



Automated columnar microstructure analysis using CoCo (Column Counter): Insights from EB-PVD TBCs[☆]

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ABSTRACT

Thermal barrier coatings (TBCs) are essential for protecting gas turbine components from extreme heat. The columnar microstructures produced by conventional electron beam physical vapour deposition (EB-PVD) provide pathways for the transport of heat and molten calcium–magnesium–alumino–silicates (CMAS), compromising their insulation capability and durability. Modifications to the columnar grain morphology have been shown to improve the performance and durability of EB-PVD TBCs, but replicable quantification of these key morphologic parameters remains elusive. In the present work, we present an automated method for the measurement of column width, Column Counter (CoCo). This method is applied to characterize a wide array of microstructures produced by systematically varying substrate temperature (430–1030 °C) and rotation speed (1–8 rpm). The wide spectrum of novel microstructures produced, ranging from columns with periodic porosity bands to layered architectures, markedly diverge from standard columnar TBCs. The morphological analysis is complemented by advanced characterization via X-ray diffraction (XRD) and electron backscattered diffraction (EBSD), revealing how the deposition parameters control column width, crystallographic texture strength and grain multiplicity within columns. Lower temperatures and slower rotations promote finer, less strongly textured coatings with reduced intercolumnar pathways. The results obtained through CoCo showcase the potential of automated morphological analysis in the tailored design of TBCs for improved performance and durability.

1. Introduction

Thermal Barrier Coatings (TBCs) with columnar microstructures have contributed to the development of efficient, durable gas turbines [1,2]. The initial development of columnar TBCs, produced via Electron Beam Physical Vapour Deposition (EB-PVD) was undertaken to overcome the shortcomings in cyclic oxidation life exhibited by Atmospheric Plasma Sprayed (APS) TBCs with a lamellar microstructure [2,3]. This columnar microstructure also provides EB-PVD TBCs with a higher particle impact resistance when compared to sprayed TBCs [4,5]. However, the intercolumnar porosity has been shown to have a detrimental effect with regard to thermal insulation [6–8] and resistance to infiltration by calcium–magnesium–alumino–silicate (CMAS) slags, making EB-PVD TBCs more susceptible to this fluxing attack than APS TBCs [9,10].

The continued efforts to increase the Turbine Inlet Temperature (TIT) in modern jet engines is increasingly raising the relevance of

CMAS as a life-limiting failure mechanism for TBCs [9]. A significant research effort is being undertaken to explore alternatives to EB-PVD TBCs made of 7 wt. % Ytria Stabilized Zirconia (7YSZ). The main avenues of research include the evaluation of novel materials [11], and alternative methods of manufacturing columnar TBCs [12,13].

A number of material families have been explored as CMAS resistant alternatives to 7YSZ, including 7YSZ doped with reactive elements [14,15], Rare earth zirconates such as Gd₂Zr₂O₇ [11,13] or La₂Zr₂O₇ [16], Magnetoplumbites [17,18] and Perovskites [11] among others. However, no clear material candidate seems to provide an overall improvement in CMAS performance without significantly affecting erosion performance [5,19]. A promising avenue seems to be the addition of Al₂O₃ to 7YSZ TBCs [15,20–23], to promote intrinsic crystallization of the melt.

The exploration of alternative methods of manufacturing columnar TBCs, via Suspension Plasma Spray (SPS) and Plasma Sprayed Physical

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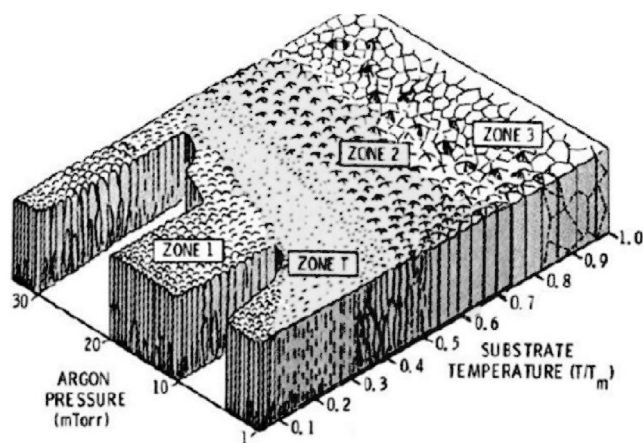


Fig. 1. Structure Zone Model as proposed by Thornton [33]. Reproduced with permission from [34].

Vapour Deposition (PS-PVD), have so far yielded mixed results [24–26], with no clear alternative that increases the durability of TBCs with respect to erosion, CMAS attack, and cyclic oxidation.

A research area that has not been extensively explored is the modification of TBC microstructure produced via EB-PVD. The existing studies, suggest that a refinement of the columnar microstructure could increase both the resistance to impact [27], to ingress by molten CMAS [28,29]. Additionally, refined EB-PVD columns have shown enhanced thermal insulation capabilities [30]. However, in the absence of replicable, quantitative methods for the characterization of columnar microstructure morphology, as discussed by Scotson and coworkers [31], the effect of EB-PVD microstructural features on durability cannot be quantitatively established.

Structure zone models have been developed [32,33] to capture the effect of process parameters on microstructures produced by Physical Vapour Deposition processes, specially homologous temperature and vapour pressure, as shown in Fig. 1.

These structure zone models attempt to capture the mechanisms for crystal nucleation and growth depending on the dominant forces in the process: condensation and diffusion. Each of these is influenced by local pressure conditions, self-shadowing and energy available for adatom mobility.

This work aims to address the absence of published replicable methods for quantifying microstructural features in Thermal Barrier Coatings, introducing a newly-developed image analysis algorithm, CoCo. This algorithm is used to determine the column width of TBCs deposited via EB-PVD by analysing electron microscope images of coating cross-sections. TBCs with diverse microstructures were deposited by varying deposition parameters, and used as case study to investigate the ability of CoCo to discriminate between them. The main morphological features of these novel microstructures are reported. The morphological characterization undertaken using CoCo is complemented by an advanced crystallographic study using Electron Back Scattered Diffraction (EBSD), with the additional aim of shedding light on the specific balance of crystal nucleation vs growth in EB-PVD Thermal Barrier Coatings and its contribution to the behaviour described by Structure Zone Models.

2. Experimental, characterization and analysis methods

2.1. Substrate and coating materials

The coatings were deposited on 1.6 mm thick, 25 x 25 mm samples made of Nimonic-75 (William Gregor Ltd.), polished to P1200 standard. Aluminizing was conducted following a High Temperature Low Activity

process, using AlF_3 (Prince Minerals) and Al-Cr alloy chips (Reading Alloys 40wt%Cr-60wt%Al). The ceramic coating was produced through evaporation of Partially Yttria Stabilized Zirconia. A light grit blasting operation was conducted prior to each coating deposition process to remove surface contamination, followed by solvent cleaning using isopropanol (Fischer Scientific, $\geq 99.8\%$ purity). The grit blasting process was conducted in a Guyson F1600 cabinet using 220 grit Saftigrit white alumina (Guyson International Ltd.) at 2.0 bar air pressure.

2.2. Coating deposition

A nickel aluminide bond coat, between 20 and 30 μm thick, was produced by aluminizing the Nimonic-75 samples in the Chemical Vapour Deposition plant at Cranfield University. Aluminizing was conducted at 1030 $^{\circ}\text{C}$ for 5 h. A full description of the high-temperature, low-activity process used is provided by Chirivi [35].

The EB-PVD coater at Cranfield University, comprising a customized vacuum chamber, fitted with a Von Ardenne Anlagentechnik GmbH EH150V electron beam gun (150 kW, 40 kV) and a custom-made hearth with capacity for 3 ingots - see Fig. 2 - was used to deposit the ceramic coatings. A custom-built furnace within the evaporation chamber is used to control the temperature of the substrates during deposition. A sample manipulation system allows for the translation of the substrates in and out of the plume from each ingot, as well as controlled rotation of the samples.

The effect of varying furnace set temperature and substrate rotation speed were explored in this study. It should be noted that actual component temperatures can vary with respect to furnace set temperature, due to heat radiated by the ingot melt pool, electron-beam reflection and convective transport from the vapour flux. To account for these effects, regular thermal surveys are conducted, allowing to relate substrate temperatures to those measured by a process control thermocouple.

The conditions used in the deposition of the PYSZ coating via EB-PVD, including the thermal survey-adjusted substrate temperatures at the beginning and end of the coating runs, as well as the nomenclature used to designate the resulting systems is summarized in Table 1.

It should be noted that the beginning of coating runs is defined as the moment the samples to be coated are in position, fully exposed to the evaporation plume, and the end is marked by the turning off of the electron beam, and the removal of the substrates from the plume. The electron beam is turned on a few minutes prior to the coating run start, to establish a stable melt pool and vapour plume.

