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Processing of Functionally Gradient Ceramic Membrane Substrates for Enhanced Porosity

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A method to cast functionally gradient porous ceramics was conceived and established. A previous initial study had established viability of the technique: samples were shown to have a functionally gradient cross section with a continuously increasing mean particle size from top to bottom. This article reports on a modified two-level factorial experimental design that was undertaken to determine the interdependent effects of pH, polyelectrolyte additive concentration, sintering temperature, and powder blend on the sintered microstructure. Ceramic disks ~45 mm in diameter and 3.3 mm thick were cast by sedimentation. The green bodies were dried prior to sintering. For each point in the experimental space, mercury porosimetry was used to obtain the porosity and pore-size distribution in the solid sample. From metastable suspensions, it was possible to form functionally gradient porous structures. Porosimetric data obtained in this study corroborated previous observations. Structures were produced with a wide pore-size range and high porosity (up to 0.68). These structures, formed from a one-step process, could be used as-is for ultrafiltration applications, but they also had a sufficiently fine top layer for facilitating subsequent thin-coating operations.

I. 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. 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 support structure preparation via a polydisperse slurry method, where the objective is to fabricate a functionally gradient material by a colloidal processing technique. The benefit of creating an asymmetric microstructure is to produce a smaller substrate pore size over a thinner region for a given bulk density.

The key for achieving asymmetry is 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 produces a functionally gradient, or continuously finer, mean particle diameter profile from bottom to top over the cross section of the consolidated structure. The particle-size distribution control can be achieved by blending different powder samples. In

terms of volume fraction, the continuous particle-size distribution of the powder used to make the suspension should be coarse-rich. Preliminary results have confirmed the viability of this method.¹ Methods have been established to prepare functionally gradient samples made from α -alumina that retain a high porosity after sintering. Hardness testing has been used to demonstrate that the bodies fused and strengthened without significant densification. The dispersion of a small amount of fines throughout the body, promoted through the metastable nature of the suspensions, serve as localized sites from which sintering is enabled at lower temperatures, sufficient to fuse the sample into a contiguous, hardened porous structure. Furthermore, hardness gradients measured across the cross section reflect a functionally gradient microstructure.² Research on producing porous refractories with broad particle-size distribution powders refers to such fines as "active," and, depending on powder size, sintering of α -alumina can occur at a temperature as low as 1000°C.³

The colloidal state and suspension microstructure can be controlled by 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 that forms the consolidated green body has a direct influence 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 retaining a relatively fine-pored top surface.

A general goal is to produce a structure (substrate) that has broader application than as an improved substrate for any or all subsequent coating operations. Because 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 that extends to a relatively thin depth. This one-step-processing method makes one contiguous, solid entity, or substrate.² It is possible with such a substrate to apply thinner defect-free membrane coatings than can be applied to conventional, uniform microstructure substrates. This type of processing method is a recent development in the ceramics community, with some preliminary results available.

One study attempted the consolidation of sterically stabilized titania sol-gel particles.⁷ A functionally gradient cross section was obtained, but sintering was not attempted, because the sols had ultrafine diameters, all <180 nm. Proof-of-concept work was also demonstrated by Hong *et al.*⁸ for centrifugally cast tubular membranes. Porosimetry data showed top-layer pore sizes as small as 40 nm, but no information was given on the overall porosities of the bodies.

To obtain a defect-free membrane, it is necessary to apply a thicker coating when the top surface of the substrate is composed of larger particles, contributing to larger pores and larger overall surface roughness. A thinner coating (membrane) layer achieves similar separation performance (based on membrane layer pore-size distribution), but at a higher product rate because of the decreased flow resistance, which is directly pro-

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portional to the membrane thickness. Furthermore, a functionally gradient microstructure can eliminate the need for several intermediate layers, which are often required for priming the substrate before the final membrane coating can be applied.⁹

It has been shown previously that the metastable systems used here distribute fines by a slight colloidal association with all particle-size classes.² At a concentration of 10 vol%, no substantial particulate networking develops throughout the suspension. The sedimentation that then consolidates the solids and forms the particulate cross section proceeds in an unhindered fashion. These above phenomena, along with using a broad particle-size distribution, are the key reasons for being able to prepare the porous functionally gradient ceramics. All of the processing parameters have an important effect on the final sintered microstructure.

