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POROSIMETRIC STUDY OF FUNCTIONALLY GRADIENT CERAMIC MEMBRANE SUBSTRATES

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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 supports and are typically made with monosized particles giving a uniform cross-section. A general goal is to produce a structure (substrate) which should have broader application than just an improved substrate for any or all subsequent coating operations. Continuously functionally gradient structures can be made by slip casting with a very broad particle size distribution, producing a pore size distribution with very small diameter pores at the top surface which extend to a relatively thin depth [1]. This one-step processing method makes one contiguous solid entity, or substrate. With such a substrate it is possible to apply thinner defect-free membrane coatings than could be applied to conventional uniform microstructure substrates.

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. Methods were established to prepare functionally gradient samples which retained a high porosity after sintering. Hardness testing was 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, served as localized sites from which sintering was enabled at lower temperatures, sufficient to fuse the sample into a contiguous hardened porous structure [2]. 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 [3].

The immediate objectives of the present work were to determine the interdependent effects of relevant processing variables on the final sintered microstructure of the ceramic bodies. To this effect, a two-level factorial experimental design was conceived to test the interdependence of slurry pH, polyelectrolyte additive concentration, sintering temperature and powder blend on the resulting sintered porous microstructure.

EXPERIMENTAL

Three α -alumina powders were chosen for this work. They were: Ceralox APA-0.2, and Sumitomo AKP-15 and AKP-30. These samples provided a particle size range from 0.06 to 70 μm , and a mix of distribution characteristics. The powder particle sizing, the suspension preparation method, viscosity measurements, the slip casting and sample sintering followed the same procedures as described previously [2].

Alumina suspensions were prepared at solids loadings of 10 v/o. The pH of these suspensions was controlled by small additions of concentrated HCl, and a steric effect was provided by the addition of an ammonium polymethacrylic acid electrolyte ($\text{NH}_4^+\text{PMA}^-$) of molecular weight of approximately 15,000 in accordance with a stability map [4]. A Bohlin VOR rheometer was used to obtain rheological data for the ceramic suspensions. Shear stress data was obtained across a range of shear rates from 9.25×10^{-3} to 92.5 s^{-1} . The ceramic structures produced were flat discs, slip cast in 45 mm tube sections over milled gypsum slabs. The discs were cast to a thickness of 3.3 mm. The green bodies were dried in an oven at 50°C .

The pore size distribution of the sintered ceramic structures was determined by mercury porosimetry measurements with a Micromeritics model 9310 pore sizer. 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 mL was used.

A two-level factorial experimental design was conducted to determine processing variables and a powder blend most suitable for substrate preparation, as well as to suggest an optimal combination of them. Three different alumina powders were used in varied proportion, along with a pH range of 3 to 6, polyelectrolyte levels of 0.0 and 1.0 mg/m² of powder and sintering temperatures of 1200 and 1350°C. With 7 different combinations of the 3 powders and 3 other input variables, a total of $(7 \times 2^3) = 56$ experiments were required to demonstrate parameter interdependencies. Figure 1 shows a schematic of the experimental space. Microstructures of suitable functionally gradient character had been produced within the above variable ranges.

RESULTS AND DISCUSSION

Factorial Model - Screening Study

A number of responses from the 6 variable screening study were analyzed over the range of variables with a multivariate regression routine, summarized in Table 1. The regression analysis itself was of limited use. Looking under the "significant terms" column in Table 1, it can be seen that with a *t*-statistic of 2.00 ($\approx 95\%$ confidence interval), most of the 65 possible terms were deemed significant and retained in the model, showing substantial interdependence of all the input variables. Without obvious monotonic trends, the data were evaluated in view of the general objectives.

For a tight-skinned, yet porous structure, a small finest pore size is desired along with a large mean, largest and range of pore sizes. The metastable suspensions, at pH of 3 and electrolyte concentration of 1.0 mg/m² provided these properties. The powder blends found to have produced these favourable properties were A, B, E or F. This composition is from one side of the ternary map, shown as the shaded region in Figure 1.

