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Investigation of grain-boundary geometry and pores morphology in dense and porous cubic zirconia polycrystals

Piotr Bobrowski [a,*], Marek Faryna [a], Zbigniew Pędzich [b]

[a] Institute of Metallurgy and Materials Science, 25 Reymonta Street, PL 30-059 Kraków, Poland
[b] AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Mickiewicza 30 Street, PL 30-059 Kraków, Poland

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ABSTRACT

Three-dimensional electron backscatter diffraction technique was used for the visualization of grain boundary geometry and pore morphology in cubic zirconia. A set of four samples sintered under different conditions was investigated. Specimens which were characterized by energy dispersive spectroscopy and X-ray diffraction were entirely composed of cubic phase. Investigations of boundaries and pore structures were carried out in a dual-beam scanning electron microscope. For each sample, a volume of 1000 μm^3 was investigated. The analysis of grain boundary networks reconstructed from inverse pole figure maps revealed a strong dependence between grain boundary density and sample preparation parameters. Sintering also affects the size and distribution of pores. The total number of grains analyzed varied from 17 to 357 and the calculated volume of cavities from 0.01% to 21%. This paper shows the application of three-dimensional crystallographic orientation analysis to characterize the microstructure of yttria stabilized zirconia ceramics.

1. Introduction

Properties of polycrystalline materials are affected by the behavior of individual constituent grains, the network of grain boundaries as well as voids which can possibly occur. For a complete characterization of a porous microstructure an information about grains (size, shape, and crystallographic orientation), voids (size, distribution, interfacial area and connectivity) and grain boundaries (boundary plane and misorientation) is required. While most of the necessary data can be obtained from regular cross sections of a sample, the information about pore distribution, pore connectivity, grain boundary planes and structure formed by grains require three-dimensional analysis to be fully characterized. Stereological techniques based on statistical calculations can be applied to obtain some information about features in the third dimension within material [1]. However, when statistical considerations cannot provide satisfactory results, three-dimensional characterization of the material is needed. Such cases, when the real 3D data are indispensable, include shape and size of strain regions in deformation studies [2], shape and connectivity investigations of porous structures [3] and complete characterization of grain boundaries in polycrystalline materials [4,5].

Three-dimensional microstructural data can be collected by use of several methods. X-ray tomography is one of the earliest techniques for 3D imaging. It is a non-destructive method, however the resolution obtained by this technique, ranging from 1.5 to 170 μm, is insufficient for analysis of microporous materials [6]. Electron tomography in transmission electron microscope is capable of achieving nanoscale resolution but at the cost of very limited volume of investigated material [7]. Atom-probe tomography can also obtain nanometer scale resolution but it is rather suitable for chemical composition analysis and requires preparation of needle-shaped samples [8]. In recent years, focused ion beam (FIB) combined with scanning electron microscope (SEM) emerged as a useful tool for comprehensive three-dimensional analysis in micro- and nanoscale [9,10]. The measurement is based on repetitive creation of cross sections of a sample followed by acquisition of microstructural information. The SEM can be equipped with various detectors for different applications, i.e. backscattered electrons (BSE) detector for imaging, energy dispersive spectrometer (EDS) for analysis of chemical composition and electron backscatter diffraction (EBSD) camera for acquisition of crystallographic data.

* Corresponding author at: Polish Academy of Sciences, Institute of Metallurgy and Materials Science, 25 Reymonta street, 30-059 Kraków, Poland. Tel.: +48 12 2952837.
E-mail address: bobrowski.piotrek@gmail.com (P. Bobrowski).

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The EBSD technique incorporated into FIB–SEM machine (3D-EBSD) is the only experimental technique which can provide information about grain boundary geometry in micrometer scale. For example, Rohrer et al. [11] calculated grain boundary character distributions (GBCD) and estimated relative boundary energies in the Ni based superalloy and found correlations between these parameters. The same research group analyzed grain boundary distributions in ceramic materials such as dense yttria stabilized zirconia (YSZ) [12] as well as pure yttria [13]. Their dense YSZ samples were manufactured by casting tapes from slurry [14]. The applied specimen preparation procedure involved polishing of the material to the final thickness in the range of 20–60 μm followed by disintegration into triangular fragments, which were further FIB milled to obtain needle shaped samples. The sample preparation procedure described in [14], although it proved successful, was quite tedious and time consuming.

An important aspect in the study of YSZ ceramics is the morphology of cavities being always present. A few papers described the application of FIB–SEM equipment to analyze porous zirconia and zirconia based composites with a view to their application in solid oxide fuel cell (SOFC) production [3,15–17]. Xia et al. [18] reconstructed microstructures of pores in a series of ZrO_2 samples based on BSE images. The obtained experimental data was used as an input for calculations of pore connectivity, pore number, pore-grain interfacial area and tortuosity.

