Morphology and thermal conductivity of yttria-stabilized zirconia coatings

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Abstract

An electron beam directed vapor deposition method was used to grow 7 wt.% Y$_2$O$_3$–ZrO$_2$ (7YSZ) coatings and the effects of substrate rotation upon the coating porosity, morphology, texture, and thermal conductivity were explored. As the rotation rate was increased, the texture changed from (111) to (100). Under stationary deposition, the coatings were composed of straight columns, while low-frequency rotation resulted in wavy columns. Increases in rotation rate resulted in a gradual straightening and narrowing of the growth columns. The pore fraction slowly decreased as the rotation rate increased. The thermal conductivity was found to be inversely related to the pore fraction. The structural and thermal conductivity alterations are a result of changes to flux shadowing associated with specimen rotation in a gas jet-entrained vapor plume. The minimum thermal conductivity at a low rotation rate is 0.8 W/(m K), well below that of conventionally deposited coatings.

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1. Introduction

Thermal barrier coating (TBC) systems are widely used to protect the hot, internally cooled components of gas turbine engines by reducing the metal substrate temperatures and increasing their oxidation and corrosion resistance [1,2]. Current TBC systems consist of two layers. Either a platinum-modified nickel aluminide (NiAl + Pt) diffusion coating [3] or an MCrAlY (M refers to one or more of the elements Co, Ni, and Fe) [4] overlayer bond coat is used to provide substrate oxidation/corrosion protection [5]. A ceramic topcoat composed of partially yttria-stabilized zirconia (YSZ) is then applied to provide thermal insulation [1]. This ceramic layer is currently applied either by electron beam physical vapor deposition (EB-PVD) [6–8] or by air plasma spraying (APS) [9]. In order to avoid high-temperature phase transitions, the zirconia is usually stabilized with 6–8 wt.% Y$_2$O$_3$ [1].

Fully dense, large grain size YSZ with 6–8 wt.% Y$_2$O$_3$ stabilization has a reported thermal conductivity in the range 2.2–2.9 W/(m K) [10]. It has a high melting point (approximately 2700 °C) [11], a relatively high coefficient of thermal expansion (11.0 × 10$^{-6}$/K) [12], and is chemically inert in the hydrocarbon combustion atmospheres of gas turbine engines [2]. However, zirconia also has a high oxygen ion conductivity at the use temperature of TBC systems, and this, combined with extensive, interconnected networks of pores, results in rapid oxygen migration through the ceramic layer to the bond coat. This results in the formation of a thermally grown oxide (TGO) layer on the bond coat surface whose growth rate increases strongly with temperature [13]. The TGO plays an important role in TBC performance; failure in EB-PVD TBCs is often initiated at or near the TGO bond coat/YSZ interface [12].

The thermal conductivity of the ceramic layer has been found to depend on the pore morphology within a coating...
In APS coatings, inter-splat pores are roughly aligned parallel to the substrate surface and are accompanied by microcracks and a fine grain size [15]. This pore orientation is highly effective at impeding the flow of the heat through the coating. APS coatings therefore have low effective thermal conductivities of 0.8–1.1 W/(m K) [10]. However, this is achieved at the expense of surface smoothness, in-plane strain tolerance, and erosion resistance [12,15]. These limitations constrain their use to low thermal cyclic environments [12,16]. Modifications to the APS deposition conditions have enabled dense, vertically cracked (DVC) coatings to be deposited [17]. A new, potentially lower-cost solution precursor plasma spray (SPPS) deposition process has also been proposed [18]. It has the potential for creating more durable TBCs with reduced strain compatibility limitations compared to conventional APS TBCs.

EB-PVD coatings consist of collinear elongated single-crystal columns with a predominantly (100) orientation [8,19]. They contain a small volume fraction of intercolumnar pores which are oriented perpendicular to the coating interface [20]. Due to these elongated intercolumnar pores, EB-PVD coatings are more strain tolerant in directions normal to the columns (in-plane directions) and they are more resistant to spallation than APS coatings [15]. A finer distribution of intracolumn pores is also present within the columns [20]. Modeling has shown that these are much more effective at impeding heat flow through the coating as they are generally inclined to the heat flow [20]. Nevertheless, EB-PVD coatings have higher thermal conductivities (approximately 1.5–1.9 W/(m K)) [10,21] than their APS counterparts. A practical challenge confronting current EB-PVD ceramic layer growth is to develop processes that result in a thermal conductivity similar to that of the APS process while retaining the other beneficial coating characteristics.