Viscosity Measurement

The particle Reynolds numbers corresponding to sedimentation rates during slip casting are extremely low ($Re \approx 2 \times 10^{-9}$ for a 1 μm alumina particle), making a zero-shear viscosity value meaningful. The Cross model[5], incorporating zero-shear and high-shear parameters was selected as a relevant reference model. There is a visual inverse correspondence between its powder-based ternary contours (Figure 2-a) and the ternary contours of the sintered porosity obtained under the same sample conditions (Figure 2-c).

Porosity Measurement

The raw porosimetric data provided a cumulative pore size distribution. Also of interest was the overall porosity of the the sintered structure. Figures 2-c/d show the sintered porosities of the the structures as a function of the ternary powder system. The pore size range, defined as the range in nm spanning 90% of the distribution area is shown in Figures 2-e/f, for the 1200°C and 1350°C cases. In general, APA-0.2 gives the largest porosities. In Figure 2-c it can be seen that at 1200°C the porosity remains at larger values (ie; the 0.66 contour) with blends containing some AKP-30, perhaps due to dispersion of fines throughout the powder matrix. At 1350°C, a higher porosity is favoured more in a blended state with AKP-15. At the higher temperature, the fines which contribute to local bonding may sinter to an extent which brings about more densification than a matrix containing AKP-15. The most substantial porosity loss was in the region of high AKP-30. Also in Figure 2-e/f, the maximum in pore size range can be seen to migrate as temperature increases from AKP-15 to a near 50%-50% blend of APA-0.2 and AKP-15. This could be attributed to the 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 ($d_{0.05}$) sizes were also plotted over the ternary powder range (Figure 2-b). Inspection of these contours confirms that the section bounded by powders A, B, E and F is the region with the desired asymmetric microstructure.

Functionally Gradient Character

Porosimetry was also used to show the functionally gradient character of the structures formed with the chosen parameters. Data were numerically differentiated to produce frequency distributions.

A test was conducted to verify the presumed functionally gradient nature of several samples prepared at pH 3.0 and 1.0 mg/m² and then ground to half thickness. Top and bottom half pore size distributions were measured. The sum of the two half samples was plotted in direct comparison to the overall distribution and matches quite reasonably (Figure 3). It can be concluded from this illustration that the finer pores reside

in the upper part of the structure and the coarser pores make up the lower part. Thus, the porous nature of these ceramic structures are functionally gradient, with a continuously increasing mean pore size, from top to bottom across the body.

CONCLUSIONS

The novel process for the single step fabrication of a continuously functionally gradient ceramic substrate by slip casting has been further refined. Control of the particle size based segregation which 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 to be a highly complex non-linear function of all the input variables. A two-level factorial experimental design was used as a screening study for determining optimal system processing parameter values.

A pH near 3.0 when the suspension is combined with the $\text{NH}_4^+\text{PMA}^-$ polyelectrolyte at a concentration of 1.0 mg/m^2 of powder produces the most porous substrates. A particle size distribution of alumina powder from the shaded region of Figure 1 is favoured for producing a better functionally gradient substrate microstructure. Temperatures nearer 1200°C were more suitable for producing a desirable functionally gradient structure without excessive grain growth and pore expansion.

Functionally gradient pore size distributions were observed across the substrate cross-sections, with generally high overall porosity, between 45 and 70%. Porosimetry data were able to show top layer pore sizes as fine as 20 nm, well within the ultrafiltration regime. Such structures could be used as ultrafiltration membranes directly, or as substrates for applying thin coats of finer material to produce membranes for reverse osmosis or gas separation.

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response	significant terms ($x/65$)	desired extremum	optimal parameters			
			pH	mg/m^2 $\text{NH}_4^+\text{PMA}^-$	T [$^\circ\text{C}$]	powder
green porosity	28/32	MAX	3	1.0	NA	E
sintered porosity	57	MAX	3	1.0	1200	E
mean pore size ($d_{0.50}$)	61	MAX	3	1.0	1200	F
finest pore size ($d_{0.05}$)	61	MIN	3	1.0	1200	A
largest pore size ($d_{0.95}$)	63	MAX	3	1.0	1200	F
pore size range ($d_{0.05} - d_{0.95}$)	64	MAX	3	1.0	1350	B

Table 1: Results of two-level factorial experimental design screening study.

