NRC Publications Archive Archives des publications du CNRC

Sintering effects related to filtration properties of porous continuously gradient ceramic structures

Darcovich, K.; Roussel, D.; Toll, F. N.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. /
La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

Publisher's version / Version de l'éditeur:

Journal of Membrane Science, 183, 2001

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=66f4b689-f809-45ed-8e4a-cc139a39faa7>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=66f4b689-f809-45ed-8e4a-cc139a39faa7>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

Sintering effects related to filtration properties of porous continuously gradient ceramic structures[☆]

K. Darcovich^{a,*}, D. Roussel^b, F.N. Toll^a

^a National Research Council of Canada, Institute for Chemical Process and Environmental Technology,
Ottawa, Ont., Canada K1A 0R6

^b ICAM-Toulouse, 75, av. de Grande Bretagne, 31300 Toulouse, France

Accepted 22 September 2000

Abstract

A single-step processing method has been previously established to prepare porous alumina microstructures by a controlled sedimentation technique whereby fine powder from an aqueous suspension consolidates over a casting slab. Metastable surface chemical control of the suspension properties was able to produce a highly porous flat disc structure with a continuously increasing mean pore size from top to bottom. Formation of this gradient structure was facilitated by using a relatively broad particle size distribution. Top layer pore sizes less than 50 nm have been achieved. Without modification, these structures are suitable for use as ultrafiltration media.

The present work presents a comparison of properties and performance data for samples made with the above mentioned functionally gradient characteristics, to samples made with a more uniform microstructure. The effects of sintering time and temperature were analysed in view of overall porosity, pore size distribution and the extent of densification from the green state. These results are presented along with permeation measurements from a filtration test module. Crown Copyright © 2001 Published by Elsevier Science B.V. All rights reserved.

Keywords: Ceramic support structure; Functionally gradient material; Porosimetry; Permeation and separation tests

1. Introduction

In order to prepare ceramic membranes, a porous ceramic support is typically required as a substrate, which is then coated with a thin dense layer of additional ceramic material. Conventional ceramic support structures are not necessarily designed as membrane support substrates, rather they are simply commercially available porous ceramics. They are typically

made with monosized particles and have a uniform cross-section.

The present research investigates the characterisation of support structures prepared via a polydisperse slurry sedimentation method, which provided a functionally gradient material. The benefit of creating an asymmetric microstructure is to produce a smaller substrate pore size over a thinner region, thereby imparting superior permeation properties.

Specific objectives of this paper were to compare properties of samples made from a set of similarly sized powders, but of different distribution characteristics, so that they would be processed to produce functionally gradient or uniform microstructural

[☆] NRCC No. 42016.

* Corresponding author. Tel.: +1-613-993-6848;

fax: +1-613-941-2529.

E-mail address: kdarc@sg1.chem.nrc.ca (K. Darcovich).

cross-sections. Samples were prepared at maximum sintering temperatures ranging from 1100 to 1300°C. The properties of the samples under consideration are the porosity and pore size distribution of the solid bodies as well as permeation and separation results using various solutes in a crossflow ultrafiltration module. Previous work was able to characterize the physical properties of these samples, but until now, no permeation testing equipment for them had been available.

Previous work has confirmed the viability of this method for preparing functionally gradient samples made from α -alumina which retain a high porosity after sintering [1]. Hardness testing was used to demonstrate that the bodies fused and strengthened without significant densification, and hardness gradients measured across the cross-section reflected a functionally gradient microstructure [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, sufficient to fuse the sample into a contiguous hardened porous structure. SEM images demonstrated the continuously increasing mean particle size across the cross-section of the samples [1]. Porosimetric measurements on horizontal sections of the samples corroborated the previous findings [3].

The key for achieving asymmetry was to prepare colloidally unstable or metastable suspensions of a controlled and broad particle size distribution, encouraging segregation based on particle diameter to occur during consolidation. This produced a functionally gradient, or continuously finer mean particle diameter profile from bottom to top over the cross-section of the consolidated structure. In terms of volume fraction, the continuous particle size distribution of the powder used to make the suspension was coarse-rich.

It has been shown that the colloidal state and suspension microstructure can be controlled with pH and polyelectrolyte stabilizing additives. Relevant stability criteria for systems such as presently under consideration here are available in the literature [4]. The colloidal phase state of a suspension which forms the consolidated green body has a direct bearing on the eventual microstructure of the sintered solid object [5,6]. 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.

2. Experimental

Two α -alumina powders were chosen for this work. They were: Ceralox APA-0.2 which had a broad particle size distribution, and Sumitomo AKP-30 with a narrow particle size distribution. These powders were chosen to produce consolidated ceramic pieces of differing characteristics, a functionally gradient structure with the former, and a more uniform structure with the latter.

