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Publisher's version / Version de l'éditeur:

<https://doi.org/10.1023/A:1012284522672>

Journal of Porous Materials, 8, 3, pp. 201-210, 2001

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Sintering Effects on the Porous Characteristics of Functionally Gradient Ceramic Membrane Structures

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Received June 9, 2000; Revised November 3, 2000; Accepted November 8, 2000

Abstract. A method to drain cast porous ceramics has been conceived and established, where samples were shown to have a functionally gradient cross-section with a continuously increasing mean particle size between the two principal surfaces.

Ceramic discs approximately 45 mm in diameter, and 3.3 mm thick were cast by sedimentation. These green bodies were dried prior to sintering. Maximum sintering temperature and the length of the sintering soak time were varied for samples made from suspensions of both 5 and 10 volume percent solids. Mercury porosimetry was used to obtain the porosity and pore size distribution in each sample. Additionally, a number of atomic force microscopy (AFM) measurements were made on some samples in order to correlate bulk porous properties with those on the outside surfaces.

The results showed that as the sintering temperature increased, the densification of the bodies proceeded more rapidly. In general, the longer the sintering soak time, the denser the samples became as well. For the samples prepared at the lower temperatures however, the porosity showed less of a soak time dependence. The green body had a clustered and asymmetric microstructure, which contributed to differing degrees of localized densification and coarsening effects depending on the sintering temperature. Densification effects were more pronounced with the samples made from the more concentrated suspensions.

There was an inverse correlation between the bulk and surface pore dimensions, attributable to the different size scales of particles in the two regions. The much finer surface layer particles were able to undergo some amount of densification while surface diffusion sintering mechanisms were primarily at work elsewhere in the structure.

Keywords: ceramic membrane substrate, particle size distribution, functionally gradient material, sintering effects

1. Introduction

For the production of ceramic membranes, a porous ceramic support is typically used as a substrate prior to coating with a thin dense layer of additional ceramic material.

A support structure preparation method by poly-disperse slurry sedimentation has been established, which produces a functionally gradient material [1]. The benefit of creating an asymmetric microstructure is to produce a smaller substrate pore size over a thinner region, thereby imparting superior permeation properties.

The key for achieving asymmetry is to prepare colloiddally unstable or metastable suspensions of a

controlled and broad particle size distribution, encouraging segregation based on particle diameter to occur during consolidation. This produces a functionally gradient, or continuously finer mean particle diameter profile from bottom to top over the cross-section of the consolidated structure.

Progress was made on understanding fabrication parameters for making functionally gradient samples from α -alumina which retained a high porosity after sintering [2]. The dispersion of a small amount of fines throughout the body, promoted through the metastable nature of the suspensions, served as localized sites from which sintering was enabled at lower temperatures. In this way, lower temperature sintering was sufficient to fuse the samples into a contiguous hardened porous structure without substantially densifying them.

It has been shown that the colloidal state and suspension microstructure can be controlled with pH and polyelectrolyte stabilizing additives. This has a direct bearing on the eventual microstructure of the sintered solid object [3, 4]. By controlling the dispersity of a suspension, slight aggregation and/or hierarchical clusters can contribute to overall porosity increases while at the same time retaining a relatively fine pored top surface.

A general goal is to produce a structure (substrate) which should have broad application as an improved substrate for any or all subsequent coating operations. Since this substrate is made functionally gradient by sedimentation casting with a very broad particle size distribution, the resultant functionally gradient pore size distribution can achieve very small diameter pores at the top surface which extend to a relatively thin depth. With such a substrate it is possible to reduce the thickness of defect-free membrane coating layers. Uncoated, the present method has produced top layer pore sizes in the range of 20 to 50 nm, suitable as is for microfiltration or coarser ultrafiltration.

An extensive analysis of membrane support design found that in order to obtain a smooth surface, a homogeneous packing was required, but ultimately at the expense of overall porosity and permeability [5]. Their conclusions suggested adopting a sedimentation technique to produce a functionally graded support. Work by Moritz et al. has produced functionally gradient titania structures with top layer pore sizes in the 5 nm range [6]. In this case however, the presence of sol sized particles necessitated a highly stable colloidal state and centrifugal deposition with a force of 4000 g, thereby

introducing subsequent complications for drying and sintering.

