Materials structures for 21st century energy needs

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Introduction

Demands on efficiency and environment friendliness of energy conversion and utilization dominate the beggining of the 21st century. Therefore enhancement of existing and development of new energy technologies is a major task in front of both the research community as well as industry. For example, further increase in efficiency of advanced land-based and jet turbines requires faster gains in the firing temperature compared to average about 10^{o}C per year reached during the last 50 years. Previously the progress was achieved mostly by combination of better cooling design, combustion control and improvements in base materials used. Most likely the advances in the future will come from improvements in thermal barrier coatings technology.

Thermal barrier coatings (TBC) represent an example of complex multilayer engineering system with multiscale microstructure. TBCs provide insulation to metallic structures in the hot section of land-based/aero-turbine engines and increased operating temperature of the engine and therefore enhance efficiency; enhance durability and extend life of metallic components subjected to high temperatures and high stresses; and reduce cooling requirements to metallic components. However, uncertainties about the TBC reliability have prevented engineers from taking full advantage of the TBC capabilities. In the last years the concept of "prime reliance" of these coatings has become the key for the industry. This concept requires assurance, that the TBC will not fail and therefore the underlying components do not have to be designed to survive in service without catastrophic failure. TBC applied as non-prime reliant coatings yield approximate 50^{o} C increase in operating temperature, but if these same coatings could be considered prime reliant, immediate increase in operating temperature would be few times higher.

Solid oxide fuel cells (SOFC) represent novel method of converting fossil fuel or stored hydrogen energy into electricity with enormous potential – high efficiency and environment friendliness. Ceramic SOFCs are proven technology with first pioneering commercial power plants in testing around the World. However, reaching full potential of SOFCs will require reduction in operating temperatures from current about 900^{o}C to around 600^{o}C while keeping the efficiency and performance on acceptable level. This reduction in the operating temperature requires significant advances – including optimization of reliable and fully dense electrolyte oxide-ceramic layer which can be only 10 μm thick and of highly porous ceramic (or ceramic-metal composite) anode and cathode layers.

While the above presented two examples of applications – TBC and SOFC - seem to have little in common, they pose similarly complex challenge to materials science. For the future energy needs it is imperative to gain substantial improvements in the performance of these materials and this requires qualitative and quantitative understanding of the microstructural features over many decades of length scales as well as relationships between the microstructure and functional properties. In both of the presented cases there is potential for major – "revolutionary" jump in energy efficiency by improved materials design.

Advances in computer modeling in the last years have revolutionized the engineering designs – new components are now tested "in computer" before selecting the most appropriate design for prototyping. This system is significantly more efficient. However, currently modeling success depends on availability of materials parameters and properties - which are challenging to obtain for the complex ceramic layered systems, as the examples discussed here. Significant step in the quality of computer modeling will be the capability of including the components microstructure into the models directly, bypassing the need for independent measurements of the materials properties. Ideally, such successful model would actually specify the microstructure of the materials used in different components. This would represent revolutionary method, when the properties of engineering materials in a given application could be optimized during design.

Comprehensive efforts in materials science have been underway to gain the needed insights on microstructure of these complex ceramic materials and provide useable and reliable models of microstructure-properties relationships. The sizes of microstructural features of interest range, depending on material and application, from many micrometers to Angstroms. This wide range of interest usually requires combination of various characterization techniques – for example for porosity these may be various types of microscopy, intrusion porosimetry, small angle scattering, X-ray tomography, etc… Only by combining these techniques can a "mosaic picture" of the full microstructure be created. This mosaic provides the data necessary for development of understanding of the microstructure-properties relationships. Once this is achieved, one can approach the ultimate goal of creating materials-physics based computer models for intelligent materials design.

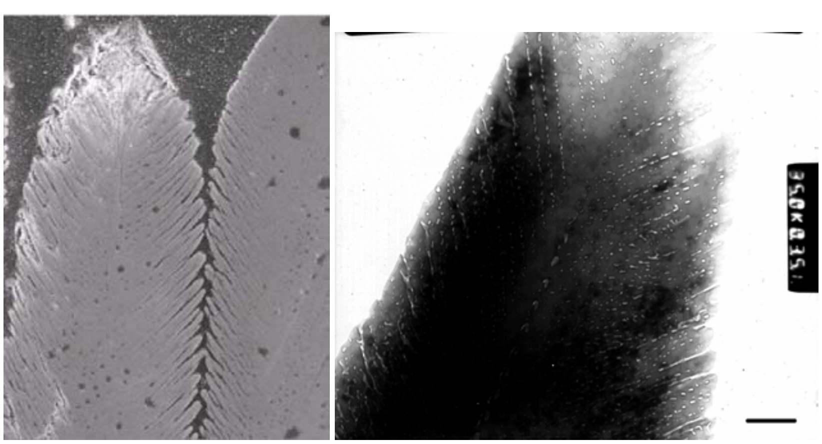

Figure 1 SEM (left) and TEM (right) micrograph of the EBPVD TBC material. Note structure between the columns (left) and intarcolumnar voids structure (right).

