Vapor deposited samarium zirconate thermal barrier coatings

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A B S T R A C T
The rare earth zirconates (M2Zr2O7, M = La→Gd) have a low intrinsic thermal conductivity and high temperature phase stability making them attractive candidates for thermal barrier coating applications. An electron-beam evaporation, directed-vapor deposition (EB-DVD) technique has been used to investigate the synthesis of Sm2Zr2O7 (SZO) coatings and to explore the relationships between the deposition conditions and the coating composition, structure, texture, pore morphology, and thermal conductivity. The coatings exhibited significant fluctuations in composition because of differences in the vapor pressures of the constituent oxides and had a metastable fluorite structure because kinetic limitations hindered the cation ordering needed to form the equilibrium pyrochlore structure. The growth morphology of the EB-DVD SZO was similar to that of EB-DVD 7YSZ and EB-PVD Gd2Zr2O7. The SZO coatings had as-deposited conductivities of 0.5 ± 0.1 W m−1 K−1, about one-half of their DVD 7YSZ counterparts. The majority of the conductivity difference appears to be associated with the lower intrinsic conductivity of this zirconate.

1. Introduction

Thermal barrier coating (TBC) systems have become an enabling materials technology for the gas turbine engines used for propulsion and power generation [1]. Through their ability to provide thermal and environmental protection, TBCs enhance superalloy component durability and/or allow an increased operating temperature with concomitant benefits for engine performance and efficiency [2]. Today’s state-of-the-art TBC systems comprise; (i) a thick (100–300 μm) thermal barrier layer typically based on 7 wt.% yttria stabilized zirconia (7YSZ), (ii) a much thinner (<10 μm) environmental barrier layer of thermally grown aluminum oxide (TGO) that protects the superalloy substrate against oxidation, and (iii) a relatively thick (50–100 μm) metallic “bond coat” layer with a chemical composition formulated to result in growth of a stable TGO over the life of the system [3,4]. A key characteristic of the thermal barrier layer is the presence of substantial porosity of various morphologies and length scales. The primary role of these pores is to increase the in-plane compliance of the thicker oxide and enhance its tolerance to strains arising from its thermal expansion mismatch with the substrate during the thermal cycling typical of engine operation [5,6]. It also results in a reduction in the thermal conductivity of the TBC, especially if thin lamellar pores are present and oriented to impede heat flow [7].

7YSZ has been used effectively in TBCs for over two decades [8] owing to its combination of low intrinsic thermal conductivity (~2.1 W m−1 K−1 at 1000 ≤ T ≤ 1200 °C [9]), its thermochemical compatibility with the underlying TGO [10,11], and its durability to thermal cycling [12]. However, its viability has become increasingly challenged as the demand for higher gas path temperatures has continued to increase. The primary concerns arise from; (i) accelerated sintering kinetics that degrade the compliance and insulating efficiency of the coating [13–16], (ii) de-stabilization of the desirable non-transformable r’ phase [10,17–20] that is responsible for the intrinsic toughness of 7YSZ [21,22], and (iii) its propensity for penetration by molten deposits of calcium–magnesium–alumino-silicates (CMAS) that degrade the strain tolerance of the coating and accelerate its destabilization [23–25]. These concerns, coupled with the potential design benefits of further reductions of the thermal conductivity relative to 7YSZ [26–28], have motivated a search for alternate thermal barrier oxides [2,10,29–33].

Among the numerous oxides that have been explored as alternate thermal barrier materials, the rare earth zirconates (REZ’s) M2Zr2O7 (M = La→Gd), with the pyrochlore structure, have attracted particular interest because of their generally lower thermal conductivity (~1.2–1.5 W m−1 K−1 at 1000 ≤ T ≤ 1200 °C) [27,34–39]. In addition, these materials are phase-stable at all temperatures relevant for gas turbine operation (T ≤ 1500 °C), Fig. 1 [40]. They also exhibit higher resistance to morphological evolution of the pore structure (sintering) than 7YSZ [39,41,42] and, notably show potential for inhibiting CMAS penetration by inducing crystallization of the silicate melt [43]. However, the REZ’s suffer two fundamental disadvantages relative to 7YSZ. First, they exhibit a thermochemical incompatibility with alumina [10,44], tending to form aluminate interphases by diffusional interactions with the TGO [45,46]. Second, as with other cubic ZrO2-based phases, they exhibit substantially lower toughness than the tetragonal phase of 7YSZ [3,21,47,48]. This has deleterious consequences for both their erosion resistance and the failure mechanisms that involve crack propagation through the TBC [3,5].
To alleviate some of these problems, zirconate TBCs are typically deposited on a tougher, TGO-compatible 7YSZ underlayer \[10,27,45,49\], although that does not address the erosion issue.