The immediate objectives of the present article are to determine the interdependent effects of relevant processing variables on the final sintered microstructure of the ceramic bodies. For dilute (10 vol%) suspensions, an experimental design has been conceived to test the interdependence of the processing parameters. Thus, the experimental variables considered are slurry pH, polyelectrolyte additive concentration, sintering temperature, and powder blend on the resulting sintered porous microstructure.

Having established the viability of the above described method for producing functionally gradient porous ceramic structures, the present article describes work undertaken to gain insight into ways to combine processing parameters in a more optimal fashion.

II. Experimental Procedure

Three α -alumina powders were chosen for this work. They were APA-0.2 (Ceralox, Tucson, AZ) and AKP-15 and AKP-30 (Sumitomo Chemicals, Tokyo, Japan). These samples provided a particle-size range from 0.06 to $>10\ \mu\text{m}$ and a mix of distribution characteristics.

(1) Powder Characterization

The particle-size distributions of the three powders were determined using a particle-size analyzer (Model 5000E, Sedi-Graph, Micromeritics Instrument Corp., Norcross, GA) consisting of 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 a dispersing agent (A-12, Sedisperse, Micromeritics Instrument Corp.) as the liquid phase. This dispersing agent was a highly purified, nonpolar, saturated aliphatic hydrocarbon of viscosity 4 mPa·s, formulated for dispersing metal oxides.

The cumulative particle-size distributions of these powders are shown in Fig. 1. Table I provides additional data describing the powders. The very high specific surface area for the APA-0.2 sample suggested that it was in the form of aggregates of quite fine particles. The values for specific surface area were taken from product technical information provided by the suppliers.

(2) Sample Preparation

Aqueous alumina suspensions were prepared at solids loadings of 10 vol%. A steric effect was provided by the addition of an ammonium poly(methylacrylic acid) electrolyte ($\text{NH}_4^+\text{PMA}^-$) of molecular weight of $\sim 15\ 000$ (Darvan C, R. T. Vanderbilt Co., Inc., Norwalk, CT), in accordance with a stability map.¹⁰ The required amount of polyelectrolyte was mixed with $\sim 90\%$ of the required water (distilled), then the alumina powder was slowly added under continuous stirring. The pH was then adjusted with concentrated hydrochloric acid, and the remaining volume to make 10 vol% solids was provided by adding the necessary amount of distilled water.

The ceramic structures were then produced by sedimentation

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

in the form of flat disks in 45 mm diameter tube sections over milled gypsum slabs. The disks 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.

(3) Porosimetry

To investigate the pore-size distribution of the sintered ceramic structures, mercury porosimetry measurements were made using a pore sizer (Model 9310, Micromeritics Instruments Corp.). A pore-size distribution representing a bulk value for the entire cross section was obtained for each sample. The ceramic disk was cut into small pieces with a water-cooled diamond saw. The pieces were dried at 100°C . A porosimeter penetrometer volume of 3 mL was used.

(4) Experimental Design

A simple two-level factorial experimental design was conducted to determine an improved combination of processing variables and a powder blend most suitable for substrate preparation.

An experimental system with five independent variables was conceived. Three different alumina powders were used (two independent variables), and their proportions varied, along with the pH, the polymer concentration, and the maximum sintering temperature. A first-order two-dimensional model (equilateral triangle) design was used to specify the proportions of powders that determined the particle-size distribution. Because there were seven different combinations of the three powders and eight different combinations of the other input variables, a total of $7 \times 8 = 56$ experiments were required. This experimental design demonstrated possible interactions between these independent variables. Figure 3 shows a schematic of the experimental space.

The variable levels were selected from preliminary results. At $\text{pH} < 6$, the colloidal state of the suspension exhibited metastable characteristics with a small level of polyelectrolyte additive. This was determined by viscosity measurements that showed higher viscosities within 1 order of magnitude relative to disperse suspensions, either electrostatically or sterically stabilized. The viscosities of suspensions with no steric stabilizers near the isoelectric point, were >2 orders of magnitude higher than disperse values.² Depending on the suspension characteristics, a wide range of fusion and densification was observed at sintering temperatures between 1100° and 1400°C . As a result of these previous findings, the following values of the experimental variables were selected: the pH levels were 3 and 6, the polyelectrolyte levels were 0.0 and $1.0\ \text{mg}/(\text{m}^2\ \text{of powder})$, and the sintering temperatures were 1200° and 1350°C . Microstructures of varying degrees of suitable functionally gradient character have been produced within the above variable ranges.

