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Predicting grain size distributions in perovskite-structured Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ oxygen transport membranes

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Abstract

This study is conducted over a 3×3 time-temperature matrix on Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ (BSCF) ceramics, and sintered bodies above 93% dense are obtained. The electron backscatter diffraction (EBSD) band contrast micrographs of the polished sintered samples are analysed for characterising the grain size distributions. This study develops an algorithm for predicting the grain size distributions (GSDs) of BSCF dependence of sintering condition (time and temperature). In addition, the GSDs predicted by the algorithm agree reasonably with those experimentally observed. When individual grain size is nondimensionalised by the median grain size, the GSDs data of all BSCF samples reduces to a single
self-similar GSD curve. The median grain size is predicted by the classical kinetics equation, $D^n = tK_0 \exp(-Q/RT)$.

Keywords: BSCF; Grain growth kinetics; Grain size distribution; Microstructure

1 Introduction

Mixed ionic and electronic conducting (MIEC) materials have attracted great attention to be studied due to their application in oxygen separation [1, 2] and solid oxide fuel cells [3, 4]. Among these MIEC materials, the perovskite-structured Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ (BSCF) was found to be a promising material for oxygen permeation[5]. Generally, the oxygen permeability of ceramic membranes highly depends on many factors, including compositions, thickness, microstructure, and temperature[6]. Many studies have shown that the permeability of the membranes was greatly influenced by grain size. For example, the oxygen permeability of SrCo$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ increases significantly with decreasing grain size, because grain boundary hinders the transfer of oxygen ions[7]. However, the permeability of SrCo(Fe,Cu)O$_{3-\delta}$[8] and Ba$_{0.5}$Sr$_{0.5}$Fe$_{0.3}$Zn$_{0.2}$O$_{3-\delta}$ [9] materials increase with increasing the average grain size. In the case of BSCF, Arnold et al. [10] have reported that the permeability increases with decreasing the average grain size. On the contrary, Wang et al. have reported the permeability increases considerably with increasing average grain size[11]. Other properties of polycrystalline ceramics also highly depend on the
microstructure, so that it is very important in a general sense to fundamentally
understand the microstructural development of ceramics. In the case of electrical
property, it has been reported that the area specific resistance (ASR) of BSCF
materials with nano-scale grain sizes is much lower than those with micro-scale grain
sizes[12]. Although there is no literature to report the influence of grain size on
mechanical properties of BSCF, fracture stress and fracture toughness were highly
related to grain size for some other ceramic materials[13]. For example, the strength
of Ti$_3$SiC$_2$ increases with decreasing the average grain size in the temperature range of
25 °C to 1300 °C[14] and fracture toughness of Si$_3$N$_4$ with broader grain size
distribution was higher than that with narrower one due to crack deflection[13].
Therefore, the properties of ceramics can be modified by these microstructural
characteristics.

For most of these works mentioned above, an average grain size obtained from
scanning electron micrographs is usually determined by the lineal intercept
technique[15]. Image analysers are normally being used to quantify the grain
sizes[16]. The average grain size thus measured was used to analyse an activation of
the kinetic parameters of BSCF grain growth, namely the apparent activation energy
and the kinetic grain growth exponent. These parameters can be determined from the
following equation[17]

\[ D^n = K_0 t \exp\left(-\frac{Q}{RT}\right) \]  (1)
where $D$ is the average grain size ($\mu$m) after sintering the specimen for time $t$ at $T$

temperature; $Q$ the apparent activation energy; $n$ grain growth exponent; $K_0$ is a
constant; $R$ the gas constant; and $T$ the absolute temperature.

In this way, only an average grain size representing the multitude of grains of sintered
bodies is related with the sintering time-temperature conditions. However, the sintered
bodies normally have a wide distribution of grain sizes. In other words, larger grains
and smaller ones exist at the same time. Therefore, how grain size distributions in a
ceramic body influenced by the sintering time-temperature schedule need to be
investigated.

As introduced above, grain sizes and their distributions in sintered bodies are worthy
studying. To the best of our knowledge, there is no relevant report about the
prediction of BSCF grain size distributions because of the challenge in preparing
appropriate samples for image based analysis. In order to attain a deeper
understanding of grain size distributions of BSCF materials, the parameters of grain
growth kinetics used to predict its grain size distributions and the requirement for
tailoring ceramic microstructures, the present study was conducted with the technical
support of electron backscatter diffraction (EBSD) to fulfill the accurate grain size
and grain boundary determination without special sample preparation process, like
chemical or thermal etching (> 800 °C) which could introduce the error in grain size
in forms of unexpected grain boundary damage or grain growth during the etching
process.