Given the background of the project, the present objectives were to investigate the effect of the sintering profiles chosen for fusing the structures. Using a sample preparation route known to produce functionally gradient structures, maximum sintering temperatures and soak times were to be varied to assess these effects on the microstructural evolution of the pores. Mercury porosimetry was available for bulk characterization, while atomic force microscopy (AFM) was selected for characterizing the surface pores. Analysis of the results should provide guidance for designing sintering profiles to preserve a highly porous structure, while also allowing the pieces to fuse to a sufficient extent to provide serviceable material strength. Further, with clustered fine powder, densification, coarsening and pore growth can all occur under sintering. The data set should help in selecting a sintering profile that best manages these competing effects, given that the desired fused product is intended as a filtration medium.

2. Experimental

An α -alumina powder (Ceralox APA-0.2) known to drain cast into a functionally gradient cross-section was chosen for this work. This powder has a specific surface area of 40.0 g/m², and a broad diameter range from about 0.05 to over 5 μ m. The powder is in the form of aggregates of quite fine particles. Distribution measurements and characteristics are given in more detail in [2].

2.1. Sample Preparation

Aqueous alumina suspensions were prepared at solids loadings of 5 and 10 volume percent solids (v/o). A steric effect was provided by the addition of an ammonium polymethacrylic acid electrolyte (NH_4^+ -PMAA⁻) of molecular weight of approximately 15,000 (Darvan C, R.T. Vanderbilt Co. Inc., Norwalk, CT). The stabilizing influence of this polyelectrolyte is described by Cesarano and Aksay [7]. Additionally, it has been reported that the adsorption of long PMAA chains on alumina inhibits particle contact during drying, resulting in a higher structural porosity [8]. This is an attractive feature in the fabrication of a filtration medium.

Figure 1. Sintering time—temperature profiles outlining the experimental space under consideration.

Polyelectrolyte was mixed with about 90% of the required water (distilled) at a concentration of 1.0 mg/m^2 of powder. The alumina was slowly added under continuous stirring. The pH was then adjusted to 3.0 with concentrated HCl and the remaining volume to make the required solids loading was provided by adding the necessary amount of distilled water.

The ceramic structures were then produced by sedimentation. They were drain cast into the form of flat discs, in 45 mm diameter tube sections over milled gypsum slabs. The discs were cast to a thickness of 3.3 mm. Prior to sintering, the green bodies were dried in an oven at 50°C . The sintering ramp and soak profiles followed in the experiments are shown in Fig. 1. A brief soak period at 850°C (prior to any morphological change in the alumina) was included to allow organic burnout.

2.2. Porosimetry

To investigate the pore size distribution of the sintered ceramic structures, mercury porosimetry measurements were done with a Quantachrome Pore Master 60 porosimeter. A pore size distribution representing the bulk properties of the entire cross-section was obtained for each sample. The ceramic disc was cut into small pieces with a water-cooled diamond saw. The

pieces were dried at 100°C . A porosimeter penetrometer volume of 3.9 cm^3 was used.

2.3. Atomic Force Microscopy

An atomic force microscope (Nanoscope IIIa, Digital Instruments) [9] has been used for measurement of surface topography, roughness and pore characteristics. The AFM is a powerful tool for high-resolution imaging and analysis of ceramic materials due to its minimal requirements for sample pretreatment. It utilizes an extremely sharp tip at the end of a cantilever to track the surface during raster scanning of a sample attached to a piezoelectric ceramic material. A laser reflected off the back of the cantilever is sensed by a detector and used to recreate the three-dimensional surface topography from the motion required by the piezo to keep the force between the tip and sample constant. All surface property evaluations were done on $50 \times 50 \mu\text{m}$ images.

2.4. Experimental Design

A set of experiments was organized to compare the microstructure of samples prepared from colloiddally metastable suspensions at solids loading of 5 and 10 v/o. Samples were prepared at maximum sintering temperatures from 1150°C to 1250°C , and with soak times

at these maximums ranging from 30 minutes to 5 hours. An overview of all the samples tested is shown in Fig. 1. Each parameter combination listed here was tested in triplicate as a measure of reproducibility.

A number of samples representative of the experimental space were examined by AFM for surface properties.

