Modeling of Anisotropic USAXS Data from Multicomponent Microstructures

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Introduction
In advanced gas turbine applications, electron-beam physical-vapor deposition (EB-PVD) has become a major means of depositing the ceramic thermal barrier coating (TBC) on the turbine blades to protect them from the increasingly high operating temperatures that they must withstand. Anisotropic ultrasmall-angle x-ray scattering (USAXS) can characterize highly anisotropic microstructures such as those in EB-PVD TBCs [1]. Such microstructure characterization must be quantitative in order to establish the processing-microstructure-property correlations that will aid in TBC design. Thus, a mathematical formulation is required to describe the anisotropic and orientation-dependent small-angle scattering from several populations of scattering features.

To address this need, an anisotropic four-component void model has been developed and applied successfully in interpreting the USAXS data collected from a typical EB-PVD TBC. For the first time, quantitative results have been obtained for describing the individual EB-PVD void populations and the changes introduced during thermal cycling [2].

Methods and Materials
The yttria-stabilized zirconia (YSZ) EB-PVD samples were prepared by depositing YSZ from a rotating vapor plume onto a stationary bond-coat and superalloy (blade) substrate, to a coating thickness of 0.5 mm. The coating and substrate were sectioned together to produce <0.2-mm-thick slices, and these were studied “in section” with the incident x-ray beam perpendicular to the slice. Two orthogonal sections were studied for each coating, here denoted as having Y and Z orientations with reference to the incident beam direction. A third sample was made for each coating by removing it from the substrate and thinning it down to <0.2 mm in thickness. This sample was measured in the X orientation, with the incident beam orthogonal to the coating plane. These orientations are shown in Fig. 1.

The scattering measurements were performed at UNICAT beamline 33-ID at the APS. The x-ray energy used was 16.9 keV in order to decrease the amount of linear absorption and multiple scattering within the sample.

For anisotropic USAXS studies, side-reflection crystal optics were introduced to remove the intrinsic slit-smearing effect of regular USAXS and provide effective 2-D-collimated scattering. The Q range measured was 0.0001 to 0.05 A⁻¹. The anisotropy of the scattering was investigated by repeated USAXS scans over the range of the scattering vector Q for different azimuthal orientations of the sample about the incident beam direction. Both USAXS scans as a function of Q for a given azimuthal angle and anisotropic scans of the azimuthal angle at fixed Q were made in order to characterize the scattering anisotropy.

To model the scattering observed, a four-component spheroid model was used to represent the void populations. The four void populations were intercolumnar and subcolumnar voids, coarse intracolumnar feather voids, fine feathers, and nanometer-scale pores within the EB-PVD columns. Each population was approximated to a non-random-orientation distribution of spheroids. The cross section for a given spheroid orientation was well known. Thus, the mean small-angle scattering cross section dσ/dΩ per spheroid in the population was given by a weighted orientational average over all orientations of the scattering vector Q:
\[
d\sigma\bigg|_{d\Omega_p} = \pi^{1/2} d\alpha \int_0^{2\pi} P(\alpha, \omega) d\sigma(Q, X) \sin \alpha \int_0^{2\pi} \sin \omega \, d\omega
\]

where \( P(\alpha, \omega) \) is the orientational probability for spheroid orientation \( X \) with respect to the direction of \( Q \). (For a spheroid with orthogonal radii \( R_o, R_o, \) and \( \beta R_o \), oriented with angle \( \eta \) between the \( \beta R_o \) axis and the direction of \( Q \), \( X = \cos \eta \).) The angles \( \alpha \) and \( \omega \) are, respectively, the polar and azimuthal orientation angles of \( Q \) with respect to the normal direction to the substrate plane. The mean scattering cross section (for a given \( Q \) orientation) must then be summed over each population and weighted for the different component volume fractions.

For empirically determined aspect ratios \( \beta \) and orientation distributions \( P(\alpha, \omega) \), for each void component, values of the component volume fractions and spheroid sizes \( R_o \) are fitted simultaneously to the USAXS data obtained for several different \( Q \) directions and sample orientations. For a set of fits obtained for the USAXS data, the predicted anisotropy at a given \( Q \) can be calculated for any of the three orthogonal sample orientations and compared with the experimentally measured anisotropies. The component \( P(\alpha, \omega) \) and \( \beta \) values can be adjusted to optimize the USAXS fitting and predicted scattering anisotropies. Once an acceptable set of microstructure parameters has been obtained, other quantities such as the component surface areas, may be calculated.

**Results**

Figures 2 to 5 present sets of fits to the USAXS data obtained from the as-deposited and corresponding thermally cycled EB-PVD deposits, together with a comparison of the experimentally measured and theoretically predicted scattering anisotropies. Table 1 presents the component void volume fractions obtained for both the as-deposited and the thermally cycled EB-PVD.

**FIG. 2.** USAXS scans with fits for selected \( Q \) directions and sample orientations for typical as-deposited EB-PVD.

**FIG. 3.** Experimental and predicted USAXS anisotropies at selected \( Q \) values associated with specific void components in as-deposited EB-PVD.

**FIG. 4.** USAXS scans with fits for selected \( Q \) directions and sample orientations for typical thermally cycled EB-PVD.

**FIG. 5.** Experimental and predicted USAXS anisotropies at \( Q \) values associated with specific void components in thermally cycled EB-PVD.
### Table 1. Component Void Fractions in As-Deposited and Thermally Cycled EB-PVD.

<table>
<thead>
<tr>
<th>Void Population</th>
<th>As-deposited (%)</th>
<th>Thermally cycled (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercolumnar</td>
<td>8.9 ±0.3</td>
<td>9.1 ±0.1</td>
</tr>
<tr>
<td>Subcolumnar</td>
<td>1.7 ±0.1</td>
<td>6.1 ±0.3</td>
</tr>
<tr>
<td>Coarse intracolumnar feathers</td>
<td>2.6 ±0.3</td>
<td>4.8 ±0.6</td>
</tr>
<tr>
<td>Fine feathers</td>
<td>4.1 ±0.1</td>
<td>0.6 ±0.1</td>
</tr>
<tr>
<td>Nanometer pores</td>
<td>4.6 ±0.6</td>
<td>3.4 ±0.8</td>
</tr>
<tr>
<td>Total</td>
<td>21.9 ±0.1</td>
<td>24.0 ±0.7</td>
</tr>
</tbody>
</table>

In Table 1, it has been possible to identify five void components of physical significance through the use of a $P(\alpha,\omega)$ orientation probability function that is bimodal in $\omega$. While the mean opening dimensions and preferred orientations for each void component are not shown here, thermal cycling has sintered the fine feather population the most, while the nanometer pores sinter only slightly. Meanwhile, the coarse feather and subcolumnar void porosities increase significantly.

### Discussion

A multicomponent model for interpreting anisotropic USAXS data that were obtained from using different sample orientations has been developed. Application of this model has quantified the component void structures in EB-PVD microstructures to a degree not previously possible. Systematic changes have been characterized for each void component. In particular, the USAXS studies have revealed and quantified a “subcolumnar” void component in as-deposited EB-PVD that becomes more prominent upon thermal cycling.

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### References