Studies of the Anisotropic Microstructure of Dicalcium Silicate Thermal Barrier Coatings by Pinhole-Geometry Ultra-Small-Angle X-ray Scattering

J. Ilavsky,[1] A. J. Allen,[1] P. R. Jemian,[2] G. G. Long,[1] F. Jansen[3]

[1] *National Institute of Standards and Technology, Gaithersburg, MD, U.S.A.*

[2] *Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, IL, U.S.A.*

[3] *Sulzer Innotech, Winterthur, Switzerland*

Introduction

Thermally sprayed dicalcium silicate (Ca_2SiO_4) deposits are currently being developed for use as thermal barrier coatings (TBCs) in gas turbines.[1] They promise superior damage resistance to fuel contaminants and improved cost effectiveness compared to current yttria-stabilized zirconia TBCs. Since the void microstructures[2] of thermally sprayed deposits control their properties, performance, and reliability, significant effort has been invested in gaining a better understanding of these microstructures. Small-angle scattering techniques are among the best methods for quantifying voids in these materials over a wide size range.[3,4] Ultra-small-angle x-ray scattering (USAXS) is particularly powerful, providing information on voids up to several micrometers in size. While the void microstructures of TBCs are usually axially symmetric about the spray direction, they exhibit considerable anisotropy in the deposit cross-section plane. Thus they are unsuited for measurement in the slit-smeared geometry of USAXS. This limitation of standard USAXS has been overcome on UNICAT sector 33-ID through the implementation of an effective pinhole-geometry USAXS that has proven successful for the characterization of anisotropic microstructures.

Methods and Materials

Bonse-Hart USAXS cameras[5] that make use of vertically collimating and analyzing crystals exhibit inherent slit smearing that prohibits studies of anisotropic materials. At UNICAT, effective pinhole collimation geometry has been achieved by adding horizontally collimating and analyzing crystals[6] before and after the sample. The sample itself is mounted on an azimuthal rotation stage and measured at different azimuthal orientations.

TBCs contain three major void systems: interlamellar pores mostly parallel to the substrate, intralamellar cracks mostly perpendicular to the substrate, and globular pores. Each of these void systems evolves during service life. Quantitative and separate characterization of these void systems, important for understanding the deposit properties, can be obtained from USAXS data by determination of the anisotropic apparent Porod surface area distribution.[2,3] These data provide calibrated specific surface areas for the two dominating anisotropic void systems, and they provide information on the void microstructure anisotropy as well.

Details of the spray and feedstock conditions are given elsewhere.[1] Dicalcium silicate deposits 0.3 mm thick were cut parallel to the cross-section plane and ground to thicknesses ranging from 0.15 mm to 0.25 mm using metallographic methods. A 0.2 mm x 0.2 mm x-ray beam illuminated the samples. USAXS scans were made in azimuthal increments of 5°, and the Porod constant [2,7] was measured from the Porod Q^{-4} terminal slope of the scattering in the scattering vector, |Q|, range between 0.002 $Å^{-1}$ and 0.02 $Å^{-1}$.

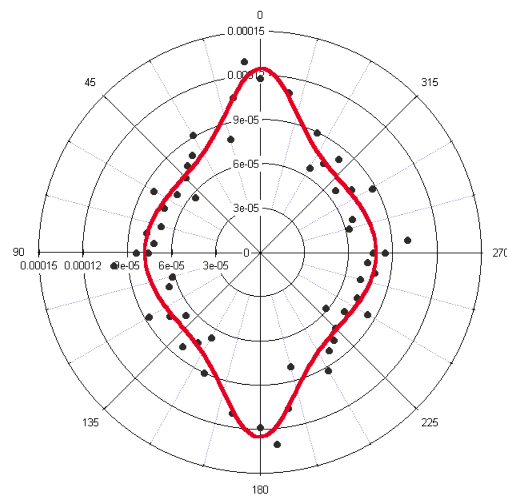

FIG. 1. Measured Porod constant distribution in the cross-section plane of a dicalcium silicate thermally sprayed deposit.