Table I. Powder-Size Distribution Properties

Powder	d_{50} (mm)	$d_{10} - d_{90}$ (mm)	Distribution characteristic	Specific surface area (m ² /g)
E (APA-0.2)	3.73	0.40–9.79	Broad	40.0
F (AKP-15)	0.71	0.40–1.30	Narrow	2.5
G (AKP-30)	0.20	0.09–3.64	Narrow	8.6

Fig. 2. Ramp and soak sintering profiles.

III. Results and Discussion

(1) Screening Study

A full, two-level factorial design with three parameters, coupled with a centered ternary powder system requiring ($2^3 \times 7$) 56 experiments was used for initial screening. This was an effective way to minimize the number of experiments required to check on all possible variable interdependencies.¹¹ Fractional two-level designs were not considered because the assumption of insignificant high-order interactions was suspect.

Several measured data or “responses” were considered for analysis over the range of variables. These quantities are summarized in Table II.

An initial examination of the responses from the five-variable screening study yielded some insight for the determination of processing parameters for making porous ceramics.

The responses were modeled with a multivariate regression routine (IMSL: DRGLM). This modeling exercise served as a means to detect any single linear dependencies of the responses on the input variables. In this way, insignificant variables were screened out of the experiment and, thereby, simplified the system. On the other hand, if the set of model coefficients proved to be fully populated, then it served notice that further research toward refining the ceramic microstructure must consider the simultaneous effect that all the compositional and processing variables have on the final result.

The general linear functional form, expressed in tensor notation (which represents a summation of terms over a repeated index), for a response y_i is¹²

$$y_i = \beta_0 + \beta_j x_j + \beta_{jk} x_j x_k + \beta_{jkl} x_j x_k x_l + \beta_{jklm} x_j x_k x_l x_m + \beta_{jklmn} x_j x_k x_l x_m x_n + \varepsilon$$

where β_i are the regression coefficients, x_i the independent variables, ε an error term, and j, k, l, m, n the coefficient indexes 1, 2, 3, 4, 5, respectively. For a linear case, among the indexes, $j \neq k \neq l$, etc. With five independent variables, there are 32 terms in the above expression. Statistical analysis of the regression model can determine which of these 32 coefficients are quantitatively significant.

The regression analysis produces a model that is of limited use. The “significant terms” column in Table II shows that,

with a t -statistic of 2.00 (–95% confidence interval), most of the 32 possible terms are deemed significant and retained in the model. Statistically, this shows that there is substantial interdependence of all the input variables and that all variables are significant. Furthermore, obvious monotonic trends do not result from the regressions.

Each response can be examined from the perspective of what is desirable in a functionally gradient porous membrane substrate structure. In this case, a high porosity, a wide pore-size range, and small finest pores are good properties. This concept is expressed as the “desired extremum” and is listed for each response in Table II, with the parameter values corresponding to this extremum. For a tight-skinned, yet porous structure, a small finest pore size is desired with a large mean and largest range of pore sizes. The metastable suspensions, at pH 3 and electrolyte concentration of 1.0 mg/m², provide these properties. In general, the lower sintering temperature of 1200°C is better. The powder blends that produce these favorable properties are A, B, E, or F. This composition is from one side of the ternary map, shown as the shaded region in Fig. 3. These powder blends generally have a broad particle-size distribution with a significant quantity of fines. Therefore, an affiliation of the fines with the other size classes is enabled. This affiliation allows some degree of fusion under sintering without substantial densification, because the fines act as bridging sites. It is less likely that this metastable affiliation provides any benefit in structures produced from a more monosized powder blend. Powder F results as the blend with the largest mean pore size, likely as a direct consequence of a lesser packing density because of its narrow distribution.

Some explanation can be offered on why the preferred microstructural properties are obtained at pH 3, 1.0 mg/m² polyelectrolyte, and 1200°C sintering. From rheological measurements in previous work, the only suspensions with intermediate viscosity values indicative of a metastable state are with the combination of pH 3 and 1.0 mg/m² polyelectrolyte.² Under these conditions, the colloidal interaction forces suggest that there is the smallest energy barrier to flocculation between the fines in the particle-size distribution and all other size classes, thereby facilitating a presence of fines at all points in the compact. This allows lower-temperature site sintering, where fusion occurs without much densification. In general, samples sintered at 1200°C, compared with 1350°C, exhibit fusion without substantial densification. Figure 4 shows more explicitly, for one case, the sintering temperature effect on pore-size distribution. The region of fine pores is more substantial and extends to smaller diameters (25 nm) for the 1200°C case. Grain growth at the higher sintering temperature is the likely mechanism for the coarsening of the pore-size distribution.