Other relevant deposition parameters were kept constant across coating runs. The chamber pressure was set at 5.0×10^{-3} mbar, beam power fluctuated around 26–28 kW yielding a power density of 21.2–22.8 W/mm^2 for the 39.5 mm diameter ingots used. An ingot feed rate of around 3–3.5 mm/min was targeted, but adjusted to ensure that the melt pool was level with the water-cooled hearth. The sample to source (ingot) distance was kept constant at around 35 cm.

2.3. Analytical equipment

The analytical equipment used to characterize the morphology and crystallography of deposited coatings is summarized in Table 2.

2.4. Image analysis

Characterizing the morphology of coating microstructures relies on image analysis, be it qualitative or quantitative. Qualitative assessments of the microstructure morphology as “columnar” or “cauliflower-like” [37], as well as manual measurement of microstructural features constitute a form of image analysis. In that sense, both qualitative assessments of this type, as well as image analysis techniques relying primarily on computational means were used for characterizing the microstructural features of the deposited coatings.

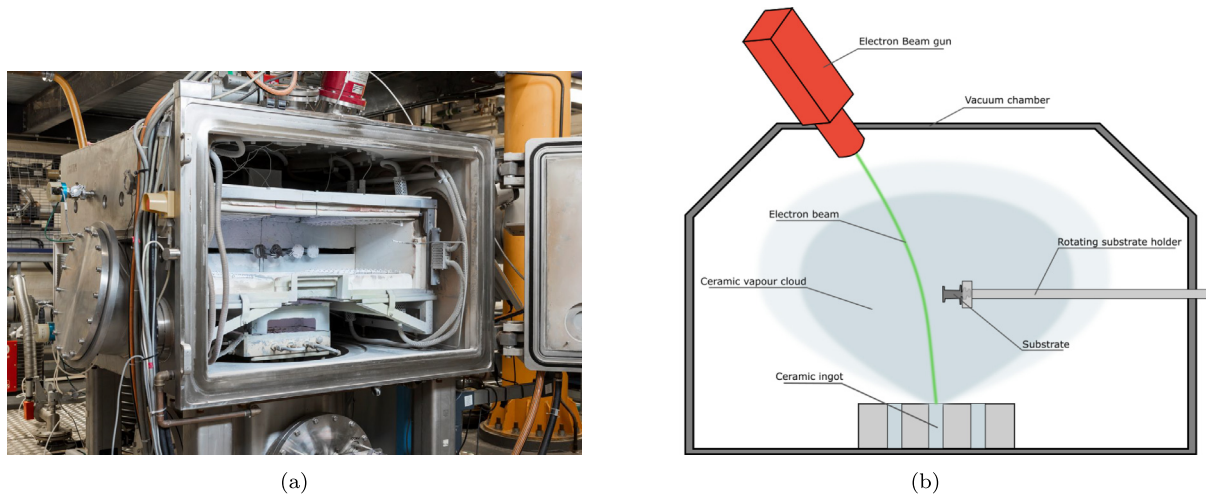


Fig. 2. (a) Image of the Cranfield University EB-PVD coater and (b) diagram of a multi-source EB-PVD coating chamber components [36] - reproduced under CC-BY-4.0.

Table 1

Manufacturing conditions and nomenclature of the TBC systems deposited in the present study.

	Rotation speed [rpm]	Furnace set T [°C]	Calibrated sample T coating start [°C]	Calibrated sample T coating end [°C]
PYSZ-Nom	8	1030	953	999
PYSZ-LR	1	1030	948	1005
PYSZ-LT	8	730	850	880
PYSZ-LTLR	1	730	843	877
PYSZ-LLT	8	430	789	886

Table 2

List of analytical equipment used in the characterization of the coating systems in this study.

Equipment	Manufacturer	Component/Model
Scanning Electron Microscope	Tescan	Microscope - S8000G
		SE detector - Everhart-Thornley
	Oxford instruments	BSE detector - Scintillator based
X-Ray Diffractometer	Bruker	EDS detector - Ultim-max 100
		EBSD detector - Symmetry S1
		D5005

Any method for quantifying the morphological features of TBC microstructures necessarily introduces subjective aspects in the analysis. This subjectivity manifests through the manual selection of the parameters used in the analysis and the selection of the subject of the analysis themselves. Some examples of specifically subjective aspects introduced in the analysis of column dimensions based on cross sectional micrographs are:

- Regarding column width:
 - Choice of columns to be measured
 - Choice of through-thickness position for column width measurement
 - Determination of “column” as an entity to be measured
- For the porosity analysis:
 - Determination of area covered by TBCs
 - Setting threshold values for porosity/non-porosity

Note that even the selection of micrographs and cross-sectioned samples as the subject for analysis is a subjective aspect that determines the subsequent analysis possible to be carried out.

In this context, the computational method described below is a proposal to systematize the subjective aspects of the analysis. The microstructural feature chosen as subject of quantification was column width, which has shown – based on data acquired using manual

methods – qualitative correlation to erosion [38] and CMAS [28] resistance.

2.4.1. Column counter

The method proposed consists of a four step treatment of the captured images and the data obtained from them. Given the focus on quantifying the column width, the algorithm developed was called Column Counter (CoCo) [39]. The algorithm uses a combination of image analysis software FIJI [40] and computational science tool SciPy [41] as follows:

1. Image scaling and cropping
2. TBC edge detection
3. Inter-columnar porosity identification
4. Counting of inter-columnar pores

The first step consists in the automatic scaling and cropping of the acquired images, leveraging the metadata files produced by the TESCAN Essence software during image acquisition.

In the second step, the TBC edges are detected, to confine the column width analysis to the area of the image occupied by the TBC, disregarding both the substrate and the resin used to mount the cross section. This step was performed through use of the trainable

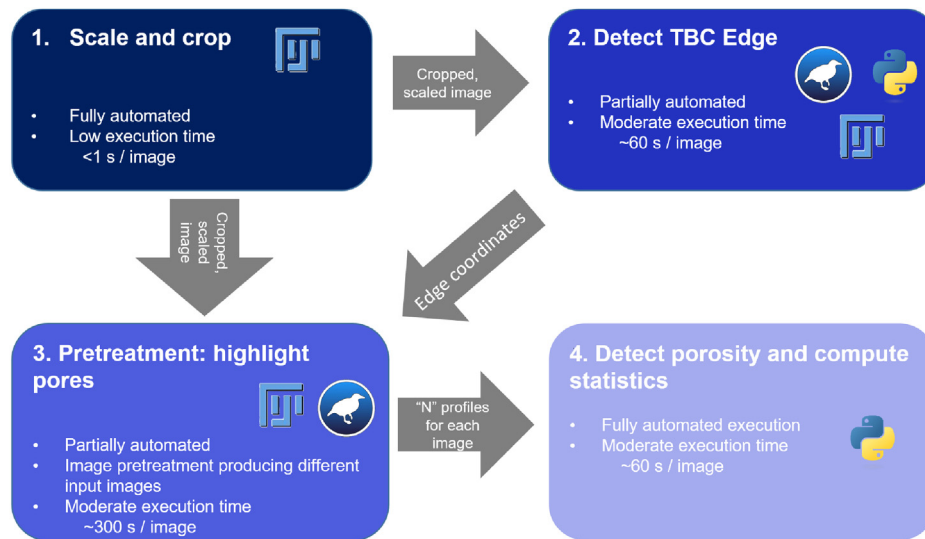


Fig. 3. Diagram showing the steps in the quantitative evaluation of column width (CoCo). FIJI [40], WEKA [42] and Python are used at different steps of the algorithm, as indicated by the corresponding logo.

WEKA¹ [42] segmentation plug-in in FIJI. The average coordinates of the upper and lower bounds of the class identified as “TBC” through semantic segmentation were subsequently computed in Python.

Going back to the caveat regarding the determination of “column” as an entity to be measured, for the purposes of this step, the proposed method relies on having a definition of a column. In the context of the growth mechanism for TBCs via EB-PVD, the definition used is equivalent to that for crystallographic grain, that is to say, “Contiguous material sharing a common crystallographic orientation”. However, given the limitation posed by the use of electron images, which do not provide crystallographic orientation information, but can be used to determine the limits for the condition of material being contiguous, the working definition for the development of the method is: “Material appearing contiguous in the horizontal dimension” or put in another way, “Material bound by discontinuities apparent in the horizontal dimension”.

The third step consists in the identification of these discontinuities in the form of porosity, which, as far as the method is concerned, represent the limits between the different columns. This is achieved by using the difference in contrast of the discontinuities to the contiguous material. The pixel values (greyscale, RGB...) for all the pixels in a horizontal line are plotted against their horizontal coordinate.

The extreme values of these profile plots, either peaks or troughs depending on whether the discontinuities show relatively high or low contrast values, are identified as porosity, and, therefore, boundaries between the columns. The location of the boundaries is consequently tantamount to the detection of the peaks in the profile plot.

