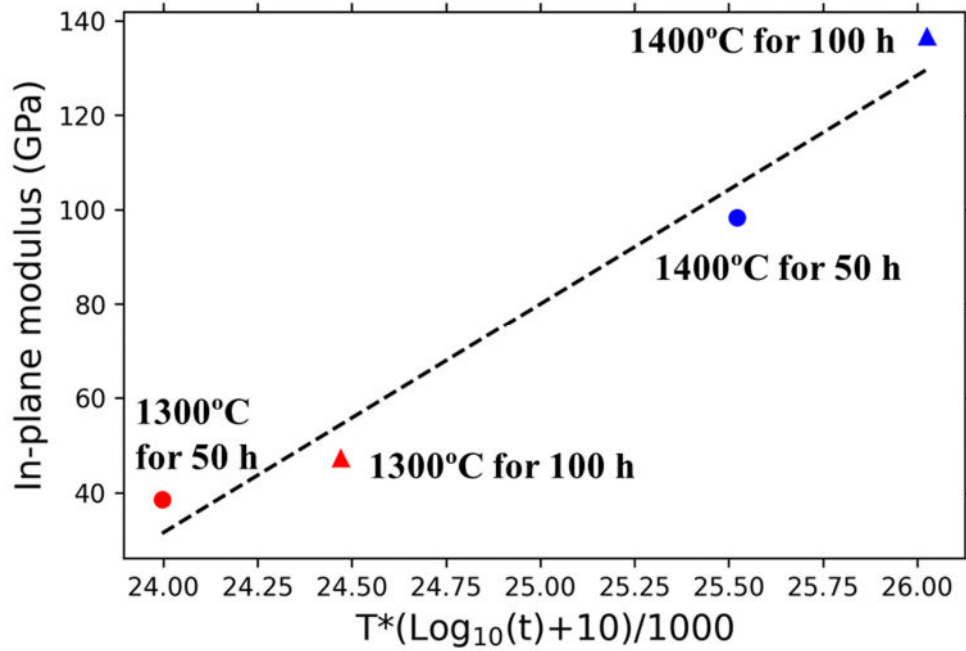


Fig.11 Formulated global in-plane modulus fitted as a linear function of the LMP (data via beam bending is used).

We now estimate the driving force for the propagation of a horizontal delamination crack that lies within the YSZ topcoat close to the interface for a given temperature distribution through the coatings thickness direction, as demonstrated by Fleck et al [26] and Appendix. For simplicity, we assume that during sintering, the in-plane stress within the topcoat is fully relaxed by the creep of the YSZ columns even though a temperature gradient exists for the

practical service condition. A coating with a thickness of 200 μm is considered. The in-plane stress within the YSZ topcoat develops as a result of the different thermal expansion coefficients between the YSZ coating ($1 \times 10^{-5} \text{ K}^{-1}$) and the metallic substrate ($1.5 \times 10^{-5} \text{ K}^{-1}$). The energy release rate for the propagation of a delamination crack near the interface can be determined for an instantaneous temperature distribution across the YSZ topcoat. Three scenarios have been considered to elucidate how the sintering of YSZ topcoat and CMAS infiltration will increase the delamination driving force. In the first case, we assume that the whole TBC system is sintered isothermally. In this case, the modulus evolution within the YSZ topcoat is the same everywhere. This represents the more simplified furnace sintering test usually conducted in the lab. In the second case, we consider the gradual infiltration of CMAS from the top surface of the TBC. This essentially leads to a step in the modulus of the YSZ topcoat. The top layer has a modulus of CMAS-infiltrated YSZ i.e. 165 GPa and is gradually increasing in thickness while the bottom layer has a modulus of the as-deposited coating. In the third case, we assume a temperature gradient in the YSZ topcoat during sintering. This will lead to faster sintering near the top surface and a relatively slower sintering near the interface. This temperature distribution during sintering will also lead to a higher contraction near the top surface upon cooldown to room temperature as the top surface sees a higher temperature change. Moreover, CMAS is assumed to infiltrate to a fixed depth into the topcoat. This assumption is reasonable since CMAS will solidify as the temperature decreases towards the topcoat/substrate interface. As a result, only the top part of the YSZ topcoat becomes infiltrated by CMAS. It is worth noticing that the infiltrated CMAS will undergo transition from a glassy state at high temperature to a crystalline state at lower temperature [29,30]. It is expected that the Young's modulus of the CMAS-infiltrated coating will remain low above the transition temperature. In this work, we intend to assess the significance of the CMAS infiltration on coating delamination to a first order. Therefore, we have simplified the problem by assuming that the CMAS-infiltrated coating has a constant Young's modulus, i.e. 165 GPa as we measured at room temperature. The resultant energy release rate for delamination crack will serve as an upper bond. The effects of the variation of the CMAS Young's modulus with temperature will be explored in detailed in future work.