Results

The measured anisotropic variation of the Porod constant in the cross-section plane of a typical dicalcium silicate sample is shown in Fig. 1. By exploiting the axial symmetry of the microstructure about the spray direction (vertical in Fig. 1) a 3D distribution of the Porod constant can be reconstructed as shown in Fig. 2. As described elsewhere,[2] if the anisotropic variation of the Porod constant is known over all 4π steradians, the weighted 3D average can be calculated and the quantitative specific surface

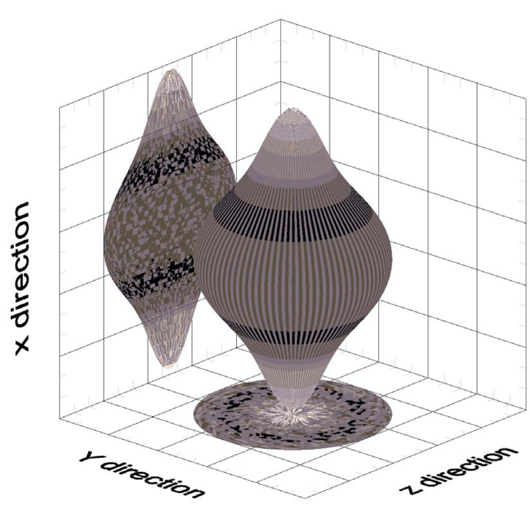

FIG. 2. 3D Porod constant distribution for a dicalcium silicate deposit reconstructed from Fig. 1.

area of the voids can be deduced using the x-ray scattering contrast of the material. Furthermore, the anisotropic void systems can be characterized separately if they can be distinguished as two distinct Porod constant distributions. In these deposits, the interlamellar pores (projection to XZ plane in Fig. 2) and intralamellar cracks (projection to YZ plane in Fig. 2) can be characterized separately, as they dominate the total internal surface area. The globular pores cannot be observed in this way since their surface area is small and isotropic even though their fraction of the porosity is significant.

Discussion and Conclusions

Our results demonstrate that different populations of voids can be observed and quantified by USAXS studies. These data can be related to the feedstock and manufacturing conditions and to the deposit properties. Such knowledge is currently being used to optimize the microstructure for particular engineering applications. At this time, anisotropic USAXS is unique in being able to characterize, separately, the different void populations at a selected location within the cross section of thin deposits.

Acknowledgment

Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38. The UNICAT facility at the Advanced Photon Source (APS) is supported by the University of Illinois at Urbana-Champaign, Materials Research Laboratory (U.S. DOE, the State of Illinois-IBHE-HECA, and the NSF), the Oak Ridge National Laboratory (U.S. DOE under contract with UT-Battelle LLC), the National Institute of Standards and Technology (U.S. Department of Commerce) and UOP LLC.

References

[1] F. Jansen, X. Wei, M.R. Dorfman, J.A. Peters, and D.R. Nagy, Performance of Dicalcium Silicate Coatings in Hot-Corrosive Environment, The International Conference On Metallurgical Coatings And Thin Films, San Diego, CA, April 10 - 14, 2000.

[2] J. Ilavsky, A.J. Allen, G.G. Long, et al., J. Am. Ceram. Soc. **80**, 733-742 (1997).

[3] J. Ilavsky, G.G. Long, A.J. Allen, et al., Ceramics-Silikaty **42**, 81-89 (1998).

[4] J. Ilavsky, G.G. Long, A.J. Allen, et al., "Anisotropic Microstructure of Plasma-Sprayed Deposits," presented at the 15th International Thermal Spray Conference - Thermal Spray: Meeting the Challenges of the 21st Century, Nice, France, 1998 (unpublished).

[5] G.G. Long, A.J. Allen, J. Ilavsky, P.R. Jemian, and P. Zschack, in **CP521**, *Synchrotron Radiation Instrumentation: 11th US National Conference*, P. Pianetta and H. Winick, eds. (AIP, College Park, 2000) p.183.

[6] U. Bonse and M. Hart, Zeit. für Phyzik **189**, 151 (1966).

[7] J. Ilavsky, G.G. Long, A.J. Allen, et al., J. Thermal Spray Techn., **8**, 414-420 (1999).