2.1. Powder characterization

The particle size distributions of the two powders were determined using a SediGraph 5000E Particle Size Analyzer, which is an X-ray sedimentation device operating in the Stokes regime and giving a cumulative mass percent distribution in terms of spherical diameter. Stable suspensions were prepared using Sedisperse A-12 dispersing agent as the liquid phase. Sedisperse A-12 is a highly purified, non-polar, saturated aliphatic hydrocarbon of viscosity ≈ 4 mPa/s, formulated for dispersing metal oxides. It is supplied by Micromeritics Instrument Corp.

Through differentiating the raw data, the frequency particle size distributions of these powders are shown in Fig. 1. The AKP-30 powder had a specific surface area of $8.6 \text{ m}^2/\text{g}$ and the APA-0.2 powder had a value of $40.0 \text{ m}^2/\text{g}$. Although the mode diameter may be slightly higher in the case of APA-0.2, its very high specific surface area arises because it has a substantial tail of fines in the distribution, and it occurs in the form of aggregates of ultra-fine particles. The values for specific surface area were taken from product technical information provided by the suppliers. The powders were chosen because they have a similar mean sub-micron diameter, but with different distribution characteristics. The APA-0.2 sample has a much broader particle size distribution, which will contribute to a continuously gradient ceramic cross-section for samples prepared by the sedimentation technique. It must be remembered that the distributions shown in Fig. 1 are plotted on a logarithmic axis so that dis-

Fig. 1. Frequency mass distributions of the alumina powder samples.

tributions extending into larger diameters would have their breadth extended exponentially.

2.2. Sample preparation

Aqueous alumina suspensions were prepared at solids loadings of 10 volume percent solids (v/o). A steric effect was provided by the addition of an ammonium polymethylacrylic acid electrolyte ($\text{NH}_4^+\text{PMA}^-$) of molecular weight of approximately 15,000 (C. Darvan, R.T. Vanderbilt Co. Inc., Norwalk, CT), in accordance with a stability map [7]. The required amount of polyelectrolyte was mixed with

about 90% of the required water (distilled), then the alumina powder was slowly added under continuous stirring. The pH was then adjusted with concentrated HCl and the remaining volume to make 10 v/o solids was provided by adding the necessary amount of distilled water.

The ceramic structures were then produced by sedimentation 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. 2.

Fig. 2. Ramp and soak sintering profiles.

2.3. 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 a bulk value for 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 cm³ was used.

2.4. Permeation and separation testing

A cross-flow module was used to test the ceramic structures for permeation and separation properties under a number of conditions. Cross-flow velocities of 1.0 and 2.0 m/s were tested, at pressures of both 25 and 50 psi. Details of the cell and its configuration can be found elsewhere [8,9]. Pure water permeation (PWP) tests were run, as well as ultrafiltration tests using solutes of 35 K MW polyethylene glycol (PEG, Fluka) and 300 and 900 K MW polyethylene oxide (PEO, Aldrich) in distilled water. Permeation tests were run with solute concentrations in the feed of approximately 200 ppm. The concentrations of the feed and permeate samples were measured with a Shimadzu model TOC-5050 Total Organic Carbon Analyzer.

2.5. Experimental design

A set of experiments was organized to compare microstructure and permeation properties of both uniform and functionally gradient structures. A stable colloidal state was chosen to make uniform cross-sections with the AKP-30 powder, at pH 9 and polyelectrolyte concentration of 2.0 mg/m² of powder. A metastable state was chosen for the APA-0.2 powder to make a continuously gradient structure, at pH 5 and polyelectrolyte concentration of 1.0 mg/m² of powder [2].

A range of maximum sintering temperatures from 1100 to 1300°C was tested for each sample type. An overview of all the samples tested is shown in Table 1.

3. Results and discussion

For each sample prepared, a number of data were collected to characterize the microstructure of the

Table 1
Outline of sample preparation parameters

No.	Sample	Sintering temperature (°C)
1	Uniform	1100
2	AKP-30	1150
3	pH = 9	1200
4	[pol] = 2 mg/m ²	1250
5		1300
6	Functionally gradient	1100
7	APA-0.2	1150
8	pH = 5	1200
9	[pol] = 1 mg/m ²	1250
10		1300

ceramic body corresponding to its processing parameters. The mean pore size, overall porosity, PWP and separation results can all be shown as a function of the sintering temperature, where the functionally gradient samples are compared with the uniform samples.

While mechanical properties of ceramic structures are an important consideration, they were not included in the scope of the present project. All of the samples tested were not affected by 50 psi of pressure in the test module. Exploratory tests indicated that some of the samples from the lower end of the sintering temperature range would crack at pressures between 90 and 100 psi. This problem likely resulted from shrinkage derived irregularities at the bottom surface. Milling the bottoms of the pieces flat and seating them on a spongy porous backing substantially improved their mechanical resistance to elevated pressures.