Full exploitation of REZ’s as thermal barrier oxides requires not only strategies to circumvent their limitations relative to 7YSZ, but also the development of suitable processing approaches. In general, the deposition of rare earth zirconate coatings is more challenging than 7YSZ. The atmospheric plasma spray (APS) process must confront the higher melting temperatures of the stoichiometric phases while the electron-beam physical vapor deposition (EB-PVD) approach must overcome the sometimes significant differences in vapor pressure of the constituent oxides \[50\] which hinders achievement of the desired composition during evaporation \[51\]. Experience suggests that Gd$_2$Zr$_2$O$_7$ (GZO) is more amenable to EB-PVD than La$_2$Zr$_2$O$_7$ (LZO) and is consistent with the relative magnitudes of their vapor pressures \[50\]. Samarium zirconate, Sm$_2$Zr$_2$O$_7$ (SZO), is reported to be suitable for vapor deposition \[42\] but its behavior during vapor phase processing has not been well documented. Moreover, the high cost of the rare-earth oxides and their high content in zirconate TBCs exacerbates concerns about the low deposition efficiency (a few percent) of conventional EB-PVD.

Gas-jet based evaporation techniques such as electron-beam directed-vapor deposition (EB-DVD) offer high material deposition efficiency \[52\] and their multi-source capability facilitates the deposition of the preferred multilayer (e.g. REZ/7YSZ) \[10,27,45,49\] and/or the option of co-evaporation and deposition of the constituent oxides if challenges posed by their vapor pressure differences are insurmountable. This investigation is motivated by the need to develop a processing science for the deposition of REZ TBCs using a DVD approach. The specific emphasis is on samarium zirconate. The viability of depositing uniform compositions is assessed and the influence of substrate rotation rate and deposition temperature on the coating’s density, pore morphology, texture and microstructure, and their related impacts on coating thermal conductivity are investigated. The observations are compared with those reported recently for identically grown 7YSZ coatings \[53\].

2. Experimental methods

2.1. Samarium zirconate deposition

Samarium zirconate coatings were deposited on both stationary and rotated substrates using an EB-DVD technique \[52\] with the configuration illustrated in Fig. 2. The deposition conditions were nominally identical to those used for 7YSZ which are described elsewhere \[53\]. The coatings were applied to 25.4 mm diameter Hastelloy-X substrates (provided by GE Aviation, Evendale, OH) oriented as shown in Fig. 2. Prior to deposition the substrates were EB-PVD coated with a 100–200 μm thick Ni–22Co–20Cr–10Al–0.5Y (in wt.%) alloy, and subsequently hand polished using 1200 grit paper and then 1 μm diamond finish. The evaporation source was a 12.5 mm diameter SZO rod (TCI Ceramics Inc., MD), positioned in the throat of a water-cooled copper nozzle with a coaxial He/O$_2$ gas jet at its periphery, as illustrated in Fig. 2. The chemical composition of the rod measured by energy-dispersive X-ray spectroscopy (EDS) was 48ZrO$_2$–52SmO$_{1.5}$ (in mol%). The electron-beam accelerating voltage was 70 kV and the incident beam power was 2.45 kW. The substrate temperature was monitored and maintained at a prescribed level during deposition using a thermocouple placed very close to the substrate. We note that there is a difference between the actual temperature of the deposition surface and that measured by the thermocouple, but for the purposes of this comparative analysis they are assumed to be the same. A systematic investigation of the effect of the putative substrate temperature (900–1100 °C) and rotation rate (0–20 rpm) upon the coating morphology, density and thermal conductivity was then conducted. The deposition rate was 10±2 μm/ min for the samples deposited without rotation and approximately 3–4 μm/min for all others.