In the first case, we assume that sintering has been conducted isothermally at 1300°C and the energy release rate for a delamination crack near the interface has been plotted as a function

of sintering time in Fig.12. Also, the plotted red dot is the energy release rate upon cooldown when the TBC becomes fully infiltrated by CMAS at 1300°C within 0.5 h. The interfacial fracture toughness at TBCs/substrates of EB-PVD TBCs system is about 100 J/m² [3, 27, 28]. Coating delamination can be expected upon cooldown after sintering for 30 h at 1300°C without CMAS infiltration. An important observation is that when CMAS fully infiltrates the YSZ topcoat after only 0.5 h at 1300°C, the energy release rate induced upon cooldown to room temperature far exceeds that induced by sintering and will cause coating delamination.

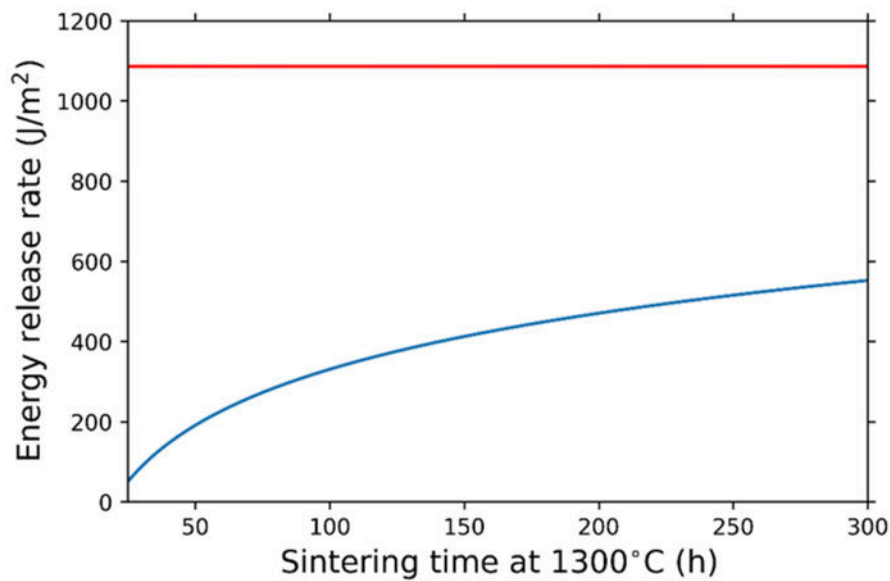


Fig.12 Energy release rate as a function of sintering time (no CMAS infiltration), Red line: energy release rate when the coating is fully infiltrated by CMAS at 1300°C for 0.5 h.

The energy release rate for delamination upon cool-down to room temperature from 1300°C is plotted against the CMAS infiltration depth for the second case considered in Fig.13. According to Fig.13, the energy release rate scales almost linearly with the CMAS infiltration depth. This occurs as the modulus of the infiltrated portion of topcoat (165 GPa) is much larger than that of the un-infiltrated portion (6.6 GPa). The elastically stored strain energy that drives delamination is dominated by the much stiffer CMAS-infiltrated layer.