Both experimental and recent atomistic modeling studies of vapor deposited coatings indicate that the pore morphology can be influenced by process variables which affect the vapor atoms’ incidence angle and the mobility of condensed species on the solid–vapor interface. These variables include the substrates temperature [22,23], the deposition rate [22,24], the background gas pressure [22,25,26], the vapor plume composition [27], and the substrates initial roughness [28]. Experimental studies indicate that highly porous columnar morphologies are associated with low kinetic energy, oblique vapor incidence angles, low substrate temperatures, high deposition rates, rough substrates, and high chamber pressures [22,28–30]. Atomistic models of coating growth support these observations [31,32] and link pore formation to flux shadowing under conditions of restricted adatom mobility on the coating surface.

Access to the conditions that produce optimal pore structures are limited by the design of current EB-PVD systems. Low chamber pressures (<10^-3 Pa) are needed to facilitate electron beam propagation and this results in less collisional vapor transport to the substrate. This in turn leads to a narrow range of flux incidence angles when the vapor impacts a flat, stationary substrate. Flux shadowing is then promoted by substrate rotation, which broadens the effective flux incidence angle distribution leading to increases in porosity [33]. This rotation also has a practical value. It enables the uniform coating of complex shaped components such as the airfoils and guide vanes used in gas turbine engines. Schulz et al. [19] have explored the effects of rotation on the microstructure and texture of conventional EB-PVD coatings. They, and others [8], have found through pole figure analysis that rotation produces a transition from (111) to (100) out-of-plane texture and the development of an in-plane orientation relationship between the growth columns.

There are many ways in which the incidence angle of a condensing flux (and thus a coating’s pore morphology) can be manipulated. Hass et al. [34] inclined a substrate between two fixed angles to produce a symmetrical coating with zigzag-shaped columns over the entire thickness. In this structure, the intercolumnar gaps (primary pores) were orientated obliquely to more effectively impede the heat transport across the coating. A second approach is to use high-pressure environments to broaden the incidence angle distribution of the flux [35]. In directed vapor deposition (DVD) [3,36], the flux is entrained in a supersonic gas jet that is directed towards the substrate. With the jet present, chamber pressures are much higher and the mean free path is greatly reduced so that many vapor phase collisions occur. Multiple scattering events during the transport of vapor towards the substrate, and especially during its passage above the surface, broaden the angular incidence distribution significantly. It can also increase the frequency of three-body collisions and the probability of nucleating vapor-phase clusters, which provide a different mechanism of coating morphology manipulation. Previous preliminary studies have indicated that YSZ layers deposited onto stationary substrates have highly porous, columnar morphologies with hierarchical pore distributions which could be manipulated by the jet flow conditions [34,35]. By combining the DVD approach with substrate tilting, Hass et al. created zigzag structures with through-thickness thermal conductivities as low as 0.8 W/(m K) [34].

Here, this EB-DVD process has been used to deposit YSZ coatings. The study focuses upon the relationship between pore morphology, thermal conductivity, and substrate rotation under high growth pressure conditions. The morphology, texture, and pore volume fraction of YSZ films deposited at different rotation rates are systematically investigated and linked to the thermal conductivity and density of the coatings. We show that coatings with a thermal conductivity as low as 0.8 W/(m K) can be grown under lower rotation rate, high-pressure growth conditions. Interestingly, we find that this conductivity only rises slightly (to ~1 W/(m K)) when much higher rotation rates are used.
2. Experimental