2.2. Sample characterization

The microstructure of the coatings was characterized by scanning electron microscopy (SEM) of the growth surfaces as well as through-thickness polished cross-sections and fracture surfaces. The chemical content in zirconate TBCs exacerbates concerns about the low deposition efficiency [52].
composition in this paper is given in a stoichiometric compound. The orientation and phase constitution of the coatings were determined by X-ray diffraction (XRD) using a XDS 2000 powder diffractometer (Scintag Inc., USA), CuKα radiation, a scan angle range $10^\circ \leq 2\theta \leq 90^\circ$, and a step size of 0.02°. Lattice parameters were determined from refined cell dimensions using a software package based on Cohen’s method of least squares [54]. A full texture analysis was conducted using an X1 Texture instrument (Scintag Inc., USA) by varying the tilt angle $\alpha$ from 0 to 90° and rotating the sample over a range $0^\circ \leq \psi \leq 360^\circ$ about the substrate normal. The step sizes for both rotation and tilting were 5°. The thermal conductivities of the coatings were measured at room temperature by the phase-of-thermal-emission spectroscopy method [55], as described in the earlier study on 7YSZ [53].

### 3. Results

Typical microstructures of the EB-DVD SZO coatings are illustrated in Fig. 3. Measured thicknesses ranged from ~65 to 110 $\mu$m. The average bulk composition was Sm$_{2.1}$Zr$_{1.9}$O$_7$: slightly off stoichiometry but relatively consistent with that measured for the source rod. In contrast, the backscattered electron images in Fig. 3 reveal fluctuations from the average Sm$_{1.5}$ content within each coating. The amplitude of these fluctuations varied from sample to sample. The lowest variation of $\pm 5\%$ was found for a non-rotated specimen, Fig. 3 (a), but some of the rotated coatings had higher variations (up to $\pm 12\%$ for the specimen rotated at 20 rpm), Fig. 3 (b). There was no apparent correlation between the deposition conditions and the extent of compositional heterogeneity. Rather, it appears that the significant vapor pressure difference of the constituent species has created melt instabilities leading to unsteady evaporation of the two species. As with 7YSZ, the texture and morphology of the SZO coatings grown by DVD were highly sensitive to the growth conditions. The salient observations are described below.

#### 3.1. Deposition temperature effects

The morphology of the SZO coatings was strongly affected by the substrate temperature during deposition. Fig. 4 shows surface and through-thickness fracture surface images of coatings deposited at 900°, 1000° and 1100° C using a fixed substrate rotation rate of 6 rpm. All three coatings were composed of relatively tightly packed growth columns with faceted tips. At the higher temperatures, Fig. 4 (c), the tips had a well-defined 4-sided pyramidal shape typical of flouite derivative structures and were similar to those seen in 7YSZ [56,57] and other zirconates [51]. The growth columns had a strong (200) preferred orientation. As the deposition temperature decreased, secondary crystals started to appear on the growth surface, e.g. Fig. 4 (b), and these became sufficiently numerous at 900 °C to make the shape of the tips appear rough and indistinct, Fig. 4 (a).

Examination of the through-thickness fracture surfaces, Fig. 4 (d–f), reveals a fairly typical columnar structure for coatings grown at the higher temperatures. These are again reminiscent of those seen in EB-PVD coatings [58]. The structure formed at 1100 °C, Fig. 4 (f), appears more regular than one might infer from the top view, Fig. 4 (c), with columns separated by distinct intercolumnar gaps and well-developed feathery pores within the columns. These have been designated in earlier papers as Type I and II porosity respectively [53,59]. As the temperature decreases to 1000 °C the fracture surface reveals incipient branch growing off the column sides, Fig. 4 (e), but the main columns are still clearly identifiable. Further reduction in deposition temperature to 900 °C, however, leads to highly branched columns with an apparent loss of the feathery morphology. The distinction between intra- and intercolumnar pores on the fracture surface also becomes blurred, as seen by comparing Fig. 4 (d) and (f). One might envisage the structure in Fig. 4 (d) as containing two main columns each consisting of multiple sub-columns oriented on average along the vertical axis. Examination of polished cross-sections corresponding to this sample revealed that the scale of the branching increased with distance from the substrate (Fig. 5). Even so, some of the coarser “branches” under the surface still exhibited the fine feathery pore structure associated with a high through-thickness thermal resistance.

XRD patterns of coatings deposited at the different substrate temperatures (all at 6 rpm) are shown in Fig. 6. All of the peak positions are consistent with the flouite (disordered) form of Sm$_2$Zr$_2$O$_7$ [60] with a lattice parameter 0.5285 nm. When doubled to account for the ordering in the pyrochlore structure, this is slightly lower than the reported value of 1.0594 nm for samarium zirconate [60]. The peak intensities reveal a predominant (200) out of plane texture at all temperatures, with minor amounts of secondary orientations present at the higher temperatures (most notably (111)). The consistency of the (200) texture across the temperature range is rather remarkable in the context of the substantial changes in the columnar structure in Fig. 4. Pole figures (not shown) also suggested preferred in-plane orientations but these are less distinct than those reported for conventional EB-PVD 7YSZ [56,58] and gadolinium zirconate [48].