The detection of these peaks constitutes the fourth and final step of CoCo. A vast variety of peak detection algorithms exist, due to the broad scope of problems where the detection of peaks is critical for the accuracy of the solution obtained, from detecting energy levels in analytical techniques for materials science and chemistry [43–45], to signal processing [46] and neuroscience [47]. It is thus unsurprising that FIJI incorporates a peak detection algorithm - “Find peaks” - within the Broadly Applicable Routines (BAR) collection [48]. “Find peaks” detects both maxima and minima in a given profile. Despite this functionality, the use of BAR within FIJI to process the large number of profiles produced by CoCo has the disadvantage of incurring a significant computational overhead. This overhead results from the Graphical User Interface focus of FIJI, which, in the case of Find Peaks,

requires opening and closing 3 windows per profile. A popular alternative for peak detection is the signal processing subpackage provided with scientific computing library SciPy [41]. The ‘find_peaks’ function in SciPy.signal takes 3 arguments as detailed in Table 3.

A diagram illustrating the operation of CoCo is shown in Fig. 3.

CoCo was also applied to crystallographic images obtained via EBSD. Grain boundaries were determined by the identification of adjacent pixels having a misalignment greater than 5°, as the default setting for grain boundary determination used by crystallographic analysis software AZtec [49]. The grain boundary images thus obtained consist of binary images with pixels either classed as boundaries (value = 1, represented in black) or not boundaries (value = 0, white). An example of an EBSD orientation map and the corresponding grain boundary map is shown in Fig. 4.

Additionally, the size distribution of the crystallographic grains of the produced coatings was calculated based on the grain boundaries determined from EBSD data, filtering out grains smaller than 100 pixels in area, as per point 12.4 in ASTM E2627-13 [50]. Kernel Density Estimation (KDE) was applied for approximating the probability density function of the grain size distributions of the novel coatings deposited, for ease of comparison.

Given a number n of samples from a distribution of unknown density, the KDE [51,52] is a function that results from the sum of functions (Kernels, $K(x)$) defined around each of the samples (x_i), as per Eq. (1):

$$\hat{f} = 1/(nh) \sum_{i=1}^n (x - x_i)/h \quad (1)$$

The bandwidth parameter h defines the ‘smoothness’ of the approximated density function thus defined. In the approximation of the KDE for the grain size distributions presented here, gaussian function kernels with the default bandwidth of the ‘gaussian_kde’ function provided with the Scipy library [41] were used. This default bandwidth is selected using “Scott’s Rule”, whereby the value of h is determined by:

$$h = n^{-1/(d+4)} \xrightarrow{\text{for } d=1} h = n^{-1/5} = 1/\sqrt[5]{n} \quad (2)$$

Where d is the number of dimensions of the density function being approximated. For an univariate distribution, $d = 1$. For a discussion on the use of KDE in statistics and data analysis, the reader is referred to the work of Scott [53] and Silverman [54].

¹ Waikato Environment for Knowledge Analysis

Table 3
Arguments taken by ‘find_peaks’ function in signal processing library SciPy.signal and their default values.

Argument	Explanation	Default
Prominence	Smallest depth that a qualified valley must exceed	Stdev. of Data
Distance	Smallest separation between peaks — iterated from highest	0
Peak Height	Threshold minimum absolute value for maxima	None (inactive)

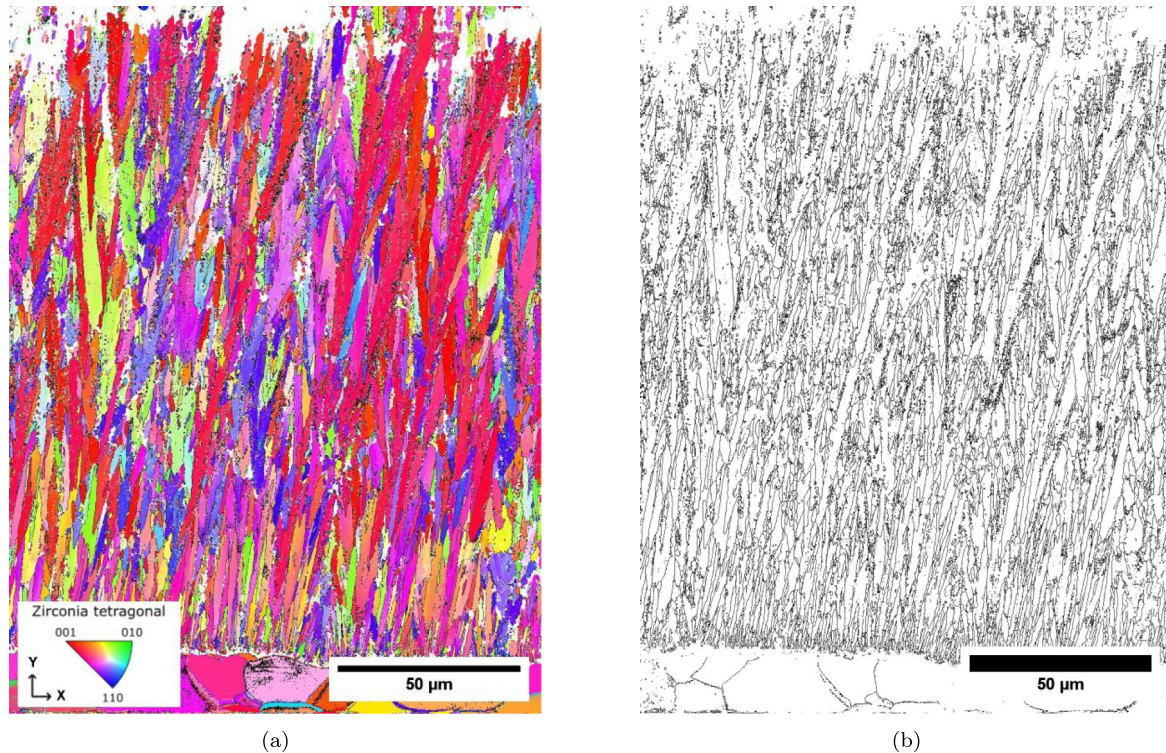


Fig. 4. (a) EBSD orientation map and (b) grain boundary map for PYSZ-LT coating obtained through analysis of pixel-wise misalignment of EBSD map data.

3. Results and discussion

3.1. Microstructure of produced coatings

A difference in the size and shape of the column tips can be observed when comparing the coatings produced under different deposition conditions. Looking at the column tip morphology, Fig. 5, the main difference observed is the rounded column tip morphology observed at lower temperatures, contrasting with the angular tips of columns deposited at high temperature.

The coating deposited under nominal conditions (PYSZ-Nom.) shows the characteristic tetragonal pyramid shaped-column tips. An interesting observation is the apparently larger width of columns deposited at high temperature but lower rotation speeds (Figs. 5(a) vs. 5(b)) as well as the resulting shape anisotropy. Column tips present as elongated grains with aspect ratios > 1 . PYSZ-Nom exhibit approximately equiaxed column tips. This apparent widening of the columns may contrast with the proposed effect of rotation on the structure-zone models as proposed by Schulz et al. [55]. This contrast is, however, qualitative. Comparing the cross sections of PYSZ-Nom and PYSZ-LR, depicted in Fig. 6, wider columns are observable for the PYSZ-LR sample, in line with the surface pyramid shape observations.

It should also be noted that the PYSZ-Nom coating shows, on cross section, less clearly defined column tips than the surface SEM images would suggest. The cause of this rounding of the tips is unclear, but may be related to metallographic preparation of the cross-section.

The effect of lower rotation speeds that is most clearly observable in the cross sectional images is the appearance of periodic features in the microstructure (Figs. 6(b) & 6(d)). These features correspond

to increased porosity zones which correlate with each rotation cycle, with the number of these periodic features coinciding with the coating deposition length in minutes divided by the rotation speed in RPM.

The low rotation-deposited coatings also exhibit a c-shaped periodic morphology in the sections of the coating between adjacent porosity features. This curvature can be explained by the effect of self-shadowing. The self-shadowing induced by the slow rotation results in subgrains growing in the direction of the incoming vapour flux, which changes slowly as the substrate rotates, hence resulting in a c-shape.

The presence of these c-shaped features and increased porosity zones has previously been observed, reported as ‘banana’-shaped elongated intra-columnar pores and intra-columnar pore arrays, respectively by Flores Renteria et al. [30]. Also notable is the similarity between the ‘fine’ microstructure Flores Renteria and coworkers report and PYSZ-LT.

While the coatings deposited at lower temperature seem to exhibit thinner columns in line with the structure zone model predictions, this qualitative evaluation is complicated by the loss of features clearly identifiable as ‘Columns’ in the case of PYSZ-LTLR coatings. These coatings display features that do not create clear clusters distinct from adjacent material. In cross section, the C-shaped or fibrous grains originating from the periodic porosity were apparent. Establishing the lateral extent of these, however, is challenging. This difficulty is shared by the surface topography images, where triangular facets or crystallites are apparent, but do not result in distinct groups that could be classed as “columns”.