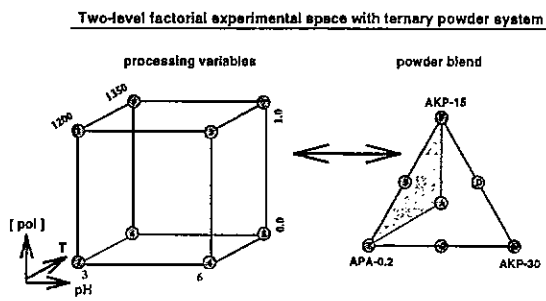


Figure 1. Schematic of the experimental design space. The powder blend system is superimposed over each processing point, or vice versa.

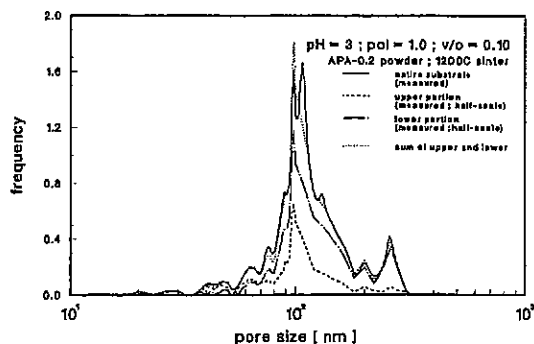


Figure 3. Comparison of the pore size distributions obtained by porosimetric measurements made with separate upper and lower sections of a ceramic structure.

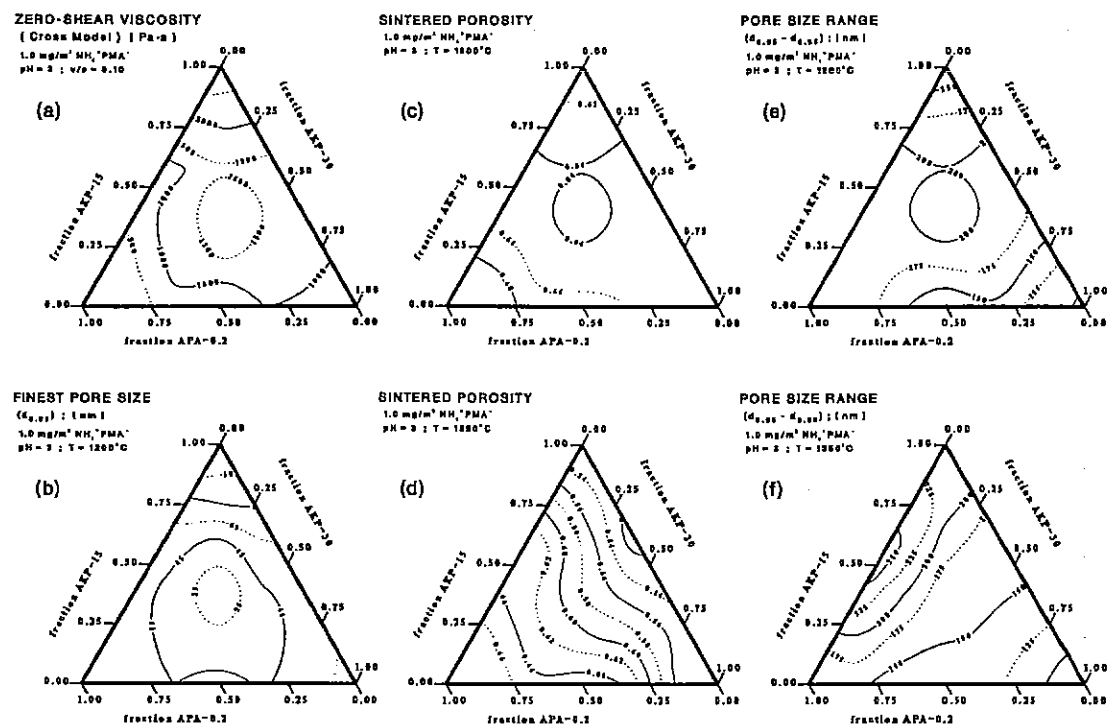


Figure 2. Responses as function of ternary powder composition. (a) Cross model zero-shear viscosity. (b) Finest pore size. (c) Sintered porosity at 1200°C. (d) Sintered porosity at 1350°C. (e) Pore size range at 1200°C. (f) Pore size range at 1350°C.



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