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1 Crystallographic notation referred to the flouite structure. The equivalent pyrochlore planes have doubled indices, i.e. (200)$_p$ = (400)$_p$. 

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Fig. 3. Back scattered electron images of typical SZO coating microstructures deposited at 1000 °C with superposed composition profiles determined by EDS. The banding is a manifestation of variation in the samarium content through the thickness. (a) Coating deposited without rotation, exhibiting a samarium fluctuation of $<\pm 5$ at.%. (b) A coating deposited at a high rotation rate where the fluctuation was up to $\pm 12$ at.%.
The density ($\rho$) and through-thickness thermal conductivity ($k$) of the SZO coatings were measured as a function of the deposition temperature and are compared on a normalized basis with data for similarly grown 7YSZ coatings in Fig. 7. The conductivities ($k_0$) of the theoretically fully dense ($\rho_0$) 7YSZ and SZO at ambient temperature are taken as 3 and 2 W m$^{-1}$ K$^{-1}$ based on [38]. Both normalized properties for SZO are lower than for 7YSZ, by ~5% for $\rho/\rho_0$ and ~8% by $k/k_0$. The porosity content of the zirconate is therefore slightly higher and slightly more effective at hindering heat transport in the through-thickness direction. One should note, however, that these differences are close to the typical scatter of the measurement techniques utilized [55]. Both properties increase with coating deposition temperature, reflecting a concomitant decrease in porosity. However, the relative conductivity for SZO rises comparatively faster than its relative density with increasing deposition temperature. Relative conductivities after aging (Fig. 7b) are also lower for the zirconate, and it is notable that the values for the higher temperature are now distinctly separated, whereas those for the lower temperature are closer together.

3.2 Rotation rate effects

Examples of the morphology of columnar coatings grown at 1000 °C on stationary substrates as well as those corresponding to the slowest (0.5 rpm) and highest (20 rpm) rotation rates are shown in Fig. 8. (Those for 6 rpm were shown in Fig. 4b and e). Polished cross-sections are chosen for Fig. 8(d–f) instead of fracture surfaces (cf. Fig. 4(d–f)) because the latter were less informative, especially for the lowest rotation rate.
When the coatings were grown on stationary substrates under nominally normal incidence, as in Fig. 8(a), the growth surface was composed of column tips bound by triangular facets and was much more planar than those observed in YSZ grown under the same conditions [53], or on the samarium zirconate coatings grown with rotation, Fig. 8(b) and (c), which exhibited square-based pyramidal column tips bound by curved triangular faces. Some pyramidal tips are also evident in Fig. 8(a), but the majority of the triangular facets were oriented closer to the plane of the substrate. It is also noted that these facets show ledge-like features predominantly parallel to one of the sides.

The cross-sectional views in Fig. 8 show that the coating grown without rotation comprises closely packed columns with much narrower intercolumnar gaps than those grown with rotation. Interestingly, the columns in Fig. 8(d) still show "feathery" branches that are more similar to those found in rotated EB-PVD coatings than to those grown with stationary substrates [56]. Slow rotation at 0.5 rpm resulted in pronounced C-shaped columnar structures with a wavelength of ~10.8 μm and similarly shaped intercolumnar gaps, Fig. 8(e). The wavelength is consistent with the rate of deposition and the period of a single revolution of the substrate. The columns are clearly defined and very thin near the substrate, but they become less distinct as they grow. This is a result of the concomitant widening and segmentation of the column tips, evident in Fig. 8(e), apparently occurring as the vapor flux orientation transitions from the "sunset" to "sunrise" part of the next rotation cycle [58]. With increasing rotation rate the C-shaped features become smaller and rapidly lose their identity as the growth front moves away from the substrate. The columns then adopt the more typical structure, as shown for the 20 rpm case in Figs. 3(b) and 8(f). The intercolumnar gaps are aligned close to the substrate normal, with typical feathery pores within each column.