2.1. EB-DVD

The EB-DVD system is schematically illustrated in Fig. 1. It combines high-rate, low-vacuum electron beam evaporation with a rarefied gas jet to entrain vapor and transport it to a substrate. The EB-DVD gun system used here has a maximum power of 10 kW, a beam accelerating voltage of 70 kV to facilitate propagation through a high-pressure deposition chamber, and includes a high-speed electron beam scanning system that enabled up to 100 kHz rastering of a 0.5 mm diameter electron beam over the source surface. Vacuum chamber pressures between 3.3 and 13.3 Pa can be accessed by a multi-pump vacuum system. The evaporation source was positioned in the throat of a water-cooled copper nozzle and a He/O₂ gas jet was formed in the vicinity of the evaporation surface. During operation, the source material was vaporized and gas jet atom collisions with the vapor plume directed the vapor towards the substrate. Using jet conditions that enable all the vapor to be entrained in the gas jet flow facilitates deposition of a large fraction of the evaporated flux on the substrate. This results in high materials utilization efficiency and concomitantly high deposition rates [37].

The gas jet flow speed and density can be controlled by the choice of upstream and downstream pressure ratio and the nozzle dimensions. Hass et al. [36] have shown that DVD can provide non-line-of-sight deposition on non-planar substrates. The degree of non-line-of-sight deposition and thus the coating thickness uniformity depends on the gas jet flow conditions. The coating thickness uniformity dramatically increased as the pressure ratio $P_u/P_o$ (upstream pressure $P_u$ of a nozzle opening and a lower downstream or chamber pressure $P_o$) was decreased. In this paper, a large pressure ratio condition was used, which resulted in a more line-of-sight deposition process similar to that of conventional EB-PVD processes. A detailed description of the method and analyses of it can be found in various references [11,36,38].

2.2. TBC deposition

The EB-DVD approach was used to deposit 7YSZ (zirconia stabilized with 7 wt.% yttria) layers on stationary and rotated substrates as shown in Fig. 1. The disc-shaped substrates were mounted on a holder rotating around a horizontal axis normal to a 1.25 cm diameter source ingot (and vapor plume) axis. The substrates (provided by GE Aircraft Engines) were 2.54 cm in diameter and made from a Hastelloy-X alloy. They were coated with a 200 $\mu$m thick Ni₀.475Co₀.22Cr₀.2Al₀.1Y₀.005 bond coat. Prior to the deposition process, their surfaces were polished. The substrates were then solvent cleaned and pre-heated to 500°C for further surface cleaning, and then heated to the nominal deposition temperature of 1000°C. The substrate temperature was monitored and maintained at 1000 ± 20°C during deposition using a thermocouple placed very close to the substrate.

The 1.25 cm cylindrical source rod had a composition of 93 wt.% ZrO₂–7 wt.% Y₂O₃ and was supplied by TCI Ceramics, Inc. (Hagerstown, MD). A 2.45 kW power electron beam with a 0.5 mm beam spot size and a 100 Hz scan rate was used for evaporation. A scanning pattern was chosen from a programmed pattern library that enabled complete source rod evaporation without ejection of source droplets. The gas jet used in this process was created by maintaining a high upstream pressure $P_u$ (140 Pa) of a nozzle opening and a lower downstream (or chamber) pressure $P_o$ (16 Pa). The pressure ratio, $P_u/P_o$, was set at 8.75. The evaporated flux was entrained in a 10.0 standard liter per minute (slm) helium–1.0 slm oxygen gas flow. The oxygen in the gas flow compensated for oxygen depletion in the ceramic source during evaporation. The evaporated 7YSZ vapor flux was entrained in a rarefied, supersonic jet and directed towards the substrate. A high carrier gas flow condition was chosen to both increase the deposition rate [37] and the pore fraction [11]. The resulting deposition rate was around 4 ± 1 $\mu$m/min during experiments with substrate rotation. It was higher (~10 ± 2 $\mu$m/min) when the substrate was stationary. Similar deposition parameters were used for all the experiments and are shown in Table 1.
2.3. Characterization