Case example – Thermal Barrier Coatings

The small-angle X-ray and neutron scattering technique was previously developed to characterize - separately and quantitatively - void systems in TBC ceramic layers (electron-beam physically vapor deposited – EBPVD). The complex microstructure (see Figure 1) made this project challenging.

Success was achieved by design of representative computer model of void system and calculating the small-angle scattering patterns produced by this model. Microscopy images (SEM, TEM, and Optical) were used to develop realistic model and used as guidance to obtain reasonable estimates for shapes, anisotropy, aspect ratios and size ranges of the voids in each of the four subsystems modeled. Intrusion porosimetry was used to obtain total volumes of voids.

The calculated SAXS data from the model were then compared with measured small-angle scattering data obtained using 2-D collimated USAXS instrument at UNICAT, Advanced Photon Source. Using fitting procedure we were able to extract quantitative and separate data on void subsystems in these materials, as shown in the Figure 2.

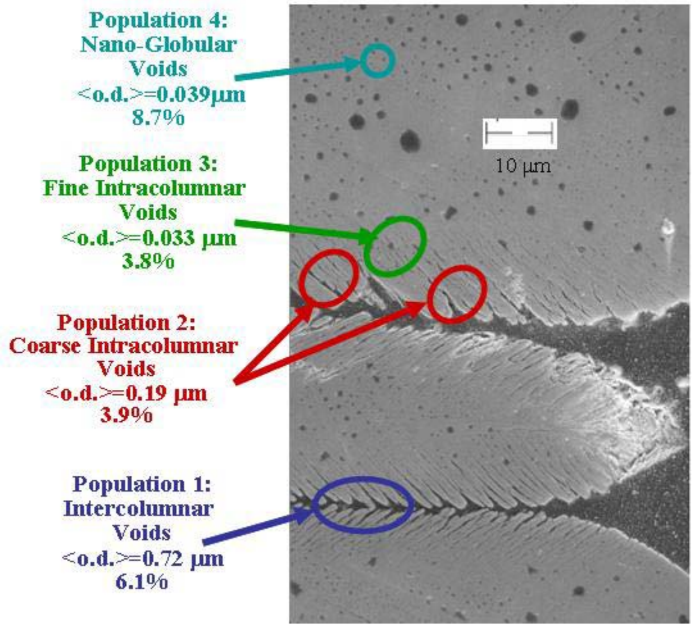

Figure 2 – results from analysis of USAXS measurements.

The data were complemented by tomography measurements on the same samples at 2-BM beamline (XOR, Advance Photon Source) – see Figure 3 for examples. While quantitative data are not presented here, with appropriate processing number of microstructure descriptors (such as voids volume) can be extracted. By combining methods described above together we have already obtained description of microstructure on level never seen before.

Conclusions

The need for wide-range, statistically representative and quantitative microstructural data requires the use of advanced techniques and possible development of new ones. While the presented combination of techniques currently is capable producing the data on basic level needed, better data are required for the future.

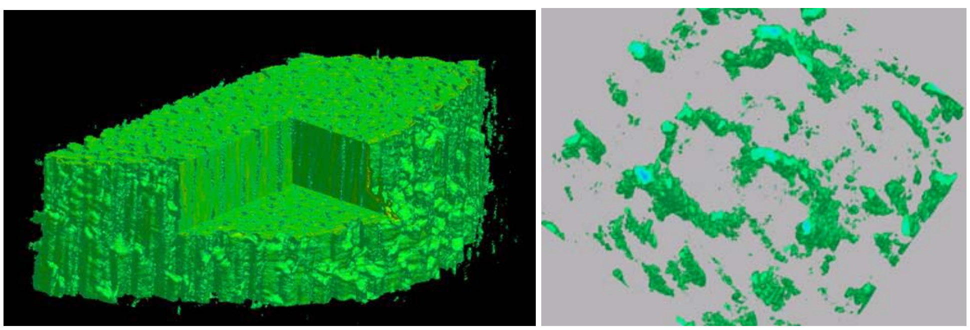

Figure 3 - Tomography images of EBPVD TBC deposit. Left – side view on the deposit with cut out. Right – top view on voids between the columns (inverted threshold).

The two presented X-ray techniques – small-angle scattering and tomography - currently complement themselves without overlap, leaving part of the microstructure "out of view". The current tomography setup at 2-BM is capable of resolution limit about 1 – 1.5 micrometers, while the USAXS instrument maximum size, which can be reliably characterized is on the order of 1 micrometer.

The tomography is attractive for its ability to generate 3-dimensional datasets which can be used as input data in various models predicting materials properties (OOF, NIST, and various other finite element methods). Major advantage of the tomography data is relative confidence of scientific community with the data and minimum modifications necessary for use in models developed with 2d data from imaging techniques.

For full utilization of tomography, it is necessary to extend the capabilities of the tomography instrumentation. We will need to be able to characterize the complex ceramic materials structures with improved resolution (at least 100nm, but ideally 10 – 20 nm) in meaningful sample volumes – and that means that we need to retain field of view of at least 200 micrometers to provide statistically representative data. Element specific capabilities would be very useful addition, as well as various in-situ capabilities (furnace and chemical reactor).

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