XRD patterns in Fig. 9 are again indexable to the (disordered) fluorite form of the zirconate, regardless of the rotation rate. However, the relative intensity of the diffraction peaks changed with rotation rate, indicative of a change in the out-of-plane texture. Coatings grown on stationary substrates exhibit a dominant (111) peak, consistent with prior observations on similarly grown 7YSZ coatings [53] but with significant amounts of (220) and (311) reflections, which were not present in the latter. The implication is that the texture is mixed, as suggested by the top views of the growth surface in Fig. 8(a). The (200) reflections are much smaller in this case, but grow in intensity relative to (111) as the rotation rate increases, while the (220) and (311) peaks rapidly disappear. This was accompanied by a change in surface morphology from triangular facets in Fig. 8(a) to the pyramidal column tips characteristic of (200) growth in 7YSZ under similar conditions [53].

The relative density and normalized thermal conductivity for the SZO coatings are shown as a function of the rotation rate in Fig. 10, and compared with similar data for 7YSZ [53]. Both materials exhibit similar trends with rotation rate in the as-deposited condition, with the individual property values being consistently lower for the
4. Discussion

Salient findings from this study include: (i) confirmation that SZO can be deposited by DVD with microstructures suitable for thermal barrier coating applications albeit with some composition variability that requires further study; (ii) SZO is deposited with a metastable fluorite structure instead of the stable pyrochlore form; (iii) there exists overall similarity in crystallographic texture with 7YSZ grown under comparable conditions but the pore morphology appears to be more sensitive to deposition temperature in SZO; and (iv) there are differences in porosity content and its evolution during high temperature aging that impact the thermal conductivity. These findings are further discussed below.

4.1. Coating composition

In principle, the composition of a multi-component vapor should be different from that of the melt from which it emanates, as dictated by the vapor pressures of the pure components and their activities in the melt. In the case of oxides, there are additional concerns about dissociation reactions, e.g. the vapor of a $\text{ZrO}_2$–$\text{MO}_{1.5}$ ($\text{M= Y or rare earth}$) alloy may contain $\text{Zr, ZrO, ZrO}_2, \text{M, MO, O and O}_2$ [61]. It is also known that one may establish a steady state evaporation condition wherein a solid is continuously fed into its melt and the vapor forming from the melt has the same composition as the solid, albeit not that of the melt. This is claimed to be feasible as long as the vapor pressures of the components are not too dissimilar (reported by no more than two orders of magnitude) [62].

Information on the vapor pressures of the relevant species over $\text{ZrO}_2$–$\text{MO}_x$ melts is generally not available in the literature, although estimates could be made based on data for the corresponding solids. (The slope should change moderately at the melting point but the curve should be essentially continuous.) The available (calculated) data for the relevant solids is summarized in Fig. 11, plotted as ratios to the total vapor pressure of the two dominant $\text{Zr}$-bearing species, i.e. $\frac{p_{\text{MO}}}{p(\text{ZrO} + \text{ZrO}_2)}$. It is reported that for all the other oxides in this figure the dominant species is the sub-oxide $\text{MO}$ [61]. Also plotted are the vapor pressures of $\text{MO}$ and $\text{ZrO}$ over two equi-molar compositions, namely $\text{Zr}_0.5\text{M}_0.5\text{O}_{1.75}$, where $\text{M}=\text{Y, La}$. (La occurs as a pyrochlore compound that melts congruently, whereas the equivalent Y composition is a fluorite solid solution and melts incongruently.) The relevant temperature range is above the liquidus, $T_L$, which is marked in Fig. 11 for 7YSZ and the three zirconates that have attracted the most interest for TBC technology.\footnote{Note that the curve for $\text{LaO}_1.5$ does not bend at the liquidus temperature of $\text{LaO}_1$, suggesting the calculation in [61] ignores the solid/liquid transition.}