2 Experimental procedure

Ba₀.₅Sr₀.₅Co₀.₈Fe₀.₂O₃₋₈ powders were supplied by Treibacher Industrie AG, Austria. The powder was packed in a cylindrical stainless steel die with a diameter 28 mm, and uniaxially pressed under a pressure of 100 MPa. The BSCF samples were sintered as the following 3×3 temperature-time matrix. The sintering temperatures were 1075°C, 1100°C and 1125°C and the dwell times were 5, 10, and 24 hours. The heating rate and the cooling rate during the process of sintering were set to 180°C/hour. The relative densities of all the BSCF samples determined by the Archimedes method in distilled water were over 93%. The samples were then ground using several different sizes of SiC grinding papers from P400 to P1200, and then polished with diamond paste descending from 6 μm to 0.25 μm. The colloidal silica was used for 15 minutes in the final polishing stage. The phase composition of all the BSCF was determined to be a single cubic phase by X-ray diffraction. Grain sizes were analysed by scanning electron microscopy (SEM; Quanta FEG-650, FEI) equipped with electron backscatter diffraction (EBSD, NordlysNano, Oxford Instruments). The grain size was analysed by EBSD method using the area counting technique. To be more specific, the diameter was calculated by the equivalent area (D = \( \sqrt{\frac{4S}{\pi}} \)). A large number of grains were analysed to ensure that a representative average value could be measured for the samples.
3 Results and discussion

3.1 Comparing the grain size distributions in the sintered BSCF ceramics

Figure 1 shows the EBSD band contrast micrographs of the same sintered samples at two different fields. It can be clearly inferred that microstructural features in these two fields are very similar in appearance. Figure 2 shows the relationship between the cumulative frequencies of the grain undersize against the grain size for the two electronic micrographs of Figure 1. It is clearly observed that the microstructures exhibit a close quantitative match. The overlap of grain size distributions in Figure 2 proves that the grain size analysis by EBSD method is repeatable and reproducible. This indicates that EBSD method is suitable for making further analysis in this study.

Figure 3 shows the grain size distributions of the sintered samples obtained under various sintering conditions. These four plots were selected because they were reasonably far apart from each other, making it possible clearly distinguish the data points. It is clearly evident from the plots presented in Figure 3 and Figure 4, that, whereas the shape of the grain size distribution profile of each curve remains essentially similar, the grain size distribution curve shifts toward the coarser end of the size profile as a function of prolonging dwell time and/or increasing temperature. Then, it is possible to give basically the same grain size distribution under appropriate
conditions for different combinations of time and temperature. It can be inferred from Equation (1) that the combination of a high sintering temperature and short dwell time would give the same average grain size and grain size distribution as that of a relatively lower temperature and longer time.

Unexpectedly, even within the inadequate number of the sintered bodies, this provisional study was demonstrated experimentally. Figure 5 shows that the EBSD band contrast micrographs of microstructures of the sintered bodies under different conditions look visually similar. It has been demonstrated that the grain size distributions of these two samples in Figure 5 are plotted similarly, as shown in Figure 6.

3.2 Self-similar grain size distributions in sintered BSCF

It is noted above that while the plot profile tends towards a coarse grain size range during grain growth, the shape of the grain size distribution profiles remain similar in Figure 3 and Figure 4. When the grain size distributions of these samples are replotted based on a nondimensionalised size, defined as the median size of the individual distribution, several plots are obtained as shown in Figure 7. Grain size distributions with this characteristic are regarded as self-similar size spectra. Self-similar characteristics suggests that the same dominant mechanism governs grain growth kinetics[16].
For the grain size distribution curves in Figure 7, the nondimensional grain size is defined as \[X = \frac{x}{x_{0.5}}\] (2) where \(X\) is the defined dimensionless grain size corresponding to the grain with a size \(x\) (\(\mu m\)), and is the number-based median size (\(\mu m\)) of the distribution.

Figure 7 shows the dimensionless grain size distributions for the data obtained under different sintering conditions. As replotted in this way, the different GSD curves shown in Figure 7(A) and 7(B) overlap into a single curve in Figure 7(C) and 7(D), respectively. Thus, the standard of self-similarity can be used in sintered bodies as well, which are consisting of numerous connected grains arranged in this system[16].

As aforementioned the dominant grain growth mechanism in the systems with self-similarity, this implies that the appropriate time-temperature region for normal grain growth can be predicted. Self-similarity for ceramics during grain growth has been reported. For example, Burke et al. [18] have reported that the shape of the grain size distribution curve does not depend on the grain size. Self-similar grain size distributions suggest that the nondimensional grain size distributions in sintered bodies for the BSCF ceramics are irrespective of the sintering histories. It can be inferred that with respect to the width of the distribution, the ratio of the largest grain to the smallest grain can be irrespective of the sintering history. Therefore,
self-similarity has important implications, although a limited range of sintering conditions are used in this study. First, when the sintering temperature-time programmes are changed, it is accompanied by translation of the whole grain size distribution plot horizontally along the temperature axis rather than shifting any point in the plot. Second, the single measurement of any distribution, specifically its median size, can predict the entire grain size distribution if the characteristic self-similarity and grain size distributions plots have been already obtained. This phenomena is also observed in alumina[16].