Interestingly, the columnar microstructure is somewhat maintained in the PYSZ-LLT or PYSZ-LT coatings, albeit with a modified morphology. In the case of PYSZ-LT coatings, each column shows a tendency to ‘branch’, incorporating clearly defined porosity within a main grain.

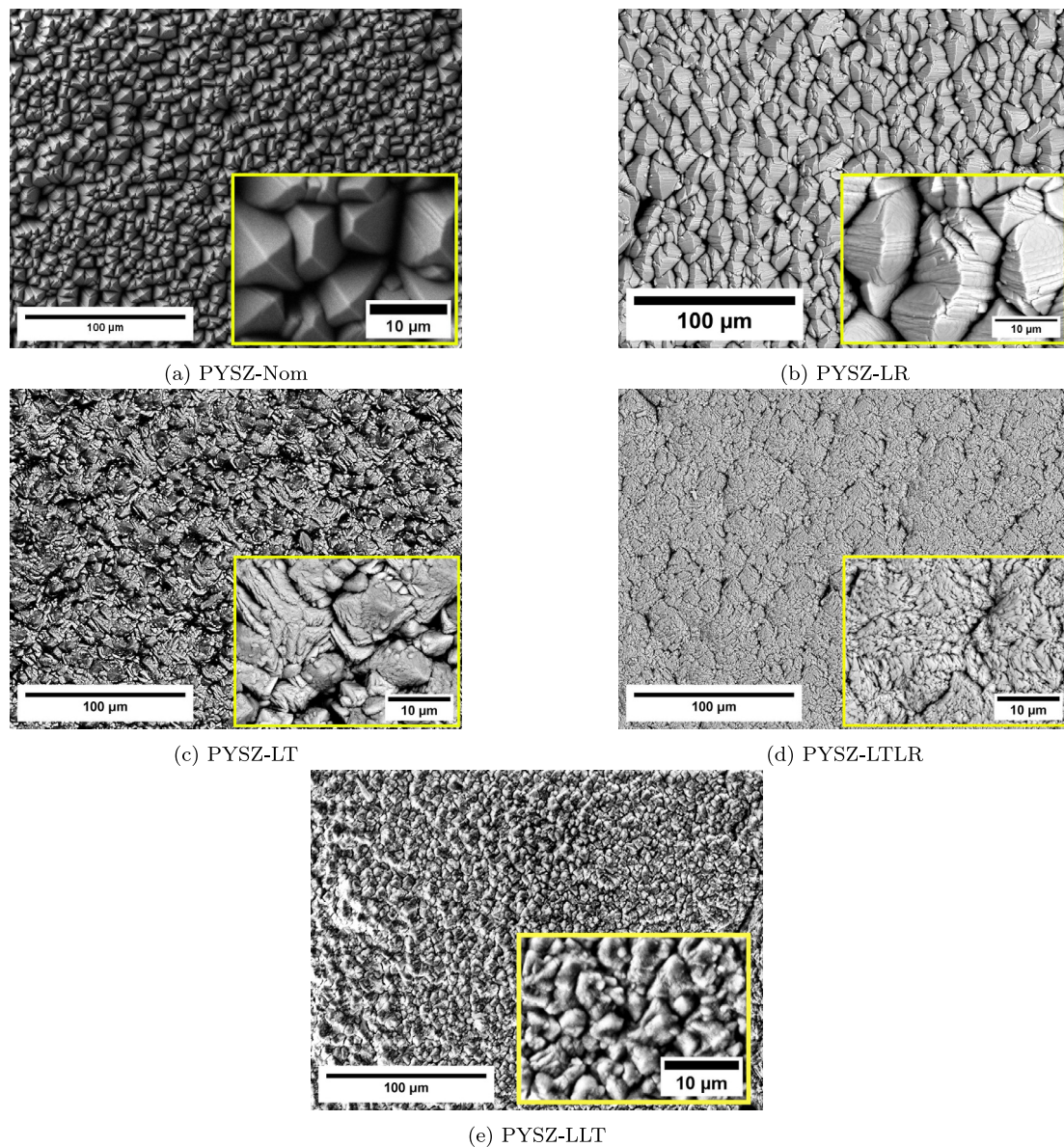


Fig. 5. Coating surface SEM images for the different PYSZ systems.

In the case of PYSZ-LLT coatings, despite the lack of a clear column-like microstructure for the bottom 3/5 to 2/3 of the coating thickness, clearly distinct columns can be identified at the coating surface. The red dashed line in Fig. 6(e) demarcates the boundary between both zones.

For both systems, this retention of ‘columnarity’ is true both in cross section and in the surface view, even if the column tip morphology is rounded. This suggests that these columns consist in a collection of crystals rather than a single crystal with clearly defined facets, such as the ones observed in PYSZ-Nom and PYSZ-LR.

The PYSZ-LLT coating showed extensive delamination in the as-deposited condition. While the cause for this delamination cannot be clearly established at time of writing, it can be hypothesized that thermomechanical loading due to CTE mismatch during cool-down following the coating run played a significant role.

This hypothesis is based on three observations. Firstly, only the coatings deposited in metallic substrates spalled. Note that additional substrates, consisting of polycrystalline alumina were also coated in the same coating run.

Secondly, a quicker cool-down is expected to have happened for the LLT system, given the relatively more important contribution to

substrate temperature provided by the electron beam and vapour flux, as indicated by the significant raise in temperature before the coating start and during the coating run — see Table 1. The removal of this heat source at the end of the run, when the electron beam is turned off would have resulted in a quick drop in temperature.

Lastly, the slight peak shifts observed in the XRD pattern for PYSZ-LLT, particularly for orientations $\langle 110 \rangle$ and $\langle 220 \rangle$ in Fig. 8 indicate that the coating may be under residual stress. However, no XRD stress measurement were conducted for the coatings in the present study.

3.2. Crystallographic study of produced coatings

Two methods have been compared in the present study for the crystallographic study of the PYSZ coatings; X-ray Diffraction (XRD) and Electron BackScattered Diffraction (EBSD).

The advantage of EBSD for the investigation of column and crystal size is the ability to acquire crystal orientation and phase data with a spatial resolution able to resolve sub-micron grains with the appropriate sample preparation. EBSD is based on a similar principle to XRD, with some differences. Both methods detect the intensity of radiation

