USAXS Studies of Directed Vapor-deposited Y_2O_3-stabilized ZrO_2 Coatings

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Introduction

Thermal barrier coatings (TBCs) are used to protect blade and vane components in turbine applications operating at elevated temperatures. These coatings have enabled improvements to be made in both engine efficiency (by allowing higher operating temperatures for given service life) and engine component life (by extending the service life at a given operating temperature) [1]. Current TBCs make up a 200- to 300-µm-thick insulating layer of 6-8% mass-fraction Y_2O_3-stabilized ZrO_2 (YSZ) [2]. This work is concerned with understanding the nature of voids in directed vapor-deposited YSZ coatings and how they might be controlled by processing [3]. It has been shown that the small-angle scattering (SAS) of x-rays or neutrons (small-angle x-ray scattering [SAXS] or small-angle neutron scattering [SANS]) can nondestructively quantify the representative void microstructures in TBCs over a scale range from nanometers to micrometers [4].

For the most demanding applications involving the moving parts of an advanced gas turbine, TBCs are increasingly produced by physical vapor deposition (PVD). Multiscale anisotropic voids with preferred orientations are formed during deposition in regions both between (intercolumnar) and within (intracolumnar) the PVD columns. In the case of directed vapor deposition (DVD), an inert gas directs the vapor cloud toward the substrate, resulting in alternative microstructures having a higher volume fraction of voids within the columns. Figure 1 shows the DVD microstructure for deposition under normal conditions (chamber pressure = 0.18 Torr; deposition temperature = 1050°C). Ultrasmall-angle x-ray scattering (USAXS) is used to relate processing conditions to void volume fraction and size.

In recent years, the technique of USAXS has been significantly advanced by the availability of new high-brilliance x-ray synchrotron sources. Currently, USAXS studies can interrogate the microstructure features in a size scale ranging from nanometers to micrometers by using an x-ray beam size of 0.3 × 0.3 mm and provide quantitative volume fractions, surface areas, and size on a calibrated absolute scale. A 2-D collimated modification of USAXS [5] was used to study highly anisotropic structures by adjusting the sample’s azimuthal rotation angle in the x-ray beam. The combination of extreme anisotropic capability, submillimeter beam size (hence spatial resolution), and absolute calibration made 2-D USAXS a viable means for quantifying electron beam physical vapor deposition (EBPVD) TBC microstructures.

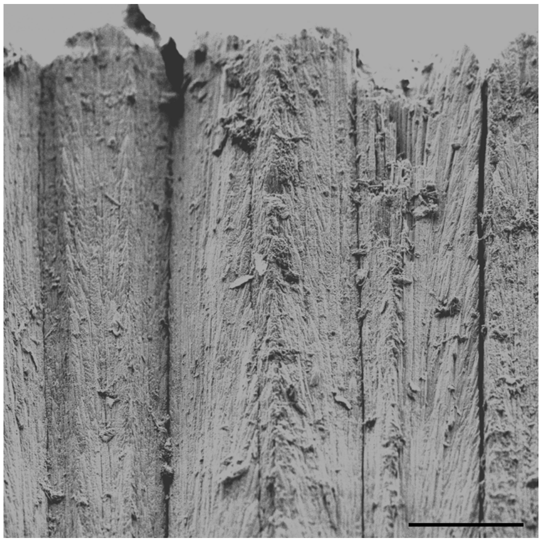

FIG. 1. Columnar microstructure of DVD coating. Marker is 20 µm.

Methods and Materials

In the present study, scattering from the highly anisotropic and preferentially oriented voids in DVD YSZ coatings deposited under varying chamber pressures is measured. Table 1 shows the deposition conditions. SAXS intensities are measured as a function of the scattering vector **Q**, which bisects the incident and scattered x-rays, with magnitude **|Q|** defined by:

$$|\mathbf{Q}| = \frac{4\pi}{\lambda} \sin\theta , \qquad (1)$$

where 2θ is the scattering angle. For anisotropic microstructures having preferentially aligned, nonspherical voids, the direction of **Q** defines the direction within the

TABLE 1. DVD coatings made using various conditions.

Sample No.	Chamber Pressure (Torr)	Chamber Temperature (^{o}C)
1	0.18	1050
2	0.10	1050
3	0.056	1050

sample for which structural information can be obtained from the scattering measured as a function of |**Q**|.