3. Results and Discussion

The choice of sintering profile has an important influence on evolution of the pore size distribution in a porous ceramic body. While some of these time and temperature effects are well known for bodies made from uniform microstructures, the present study considers asymmetric bodies cast from colloiddally metastable suspensions.

3.1. Bulk Porosity

All of the samples outlined in Fig. 1 were examined by intrusion porosimetry with mercury to determine their overall porosities as well as their pore size distributions. The effects of the two independent variables, the maximum sintering temperature and the total soak time were found to be complex and interdependent, so consequently, the porosity is presented as contours over the experimental range. Figures 2 and 3 show the porosity response surfaces for over 30 different samples prepared from 5 v/o and 10 v/o suspensions respectively. At least three samples were made with each set of processing parameters. The measured variation of both the porosities and the mean pore diameters were within 5% over the entire experimental range. Inspection of the contours shows that the bulk porosity decreases with maximum sintering temperature given a minimal soak time. This porosity decrease effect is much more pronounced with the samples from the more concentrated suspensions. At 1250°C the porosity decreased to a greater extent as the soak time increased, since all the size classes would be active in the sintering process. At 1200°C or less, this strong dependence on soak time is not observed as the sintering process is likely nearly complete for the smaller range of active size classes. Dilatometry experiments with bimodal submicron alumina samples showed that below 1200°C shrinkage did not occur [10]. Thus, the surface diffusion mechanism, with a lower activation energy, may be the only process active at the lower temperature range. Sinter-

Figure 2. Porosity contours over maximum sintering temperature and soak time ranges for samples prepared from 5 v/o suspensions.

Figure 3. Porosity contours over maximum sintering temperature and soak time ranges for samples prepared from 10 v/o suspensions.

ing by surface diffusion does not contribute to any net shrinkage or hence porosity change. In terms of the rate of densification, all samples across the sintering temperature range proceeded at a similar pace. The 10 v/o

samples were seen to be losing porosity more rapidly after about the first hour which could be attributed to their more densely packed state. At a sintering time of zero in both Figs. 2 and 3, the porosities (averaged) of the green bodies from which the samples were sintered were used as input for defining the contours.

Samples made with APA-0.2 have been shown to have some amount of sealed or closed pores in their structure [11]. It is known that mercury porosimetry has its limits in profiling extremely fine pores. In our tests however, pressures beyond which the intrusion volume did not increase were reached much below the maximum intrusion pressure of 60000 psi. In fact, closed pore volume fractions near 10% have been reported in tape cast structures made with a far more monosize powder [12]. Figures 4 and 5 show the sealed porosity response surfaces for samples prepared from 5 v/o and 10 v/o suspensions respectively. The contours start at 0.5 hours on the time scale, since it was not possible to get an estimate of the sealed pore volume for green bodies. From 1150°C to 1200°C, a larger range of the particle size distribution becomes active in sintering, and more of the clustered powder fuses to form sealed pores. At these lower temperatures, the soak time has a minor effect on the amount of sealed pores, as the diffusion effects may have come to an equilibrium. At temperatures above 1200°C, the fraction

Figure 4. Sealed porosity contours over maximum sintering temperature and soak time ranges for samples prepared from 5 v/o suspensions.

Figure 5. Sealed porosity contours over maximum sintering temperature and soak time ranges for samples prepared from 10 v/o suspensions.

of sealed pores decreases initially, but then begins to increase at longer soak times. These effects could be attributed to the hierarchical clusters in the structure undergoing simultaneous densification and pore growth at different rates, arising from the range particle size classes. It has been demonstrated that in the densification of clusters, the inhomogeneous microstructure tends to enlarge cavities during sintering [13, 14]. Pore growth in a higher particle diameter region of the structure would contribute a more marked sealed pore volume increase. These effects would only be observed at the higher temperature end of the experiment, since these elevated temperatures are required to modify the morphology surrounding the larger size classes. In general, the samples made from the 10 v/o suspensions showed a slightly lesser fraction of sealed pores. Structures with higher green densities are more able to sinter without forming closed pores.

