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Three-dimensional microstructural characterization of porous cubic zirconia

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ABSTRACT

A set of cubic zirconia samples were investigated using 3-dimensional electron backscatter diffraction (3D EBSD) to analyze the grain structure, grain boundary networks and pore morphology. 3D EBSD is a variation of conventional EBSD, whereby a focused ion beam (FIB) is used in a dual beam scanning electron microscope (SEM) i.e. FIB–SEM to mill away material and to create 'serial sections' through the material being analyzed. Each new surface revealed is subject to an EBSD scan, which continues sequentially until a desired volume of material has been removed. In this manner, many consecutive 2D EBSD scans can be rendered in 3D to gain a greater insight of microstructural features and parameters.

The three samples were examined in order to determine the effect of differences in the manufacturing process used for each. For each sample, a volume of ca. 15,000 μm^3 was studied. The analysis of several microstructure parameters revealed a strong dependence on manufacturing conditions. Subsequently, the results of 3D EBSD analysis were compared to conventional 2D EBSD. Significant differences between the values of microstructure parameters determined by 2D and 3D EBSD were observed.

1. Introduction

Three-dimensional electron backscatter diffraction (3D-EBSD) is based on incorporating a focused ion beam (FIB) column into a conventional scanning electron microscope (SEM). Such instruments are thus referred to as FIB–SEMs. The measurement is carried out by repetitive iteration of two basic steps: cross-section milling using the ion beam and acquisition of orientation data using the electron beam (Uchic et al., 2011; Konrad et al., 2006). The method is applied to comprehensive microstructural analysis of various materials based on information about local crystallographic orientation (Zaefferer et al., 2008; Bastos et al., 2008).

FIB serial sectioning can be applied to various kinds of materials, metals, ceramics and even organic ones (Zankel et al., 2014; Peddie and Collinson, 2014). One of the first attempts to apply the 3D-EBSD technique to ceramics reported by Dillon and Rohrer (2009a) showed the possibility to conduct such measurements on non-conductive samples. Wilson et al. (Wilson et al., 2011; Wilson et al., 2009; Chen et al., 2011) carried out comprehensive research on zirconia-based composites in three dimensions. However, only the backscatter electron (BSE) signal was used to distinguish different phases. Crystallographic characterization of grain boundaries in bulk yttria and yttria stabilized zirconia by use of FIB–SEM was presented in (Helmick et al., 2011; Dillon and Rohrer, 2009b). A successful measurement on a series of bulk zirconia samples were performed by Bobrowski et al. (2014), however the investigated volumes of material (1000 μm^3) were insufficient for reliable statistical analysis. In this paper we present the data acquired from significantly larger regions of interest (ROI) (ca. 15,000 μm^3), comparable with the largest datasets reported in literature so far (Zaafarani et al., 2006; Zaefferer et al., 2008), followed by statistical characterization of the material based on calculations of several microstructural parameters.

Among the most important parameters required for a complete characterization of a microstructure of polycrystalline material, either bulk or porous, is the size and shape of grains and voids, as well as the areas of interfaces and grain boundaries. Some of these parameters (e.g. grain size) can be calculated based on 2D experimental data, while the others (e.g. areas of interfaces) can be estimated by 3D analysis only. In the case of the parameters which can be obtained from both 2D and 3D measurements, it is important to evaluate whether they yield comparable results. An experimental 3D analysis is an attractive tool to verify the accuracy of stereological methods extrapolated from 2D data sets. To compare the results obtained from 2D and 3D analyses, the microstruc-

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Table 1
Manufacturing parameters and sample nomenclature explanation.

Name of the sample	T1600	T1650	S1600
Sintering temperature [°C]	1600	1650	1600
Heating rate [°C/min]	3	3	5

tural parameters should be reduced to the same dimensions. For example, grain volume and grain area can be reduced to equivalent sphere and circle diameters (ESD and ECD). However, this can only be done assuming that material is composed of equiaxed grains which can be approximated by round shapes (Underwood, 1970). In case of grain boundary length in 2D and grain boundary area in 3D, both values can be reduced to grain boundary density by normalizing them with respect to the investigated area and investigated volume for the 2D and 3D cases, respectively.

The most common method to distinguish various phases in the SEM is based on the BSE signal. In our previous paper we proved that it is also possible to analyze porous microstructures using the Image Quality (IQ) parameter of electron backscatter diffraction (Bobrowski et al., 2014). The IQ parameter (Kunze et al., 1993) is very sensitive to various surface irregularities such as voids or scratches. It can be also used for precise identification of pores in the material. An important feature of such an approach is the fact that IQ values are stored in the same files as EBSD orientation data and have the same spatial resolution as EBSD and do not require any alignments of the experimental data, as opposed by BSE images acquired before or after EBSD mapping runs, which may be subject to sample drift.