The microstructure of fractured coatings was characterized using scanning electron microscopy (SEM). Texture was measured from X-ray diffraction (XRD) patterns recorded with an XDS 2000 powder diffractometer using Cu Kα radiation. The scan angle range \(2\theta\) (\(\theta\) is the angle between incident beam and coating surface) was changed from 10° to 90°. The step size was 0.02° and the scan rate was 1°/min. A more complete texture analysis was conducted using a Scintag X1 Texture instrument. The tilt angle \(\alpha\) was varied from 0° to 90° and the sample was rotated 360° around the center. The step size for both rotation and tilting was 5°. Pole figures were plotted with their east–west axis oriented parallel to the rotation axis. Coating density was measured in the experiment. The factors that affect the measurement accuracy are from the measurement of thickness and weight of coatings. Thermal conductivities were measured at 300 K using a laser-based harmonic heating method [39]. A schematic of the method used here is shown in Fig. 2. The resulting temperature field in the sample was interrogated through its thermal time-dependent emission. The phase of the thermal emission carries information related to the coating’s thermal properties, its thickness and the thermal contrast between the substrate and the coating. A model [39] can be used to relate the phase difference between the laser and the thermal emission and coating properties from which the thermal conductivity can be deduced. The factors that influence the experimental accuracy involved in measurements are temperature and frequency dependence of the measurement system as well as the coating thickness measurement. The uncertainties in thermal conductivity associated with this approach were estimated to be less than 10%.

3. Results

3.1. Coating morphology

The surface morphologies of coatings deposited at rotation rates of 0, 0.5, 1.0, 12, 20, and 30 rpm are shown in Fig. 3. There is a distinct difference between the surface topologies of the stationary and the rotated samples. Under stationary deposition, the coating surface is dominated by triangular (three-sided) columns whose tips consist of three triangular facets. This surface morphology is similar to that reported for coatings made by conventional EB-PVD techniques without rotation [8]. The rotated sample surfaces are covered by four-sided square columns that are terminated by four facets (Fig. 3b–f). The sides of these pyramids are consistent with \{111\} facets bounding the tips of \{100\} oriented growth columns, which would be consistent with EB-PVD observations of coatings grown at 1000 °C with rotation [8,19]. Increases of the rotation rate reduced the column diameter. However, this trend eventually reversed and the highest rotation rates resulted in coarser columns consisting of several smaller columns each capped by small pyramids with square facets. The growth columns appeared most closely packed together in the sample deposited under stationary conditions.

Fig. 4 shows cross-sectional views of coating fracture surfaces. The growth direction was vertically upwards in each figure. The cross-sectional morphology of the coatings was very sensitive to the rotation rate. Fig. 4a shows the structure of a coating deposited onto a stationary substrate whose surface was perpendicular to the vapor plume axis. The growth columns are about 1.5 μm in width, do not change in width with coating depth, and exhibit little inter-column porosity. At low rotation rates of 0.5 and 1 rpm (Figs. 4b and c), the prominent feature is the wavy

![Fig. 2. Experimental set-up for the measurement of the thermal conductivity.](image-url)
columnar structure (C-shape), which is caused by changes of the flux incident angle to the substrate. Each wave corresponds to one cycle of substrate rotation. Altering the rotation rate affects both the wavelength and amplitude of the wavy structure. The wavelength of the coating is about 10 μm per cycle at 0.5 rpm and 2.75 μm per cycle at 1 rpm. The amplitudes are 2.5 μm and 0.5 μm, respectively. At higher rotation rates of 12, 20, and 30 rpm, the wavy structure disappeared and relatively straight column grains were formed in the coating.

The column diameters measured from Fig. 4a–f are 1.5, 7, 4, 0.5, 0.7, and 0.85 μm for 0, 0.5, 1.0, 12, 20, and 30 rpm samples, respectively. The width of the primary growth columns did not vary significantly through the coating thickness. The column growth direction in all cases was parallel to the substrate surface normal. Three types of pores were present in all samples. Type I pores (the gaps between the primary growth columns [20,34]) can be observed in the micrographs shown in Fig. 4. These extend from the bond coat/ceramic interface to the top of the ceramic layer. Those in the slowly rotated samples were not straight, forming a C-shape pattern. Fig. 5a–f shows a much finer, Type II pore morphology present within the growth columns. These Type II pores were long narrow pores that separated smaller diameter, secondary growth columns within the primary columns [20,34]. They were oriented in the direction of the primary column growth. However, unlike the Type I pores, they did not extend through the coating.
majority of the coating thickness. Coatings grown with rotation have columns with a more “feathery” structure than those grown under stationary conditions. Type III, spheroidal nanopores were present within the secondary growth columns of the stationary and slowly rotated coatings (Fig. 5). These became much longer and were aligned almost transversely to the secondary column growth direction in the most rapidly rotated coatings (Fig. 5f).