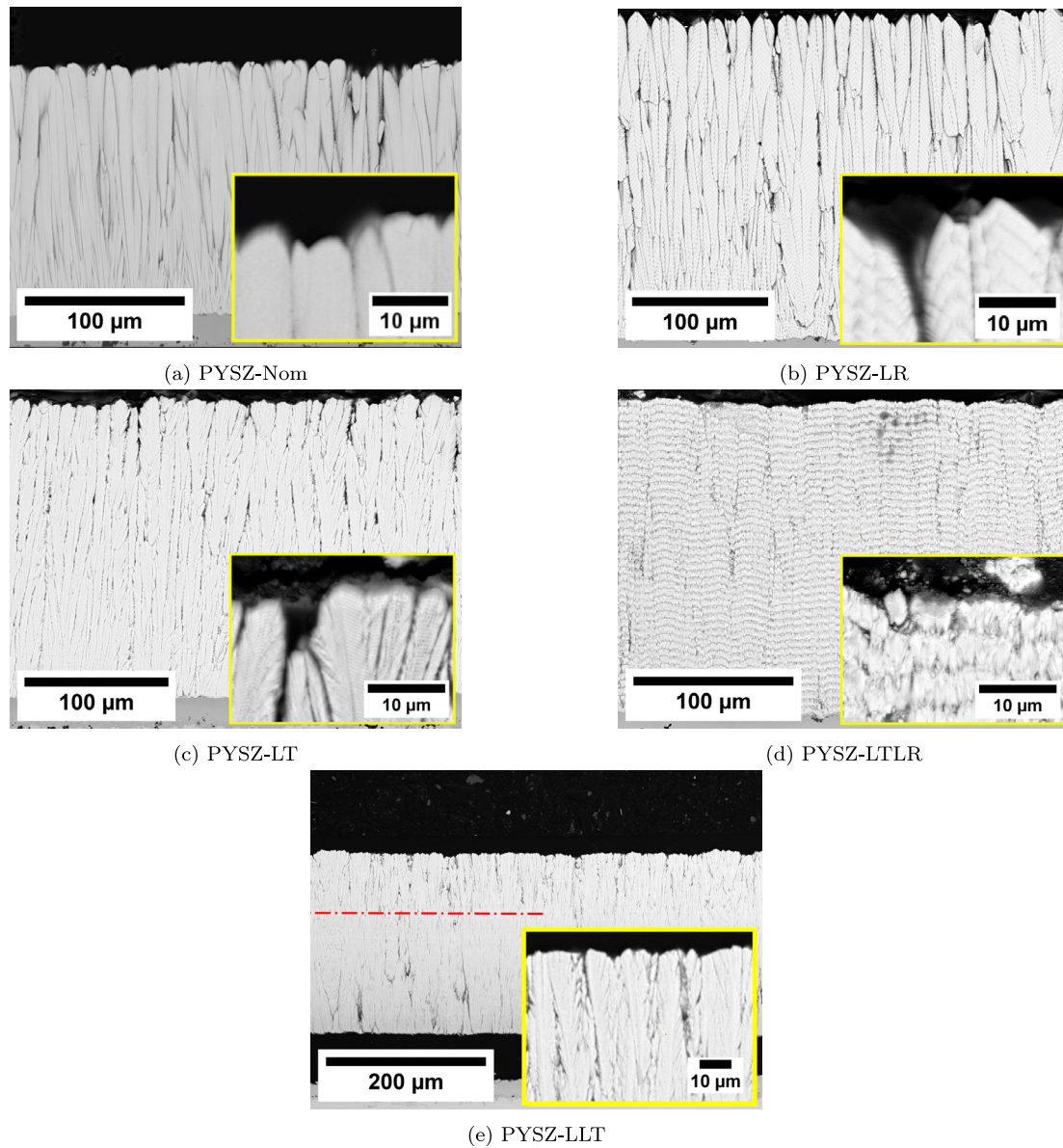


Fig. 6. SEM micrographs of cross sections for the different PYSZ systems.

diffracted according to Bragg's law. XRD resolves the crystal parameters and phases by interrogating the intensity of X-rays diffracted at different angles.

EBSD captures the size and orientation of the crystalline phase in every pixel by capturing a diffracted beam of electrons as it is projected in a sensor screen. The diffraction pattern takes the form of diffraction bands with a given arrangement in space, which varies from point to point. This arrangement can be analysed to determine the characteristics of the crystalline phase present. Since EBSD can gather data equivalent to a Megapixel (MP) sized image for each pixel in the FoV analysed, the resulting image is, consequently, significantly richer in information than an equivalent electron image.

As can be seen in the orientation map (Fig. 4), the classification of the pixels by crystal orientation allows for qualitative assessment of the level of texture of a given coating. Highly textured coatings appear close-to-monochrome, whereas low texture coatings display a more uniform colour distribution. Note that the orientation map only displays the projection of the crystallographic orientation with regard to the through-thickness Y axis. This orientation data allows for calculating the misalignment between adjacent pixels, used to determine grain boundaries.

In order to draw the boundaries between grains, which may appear to have a very similar orientation depending on the axis along which the crystal orientation is projected, describing their relative orientation in three dimensional space is required. This orientation is expressed, relative to a given frame of reference, through the rotation matrix R , as described in Eq. (3).

$$R = \begin{bmatrix} \omega_{11} & \omega_{12} & \omega_{13} \\ \omega_{21} & \omega_{22} & \omega_{23} \\ \omega_{31} & \omega_{32} & \omega_{33} \end{bmatrix} \quad (3)$$

This three dimensional rotation can be reduced to a rotation around the eigenvector $\hat{u}$ of matrix R of a given magnitude θ , representing the three dimensional misalignment, or rotation angle between the two areas being considered. For a non-symmetric rotation matrix, $\hat{u}$ and θ can be calculated using Eqs. (4) and (5).

$$\hat{u} = (\omega_{32} - \omega_{23}), (\omega_{13} - \omega_{31}), (\omega_{21} - \omega_{12}) \quad (4)$$

$$2 \cdot \cos(\theta) = \text{Tr}(R) - 1 = (\omega_{11} + \omega_{22} + \omega_{33}) - 1 \quad (5)$$

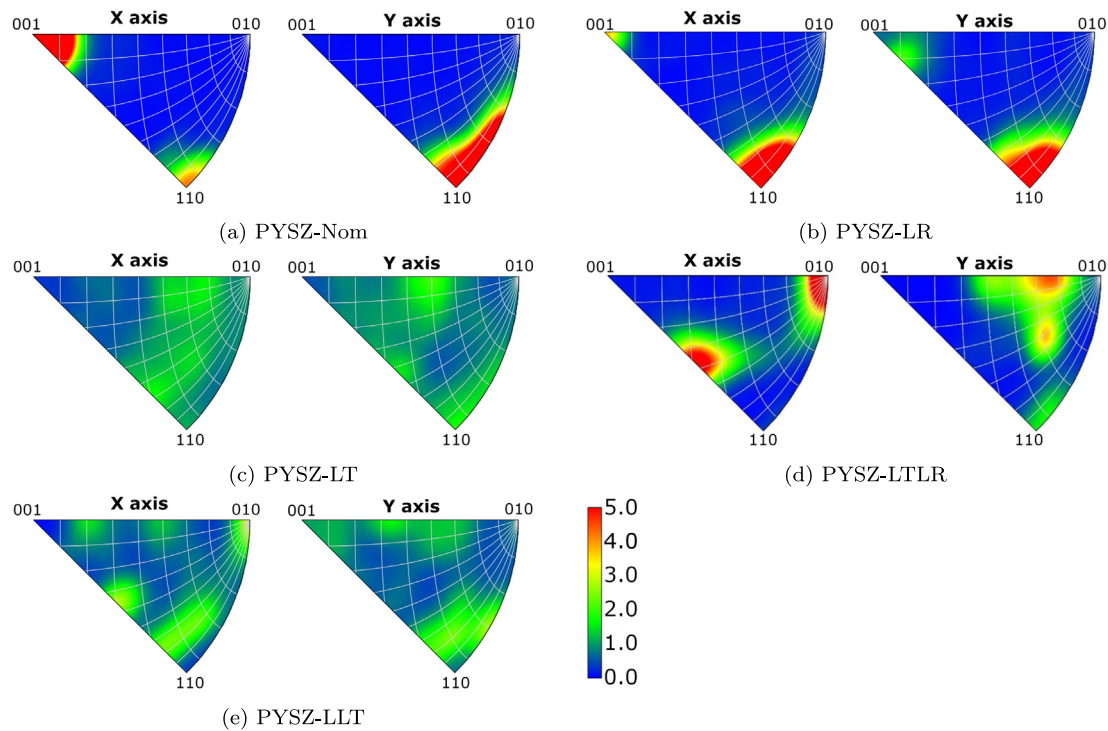


Fig. 7. Inverse Pole Figures (IPFs) for the tetragonal zirconia phase of PYSZ coatings deposited under different conditions – all IPF projected on Y direction – see Fig. 4 for the orientation of the coordinate system. The colour bar is standardized across all subfigures, and represents the Multiple of Uniform Density (MUD) for the IPFs.

Where $\text{Tr}(\mathbf{R})$ refers to the trace of matrix $\mathbf{R}$. The threshold value of 5° is applied to the magnitude θ for the determination of grain boundaries and subsequent crystal size analysis.

Beyond the immediate, qualitative, colour distribution description of texture given above, crystallographic texture refers to the extent to which different grains align in a preferred spatial orientation and the preferential crystallographic orientation relative to a specific orientation in space. Crystallographic texture plays an important role in defining the behaviour of polycrystalline materials, especially those with anisotropic crystal structures, such as tetragonal zirconia. TBCs deposited by EB-PVD have been shown to develop a strong crystallographic texture when deposited under “Nominal” conditions, i.e. at high temperature and rotation speed. The orientation data for each of the phases measured in a given EBSD map can be used to assess the texture and preferential crystallographic orientation of the deposited material.

A semi-quantitative assessment of crystal texture is performed through the generation of Inverse Pole Figures (IPFs). These IPFs are generated by plotting the crystallographic orientation of each pixel, projected in each of the spatial directions (X, Y, Z) defined on the sample, over the stereographic triangle projection of the crystal system [56,57]. The X and Y directions of the sample reference frame defined for the acquisition of EBSD data are shown in Fig. 4, with Z following the right-handed convention for a Cartesian reference frame.

Fig. 7 shows the IPFs as projected in the X and Y directions. When observing the IPF for the projection along the Y axis as defined by the sample reference frame, it can be seen that the PYSZ-Nom and PYSZ-LR coatings show a strong preference for the $\langle 110 \rangle$ direction. This is consistent with the strong texture detected for PYSZ systems in nominal conditions [58]. The rest of the systems exhibit at least another orientation in the Y axis, with some showing a very diffuse IPF heat map, corresponding to a highly random crystallographic grain orientation, especially notable for the PYSZ-LT and LLT coatings.