Because of the highly anisotropic nature of voids, the Bonse-Hart USAXS double-crystal diffraction technique is applied to provide absolute-calibrated SAXS intensity data with ultrahigh Q-resolution over a range corresponding to structural dimensions from 1 nanometer to several micrometers. The standard USAXS method is intrinsically slit-smeared, with only modest angular collimation in the plane perpendicular to the diffraction plane of the collimating monochromator and with analyzer crystal monoliths before and after the sample. In the 2-D collimated modification of USAXS, transverse crystal optics are introduced immediately before and after the sample in order to de-smear the incident and scattered beams. The 2-D collimated USAXS instrument located at UNI-CAT beamline 33-ID at the APS was used for the experiments described here. The 2-D collimated USAXS instrument's dynamic range for Q is 0.00012 to 0.1 Å^{-1}, with an arbitrarily high angular anisotropic resolution within the sample plane provided simply by setting the sample azimuthal orientation angle.

Results

Figure 2 depicts the scattered intensity as a function of coating orientation, $\alpha = 0^{o}$ to 360^{o}, for DVD coatings 1, 2, and 3 at Q = 0.00414, 0.00299, and 0.00417 Å^{-1}, respectively. By convention, the substrate normal direction is at angle $\alpha = 0^{o}$. The anisotropy of the scattering depicted in Fig. 2 is related to the anisotropy of the features dominating scattering at this Q in the microstructure. Note that at this Q, the dominating maximum in scattered intensity is at about 90°. This scattering is related to the intercolumnar voids. Figure 2 also shows a second anisotropic population at about 60°, which is related to intercolumnar voids. Figure 2b and 2c do not show this second population, indicating that at this Q, this population is not yet observable. This may be related to, for example, the different sizes of these voids.

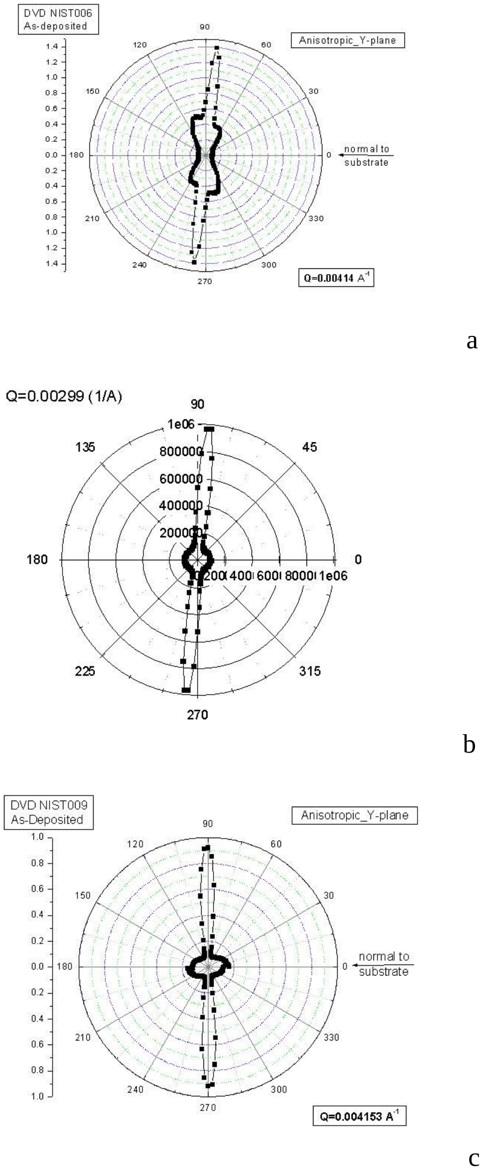

FIG. 2. Anisotropic USAXS measurement at constant Q for the three discussed DVD samples.

Similar plots at higher (or lower) Q values are then used to study anisotropy of the smaller (or larger) microstructural features. This method allows characterization of complex microstructures, such as those in these DVD coatings, that exhibit multiple size-separated populations of scatterers with different anisotropies.

An understanding of the anisotropy of the microstructure, combined with the availability of fully calibrated USAXS data for specific Q directions, enables the microstructure to be numerically modeled (this part of the evaluation is in progress) and other important physical data to be extracted. For example, the Porod regime from the full scattering curves was used to obtain the total void surface area by using Eq. (2) and sector averaging from 0° to 360°, as follows:

$$I = \frac{2\pi|\Delta\rho|^2}{Q^4} S_V \ . \qquad (2)$$

TABLE 2. Porod surface area for DVD samples deposited under varying conditions.

Sample	Total Void Surface Area (m^2/cm^3)
1	54 ±3
2	33 ±2
3	17 ±2

Discussion

Strong and complex anisotropy was found in small-angle scattering of DVD coatings. This anisotropy depends on the Q at which it is studied, documenting the presence of multiple populations of scatterers with different sizes and anisotropies. The 2-D collimated USAXS was successfully used to separately characterize these populations, demonstrating the ability to characterize voids with arbitrarily high angular anisotropy quantitatively. Important industrially relevant data were obtained. These data can be used to optimize the properties and manufacturing of these materials. This is documented by results in Tables 1 and 2, where measured microstructural characteristics were found to be directly related to the manufacturing conditions.

Acknowledgments

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