Fig. 11 reveals that the partial pressure of the dopant monoxide is usually higher than the total of the $\text{Zr}$-bearing species, but is within a factor of $\leq 10^2$ for the relevant temperature range, and also that $\frac{p_{\text{MO}}}{p(\text{ZrO} + \text{ZrO}_2)} \rightarrow 1$ for all $\text{MO}$ at some critical temperature above $T_L$. The implication is that it should be possible, to evaporate and deposit combinations of these oxides with $\text{ZrO}_2$ and preserve the original composition. Upon closer examination it is evident that $\frac{p_{\text{MO}}}{p(\text{ZrO} + \text{ZrO}_2)} \rightarrow 1$ for $\text{Y}$ at the 7YSZ liquidus but diverges progressively from unity in the order $\text{Y}_0 < \text{Gd}_0 < \text{Sm}_0 < \text{La}_0$. This is qualitatively consistent with the observed difficulty in preserving composition uniformity during deposition here and elsewhere [45,51]. The reality is, however, more complicated. Note that $p_{\text{MO}}$ diverges more from $p(\text{ZrO} + \text{ZrO}_2)$ for the $\text{Zr}_0.5\text{M}_0.5\text{O}_{1.75}$ compositions than for $\text{MO}$ above the pure $\text{M}_2\text{O}_3$ oxides, suggesting a significant effect of the relative activities of the oxide/sub-oxide species in the melt. Concomitantly, there is a change in the relative populations of $\text{ZrO}_2$ and $\text{ZrO}_2$ with the addition of the second oxide. Unfortunately, the paucity of thermodynamic information precludes any further analysis of the $\text{Zr}_0.5\text{Sm}_0.5\text{O}_{1.75}$ system. Moreover, while a full steady state is arguably not achieved, further understanding is needed of the interplay between melting and evaporation with variations in the beam power input and/or ingot feeding to explain the oscillations in composition along the thickness noted in Fig. 3. Process models that capture the complexity of the phenomena involved are necessary for this but do not exist at the present time.

4.2. Metastable fluorite structure

Deposition of SZO from the vapor occurs in a temperature range where the stable structure should be the ordered pyrochlore, as evident in Fig. 1(b), even when accounting for some deviation from stoichiometry as in the present case. However, XRD reveals no signs of ordering in the as-deposited material, Figs. 6 and 9, although the
characteristic pyrochlore reflections (331, 511, etc.) are relatively weak and could be further obscured by texturing. This behavior is similar to that observed during EB-PVD deposition of GZO [48]. Absent cation ordering, the structure is a metastable defect fluorite, as shown by removing the pyrochlore phase field from Fig. 1 and extending the relevant phase boundaries of the fluorite field. Note that in spite of the compositional heterogeneity the coatings can all be single phase fluorite, although only those with narrower fluctuations can eventually order to single phase pyrochlore.

The lack of ordering may be understood from consideration of the atomic arrangements needed to generate the pyrochlore structure during growth, Fig. 12, and the relevant kinetic constraints. Regardless of texture, active growth takes place on {111} facets and the behavior is broadly similar to that observed in 7YSZ [52,56,58,63], with some important differences. One is that 7YSZ grows directly in the \( t' \) form, where all \( \{111\} \) planes are equivalent (although slightly asymmetric because of the tetragonality). In contrast, the cubic pyrochlore structure has two types of \( \{111\} \) planes with different stoichiometry, namely \( A_3B_1 \) and \( A_1B_3 \), Fig. 12(a,b). The pyrochlore pattern is established by stacking six alternating \( A_3B_1 \) and \( A_1B_3 \) planes in a specific sequence, normal to the \( \langle 111 \rangle \) directions. When growing along the \( \langle 100 \rangle \) axes with a pyramidal habit, Fig. 12(c,d), three of the four \( \{111\} \) facets bounding the tip have one stoichiometry while the fourth has the conjugate composition. The distribution is then reversed for each alternating set of layers. Because the vapor is in principle stoichiometric, \( A \) and \( B \) atoms (with their bound oxygen’s) arrive in

Fig. 8. Surface topology (a–c) and polished cross-section (d–f) of SZO coatings deposited at rotation rates of (a and d) zero, (b and e) 0.5 and (c and f) 20 rpm at a substrate temperature of 1000 °C.
equal proportions at the surface. For the pyrochlore pattern to evolve, the crystallization mechanism must involve the cooperative growth of several layers and concomitant diffusional rearrangement of the cations. The XRD results indicate that these processes are kinetically insufficient within the time scale of the deposition. It is possible that some local short-range ordering occurs, whereupon the as-deposited columns would be conglomerates of small coherent domains with different degrees of partial order.

Fig. 9. X-ray diffraction patterns of SZO coatings deposited at a temperature of 1000 °C with rotation rates of (a) 0 rpm, (b) 0.5 rpm, and (c) 20 rpm. Compare also with coatings deposited at 6 rpm in Fig. 6(b).