3.1. Porosimetry measurements

Each sample was subjected to high pressure mercury intrusion, up to 60,000 psi. The incremental volume take-up translates into a pore size distribution. Fig. 3 shows the pore size distributions for samples sintered at 1200°C. The pore size distributions reflect the respective particle size distributions. The APA-0.2 sample produces a much broader pore size distribution, especially at the coarse end, which could be attributed to the metastable colloidal state, coupled with the aggregate nature of the powder to begin with. These factors would give rise to hierarchical clusters, and hence some of the small peaks shown at the larger diameters.

Fig. 4 shows the effect of sintering temperature on the mean pore size and the overall porosity in both the

Fig. 3. Frequency pore size distributions for samples sintered at 1200°C.

Fig. 4. Mean pore diameters and overall sample porosities plotted against sintering temperature.

Fig. 5. Theoretical and intrusion porosities versus sintering temperature. The difference between these values corresponds to closed pores.

uniform and functionally gradient samples. The porosity of the functionally gradient samples was roughly 20% greater across the test range. The overall porosity decreased slightly as the sintering temperature was increased, suggesting densification of the bodies through shrinkage and fusion. The mean pore diameter of the functionally gradient sample did not vary in the same manner, likely attributed to densification of clusters, thereby making the inter-cluster voids larger.

One further consideration was that of intrusion porosity as compared with theoretical porosity which is determined from the mass and bulk volume of a sintered sample. For a body with contiguous tortuous pores, these values should be nearly the same. In the case of the samples produced here, the theoretical porosity was larger than the intrusion porosity, which indicated that these bodies contain sealed or closed pores which would not contribute to filtration. This pore volume would not be attributable to pores of dimensions lower than could be measured by porosi-

metry, since the instrument was able to apply pressures up to 60,000 psi, while intrusion typically did not continue beyond 30,000 psi. Fig. 5 shows a plot of these porosities as a function of sintering temperature. These differences are most pronounced with the uniform samples at the middle sintering temperatures, because the tighter packing arrangement would lead to more extensive merging of neighbouring particles to produce closed pores, while at the same time, the densification rate was likely not high enough to coalesce pores. The looser packed state of the clustered APA-0.2 powder likely contributed to intra-cluster closed pores and less inter-cluster closed pores, reflected in the more regular difference between the two values of porosity across the sintering temperature range.

3.2. Permeation and separation tests

Fig. 6 shows the PWP behaviour of all the samples tested at a number of different pressures. The samples

Fig. 6. Pure water permeation data for the set of samples.

were left in the cell and monitored over time so that the PWP recorded was a stable value reached after some amount of flux reduction, often after several hours. The standard linear pressure dependence was noted. Tests were done at 20°C. The maximum PWP was observed with the samples sintered at 1200°C, corresponding to a high overall sample porosity, but not the largest mean pore diameter. Owing to their higher porosity, the functionally gradient samples had substantially higher PWP rates compared to the uniform samples. Given the initial particle size distributions, the top layer pore sizes were likely similar, so the main factor for the higher fluxes for the functionally gradient samples would be the lessened resistance across the cross-section of the body because of the high porosity with ever increasing pore sizes.

In quantitative terms, the PWP rates for these samples can be compared to other values quoted in

the literature. The best functionally gradient sample (1200°C sinter) produced a pure water flux of about 26 l/h m² bar. Laitinen et al. report γ -alumina UF membranes with a nominal pore size of 10 nm with a pure water flux of about 31 l/h m² bar (when adjusted to 20°C) [10].

Figs. 7 and 8 and show permeation and separation data for the samples tested at transmembrane pressures of 50 and 25 psi, at both 1 and 2 m/s cross-flow velocity. Solutes tested were 35 K MW PEG, 300 K PEO and 900 K PEO. Despite the complexity of the overall system, a few basic trends can be observed. The functionally gradient samples had higher permeation rates and better separations in all cases. The permeation rates with solutes followed the PWP rates in terms of functionality with the sample sintering temperature, but decreased in magnitude with increasing solute molecular weight. In general, the

Fig. 7. Permeation and separation data for the set of samples at a transmembrane pressure of 50 psi.

Fig. 8. Permeation and separation data for the set of samples at a transmembrane pressure of 25 psi.

separations increased with sample sintering temperature, attributed to finer top layer pore sizes.

At lower crossflow velocities, both the flux and the solute separation became slightly smaller. This is a typical consequence of lower surface shear.

At the lower transmembrane pressure of 25 psi, the permeation rates were of course proportionally lower than the 50 psi case, while the separation levels were similar to those achieved at the higher pressure.