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A semi-quantitative measure of texture and preferential orientation can be obtained by presenting the modes of IPF figure orientation distributions — the orientations most aligned with the hotspots. The intensity of a given orientation in the IPF can be interpreted as analogous to the relative XRD peak intensity for different crystalline orientations

For the semi-quantitative comparison to the XRD data, the hotspots aligned with known preferential growth orientations of EB-PVD tetragonal zirconia, $\langle 110 \rangle$ and $\langle 101 \rangle$, are investigated. This is further complemented by using an indicator of the fabric (texture) strength; the J-index [57].

For a succinct interpretation of the meaning of the texture J-index, the Orientation Distribution Function (ODF) must first be understood. Given an orientation g in space, the ODF, $(f(g))$ gives the volume or area percentage of crystals that are aligned with g . The ODF of a theoretical polycrystalline sample with a uniform orientation distribution is 1. The ODF for a given orientation can therefore be considered as the equivalent to the multiplier of the random distribution, meaning that the frequency of grains showing orientation g are ODF times those expected in a randomly textured sample.

The J-index provides a practical and compact description of texture strength. Statistically speaking, the J-index corresponds to the second moment (equivalent to the variance) of the orientation distribution function (ODF) [59]. The texture index is obtained by integrating the ODF for all the crystal orientations present in the sample with regard to the differential volume element of the Euler angle space [60], according to Eq. (6) [61].

$$J = \int |f(g)|^2 dg \quad (6)$$

Thus defined, the expected values of the J-Index range from 1 for a sample comprised of randomly distributed grains to infinity for

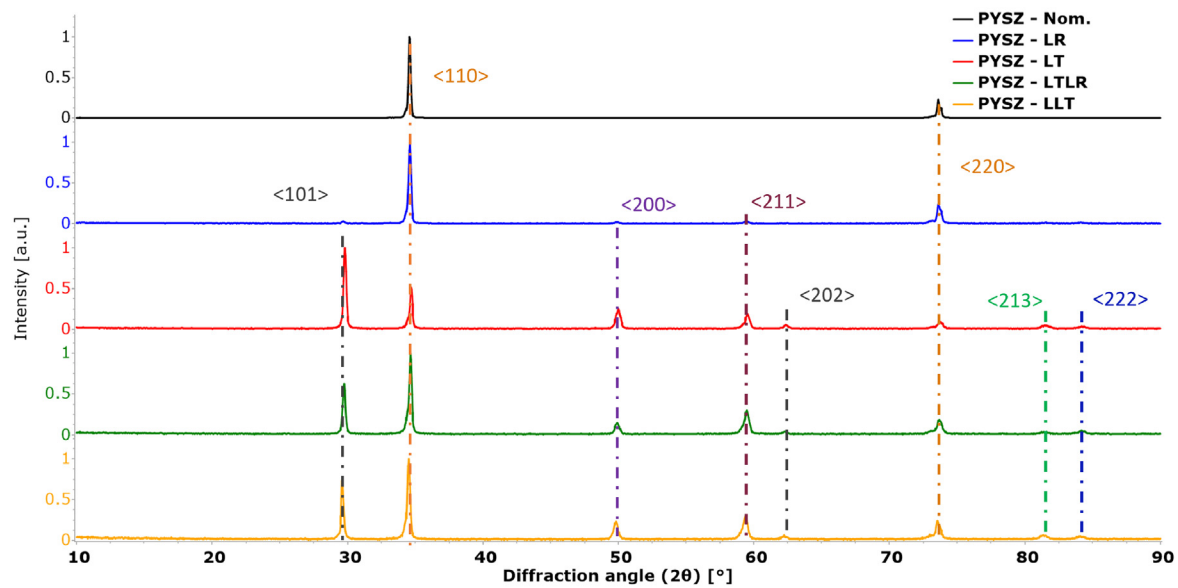


Fig. 8. XRD patterns of PYSZ coatings and crystallographic orientations corresponding to each peak. Peaks annotated with the same colour correspond to equivalent orientations with different d-spacings between planes.

Table 4

Orientations and intensities obtained for the orientations corresponding to the two main peaks of tetragonal zirconia — see Fig. 8 — from IPFs for PYSZ coating systems and corresponding J-index for crystallographic texture.

Coating system	IPF orientation (Corresponding intensity)	Texture J-index
PYSZ-Nom	$\langle 101 \rangle$ (0.05) $\langle 110 \rangle$ (11.01)	52.93
PYSZ-LR	$\langle 101 \rangle$ (1.07) $\langle 110 \rangle$ (9.34)	15.18
PYSZ-LT	$\langle 101 \rangle$ (1.11) $\langle 110 \rangle$ (1.82)	3.35
PYSZ-LTLR	$\langle 101 \rangle$ (2.37) $\langle 110 \rangle$ (1.68)	10.14
PYSZ-LLT	$\langle 101 \rangle$ (1.58) $\langle 110 \rangle$ (0.75)	11.05

a single crystal [59]. While this is a compact descriptor, having a range including infinity in it complicates the intuitive understanding of texture strength without prior knowledge of the typical range of J-index exhibited by the material system in question.

The preferential orientations and corresponding IPF intensities from the IPFs, as well as the calculated J-index for the coating systems is summarized in Table 4.

The semi-quantitative assessment of the IPF peak intensity and orientation conforms to the qualitative observation of the IPFs in Fig. 7. When compared to the XRD peak patterns, displayed in Fig. 8, a significant correlation between the IPF modes and orientation of largest peaks for each coating can be observed.

Specifically, the ratio of the intensities displayed by the $\langle 101 \rangle$ and $\langle 110 \rangle$ orientations in the IPFs parallels, if not replicates, that obtained from the XRD peaks. As an example, the minute peak exhibited by PYSZ-LR in the $\langle 101 \rangle$ direction is captured by an appreciable intensity in the IPF, whereas it is as absent from both in the PYSZ-Nom coating system.

The self shadowing due to the reduced rotation speed does not seem to be sufficient to promote a substantial change in the preferential growth direction of the grains at high temperature, instead resulting in a reduced texture compared to nominal conditions and only incipient appearance of secondary growth orientations. It is notable that the lower deposition temperature did, however, result in both a reduced texture and a change in the preferential growth direction, shifting to $\langle 101 \rangle$ from $\langle 110 \rangle$.

As for the texture strength, as indicated by the J-index, it can be seen that, relative to the coatings deposited in nominal conditions,

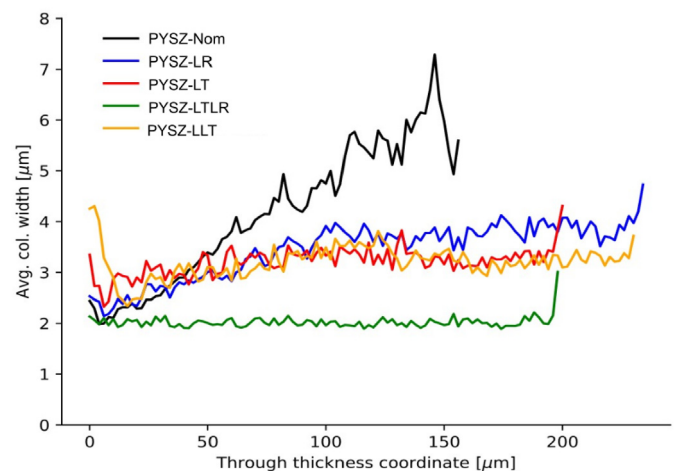


Fig. 9. Column width profiles obtained through CoCo, using electron images.

a reduction in deposition temperature and substrate rotation speed results in a reduction in texture strength. However, when comparing both PYSZ-LT and PYSZ-LLT to PYSZ-LTLR, the effect of the rotation at low temperature does not conform with this trend.

3.3. Quantitative microstructural study using image analysis

3.3.1. Secondary and backscattered electron images

The differences between the coatings deposited under different deposition conditions become apparent using the analysis performed using CoCo. The column widths for the PYSZ systems, displayed in Fig. 9 exhibit a relatively large degree of variation, but with a trend of increase in column width with coating thickness. Most of the coatings show a two stage column width vs. thickness coordinate profile with thinner columns in the interface with the substrate and TGO which gradually grow in width with the coating thickness.

3.3.2. EBSD data

The well-defined grain boundaries constructed based on the crystallographic orientation data provide, in theory, an ideal input for

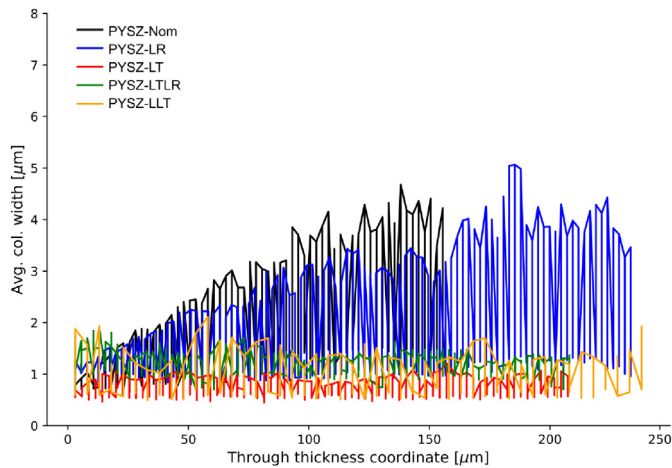


Fig. 10. Column width result for PYSZ systems, determined using CoCo on EBSD grain boundary maps.

the measurement of the through thickness column width using the method for the quantitative analysis of model TBCs discussed in the present Section. The results obtained for PYSZ systems using the grain boundary data is presented in Fig. 10.