Fig. 10. Effect of rotation rate on the (a) relative density, and relative thermal conductivity of (b) as-deposited coatings and (c) coatings heat-treated 10 h at 1100 °C. Values for 7YSZ and SZO coatings deposited at the same substrate temperature (1000 °C) are compared, normalized by the corresponding property for the dense oxide.
In general, the crystallographic aspects of the texture developed in DVD SZO coatings resemble those reported for DVD 7YSZ [53], and PVD GZO [48] albeit not for LZO [51,64]. The latter, however, were affected by much larger compositional heterogeneity (up to ±40%) and atypical columnar structures, so they are not suitable for comparison. DVD SZO coatings rotated at conventional rates (≥6 rpm) exhibit predominantly ⟨200⟩ out-of-plane textures that have been explained in YSZ as a result of evolutionary selection [65] of special orientations wherein the tip facets can capture equal amounts of flux from the vapor during a rotation cycle [56,58]. These coatings also exhibit preferred ⟨002⟩ in-plane orientations, justifiable on similar grounds. The texture of the rotated SZO coatings was generally less developed than that observed for YSZ at the same temperatures and rotation rates, i.e. minor amounts of other orientations were found mixed in with the dominant ⟨200⟩ columns. It is likely that this is due to the significantly smaller thickness of the SZO coatings, ~70 ± 5% of their 7YSZ counterparts, implying that the evolutionary selection process was more advanced in the latter and the minor orientations had been screened out.

Texture selection under stationary deposition is less understood and more sensitive to temperature than in rotated specimens. Earlier work on PVD 7YSZ revealed the changes in the population of orientations from ⟨111⟩≫⟨220⟩ at 900 °C to ⟨111⟩≫⟨220⟩≫⟨311⟩ at 1000 °C, to ⟨220⟩≫⟨311⟩≫⟨111⟩ at 1100 °C [56]. By comparison, the stationary DVD YSZ deposited at 1000 °C had a predominant ⟨111⟩ texture [53], closer to that seen in PVD coatings at 900 °C, while SMO deposited under the same conditions exhibits nearly the same pattern of orientations as PVD YSZ at 1000 °C. Some of the variability in 7YSZ might be ascribed to differences in the experimental set up, but it is more likely to result from the higher deposition rate of DVD that arguably has a similar effect on the time available for rearrangements.

![Fig. 11. Reported vapor pressures for oxide species expected during evaporation of Y and rare-earth oxides of interest and the corresponding zirconates.](image)

![Fig. 12. Atomic arrangement on the two types of (111) planes present in the pyrochlore structure (a, b), and the alternating configurations of (111) planes forming the pyramidal column tips for growth along the (001) direction. The darker circles represent the larger (Sm³⁺) cations, and the lighter ones are the (Zr⁴⁺) cations. Oxygens are omitted for clarity. Note that the stacking sequence along the (111) direction in the fully ordered pyrochlore involves 6 alternating planes of the types in (a, b) with different in-plane shifts.](image)
at the surface than a lower temperature.\(^3\) The same argument could not be used for the differences between DVD 7YSZ and SZO, but in this case the coating is significantly thinner in the zirconate, suggesting that the texture is not as developed as that in 7YSZ, an observation also made in the rotated specimens.

The samples deposited at very low rotation rates represent a special case because of the adjustments that are needed at the column tip facets as the growth direction changes over a 180° range and a long wavelength each revolution of the substrate. The tips (Fig. 8e) undergo an exacerbated segmentation because the features on one facet build up substantially on the “sunrise” part of the cycle before the “sunset” portion occurs, biasing the shadowing process. The evolutionary selection process is arguably delayed, and the segmentation adds complexity to the possible spectrum of orientations at the surface.

Branching of the columns, particularly evident at the lower deposition temperatures (Fig. 4) also complicates texture development. Similar effects have been observed in LZO deposition [51] and ascribed to the occurrence of re-nucleation, but the coatings in that case did not appear to have any preferred orientation. That is certainly not the case here, although there are obviously multiple smaller crystallites often observed on the tips of columns, e.g. Fig. 8(b) and (c). Several scenarios are then possible. In one, the “nuclei” form by cluster condensation in the vapor and subsequent landing on the growth surface. In that case the clusters may give rise to mis-oriented branches that are occluded by the growth of the larger columns, cf. Fig. 4(b) and (c). Alternatively, the clusters may be able to re-orient themselves shortly after landing on the surface and give rise to a new but oriented growth center, producing a branch because of shadowing but still being competitive in an evolutionary selection process. Finally, it is also possible that there is heterogeneous nucleation of a new crystal with a twin orientation, but that would require local ordering to develop as a separate growth center.