The micrographs suggest that the rotated samples have a lower density than the stationary sample. The measured density results support this (see Table 1). The stationary sample had the highest density 4.5 g/cm³, but this is significantly below the theoretical value of 6.0 g/cm³ for fully dense 7YSZ [40]. The lowest rotation rate sample had a density of 3.38 g/cm³. The pore volume fraction therefore increased from 26% in the stationary condition to 44% for that rotated at 0.5 rpm. As the rotation rate was increased, the average dwell time for one rotation cycle decreased and this was correlated with an increase of coating density. As shown in Table 1, samples rotated at 1.0, 12, 20, and
30 rpm had densities of 3.49, 3.58, 3.86, and 4.10 g/cm³, respectively. These pore fraction trends are in quantitative agreement with kinetic Monte Carlo simulations of deposition onto periodically inclined substrates [41].

3.2. Texture analysis

XRD patterns for coatings deposited at the different rotation rates are shown in Fig. 6. The diffraction pattern for the stationary substrate coating has very strong \{111\} type peaks. No \{200\} peaks were evident in the X-ray pattern of this sample. That implies that the coating was constructed from growth columns whose \{111\} planes were coplanar with the substrate surface. The growth columns therefore grew in the \langle111\rangle direction. The observation of three triangular planes terminating the growth columns is consistent with the columns being capped by three \{100\} type facets.

As the rotation rate was increased, new peaks appeared in the diffraction pattern and the relative intensity of these new peaks rapidly increased. For the lowest rotation rate (0.5 rpm) sample, the crystallographic features of the
stationary sample were still evident in the diffraction pattern (Fig. 6b). However, at higher rotation rates (Fig. 6c–f) {100} type peaks began to dominate the diffraction pattern and all other peaks gradually disappeared. The growth columns of the rapidly rotated coatings therefore had a large fraction of {100} type planes aligned parallel to the substrate surface. This is consistent with a {100} type column growth direction and the observation of four triangular facets capping the growth columns is consistent with these here being close-packed {111} type planes. Highly
textured coatings are therefore created using the EB-DVD technique and either \( \langle 111 \rangle \) or \( \langle 100 \rangle \) texture can be selected by choice of the rotation rate at substrate temperature of 1000 °C.

Pole figure analyses were also performed on the samples to determine in-plane orientation relationships between the growth columns. Fig. 7a shows a strong \( \{111\} \) peak located at the center of the pole figure, confirming a preferred \( \langle 111 \rangle \) through thickness column orientation. The off-axis reflections of the \( \{220\} \) pole figure Fig. 7a, shows a ring pattern of high intensity distributed around the center of the figure. This indicates that no preferred in-plane orientation of the columns developed under stationary deposition. Pole figures for the 0.5 rpm sample are shown in Fig. 7b. A region with strong \( \{200\} \) plane intensity was again located near the center of the pole figure indicating that the majority of the surface planes are parallel to the \( \langle 100 \rangle \) plane. A distorted ring pattern was evident in the \( \{220\} \) pole figure, again indicating no preferred in-plane orientation. However, as the rotation rate was further increased, Fig. 7c–f, a high intensity \( \{100\} \) peak was evident at the center of the \( \{200\} \) pole figure and the off-axis \( \{220\} \) pole figures show a four-fold symmetry structure around the \( \langle 100 \rangle \) direction. These observations are

Fig. 7. Pole figures of the samples at different rotation rates.
indicative of both a well-developed in-plane texture as well as through thickness crystallographic alignment of the growth columns.