It is immediately evident that CoCo shows a wide variation when directly using the grain boundary data. This could be explained by the noise introduced in the grain boundary map by small crystallites or areas identified as separate small grains, apparent in Fig. 4(b). These small grains appear despite data post-processing and cleaning steps used to minimize their appearance, including correction for pseudo-symmetry, commonly occurring in tetragonal zirconia. However, the upper bound of this data may be more representative of the actual distribution dependence on thickness.

Accurate indexing and orientation rely on the quality of the surface preparation with flat surfaces being preferred for signal quality. Additionally, high beam currents increase the signal intensity and improve acquisition speed. Porous ceramic systems such as TBCs exhibit low conductivity and abundant surface imperfections, this can result in low band contrast, particularly around column edges. This low band contrast can result in misorientation of the detected crystallographic phase, which in turn can lead to the detection of grain boundaries around the misoriented datapoints. Indeed, a significant proportion of the small grains in the grain boundary map in Fig. 4(b) appears to be either on the boundaries of larger grains or aligned with them.

The binary (peak-trough) nature of the column width profile shown in Fig. 10, suggests that the troughs correspond to points where the profile is encountering a disproportionate amount of these small grains, leading to a significant under-measurement of the column width. It should be noted that the upper envelope in the profiles probably also correspond to an under-measurement of column width, albeit not to the same extent as that of the troughs, as a number of small grains will also be measured along with the large grains.

The method adopted for correcting the EBSD grain boundary-based column width profiles consisted in the calculation of the upper envelope of the calculated profiles. This upper envelope was determined by detecting the peaks on each profile and linear interpolation of the resulting peak points. The results for the PYSZ system are presented in Fig. 11.

The EBSD data gathered can also be used for other morphological and crystallographic assessments of the produced systems. An interesting variable to analyse, to complement the column width, is the size of the grains, measured by their area in cross section. In the context of TBCs deposited under different conditions, with the corresponding variation in the balance between the driving forces for crystal

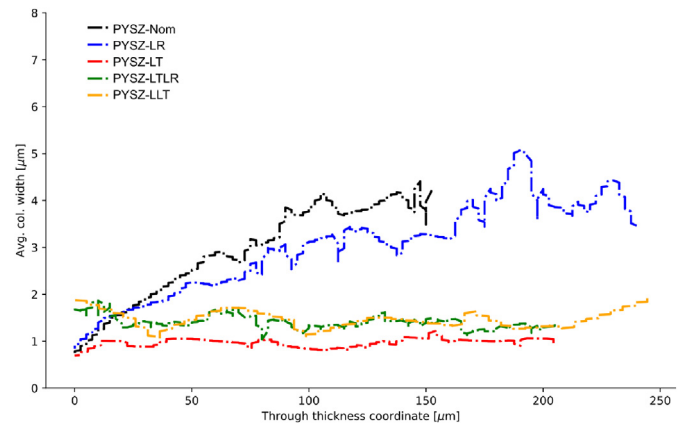


Fig. 11. Corrected column width profiles using CoCo. The profile is corrected based on an interpolation of the upper envelope of the profiles shown in Fig. 10.

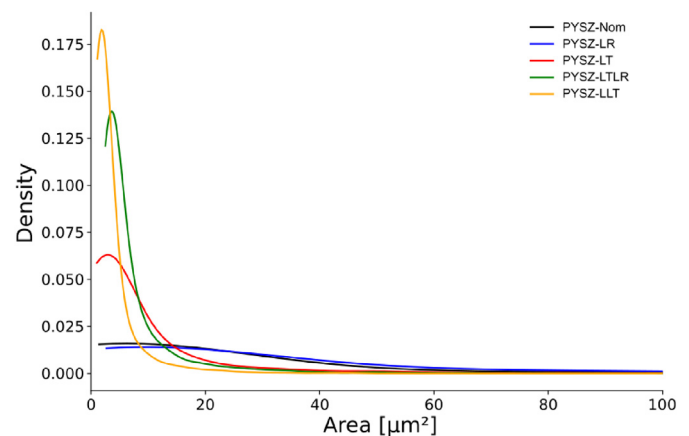


Fig. 12. Kernel Density Estimations for the grain size of PYSZ systems deposited under different deposition conditions.

nucleation and growth, analysing grain size can provide an insight into the behaviour exhibited by the model TBCs with regard to the failure modes induced by testing. The crystallographic grains detected were filtered to delete any spurious grains. A common criterion for computing grain size statistics is that grains to be included should have a minimum area of 100 pixels [50] - corresponding to $2.25 \mu\text{m}^2$ for a typical pixel size of 150 nm. Smaller grains were filtered from the dataset before computing the Kernel Density Estimation (KDE) of the resulting grain size histogram for the produced coatings. This eliminates the spurious grains observed, particularly in the PYSZ-LT system. The grain size KDE can be used to compare the distribution of grain sizes for the deposited coatings. The results obtained for the PYSZ systems are summarized in Fig. 12.

The systems deposited at high temperature – PYSZ-Nom and PYSZ-LR – show an almost identical distribution in grain sizes. Lower deposition temperatures favour nucleation, resulting in smaller grain sizes. Lower rotation speed increases the adatoms deposited on less stable lattice sites [55], which also increases the driving force for recrystallization. The grain size distributions for the coatings deposited at low temperature behave as expected based on these rotation speed and deposition temperature effects, which compound for the LTLR system, curtailing grain growth. This effect is further observed for the PYSZ-LLT systems, which exhibit a grain size distribution on the lower end of the systems analysed. The grain size mode shown by the PYSZ-LT distribution is lower than expected, which can likely be explained by

the oblique sectioning of the coating, which is shown by the absence of grains spanning the coating thickness in Fig. 4(a).

3.4. Coating microstructure morphology and crystallinity

The cause for the periodic porosity observed in the coatings deposited at low rotation speed is the line-of sight nature of EB-PVD, combined with the substrate rotation during deposition. When substrates rotate out of the evaporating ceramic plume, it is expected that a drop in their temperature will occur, concomitant with a reduction in vapour deposition rate. This expectation is based on the directional nature of substantial sources of heat, namely radiative heating from the melt pool, reflected electrons and convective heating from the vapour plume, which provide much less heat when the substrate surface is facing away from them. An observation that supports this hypothesis is the continuous increase in temperature during the deposition of all coatings shown in Table 1, which indicates that the heat provided by these sources is able to increase the temperature beyond the capability of the furnace.

This temperature drop is expected to continue until substrate surfaces are again exposed directly to the vapour flux, reflected electrons and radiation from the melt pool, at which point the deposition rate increases again. This resumption at a lower temperature enables less adatom mobility, causing the grains to grow in a disordered state, resulting in more porosity. When looking at higher magnification cross-sectional micrographs of the coatings deposited at nominal rotation speed (8RPM) - see Fig. 6(c), the same features become apparent, with an increased periodicity, albeit with a lower contrast between the embedded porosity and the solid portion of the growing crystal.

Two factors may explain the deviation that PYSZ-LT displays from the trend in terms of column width and crystalline texture: Firstly, as observed from the EBSD maps, this coating also shows the smaller grains discussed for this system. It should be mentioned that this system was mapped with a smaller than pixel size (70 nm), resulting in relatively small grains ($0.49 \mu\text{m}^2$) when applying the 100 pixel filter, as compared to $\approx 2.3 \mu\text{m}^2$ for the other systems.

Applying a grain size filter to reduce the fine grains detected for this particular system, however, does not significantly increase the texture strength J-index, which is only increased to 3.73. This filtering operation does not, unfortunately, erase the grain boundaries detected by misorientation, leaving the column width detected using CoCo on the EBSD dataset unchanged. It does, however, result in a significantly larger grain size KDE than the unfiltered dataset, as shown in Fig. 12.

The second factor relates to the observed morphology of the columns in the PYSZ-LT system, and how they affect the detected column width. The observable grains in the EBSD dataset used for the CoCo analysis of the PYSZ-LT system, shown in Fig. 7, indicate that the polished cross-section may have been slightly oblique to the TBC columnar grains. This results in apparently 'elliptical' rather than 'columnar' grains, which seem to nucleate at various points through the coating thickness, rather than growing competitively from the bond coat interface all the way to the coating surface.