In terms of the particle-size distribution of the powder, blends A, B, E, and F have a broad size range, including appreciable fine and coarse fractions. APA-0.2 (powder E) in particular is a good powder with high specific surface area, containing a large amount of fine material, which assists lower-temperature sintering.

(2) Porosity Measurement

Mercury porosimetry has been used to measure the porosity and pore-size distribution of each sample in the experiment. Data reported are bulk values for the entire 3.3 mm sample cross section. The raw porosimetric data provide a cumulative pore-size distribution; some examples are shown in Fig. 5. A

Two-level factorial experimental space with ternary powder system

Fig. 3. Schematic of the experimental design space. Powder blend system is superimposed over each processing point, or vice versa.

Table II. Results of Two-Level Factorial Experimental Design Screening Study

Response	Significant terms (x/32)	Desired extremum	Optimal parameters			
			pH	$\text{NH}_4^+\text{PMA}^-$ (mg/m ²)	Temperature (°C)	Powder
Green porosity	15/16	Maximum	3	1.0	NA	E
Sintered porosity	32	Maximum	3	1.0	1200	E
Mean pore size ($d_{0.50}$)	29	Maximum	3	1.0	1200	F
Finest pore size ($d_{0.05}$)	32	Minimum	3	1.0	1200	A
Largest pore size ($d_{0.95}$)	32	Maximum	3	1.0	1200	F
Pore size range ($d_{0.05} - d_{0.95}$)	32	Maximum	3	1.0	1350	B

Fig. 4. Sintering temperature effect on the frequency pore-size distributions for structures made from APA-0.2 powder.

Fig. 5. Cumulative pore-size distributions of structures formed from various powder blends.

more continuous pore-size distribution would be reflected by a wider diameter range, such as with APA-0.2.

However, the pore-size distributions must be considered with respect to the overall porosity of the sintered structure. Figure 6 shows interpolated ternary contours of the sintered porosities of the structures, produced from data from the seven experimental powder blends. The pore-size range, defined as

the range in nanometers spanning 90% of the distribution area, also is shown on this plot for the 1200° and 1350°C cases. In general, APA-0.2 gives the largest porosities. Figure 6 shows that, at 1200°C, the porosity remains high (i.e., the 0.66 contour) for the blend of 50% AKP-30 and 50% APA-0.2. The AKP-30 powder is quite fine; therefore, with APA-0.2, this represents a fines-rich blend. Therefore, the high porosity in

SINTERED POROSITY

1.0 mg/m² NH₄⁺PMA⁻
pH = 3 ; T = 1200°C

SINTERED POROSITY

1.0 mg/m² NH₄⁺PMA⁻
pH = 3 ; T = 1350°C

PORE SIZE RANGE

(d_{0.05} - d_{0.95}) ; [nm]

1.0 mg/m² NH₄⁺PMA⁻
pH = 3 ; T = 1200°C

PORE SIZE RANGE

(d_{0.05} - d_{0.95}) ; [nm]

1.0 mg/m² NH₄⁺PMA⁻
pH = 3 ; T = 1350°C

Fig. 6. Sintered porosity and pore-size range for 1200° and 1350°C for the ternary powder system.

this case is attributed to the metastable state in the sedimenting suspension where fines associate with coarser particles. However, with sintering at 1350°C, this blend, with regions on the ternary map with up to 50% AKP-30, shows very large porosity reductions because of grain growth and densification associated with finer and more-uniform powder. Figure 6 also shows that the maximum in pore-size range migrates from AKP-15 to almost a 50%-50% blend of APA-0.2 and AKP-15. This can be attributed to grain growth caused by dispersed fines at the mixed-powder 1350°C maximum and densification of the more-uniform AKP-15 at this higher temperature.

As a check on the pore-size range statistic, the finest ($d_{0.05}$) and coarsest ($d_{0.95}$) pore sizes also have been plotted over the ternary powder range (Fig. 7). Inspection of these contours confirms that the section bounded by powders A, B, E, and F is the region with the largest pore-size range, a desired property in a functionally gradient microstructure.

(3) Functionally Gradient Character

Preliminary work in this project presented in a previous paper demonstrates that a functionally gradient cross section is obtained by the metastable sedimentation processing method.² Mean hardness data taken over the sample cross sections and SEM images show a functionally gradient microstructure.¹ Visually, the samples are very smooth and shiny on their top surface and rougher and duller on the bottom surface. After sintering, the samples assume a slightly concave shape, shown to result with a functionally gradient microstructure.¹³ Samples prepared by the same processing methods from more-fluid and monodisperse suspensions have uniform cross-sectional characteristics.