3.3. Thermal conductivity

The effect of rotation rate upon the thermal conductivity of the coatings is shown in Fig. 8a. The stationary sample had the highest thermal conductivity of 1.55 W/(m K). This is at the low end of the range reported for conventional EB-PVD samples (1.5–1.9 W/(m K)). Both growth approaches result in coatings with a much lower thermal conductivity than fully dense 7YSZ (2.2–2.9 W/(m K)). The slowly rotated samples had a much lower thermal conductivity than their stationary counterparts (0.8 versus 1.55 W/(m K)). This very low thermal conductivity is identical to that reported for zigzag structures grown using EB-DVD techniques [34]. As the rotation rates were increased from 0.5 to 30 rpm, the measured thermal conductivities slowly increased from 0.8 to 1.06 W/(m K). This trend in thermal conductivity was similar to the variation in coating density (Fig. 8b). Fig. 9 shows the thermal conductivity as a function of the pore fraction. The largest pore fraction coating corresponded with the lowest thermal conductivity. We note that EB-PVD coatings usually have lower pore volume fractions than those reported here [42], and this additional porosity presumably accounts in part for their higher thermal conductivity.

4. Discussion

DVD processes create a flux with a broader angle of incidence distribution (under stationary substrate conditions) than that associated with EB-PVD deposition [36]. This has been shown both experimentally [11] and by kinetic Monte Carlo modeling [41] to enhance the significance of shadowing resulting in coatings with higher pore fractions. When heat is propagated through coatings at low temperatures, only phonon conduction contributes to the heat transport. Phonons are strongly scattered at pore surfaces and conduction across ellipsoidal pores with high aspect ratios introduces a high thermal resistance. The thermal conductivity is therefore strongly dependent on the volume fraction, shape, and orientation of pores [44,45]. Models of the thermal transport in porous 7YSZ coating [20,43] have shown that this lowers the thermal conductivity of EB-DVD coatings below that of their EB-PVD counterparts. Substrate rotation at low rotation rates further increases the pore fraction. It also results in wavy columns that are in some respects analogous to the zigzag structures created by alternating the inclination of a substrate [34]. The high porosity level and its favorable orientation for inhibiting heat flow results in slowly rotated coatings having thermal conductivities in the 0.8 W/(m K) range, which is comparable to that of zigzag EB-DVD and APS coatings.

Fig. 8. Effect of rotation rate on (a) the thermal conductivity and (b) the density both measured at 300 K.

Fig. 9. Thermal conductivity as a function of pore fraction at 300 K.
At low rotation rates, Type I pores are elongated and bent perpendicular to the growth direction making them longer than those in the stationary sample. The width of the pores is also greater. In the slowly rotated samples with wavy columns, the conduction distance is increased contributing to a significant impediment to the heat flow. A recent analytical study of heat conduction across the zigzag structures [20] indicated that inclined Type I pores were highly effective at disrupting through-thickness thermal transport. These models suggest that the low thermal conductivity of the C-shaped microstructures is dominated by continuous Type I and II pores even though their pore fraction is low; Type III pores, due to their random orientations in slowly rotated samples may introduce a relatively smaller effect upon the overall conductivity.

Increasing the rate of rotation significantly reduces the total pore fraction (Fig. 8b), but the thermal conductivity is restored much more slowly (Fig. 8a). Fig. 9 links the thermal conductivity to the pore volume fraction and indicates that in the 30–40% pore fraction range, the thermal conductivity is a weak function of pore fraction. The rapidly rotated EB-DVD coatings explored here therefore retain a much low thermal conductivity than their EB-PVD counterparts. The weak dependence of thermal conductivity upon rotation rate in the 5–30 rpm range appears to be the result of a change in the Type III pore morphology with increase in rotation rate.

At higher rotation rate, the Type I and II pores are vertically aligned and were not greatly affected by the substrate rotation. We therefore expect the contribution of these pores to the change in thermal resistance to be small. The retention of a low thermal conductivity in the more rapidly rotated samples must therefore be linked to a change in the morphology of Type III pores that makes them more effectively at impeding thermal transport. By comparing Fig. 5a and c, it can be seen that as the rotation rate increased, the Type III pores became aligned transverse to the growth columns in an orientation that would be highly effective at disrupting the flow of heat along the primary growth columns.