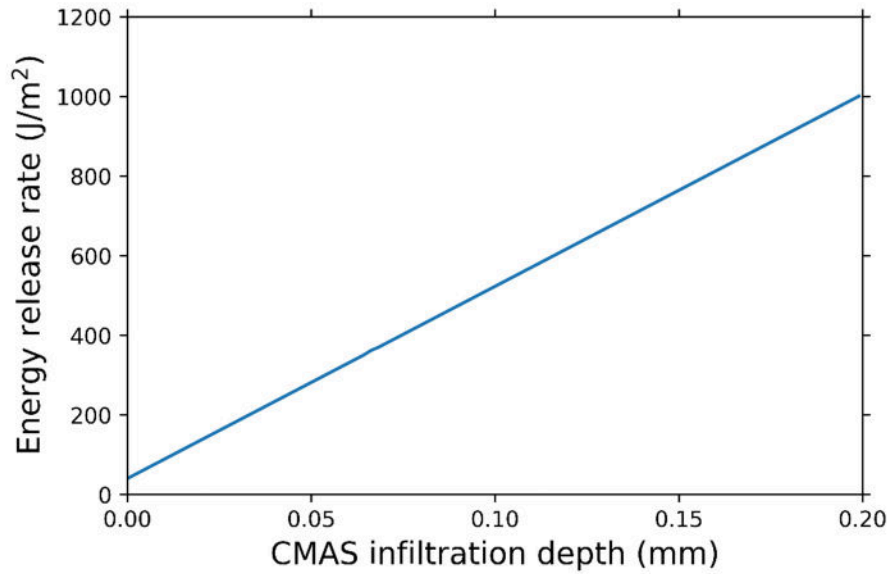


Fig.13 Energy release rate for delamination as a function of CMAS infiltration depth as the coating cools down from 1300°C to room temperature.

In the third case, the energy release rate is determined not only at room temperature but also as a function of the instantaneous temperature distribution during cyclic sintering as shown in Fig.14. Upon sintering, the surface of the YSZ topcoat has a temperature of 1400°C that decreases linearly along the coating's thickness direction to 1200°C at the interface (giving an average temperature of 1300°C). The instantaneous temperature profile is characterised by a temperature at coating surface (T_s) and a temperature at the interface (T_i) with linear variation in between. A cyclic sintering profile can thus be represented by the black dash lines in Fig.14. According to Fig.14 a, the energy release rate remains low for the prescribed temperature hysteresis. This indicates that the coating will remain intact under the prescribed temperature scenario. However, the energy release rate has increased dramatically upon CMAS infiltration by only 50 μm at the top, see Fig. 14 b. Comparison of the energy release rate contours between Fig.14 b and c indicates that similar effect can be produced by sintering under prescribed temperature profile for about 200 h.

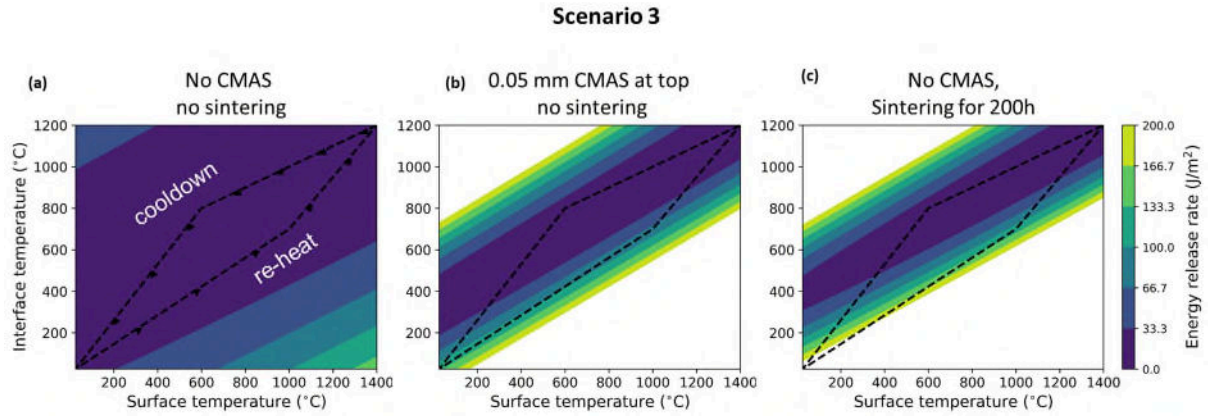


Fig.14 Contours of energy release rate as a function of the transient surface and interface temperature for (a) No CMAS and no sintering, (b) 0.05 mm CMAS at top and no sintering, (c) No CMAS and sintering for 200 h.