3.3 Predicting the complete GSDs using a kinetics approach

Therefore, the object of predicting the grain size distribution is simplified to that of obtaining the median sizes as a function of the sintering condition. Then, the predicted median size is multiplied by the dimensionless grain size in the self-similar GSD curve, the complete GSD of BSCF are obtained.

(1) Time dependence

Figure 8 shows the time dependence of the grain-growth kinetics as given in Equation (1). The slopes of these three lines are around 0.33. It indicates that the value of grain growth exponent is 3. This means that the value n of grain growth exponent equals 3, which is consistent with that obtained by other groups (n=3.1)[19] and other related
perovskite-structured materials such as PrBaCo$_2$O$_{5+δ}$ (n=3) sintered at 1150°C from 6 to 48 hours[17].

(2) Temperature Dependence

According to the Equation (1), a plot of the logarithm of the median versus the reciprocal of the sintering temperature (K) should give a straight line having a negative slope and the activation energy is determined by the slope of the curve. Figure 9 shows the Arrhenius plot for the temperature dependence of grain growth. For the sintered BSCF ceramics, the activation energy (Q) for the grain kinetics in was calculated to be 583.6±15 kJ/mol from the Arrhenius plot. Although Salehi et al.[20], Baumann et al.[21] and Yoon et al.[22] have not reported activation energies for grain growth of BSCF, analysing their data yields activation energies in the range from 372 to 741 kJ/mol as plotted in Figure 9(B), which fairly agree with the result in this study.

3.4 Grain size distributions-predicted versus experimental

As discussed above, the procedures for predicting the grain size distributions are developed as the following: (1) Produce the dimensionless GSD plot from the selected sintering experiments under different sintering conditions; (2) Calculate the activation energy (Q) for the grain growth from the Arrhenius-type equation and estimate the
grain growth exponent (n); (3) Estimate the median size of the GSD at any preset
sintering condition using the expression, \( D^r = tK_0\exp(-Q/RT) \); (4) Develop the
nondimensional grain size in the self-similar plot by the calculated median size. The
plot will give the predicted GSD curve of BSCF sintered under particular condition.

Figure 10 shows that the GSDs predicted using the algorithm was in good agreement
with that experimentally obtained under different time-temperature conditions. This
suggests that the algorithm can be used for predicting the grain size distribution of
BSCF.

4 Conclusions

This study is conducted on BSCF ceramics with densities above 93%, and the
experimental condition covers a 3×3 time-temperature matrix. All the data regarding
grain size distributions is analysed from the EBSD band contrast micrographs of the
polished samples. Subsequently, based on the processed data from the experimental
range, an appropriate prediction of the grain size distribution with respect to
temperature and dwell time is made. All the important conclusions of this study are as
follows:

(1) A combination of higher sintering temperature and shorter dwell time gives GSDs
the similar with those acquired from a combination of relatively lower
temperature and longer time for the investigated BSCF system.
When the individual grain size is nondimensionalised by its median size, the several nondimensional grain size distributions curves reduce to a single self-similar profile. Additionally, the grain size distribution curves shift toward the coarser end of the size profile as a function of prolonging sintering time and/or increasing temperature.

The grain growth exponent $n$ is determined to be 3. The activation energy for grain growth of BSCF is calculated to be 583.6 kJ/mol by an Arrhenius equation.

Based on these observations, an algorithm is proposed for predicting the complete grain size distribution as a function of the sintering time-temperature plot, and the prediction of GSDs agrees reasonably well with those experimentally obtained.

These conclusions above are useful for predicting the grain size distribution with limited experiments and valuable information is provided for designing the microstructure of BSCF materials.

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Figure 10

Cumulative frequency undersize

Symbols: Experimental
Lines: Predicted

Log(grain size/μm)
Figure 1 EBSD band contrast micrographs of the BSCF samples sintered at 1100°C for 10 hours with two different fields show similar morphology.

Figure 2 Grain size distributions for Figure 1 show the results with reproducibility.

Figure 3 Grain size distributions of BSCF having various sintering conditions expose similarity of the profile shapes.

Figure 4 Taking every tenth point of the data in Figure 3 was replotted in the distribution.

Figure 5 Scanning Electron micrographs of two BSCF samples sintered at different time-temperature conditions showing similar micro-structural features (A)1075°C-24 hours; (B)1100°C-10 hours.

Figure 6 Measured grain size distributions for the two SEM micrographs of Figure 5 are similar.

Figure 7 Comparison of normalised grain size distributions for different sintering conditions.

Figure 8 Time dependence of grain growth kinetics at three different temperatures (1075 °C, 1100 °C, and 1125 °C).

Figure 9 Arrhenius plot for grain-growth kinetics for BSCF specimens sintered at different conditions.

Figure 10 Experimental and predicted GSDs for BSCF sintered at different conditions.