The significant changes in pore morphology that accompanied an increase in rotation rate were also correlated with a change in column growth direction from (111) to (001). Similar texture changes have been reported for EB-PVD coatings [8]. Schultz et al. [19] have developed a competitive facet growth (STL) model to account for these EB-PVD observations. Briefly, in the evolutionary selection process, during deposition of a thick film, for which growth is characterized by evolutionary selection, the structure will be dominated by grains through the thickness of the film having nearly the same “fast growth” axis, resulting in a strong fiber texture to the film.

Stationary samples have the (111) preferred growth direction with growth columns capped by pyramidal type tips (Fig. 10a). Under constrained surface diffusion conditions, stable columnar growth requires that each of the facets of a column tip receive equal amounts of vapor flux. This condition is referred to as the “equal flux” requirement in the STL model [19,46]. Unfavorable columnar morphologies which do not satisfy the equal flux condition will be screened out by evolutionary selection. Experiments [46] indicate that stationary samples with oblique vapor incidence angle (45°) have a (two-sided) rooftop column tip morphology formed by the intersection of two {111} facets. The resulting column axis is then (110) direction. When such a rooftop ridge is parallel to the vapor incidence plane, each {111} facet can receive equal vapor fluxes and growth of such a structure satisfies the “equal flux” condition. Coatings grown with substrate rotation have a {100} column axis orientation with the columns capped by four {111} planes. This is consistent with the STL model, since opposing pairs of facets sequentially receive equal fluxes as the growth column axis rotates from −90° to 0° and then 0° to 90° (Fig. 11). Each period can be likened to an equivalent oblique incidence flux. The two half periods of vapor incidence angle result in equal vapor flux for the period of exposure to a different pair of rooftop column tips bounded by {111} facets with their bisectors then in a (110) direction. Square-pyramidal facet tip columns are formed with a column axis in a (100) direction (Fig. 10b).

During the growth of these columns, the formation of porosity results from flux shadowing and the Type III pore morphology reflects a complicated interplay between the actual flux that intercepts the local growth surface and the fast growth directions of the columns. Substrate rotation broadens the vapor incidence angle distribution and thus promotes the shadowing. The broader flux distribution of the EB-DVD process appears to further enhance this shadowing. The EB-DVD rotated substrate samples therefore have a high volume fraction of “feather-like” Type III pores that can be seen at the edge of columns. They are also orientated in a plane that is highly effective at disrupting thermal conduction along the column axis.

![Fig. 10. Column tip orientation during the column growth.](image-url)
5. Conclusions

An EB-DVD approach has been used to grow 7YSZ coatings and the effects of substrate rotation upon the coating density, pore morphology, and texture of the coatings were investigated and related to changes of thermal conductivity. We find that:

1. During stationary deposition, straight-sided growth columns are formed with triangular column faceted tips. Rotated samples have growth columns with square pyramidal faceted tips. This difference is accompanied by a change in preferred crystallographic growth direction from $\{111\}$ to $\{100\}$ as the substrate rotation rate increases.

2. At low rotation rates, wavy columnar structure forms due to the slow rate of change of the incidence angle of the vapor flux to the substrate. The increased conduction distance along the wavy columns combined with a high pore volume fraction results in a very low thermal conductivity of $0.8 \text{ W/(m K)}$ which is well below that of conventionally EB-PVD deposited coatings.

3. At high rotation rates, the wavy columns disappear and relatively straight-sided columns are formed in the coating. These coatings have thermal conductivities in the region of $1 \text{ W/(m K)}$ which is $50\%$ less than that reported for EB-PVD coatings grown under otherwise similar conditions. The low thermal conductivity of the rotated EB-DVD coatings appears to be a result of an increased volume fraction of Type III nanopores in the primary and secondary growth columns orientated transversely to the heat flow direction.

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