5. Conclusion

In conclusion, the Young's modulus at different length scales and microstructural evolution of EB-PVD TBCs upon different thermal exposure and separately after CMAS attack have been investigated and compared. Increased rates of modulus determined via nano indentation of TBCs upon different thermal exposures are consistent with those determined by micro indentation, whereas the global moduli of TBCs via beam bending or RFDA have dramatically increased upon sintering up to 2000%. On the finer scale (i.e. measured via nano indentation), the modulus increases from 87.3 GPa in the as-deposited coatings to 198 GPa close to that of fully dense YSZ after sintering at 1400°C for 100 h, while on the global scale, the modulus is below 6.6 GPa for the as-deposited coatings due to the relatively large inter-columnar gaps and increases to 153 GPa after identical sintering, which is largely due to the closure of the inter-columnar gaps. For the CMAS attacked coating at 1300°C for 0.5 h, the modulus values acquired by different methods are much closer, indicating that the CMAS has filled up the pores and gaps, leading to a fully dense coating. Using the measured global elastic modulus of as-sintered and CMAS infiltrated coatings, it has been found that the energy release rate of CMAS attacked TBCs at 1300°C for 0.5 h is $\sim 1200 \text{ J/m}^2$, which is equivalent to that of TBCs exposed at 1400°C for 250 h (no CMAS). Based on the energy release rate calculation, the delamination of TBCs becomes more likely once the top 50 μm thick TBCs have been infiltrated by CMAS or TBCs have been exposed for 200 h.

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Appendix: Fracture mechanics analysis for a delamination crack

For a steady-state delamination crack near the interface between a thin coating and a thick substrate,

the stress intensity factors, energy release rate and phase angle are [1, 2]:

$$\begin{aligned} K_I &= 0.434 \frac{P}{\sqrt{\hat{A}t}} + 0.558 \frac{M}{\sqrt{\hat{I}t^3}} \\ K_{II} &= 0.558 \frac{P}{\sqrt{\hat{A}t}} - 0.434 \frac{M}{\sqrt{\hat{I}t^3}} \\ G &= \frac{(1-\nu^2)}{E(t)} (K_I^2 + K_{II}^2) \\ \psi &= \tan^{-1} \left(\frac{K_{II}}{K_I} \right) \end{aligned} \tag{A1}$$

where $\hat{A}$ and $\hat{I}$ are dimensionless parameters due to the variation of modulus along the coating's thickness direction and are given by [1]:

$$\hat{A} = \int_0^t \frac{E(y)}{tE(t)} dy \tag{A2}$$

$$\hat{I} = \frac{1}{t^3} \int_0^t \frac{E(y)}{E(t)} (y - \bar{y})^2 dy \tag{A3}$$

where the position of the neutral axis $\bar{y}$ is calculated as:

$$\bar{y} = \frac{1}{\hat{A}} \int_0^t \frac{yE(y)}{tE(t)} dy \tag{A4}$$

The modulus varies along the coating's thickness due to the different sintering temperatures across the coating when sintering under a temperature gradient. Equation 12 is therefore used to evaluate the modulus at different positions within the TBC.

P and M are the equivalent end load and bending moment (per unit thickness) acting through and about the neutral axis of the equivalent section respectively (1):

$$P = \int_0^t \sigma(y) dy \quad (A5)$$

$$M = \int_0^t \sigma(y)(y - \bar{y}) dy \quad (A6)$$

$\sigma(y)$ is the in-plane thermal stress at height y from the interface which can be estimated by the mismatch in thermal expansion between the coating at this position and the substrate. For the case of a thin coating on a thick substrate, overall strain compatibility dictates the buildup of in-plane stress within the thin coating. Therefore, $\sigma(y)$ is a function of the temperature changes from the sintering condition and the coefficients of thermal expansion (CTEs) of the TBC and substrate. It can be calculated as:

$$\sigma(y) = \frac{E(y)}{(1-\nu)} [\alpha_{TBC} (T^S(y) - T(y)) - \alpha_{SUBS} (T_{SUBS}^S - T_{SUBS})] \quad (A7)$$

where $T^S(y)$ is the sintering temperature that may varies across the TBC's thickness direction; T_{SUBS}^S is the substrate temperature during sintering; α_{TBC} and α_{SUBS} are the CTEs for the TBC and substrate respectively.

Combining Eqn (A1)-(A7), the energy release rate and mode mixity can be determined as a function of the instantaneous temperature distribution assuming a linear variation from the coating's surface to its interface with the substrate.

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