A test was conducted to verify that the functionally gradient character of these samples was confirmed by the pore-size distribution measurements. Several samples were prepared under conditions 1 and E, as shown in Fig. 3. These samples were

FINEST PORE SIZE

 $(d_{0.05})$; [nm]1.0 mg/m² NH₄⁺PMA⁻
pH = 3 ; T = 1200°C

FINEST PORE SIZE

 $(d_{0.05})$; [nm]1.0 mg/m² NH₄⁺PMA⁻
pH = 3 ; T = 1350°C

LARGEST PORE SIZE

 $(d_{0.95})$; [nm]1.0 mg/m² NH₄⁺PMA⁻
pH = 3 ; T = 1200°C

LARGEST PORE SIZE

 $(d_{0.95})$; [nm]1.0 mg/m² NH₄⁺PMA⁻
pH = 3 ; T = 1350°C

Fig. 7. Finest and coarsest pore sizes for 1200° and 1350°C for the ternary powder system.

then ground to half thickness and measured for porosity. The pore-size distributions from the upper and lower portions are shown in Fig. 8, with the distribution obtained from measuring a sample from the entire structure.

The frequencies obtained for these partial distributions were divided by two and plotted to show how they might represent the upper and lower halves of the original. The finer tail of the pore distribution corresponded to the upper part of the structure, and the coarser part of the distribution corresponded to the lower part. Porosimetry showed that the porous profile of these ceramic structures was functionally gradient, with a continuously increasing mean pore size, from top to bottom across the body. The overall pore-size distribution in Fig. 8 represents a sample prepared under the same conditions as the 1200°C case in Fig. 4. Separate individual samples were prepared for each measurement, and the slight differences observed in these two pore-size distributions reflected the reproducibility of the procedure.

In terms of bulk porosity, the entire sample measured

0.686—the top half was 0.643 and the bottom half was 0.694. The top region was less porous than the bottom (by an 8% difference), but there was no substantial change in the overall porosity across the cross section.

The largest pore sizes at the bottom of the structure were just less than 0.5 μm . This was consistent with other reported values from the literature.^{14–16} Sometimes substrate pore sizes are much larger, but, to achieve a membrane coating in these cases, several intermediate laminates may be required, or the membrane itself must be made very thick to avoid defects.¹⁷

The single-step processing of these structures is important. Other projects have investigated preparing functionally gradient ceramic structures for other applications and consistently report cracking problems when sintering bodies with a non-continuous functionally gradient character and individual sintering steps are used for the different layers.^{18,19} The mechanical integrity of porous ceramics intended for membrane production is also compromised when the processing route requires more than a single sintering operation.²⁰

Fig. 8. Comparison of the pore-size distributions obtained by porosimetric measurements with separate upper and lower sections of a ceramic structure.

IV. Conclusions

The process for the single-step fabrication of a continuously functionally gradient ceramic substrate by casting into flat disks has been further refined. Control of the particle-size-based segregation that occurs during sedimentation was achieved by the properties imparted to the suspension by its composition.

The porous nature of a sintered structure formed by selecting temperature limits for sintering a green body consolidated from a given powder blend and stabilizing additive with pH control was found by statistical analysis to be a highly complex non-linear function of all the input variables.

A pH of ~ 3.0 when the suspension is combined with the $\text{NH}_4^+\text{PMA}^-$ polyelectrolyte at a concentration of $1.0 \text{ mg}/(\text{m}^2 \text{ of powder})$ produced the most-porous substrates. A broad particle-size distribution of alumina powder that included a significant quantity of fines was favored for producing a better porous substrate microstructure. A sintering temperature range of $1200^\circ\text{--}1350^\circ\text{C}$ was investigated in more detail. Using the above-mentioned particle-size distributions, temperatures of $\sim 1200^\circ\text{C}$ were more suitable for producing a desirable porous structure without excessive grain growth and pore expansion.

Broad pore-size distributions were observed across the substrate cross sections, with generally high overall porosity, between 45% and 70%. Porosimetry data showed top layer pore sizes as fine as 20 nm, well within the ultrafiltration regime. Pore-size distributions from the upper and lower halves of a sintered body were compared to the pore-size distribution of

the entire cross section to further corroborate the functionally gradient character of porous ceramic produced by metastable sedimentation.

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