In the study described in this paper, cubic YSZ was chosen as a model material to investigate grain boundary and pore structures. The samples were prepared by hydroxides co-precipitation and pressureless sintering, which enables the manufacture of polycrystalline materials with the required grain size. In our study, we decided to carry out measurements on bulk samples with a minimum of prior preparation. Difficulties resulting from charging, redeposition and anisotropic sputtering were overcome by optimization of measurement parameters. In the present analysis, we showed that it is possible to reconstruct pore microstructures from image quality (IQ) maps obtained by the EBSD technique. The IQ images are characterized by stronger contrast compared to the BSE ones that facilitates threshold-based segmentation of experimental data.

2. Experimental procedure

2.1. Sample manufacturing

Starting powders were obtained by hydroxides co-precipitation in an ammonia solution from $ZrOCl_2$ and YCl_3 precursors. The differentiation of the substrate solutions by their concentration led to gels with very different morphology. The hydroxide mixtures were calcined at 500 °C. This procedure allowed to manufacture two powders which showed different sinterability [19] denoted as '*T*' and '*S*' samples. They were densified using two heating procedures differing with maximum sintering temperature and heating rate. The soaking time was the same in each case–2 h. Four cylindrical samples with 4 mm in diameter and 1 mm thick of cubic zirconia polycrystals stabilized by 8 mol% addition of yttria were investigated. The exact values of the preparation parameters and explanation of samples names are presented in Table 1.

Table 1
Manufacturing parameters and sample nomenclature explanation.

Name of the sample	T1600	T1650	S1600	S1650
Sintering temperature (°C)	1600	1650	1600	1650
Heating rate (°C/min)	3	3	5	5

2.2. Sample characterization

Prior to SEM investigations, each sample was mechanically polished using grinding paper up to 2000 grade to obtain a smooth surface adequate for further EBSD analysis. Specimens were investigated using the SEM (Quanta 3D FEGSEM, FEI) equipped with the EDAX Trident system comprising of silicon drifted detector (SDD) for microanalysis and Hikari camera for EBSD measurements.

The chemical composition of specimens was determined by the EDS technique. Measurements were carried out in the SEM under low vacuum conditions with water vapor in the microscope chamber at a pressure of 0.45 Torr. A precise chemical composition evaluation of Zr and Y based on their *L* lines series was difficult due to the fact that their peaks overlap in this energy range. In order to excite zirconium and yttrium *K* lines, the accelerating voltage of the electron beam was set to 30 kV. Two-dimensional EBSD measurements were carried out at 20 kV. Inverse pole figure (IPF) maps were collected from 30 × 30 μm areas with a square grid pattern and the 100 nm step size. Phase identification was carried out by X-ray diffraction using a Bruker Phaser D2 X-ray diffractometer, with an energy dispersive XFlash detector and Bragg–Brentano geometry, using Cu Kα irradiation. An estimation of the grain size was made by the Rietveld method using the MAUD software.

2.3. Sample preparation for 3D-EBSD measurements

Prior to 3D-EBSD measurements, a conductive layer of gold was sputter-coated onto the sample surfaces, both on the cross section of the cylinder and the side walls. Subsequently, ion beam milling was used for final polishing of selected areas to prepare surfaces adequate for EBSD experiments. The region chosen for 3D-EBSD measurements was located near the edge of each sample to provide easy access to two perpendicular surfaces. In the chosen area, the conductive gold layer was milled away and flat, smooth surfaces were prepared on both sides of the edge. The dimensions of the milled areas were 30 × 30 μm on each side of the samples. During the preparatory milling 30 kV gallium ions were used and the applied beam current did not exceed 15 nA to avoid beam damage of the ceramics. Such procedure resulted in very good EBSD pattern quality acquired during the measurements. Though the conductive coating was sputtered away from the chosen region, the gold layer covering the adjacent area removed the electron beam induced charge.

2.4. 3D-EBSD measurements

During 3D-EBSD measurements, milling was performed using the 3 nA beam current. This value was a compromise between an acceptable time for milling and surface quality. At higher beam currents, milling time could be shorter but at the cost of side effects such as 'curtaining' resulting from anisotropic sputtering rates. Gallium ions cut the sample surface at a grazing incidence angle to mill smooth slices with well defined thickness accuracy. The secondary electron (SE) image of the analyzed area with a marker indicating position of the region of interest (ROI) is shown in Fig. 1. An additional amount of material was milled away from both sides of the region of interest to avoid shadowing by trench edges, which are formed during subsequent removal of the series of slices. The electron beam current (8 nA) was optimized to reduce charging effects in the investigated area. The diffraction acquisition rate of the Hikari camera was set to 50 frames per second. The dimensions of the region from which the EBSD patterns were recorded, were 12 × 12 × 12 μm. However, the volume which was milled away was 50 μm wide, 30 μm high and 12 μm deep to eliminate shadowing. Sets of 120 consecutive slices were milled away, each 100 nm thick.