Figure 6 shows the effect of maximum sintering temperature on the mean pore diameters in the various structures. In general, as the sintering temperature is increased, it can be said that there is increased pore growth since the samples originated from identical green bodies. Increased soak time at the maximum temperature also served to increase the mean pore diameter. For identical sintering conditions, the samples made from 10 v/o suspensions showed a smaller mean

Figure 6. Mean pore diameter versus maximum sintering temperature, plotted for 5 and 10 v/o suspension concentrations, and the various soak times.

pore diameter, arising from their more compacted green state. The one irregularity in Fig. 6 is for the 5 hour soak time at 1150°C. In this case, the 5 v/o sample reports a finer mean pore diameter, attributable to an

equilibration in the sintered state. The more compact green body from the 10 v/o sample was able to continue sintering for a longer time, such that the resulting grain growth and accompanying pore growth produced a larger mean pore diameter.

A comparison was made of the overall pore size distributions of samples prepared at opposite corners of the experimental space. Figure 7 gives pore size distributions from a 5 v/o sample sintered at 1150°C for 30 minutes, as well as a 10 v/o sample sintered at 1250°C for 5 hours. It can be seen that the characteristics of these distributions are quite different, the former being broad, and with a much higher proportion of fine pores, whereas the latter has a much less significant fines tail and a more monosized peak of larger pores. For a more compacted green body, subjected to higher heat over a longer period of time, grain growth and pore growth will occur to a more advanced extent. In view of the object of fusing a highly porous functionally gradient structure, lower temperatures and minimal soak times to ensure sufficient mechanical strength would be preferred. Pore size distributions for APA-0.2 alumina compacts prepared at denser concentrations (30 to 35 v/o), showed similar tendencies when only the suspension concentration was varied [8]. In that study, the distribution did not narrow to the same extent as in the present work, since they only considered “dried” compacts treated at 600°C, where sintering would not occur. The effect of extended soak times narrowing a pore size distribution has been confirmed elsewhere [15].

Figure 7. Pore size distributions for two samples prepared at opposite ends of the experimental space.

Figure 8. AFM image of 1250°C sintered top surface with 30 minute soak time, made from 5 v/o suspension.

3.2. Surface Properties

The AFM analysis was able to provide some information on the surface properties of some of the samples. The way these properties correlate with the bulk porosity characteristics shed useful light on the utility of a structure as a filtration medium. The surface pores are primarily responsible for what kind of separations can be achieved, and the nature of the bulk pore properties influence the achievable volumetric fluxes across the structures.

Techniques such as SANS have been used in the past to examine surface pores, but such instruments are less readily available and require very smooth surfaces to allow grazing incidence angles to differentiate pore sites [16]. AFM has been used to examine both surface roughness [17], and the surface pore size distribution [18], although in the latter case, the pore sizes were evaluated as a function of measured grain sizes, rather than by a direct imaging method.

Figure 8 is an AFM image of a sample sintered at 1250°C. The area in the view is a $50 \times 50 \mu\text{m}$ square. The relative uniformity of the surface is clearly shown. The surface roughness can be considered to be a measure of the surface grain size. For spheroidal particles, the pore sizes would be on the order of one fifth to one sixth of the grain diameters. For the samples considered in this case, this would put the surface pore sizes in the 20 to 40 nm diameter range. Figure 9 is a plot of a "bearing area" versus a normalized bearing height. What this shows is the fraction of the surface plane that is solid as a function of height, starting at the highest point in the sample region, and continuing downward until a solid signal is recorded at all points in the sample region. Thus, the slopes of these curves are indicative of the morphology of the pore sidewalls. The magnitude of the bearing height would be indicative of the vertical grain count comprising the surface layer. Based on an SEM image (Fig. 10), the surface grain sizes appear to be around 100 to 200 nm, so that the surface layer would be roughly 2 to 3 grains thick.

Figure 9. AFM bearing plot, pore area versus percent surface height.

Figure 10. SEM image of 1250°C sintered top surface with 30 minute soak time, made from 5 v/o suspension.

Figure 11. AFM surface roughness contours over maximum sintering temperature and soak time ranges for samples prepared from 5 v/o suspensions.

