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Evolution of anisotropy in hierarchical porous ceramics during sinter-forging

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ABSTRACT

When a body is sintered under non-hydrostatic stress (or strain) fields, anisotropic microstructures may develop which would have an impact on the performance of sintered products. In this study, we focus on the development of pore shape anisotropy during sintering forging. Several parameters were used to characterize the anisotropy of both intrinsic (small inter-particle pores) and extrinsic (large pores from the burnout of pore-formers). The effect of applied stress on grain growth was also investigated. As expected during sinter forging, the pore shape becomes anisotropic and the pores orient preferentially. The intrinsic pores preferentially align parallel while the extrinsic pores align perpendicular to the applied stress. For both intrinsic and extrinsic pores, the degree of anisotropy increases with applied stress, reaches a maximum and then decreases with further increase in stress. Applied stress leads to finer grain microstructures at a particular density. Possible explanations are proposed to explain these observations.

1. Introduction

Hierarchically porous ceramics are used in a variety of well-established and emerging applications, such as energy conversion and storage, metal filtration, gas separation membranes, catalysis, and refractory insulation. For many applications, the hierarchical microstructures have enhanced properties compared with single pore size porous materials due to the ability to optimize both properties that require large pore size (e.g., gas and liquid transport) and those that require small pore size (e.g., surface chemical reactions) [1]. In some of these applications, the ceramic is processed under an applied stress or in a constrained geometry (e.g., sintering of multilayered ceramics or sintering of coatings on substrates). In these approaches, either a non-isotropic stress or non-isotropic strain field is imposed on the sintering bodies. The densification under these conditions has been extensively studied (e.g., [2–8]). A continuum theory of sintering has been developed to predict sintering under these conditions with contribution by several research groups and has been periodically reviewed [9–14] Experimentally, for porous ceramics with only intrinsic pores, the application of external stresses during sintering and constrained sintering has been shown to lead to an anisotropic microstructures especially in the final stage of sintering [15–20]. It has been suggested that the non-uniform strain/stress can cause directional diffusional fluxes in sintering body and lead to elongated pores. However, the evolution of such anisotropy during the entire sintering cycle has not been well documented and is one of the focal areas of this study.

Both continuum and multi-scale approaches have been developed to analyze and simulate the anisotropic microstructures [21–24]. In Ref. [25], the formal equivalence between the two important experimental situations that lead to transversely isotropic microstructures, viz. sinter-forging and constrained sintering, was established. However, the predictions and fidelity of these approaches have not been rigorously tested.

It should also be noted that the size dependence of the pore shrinkage kinetics has been reported for free sintering and isostatic pressing of various materials [26–32]. For non-isostatic pressure-assisted sintering processes the relationship between the pore sizes and their evolution should be associated not only with the change of their volume, but also with their shape. This fact renders the possibility of the pore texture/pore orientation–based structure anisotropy imposed by sinter forging. The size dependence of this

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kind of anisotropy has not been previously studied and is another focal area of this investigation.

Thus, the purpose of this work was to investigate the evolution of anisotropy for porous materials, with both intrinsic and extrinsic pores, during pressure-assisted sintering. Sinter forging was performed on porous ceramics with bimodal starting pore size distribution at different sintering temperatures and stress levels. The evolution of anisotropic pore geometry and the key properties that affect the formation of the anisotropic porous microstructures were investigated. The analysis of these effects is of significant importance for programmable processing of ceramic materials enabling the possibility of final product structure optimization and predictable sintering outcomes.

2. Experimental procedures

The experimental studies were conducted on a standard cathode composition for a solid oxide fuel cell. The porous cathodes were of the standard cathode composition and prepared by mixing 40 vol% LSM ($La_{0.8}Sr_{0.2}MnO_3$) with 60 vol% of 8 mol% YSZ (Yitria stabilized zirconia) [33]. The LSM powder used was LSM20 (NexTech Materials, Lewis Center, OH, USA $d_{50} = 1.10\,\mu m$) and the YSZ had a $d_{50} = 0.32\,\mu m$ (Tosoh USA Inc., Grove City, OH, USA). PMMA polymer particles with a d_{50} of 7.50 μm (Arkema, Cary, NC, USA) were used to generate extrinsic pores. The weighted powders (the amount of PMMA used is based on volume fraction in the fully dense composite cathode) for the desired compositions were wet ball milled and dried on a hot plate at temperature of 373 K. Cylindrical samples (diameter 12.75 mm and height 12 mm) were made by uniaxial pressing the crushed dried powders at a uniaxial stress of 200 MPa.