The J-index does not weigh the grain orientation based on grain size, but is rather based on an unweighted variance of the grain orientation distribution. The addition of the 'extra' grains that appear through the oblique cross section may have had a significant effect on the apparent texture strength. This would be equivalent to probing multiple 'growth planes' for the LT system, as opposed to the other systems subject to study.

For the LLT system, an indexing issue too was observed, with a significant portion of the coating showing "zero solutions", i.e. areas where the crystal orientation could not be resolved. This is likely due to relatively small crystal sizes affecting the EBSD signal intensity and making effective indexing of crystallographic phase and orientation increasingly difficult.

Table 5

Comparison of column measurement results, evaluated at 90% of the coating thickness for the PYSZ model TBCs.

Coating system	Column width [μm] (Manually measured)	Column width [μm] (CoCo)
PYSZ-Nom	7.2 ± 1.0	4.1 ± 0.2
PYSZ-LR	6.3 ± 1.1	4.0 ± 0.4
PYSZ-LT	2.9 ± 1.1	1.0 ± 0.0
PYSZ-LTLR	3.5 ± 0.7	1.3 ± 0.1
PYSZ-LLT	3.0 ± 0.5	1.6 ± 0.1

There is a significant correlation between the column width measured by CoCo as applied to the electron images and the EBSD grain boundary data. The observable differences are most apparent for the LT and LLT systems. Interestingly, the column widths measured using the EBSD data for these systems are smaller than the ones measured in the electron images using CoCo. These thinner than expected results obtained from the EBSD data can be attributed to the different inherent definition of column boundaries in both datasets.

The automated method developed implicitly uses a broad definition of column boundary that is likely to detect intracolumnar as well as intercolumnar porosity as column boundaries when using electron images. The results obtained through crystallographic analysis seem to suggest that this criterion may, in part, be correct, as opposed to the visual identification of "column like" morphologies, which may count groups of distinct crystallographic grains as single columns.

The small crystallites detected by EBSD may have caused a significant underestimation of column width, particularly for systems with a more typical columnar morphology. While the presence of these, seemingly randomly occurring, small crystals, and the detection of their boundaries could indeed be diminishing the apparent column width, we believe that that the overall trend in the column width both between systems and through the coating thickness measured is representative of the grain width evolution.

An inverse relation exists between the number of grains and the average column width. This means that the column width would be relatively insensitive to additional grains in areas with large numbers of grains. This manifests as a relatively stable height of the lower envelope of the resulting profile. Conversely, the sensitivity of column width to changes in the number of grains would increase for lower numbers of spurious grains. However, as the proportion of spurious to actual grains is reduced, the measured width of the column would tend towards the width corresponding only to the actual width. The seemingly continuous shapes of the upper envelope of the signal suggest that a proportionally small number of spurious grains are affecting the measurement.

To probe this hypothesis, 10 grains of each of the PYSZ systems were manually measured using the grains apparent in the IPF maps at approximately 90% of the coating thickness, deliberately ignoring the spurious crystallites. The results of these measurements were compared to the EBSD-derived automated measurement at the equivalent relative thickness, and are presented in Table 5.

It can be noted that column widths determined by CoCo represent typically over half of the manually measured values, with the exceptions of PYSZ-LT and PYSZ-LTLR. For these systems, the automated method using EBSD grain boundary data yields about a third of the manually measured value.

This discrepancy could be explained, as already discussed, by the overestimation of the number of grain boundaries, which results in a reduction in the measured column width, as both are inversely proportional. This overestimation could stem from the aforementioned presence of spurious grains. Alternatively, it could indicate that the automated EBSD-based column width measurement was capturing sub-grain formation within the physical columns, difficult to discern visually from IPF colouring. Assuming that TBC columns could present

three sub-grain textures within a single column, a polished cross section would only reveal two of them. The presence of such sub-grains would manifest as a halving of the measured grain size.

Based on the results obtained for the column width of the coatings deposited under different conditions, a few observations can be made with regard to the Structure Zone Models for EB-PVD coatings.

The column widths determined by CoCo using electron images, combined with the grain size distributions of the resulting coatings obtained by EBSD, partially confirm the analogous effect of deposition temperature and rotation speed on grain nucleation and growth reported in the literature [55]. While the average column width seems to be lowered by the reduced lower substrate rotation speed as shown in Fig. 9, when looking at the spread of column width presented in Table 5 a significant overlap exists between the coating systems deposited at the same temperature with different substrate rotation speeds. Coatings deposited at high temperature exhibit equivalent grain size distributions.

Structure zone models and other computational models that have been developed to predict coating morphology [62–66] do not consider the crystallinity of the coating being deposited. The results obtained in the present study corroborate other crystallographic texture studies performed using XRD [58,67,68]. It is known that the faces of crystalline phases show different surface energies [69]. The preferred crystallographic orientations exhibited by the coatings grown epitaxially depend on the energy barriers presented to the adatoms during deposition, and the thermal energy provided to overcome them. The changes observed in the crystallographic orientation and texture development are the expression of the energy balance for each deposition condition. This is reflected in the microstructure through differences in the shape of the crystalline facets comprising the column tips and sides.

Based on these observations, it is proposed that both the Structure Zone Models and the microstructure prediction models could be expanded on. In the case of the SZM, the effect of micro-texture on the grain morphology could be explored. As for the computational models leveraged in the prediction of coating microstructures, the energetics used in the determination of adatom mobility and subsequent grain nucleation and growth predictions should include the differences in surface energy of the different crystal orientations of the target phases for increased accuracy.

4. Conclusions

A number of conclusions can be drawn from the reported deposition and subsequent characterization of the PYSZ coatings produced in the present study.

The TBC microstructures possible to be deposited via EB-PVD were expanded, relative to the previously reported microstructural morphology range. The diverse microstructures produced broadly conform to those expected based on modified PVD Structure Zone Models.

The CoCo algorithm for automated quantification of column width was demonstrated using both electron image and EBSD data. The results demonstrate the capabilities of CoCo to effectively measure the evolution of column width through the coating thickness, as well as discriminate between different coating systems with markedly different microstructures. The importance of sample preparation, analytical technique chosen and image acquisition parameters in the results obtained by CoCo was shown, discussing the inherent assumptions and limitations offered by each technique.

The results show that the measured quantity of ‘column’ differs between the electron image and EBSD based measurements. For the former, a column consists in a region of contiguous material, as determined by greyscale contrast and its texture, whereas grains determined by EBSD refer to crystalline regions with aligned orientation. Thus, EBSD columns could be reflecting sub-grain formation within the physical columns.

The imaging artifacts and mischaracterization of features (e.g. internal porosity, secondary grains at column edges) have been shown to impact the accuracy of the results obtained via CoCo. Hybrid approaches using image stacks comprising the greyscale images detected by SEM sensors, Forward Scattered Diode images and coloured EBSD maps to undertake semantic segmentation may help overcome these impacts.

A further limitation of this approach has been shown in the 2D nature of the obtained data, which captures a dimensionally reduced representation of the 3D system being studied. 3D data acquisition and treatment with sufficient spatial resolution to capture the features of EB-PVD coatings while capturing sufficiently representative volumes is challenging, but may be worth exploring as a means to validate results obtained from studies of cross sections.

The proposed method, CoCo, while developed to characterize the morphological features of EB-PVD TBCs, can be more broadly applied to columnar TBCs produced by other methods, such as SPS [70] or PS-PVD [71], or other columnar coatings, achieved by other Physical Vapour Deposition via magnetron sputtering [72], HiPIMS [73] or their combination with Cathodic Arc Evaporation [74].

The crystallographic study conducted through combined EBSD and XRD data acquisition has shown that the structure zone model predictions have a parallel in the temperature and rotation speed dependence exhibited by grain size distributions and texture strength. This points to the common underlying mechanisms already captured by the SZM with regard to the balance between nucleation and grain growth. To date, no SZM or computational models include a prediction of the crystallographic texture strength or preferred orientation as a function of deposition parameters. In this context, the results presented point to a significant opportunity to map these quantities for materials exhibiting different space groups. Such an enhanced SZM could potentially help identify deposition conditions for multilayer coating compatibility, where the materials belong to different space groups.

The durability and functional performance of the observed microstructures are being prepared for publication in a separate manuscript. However, based on qualitative assessments reported in the literature, coatings with thinner ‘columns’ are expected to provide an increased resistance against erosive damage and CMAS infiltration.

CRedit authorship contribution statement

Koldo Almandoz Forcén: Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Conceptualization. **Luis Isern:** Writing – review & editing, Investigation. **Alan Johnstone:** Writing – review & editing, Supervision. **Gyaneshwara Brewster:** Writing – review & editing, Supervision. **John Rayment Nicholls:** Writing – review & editing, Supervision. **Christine Chalk:** Writing – review & editing, Supervision.

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Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Koldo Almandoz Forcén reports financial support and equipment, drugs, or supplies were provided by Rolls-Royce Holdings plc. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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