2. Experimental procedure

2.1. Material

Ceramic powders were produced by using the hydroxide co-precipitation method in ammonia solution, from $ZrOCl_2$ and YCl_3 precursors. The substrate solutions differed by concentration leading to gels with different morphologies. Hydroxide mixtures were calcined at 500 °C. Subsequently, powders were densified at different heating rates and maximum sintering temperatures. The soaking time was 2 h in each case. The obtained samples were cylindrical with 10 mm in diameter and 1 mm of thickness. X-ray diffraction and energy dispersive X-ray spectroscopy (EDS) results reported in our previous paper (Bobrowski et al., 2014) showed that the samples contained a solid solution of cubic zirconia with an additive of ca. 9.5 mol% of yttria. The manufacturing parameters and sample nomenclature is given in Table 1.

2.2. Experimental procedure

Two-dimensional EBSD measurements were performed in low vacuum (LV) conditions at pressure of 0.45 Torr using a Hikari camera (a part of the EDAX Trident system attached to FEI Quanta 3D FEG-SEM). The energy of electron beam was set at 20 keV. Diffraction patterns were collected at rates of 50–100 fps using background subtraction and intensity normalization for image processing. Orientation maps were collected from 75×75 μm areas with a square grid pattern and 250 nm step size. Pore related microstructure parameters were derived from BSE images acquired from the same regions as the EBSD maps with a pixel size of 58.3 nm (step size for 2D analysis of porosity).

Before 3D data collection, all samples were sputter-coated with gold to obtain conductive layers both on the cylinder side walls and their base surfaces. Subsequently, ion beam milling was applied to prepare regions for 3D experiments located at the edges of the samples. Sputtering of the gold conductive layer from the analyzed areas did not cause any charging in the analyzed regions. The 3D-EBSD measurements were carried out in high vacuum mode due to the fact that FIB cannot operate in LV conditions. During the measurements, samples were milled using a 30 kV ion beam at 5nA. Such a value was a compromise between the surface quality required for EBSD measurements and reasonable milling rate. Additional material was sputtered away from both sides of the analyzed region to prevent 'shadowing' – obstruction of the signal recorded by the EBSD camera. The parameters of the electron beam were set at 20 kV and 8nA, sufficient to minimize the charging effect whilst sufficiently adequate to obtain indexable diffraction patterns. The acquisition rate of the EBSD camera was set 100 fps. Dimensions of the region from which the EBSD data collection took place were $27 \times 27 \times 25$ μm. Sets of 100 consecutive slices were milled away, each of 250 nm thickness. The EBSD data was acquired based on a square grid pattern with a step size of 250 nm.

2.3. Data processing

The acquired experimental data was processed using the OIM Analysis 5.0 and Dream 3D 4.2 software (Groeber and Jackson, 2014). Additionally, Amira5 Resolve RT and ParaView software were applied for visualization purposes. The EBSD maps were cleaned with minimum grain size of 10 adjacent pixels and orientation angle threshold equal to 2°. Subsequently, maps were stacked, aligned and cut to obtain a $25 \times 25 \times 25\ \mu m^3$ data volume with smooth external surfaces. The grain boundary reconstruction was performed using a 'marching cube filter' implemented in the Dream 3D program. The structure of pores was derived from IQ maps.

Stereological analysis was carried out using the same 2D-EBSD data set to facilitate identification of grain boundaries. For each sample, 20 randomly distributed horizontal and vertical lines were drawn to measure intercept lengths. According to the formula:

$$S_V = 2 \times P_L \quad (1)$$

grain boundary density in 3D volume (S_V) is proportional to the number of intersection points (P_L) between boundaries and randomly drawn lines of given lengths.

3. Results

3.1. Two-dimensional analysis

Two-dimensional EBSD data is shown in Fig. 1 as inverse pole figure (IPF) maps. Misindexed pixels with low IQ values seen as black spots in the maps were attributed to pores. The IPF maps revealed that the samples contained equiaxed, polygonal crystallites. The number of grains identified within the scanned areas varied between 589 and 733 for the T1600 and S1600 samples, respectively (Table 2). Crystallites located at the boundaries of the ROI were excluded from calculations as they could bias the analysis results. Grain areas were calculated by counting pixels attributed to each grain. Average grain areas presented in Table 2 were calculated as average values of log-normal distributions. The obtained values varied between ca. 8.5 μm^2 for both 'T' samples and 6.95 μm^2 for the S1600 sample. For a better comparison the grain areas were converted into ECD. The obtained ECD values were in the range from 2.85 μm to 3.26 μm for the S1600 and T1600 samples, respectively (Table 2). The T1650 sample sintered at the highest temperature contained the largest crystallites, although the average grain size for the T1600 sample was only slightly lower. The noticeably smaller grain size found in the S1600 sample was probably due to higher heating rate during manufacturing process.

For the calculation of grain boundary densities based on 2D data, boundaries were reconstructed as boundary segments separating particular grains in EBSD maps. Firstly, boundary segments