The sinter forging experiments were performed in a MTS loading frame (MTS Systems Cooperation, MN, USA) equipped with a high temperature furnace (temperature ranging from 293 to 1873 K). Uniaxial compression tests were performed in air from 1473 to 1573 K with stresses in range of 0–12 MPa. Sapphire disks were used to avoid direct contact between the specimen and SiC push rods. The temperature was increased from room temperature to 673 K at a heating rate of 10 K/min, held at 673 K for 30 min to burn out the binder and pore former (if any), and then increased to the final temperatures at 10 K/min followed by 90 min isothermal hold. The samples were then cooled to room temperature at 10 K/min. The compressive stress was applied when the temperature was 50 K lower than T_{max} and released at the end of the isothermal. The relative density of a sintered specimen was measured by Archimedes method and averaged for three samples processed under identical conditions.

For microstructure observation, the sintered specimens were cut in two cross-sections parallel and perpendicular to the loading direction, through the center of specimens, and polished down to 1 μm diamond finish. The microstructure was examined on the polished surfaces using scanning electron microscope (JSM 7000, JEOL-USA, Inc., Peabody, MA). Pore size and morphology and grain size were determined, after image processing, using image analysis (NIH Image J National Institutes of Health, Bethesda, MD, USA). The average grain size of sintered body was calculated using the linear intercept method with a conversion factor of 1.56 [34] for approximately 200 grains per sample. Note grain size measurement is complicated by a number of factors, such as 3-dimensional size of the grain is not constant, grain shape varies, and grain shapes can be distorted by processing procedures. However, in most cases, the grains observed on a polished cross-sectional plane exhibit a range of sizes around a central mean and individual measurements of intercept lengths (or grain areas) exhibit a normal distribution, thus the mean value of the grain size is representative.

3. Microscrutural parameters to quantify anisotropy of pores

Evolution of intrinsic and extrinsic pores during sinter forging was investigated separately. Intrinsic pores are those created due to particle packing in the green stage. They exist in the powder compacts and their size is of the order of the particle size. Extrinsic pores are pores formed from the burn out of fugitive particles (e.g., polymeric pore formers), large voids between agglomerates or formed due to evolved gases. The extrinsic pore size is much larger than the average particle diameter. Microstructures of sintered samples in our experiments have shown that extrinsic pores have pore size larger than 2 μm, and all intrinsic pores size is less than 2 μm. Therefore 2 μm was used as a threshold value to differentiate intrinsic and extrinsic pores in image processing and subsequent analysis.

Based on the microstructure analysis following from Ref. [20], four parameters, average pore angle θ, average pore elongation factor ε, average pore size dm, and pore orientation index k have been used to quantify the anisotropy of pores. Assuming each pore as an ellipsoid with three axes- major axe d_i^{maj}, minor axe d_i^{min}, and $(d_i^{maj} + d_i^{min})/2$, the four parameters are defined as follows: average pore angle θ is an arithmetic mean of the pore angle θ_i (angle between the d_i^{maj} and x-axis (x-axis is perpendicular to the loading direction)). Note the angles from 90 to 180° are mirrored across the loading direction. Average pore elongation factor ε is defined as the arithmetic mean of the aspect ratio of the pores ($\varepsilon_i = d_i^{maj}/d_i^{min}$) weighted by pore volume [20]:

$$\varepsilon = \frac{\sum_i \varepsilon_i d_i^{min}(d_i^{maj} + d_i^{min}) d_i^{maj}}{\sum_i d_i^{min}(d_i^{maj} + d_i^{min}) d_i^{maj}} \tag{1}$$

The average pore size was calculated by the arithmetic mean of $(d_i^{maj} + d_i^{min})/2$ weighted by pore volume and multiplied by the conversion factor $4/\pi$, considering observed surface could be cut from any position of an ellipsoid in a 2-D image.

$$d_m = \frac{4}{\pi}\,\frac{\sum_i d_i^{min}(d_i^{maj} + d_i^{min})^2 d_i^{maj}/2}{\sum_i d_i^{min}(d_i^{maj} + d_i^{min}) d_i^{maj}} \tag{2}$$

and the pore orientation k was quantified by using the angle θ_i [20]:

$$k = \ln\left(\frac{\sum_i \left(\varepsilon_i d_i^{maj}\sin\theta_i\right)^2}{\sum_i \left(\varepsilon_i d_i^{maj}\cos\theta_i\right)^2}\right) \tag{3}$$

The logarithm is used to introduce a difference between vertically and horizontally aligned pores. If $k = 0$, there is no preferential orientation of the pores. When $k > 0$, the pores are preferentially oriented perpendicular to the loading direction, and when $k < 0$ the pores are preferentially oriented parallel to the loading direction. Each parameter was calculated and averaged from 400 to 600 pores in corresponding SEM pictures.

4. Experimental results

4.1. Densification during sinter-forging

The effect of uniaxial stress and temperature on porosity of composite cathodes with 0 and 30 vol% PMMA is shown in Fig. 1.