Figure 11 shows the surface roughness of the samples as a function of the sintering temperature and the sintering soak time. All samples start from the same green state. The contours show that the surface is smoothed by the sintering process, and that the roughness decreases as sintering temperature is increased, and that it further decreases as the samples are subjected to these temperatures for extended peri-

ods of time. The maximum temperature attained seems to be a much stronger influence on the surface morphology. The surface diffusion mechanism which would act initially in these cases would have less of an impact on surface roughness reduction as it only transfers material without any densification, so that the grain centers do not shift relative to each other. As inter-grain neck sizes increase and curvature based driving forces are reduced, the grain boundary diffusion mechanism comes more into effect. Sintering by grain boundary diffusion will shrink the compact, and pull grain centers closer together, thereby making a more pronounced reduction in surface roughness, which can be seen at longer soak times in Fig. 11. The extent of surface smoothing appears greatest at around 1225°C. At higher temperatures, grain and pore growth arising for long soak times could counteract surface smoothing effects. The surface roughnesses of samples made at 10 v/o were similar but slightly higher than the 5 v/o samples. This would be attributable to a slightly more hindered settling condition in denser slurries, where the metastable colloidal state control is less fine.

In an experiment by Li et al. [19], it was found that a top layer pore diameter range of 100 to 300 nm on an alumina substrate was suitable for requiring only a small number of sol-gel coats to achieve a defect-free membrane for gas separations. A similar set of criteria was specified by Ismagilov et al. [20], with the additional mention of 400 nm as a desired largest defective pore diameter. The present surfaces prepared over most of the temperature and soak times considered fall well within this useful range.

The AFM images were able to show that the surface roughness at the top of the structure decreased with sintering temperature, and even at the lowest temperature had a value of less than 100 nm. These results surpass surface criteria found to be acceptable for much denser supports made with a much finer and more monosized powder [21].

3.3. Functionally Gradient Filtration Media

A positive combination of the surface and bulk porous properties aid in producing a functionally gradient porous ceramic material useful as a filtration medium. The metastable colloidal processing route gives rise to a structure with broad particle size distribution characteristics over most of the domain, the main exception being at the top surface where there are more

uniformly sized fines. In terms of microstructural evolution under sintering it has been discussed that the wider the particle size distribution of starting powder, the larger is the median pore size of a fired membrane [22]. A green compact with a wide particle size distribution contains widely distributed pores. During sintering, the smaller pores are eliminated at a much faster rate than the coarser pores, thereby leaving behind a relatively large number of coarser pores, resulting into an increase in the value of median pore size. Further, coalescence of the finer pores results in the formation of coarser pores, while retaining a similar net porosity. The evolution outlined above is most useful for the bulk region of a support structure of a ceramic membrane, in that permeate channels will be enlarged, thereby enhancing product rate.

4. Conclusions

Experiments showed well known basic results that as the sintering temperature was increased, the densification of the bodies proceeded more rapidly, producing denser samples with longer soak times.

For the samples prepared at the lower temperatures however, the porosity showed less of a soak time dependence. At higher temperatures, a wider fraction of the particles in the structure were active in the sintering, leading to densification in the finer grained regions of the body and some pore coalescence in the coarser regions. In view of these competing mechanisms, the volume of sealed pores reached a minimum at extended soak times.

The green body had a clustered and asymmetric microstructure, which contributed to differing degrees of localized densification and coarsening effects depending on the sintering temperature. Densification effects were more pronounced with the samples made from the more concentrated suspensions.

The AFM measurements indicated a decreasing surface roughness and a decreasing pore density as sintering temperature increased. Given the fine grain sizes in the top layer region of the structures, partially unconstrained surface area reduction during sintering would serve to confound any scope for estimating a pore size based on perceived grain size. While AFM bearing data was able to show that the surface region is on the order of two to three grain diameters thick, SEM images are required for analysis to provide pore size distribution information.

The ensemble of data suggests that short soak times are sufficient for producing a well fused and very porous functionally graded ceramic. At lower temperatures the relative quantity of sealed pores is less, which would provide improved permeate transport properties. Although the surface roughness is suitable for coating operations at the low end of the temperature range, the surface roughness data indicate substantial property improvements above 1200°C. For the particle size distribution considered here, short soak times and maximum sintering temperatures between 1200 and 1250°C will create an acceptable combination of the surface and bulk pore properties.

Acknowledgment

The authors gratefully acknowledge Mr. Jeffrey Fraser of NRC-IMS for his assistance with the SEM work.

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