### 4.4. Porosity and thermal conductivity

With the exception of the coatings on stationary substrates, the relative density (and pore fraction) depends rather weakly on deposition temperature, Fig. 7(a) and rotation rate, Fig. 10(a). However, the thermal conductivities of both SZO and 7YSZ exhibit a quite strong, nonlinear dependence upon pore volume fraction, Fig. 13(a). The SZO coatings grown here have thermal conductivities that range from 0.4 to 1.1 W/m·K; much lower than that of identically grown 7YSZ coatings. Data for the thermal conductivity of EB-PVD YSZ coatings is shown on Fig. 13(a) as a comparison [66,67]. Most of these coatings have a higher density and thermal conductivity than the EB-DVD coatings even though similar deposition temperatures were used. The differences in conductivity appear to arise almost entirely from the substantially different intrinsic thermal conductivities of the two materials. To illustrate this, the thermal conductivity dependence upon pore fraction has been fitted to an expression of the form:

\[
k_{\text{coating}} = K \cdot k_{\text{intrinsic}} \cdot (1 - f)^n
\]

where, \(k_{\text{coating}}\) is the coating thermal conductivity, \(k_{\text{intrinsic}}\) is the intrinsic thermal conductivity of the material from which it is made [38], \(f\) is the pore volume fraction and \(n\) is an exponent. The ambient temperature thermal conductivity of dense SZO has been measured to be -2.0 W/m·K [38], while that for bulk 7YSZ is ~3.0 W/m·K [38]. Combining DVD and PVD data, it is found that the 7YSZ and SZO behaviors in Fig. 13(a) are best fitted by an exponent, \(n = 2.5\).

\(\text{A plot of the } K \text{ factor against the pore fraction, Eq. (1), is shown in Fig. 13(b). It clearly reveals that } K \text{ is reasonably close to unity for both materials, from which one may infer that the differences in the measured thermal conductivity to first order arise from } k_{\text{intrinsic}}. \text{ The separation of the two curves in Fig. 13(b) as the pore fraction increases is likely the result of the sensitivity of the pore morphology to temperature and rotation rate. Note, for example, that the lowest density (highest porosity) corresponds to the lowest rotation rate in Fig. 10(a), wherein the heavily curved columns near the bottom provide much larger barriers to heat transfer than the straight intercolumnar gaps in conventional structures.}

Finally, it is worth noting that the heat treatment seems to have as strong an effect upon the density and thermal conductivity of the SZO DVD coatings as it does on their 7YSZ counterparts. In principle, this is inconsistent with the reportedly higher resistance to sintering of zirconates [49]. The implication is that the driving force for sintering must be dominant, presumably because of a substantially higher initial porosity contents introduced by the DVD process (cf. Figs. 7 and 10). Although the heat treatment tends to increase the thermal conductivity of the coating, the pore shape, distribution and fraction is still strongly dependent upon the as-deposited microstructure [68]. The difference in thermal conductivity of heat-treated samples still remains to be relatively larger as the as-deposited samples have.
5. Conclusion

Sm$_2$Zr$_2$O$_7$ coatings with microstructures suitable for thermal barrier coatings have been successfully synthesized by EB-DVD. The coatings exhibit compositional variation across the thickness of up to ±12%Sm$_{13}$ indicative of source instabilities induced in part by the difference in vapor pressures of the constituent oxides. SZO coatings grow with a metastable fluorite structure due to kinetically constrained cation ordering within the time scale of the deposition process. This observation is in agreement with observations on other rare earth zirconates. The coating morphology is broadly consistent with those produced in 7YSZ and GZO by EB-DVD and EB-PVD, respectively, but becomes increasingly atypical with decreasing deposition temperature and/or at low rotation rates, both of which induce extreme branching of the columns. The origin of the branching is associated with shadowing in the low rotation specimens, but is less clear in the case of the lower deposition temperature.

The thermal conductivity of SZO DVO coatings is substantially lower than that measured on DVO 7YSZ or on EB-PVD Gd zirconate. The former is primarily due to the lower intrinsic conductivity of the SZO, whereas the latter is a result of the much higher porosity content produced by the DVO process. This high level of porosity, however, appears to drive pore reconfiguration during high temperature exposure at the same rate in SZO and 7YSZ, notwithstanding the expected lower diffusion rates in SZO.

Implementation of DVO SZO in thermal barrier systems appears viable but is likely to require improved control of the composition during growth, as well as a study of the optimum levels of porosity and the processing parameters needed to achieve them.

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