A molecular weight cut-off (defined as 90% separation) could be assigned near 900 K for these samples, especially for the sintering temperatures above 1200°C. A 900 K MW PEO has a molecular radius of 24.83 nm, thereby resulting in an effective pore radius of about 32 nm. With a 35 K MW PEG, a permeation rate of about 9 l/h m² bar was obtained, which can be compared to data taken with sol-gel-coated KerafilTM membranes, where a flux of around 20 l/h m² bar was

reported after a 6 h test with 25 K MW solutes on a membrane with about a 25 K MW cut-off [11]. The permeation rates for the experimental samples here are somewhat lower than for other commercial materials. One reason for this is that at 3.3 mm in thickness, it is less straightforward to compare them to thinner filters.

Fig. 9 shows permeation and separation data for both functionally gradient and uniform samples sintered at 1250°C, and tested at 50 psi and 2 m/s cross-flow velocity. The overall performance is superior for the functionally gradient sample. The point of interest is that the functional variation across the molecular weight range is not consistent, and this is likely due to differences in the surface morphology of the two cases. At present, surface analysis methods are being sought to provide details about the sample surfaces, as of course, surface pore dimensions are the key factor in achieving solute separations.

Fig. 9. Permeation and separation data for the 1250°C samples vs. solute molecular weight.

4. Conclusions

Porosimetry and permeation and separation tests were conducted on porous ceramic samples prepared by a colloidal sedimentation technique in order to compare the properties of those with a functionally gradient cross-section to those with a uniform microstructural cross-section. It was found that the porosity and mean pore sizes of the functionally gradient samples were larger across the full range of sintering temperatures, stemming from the looser packing and hierarchically clustered structure arising from the colloidal processing parameters.

Permeation and separation tests showed superior performance for the functionally gradient samples compared to the uniform samples. Solute separation increased with increased sintering temperature, while the permeation was greatest for the functionally gradient sample sintered at 1200°C. In general, a molecular weight cut-off of about 900 K was observed. As ultrafilters, these samples performed slightly poorer, but on a comparable order of magnitude to some commercial alumina ultrafilters, the difference being attributed to their extra thickness.

This was a preliminary investigation and only two alumina powders were considered. These results should be seen as promising in view of the very basic powder samples used. Applying the processing methods developed here to a more carefully tailored particle size distribution, could produce in one step, continuously gradient porous ceramic structures suitable as ultrafilters, or as advanced substrates for subsequent coating operations.

References

- [1] K. Darcovich, M.E. Price, in: A.G. Fane (Ed.), *Microstructure Processing for Asymmetric Ceramic Membrane Substrates*, Proceedings of the International Membrane Science and Technology Conference IMSTEC'96, Sydney, Australia, 12–14 November 1996, pp. 164–166.
- [2] K. Darcovich, M.E. Price, Preparation of functionally gradient ceramic membrane substrates, *J. Can. Ceram. Soc.* 66 (2) (1997) 146–151.
- [3] K. Darcovich, C.R. Cloutier, Processing of functionally gradient ceramic membrane substrates for enhanced porosity, *J. Am. Ceram. Soc.* 82 (8) (1999) 2073–2079.
- [4] J. Cesarano III, I.A. Aksay, A. Bleier, Stability of aqueous α -Al₂O₃ suspensions with poly(methacrylic acid) polyelectrolyte, *J. Am. Ceram. Soc.* 71 (4) (1988) 250–255.
- [5] I.A. Aksay, Microstructure control through colloidal consolidation, in: J.A. Manjels, G.L. Messing (Eds.), *Advances in Ceramics*, Vol. 9, American Ceramic Society, Columbus, OH, 1984, pp. 94–104.
- [6] A.G. Lamas, M. Almeida, H.M.M. Diz, Slip-casting of alumina bodies with differential porosities, *Ceram. Int.* 19 (1993) 121–124.
- [7] J. Cesarano III, I.A. Aksay, Processing of highly concentrated aqueous α -alumina suspensions stabilized with polyelectrolytes, *J. Am. Ceram. Soc.* 71 (12) (1988) 1062–1067.
- [8] K. Darcovich, F.N. Toll, F. Paynot, E. Pélerin, Inlet plenum pressure drop calculation for a cross-flow module, *Can. J. Chem. Eng.* 77 (2) (1999) 119–121.
- [9] K. Darcovich, M.M. Dal-Cin, S. Ballèvre, J-P. Wavelet, CFD-assisted thin channel membrane characterization module design, *J. Membr. Sci.* 124 (2) (1997) 181–193.
- [10] N. Laitinen, A. Luonsi, E. Levänen, L. Grönroos, T. Mäntylä, M. Nyström, Modified and unmodified alumina membranes in ultrafiltration of board mill wastewater fractions, *Desalination* 115 (1998) 63–70.
- [11] K. Pflanz, N. Stroh, R. Riedel, Flat ceramic ultrafiltration membranes and modules coated by the sol-gel technique, *Key Eng. Mater.* 150 (1998) 135–140.