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Setting the optimal technological parameters for producing ceramic substrates

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Abstract

Geometrically similar macroporous ceramic substrates were made from quasi homo-disperse corundum grains and glassy binding material. Technological parameters, such as optimal forming pressure depending on original grain size, optimal ratio of binding material, optimal homogenisation time and sintering temperature, were determined by designed experiments and multi-regression models. Methods have been developed to examine fracturisation of corundum grain fractions by laser granulometry and homogenisation of green powder by X-ray microanalysis. With our technology, pore size of substrates in the range of 30–500 μm depends only on original grain size. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: A. Mixing; A. Pressing; B. Grain size; B. Porosity; E. Substrates

1. Introduction

Membrane separation processes are usually carried out by a thin layer of a few molecules [1] that is applied on a ceramic substrate [2]. There are issues not only in producing thin layers but also in the design of ceramics having desirable and reproducible pore size distribution. Our aim was to produce high porosity substrates made of grains and glassy binding material, the characteristic pore size and strength of which can be well designed by regression models based on designed experiments on forming pressure and content of binding material.

2. Methods and results

Filters were produced of corundum grains supported by K_2O–Na_2O–CaO–Fe_2O_3–TiO_2–B_2O_3–SiO_2 binding material. Dextrin and distilled water were added to increase plasticity. As forming process axial, pressing was applied. A sintering time of 2 h was applied at the temperature of 1300°C that is the hemisphere point of the binding material determined by heating microscopy measurements. Based on geometrical consideration, homo-disperse fractions were used in order to have the largest porosity [3].

Besides sintering temperature and quality of applied raw materials, the following technological factors were taken into consideration before designing experiments: forming pressure, ratio of binding material, grain size distribution and shape of grains.

In the first attempt, a two-factor two-level full factorial design [4] was established for prediction of porosity. Choosing one quasi homo-disperse corundum fraction (FEPA standard 120), grain size was fixed. Forming pressure and ratio of binding material were considered as factors having the largest influence on porosity (Table 1).

Thus, the model which can be established for porosity with coded factors is:

$$\mathbf{y} = 33.32 - 4.2\ \mathbf{X}_1 - 5.23\ \mathbf{X}_2 - 0.74\ \mathbf{X}_1\mathbf{X}_2 \tag{1}$$

where $\mathbf{y}$ is the real value of the porosity, $\mathbf{X}_1$ is the coded value of the forming pressure and $\mathbf{X}_2$ is the coded value of the ratio of the binding material. The porosity of filters made in the center of the design [40 MPa and 16%(m/m)] was about 33.4%. The model predicts 33.32%. Thus, it can be stated that the model [Eq. (1)] describes filters well in this experimental range. Using

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spherical geometrical model for grains with co-ordination number of 6, porosity value is 47.64%, which also fits well into the regression model. Analysing the problems, it can be seen that both the forming pressure and the ratio of binding material are in inverse ratio to porosity. Thus, for highest porosity, forming pressure and ratio of binding material are to be minimised considering strength of the filters.

Fractions of FEPA standard are not homo-disperse. To have narrower fractions, i.e. fractions with smaller geometrical standard deviation, five quasi homo-disperse fractions were produced by sieving. These were 50–63, 100–125, 200–250, 500–630 and 800–1000 μm. Shape factor of grains in different fractions was determined based on Eq. (2) by image analysis of grains [5]:

$$f = \frac{P^2}{4\pi \cdot A} \cdot \frac{1}{1.064} \tag{2}$$

where f is average shape factor, P is perimeter of projection of grains and A is area of projection of grains. Shape factor of each experimental fraction was measured. There was no significant difference between shape factors (the values were between 1.46 and 1.52), thus f value was considered as a constant in the experimental grain size range of 50–1000 μm.

In the next step, optimal forming pressure was determined for the five experimental grain fractions. It was observed that the extent of fracturisation increases with grain sizes. Two questions had to be answered: what is the optimal forming pressure for a fraction and how can the fracturisation be measured.

Grain size distribution of pressed and unpressed fractions was examined by MicroTracl000 laser-granulometer. During fracturisation caused by axial forming pressure of homo-disperse grain fractions, the average grain size decreases and the geometrical standard deviation increases. Moreover, bimodal distributions are formed for the description of which at least four variables are needed. Since the fractions made by sieving do not have normal distribution, simple statistical tools such as analysis of variance or sample statistics could not be used (Fig. 1).

Table 1
Two-factor design for estimation of porosity

Real values		Coded values		
Forming pressure (MPa)	Ratio of binding material [%(m/m)]	Forming pressure $\mathbf{X}_1$	Ratio of binding material $\mathbf{X}_2$	Porosity (%) **y**
20	10	−1	−1	42.4
20	22	−1	+1	32.8
60	10	+1	−1	35.28
60	22	+1	+1	23.06

To observe fracturisation, a method producing a simple variable was needed that can be calculated from grain size distribution and is not sensitive to the type of distribution. Calculated specific surface as a variable meets the requirements; however, in order to eliminate the effect of error of the measurements and of shape factors a quotient was formed:

$$GSS[\%] = \frac{S_{V,p}}{S_{V,0}} \cdot 100 \tag{3}$$

where $GSS[\%]$ is growth in calculated specific surface as a result of axial pressing of pressure of p, $S_{V,p}$ is the specific surface of pressed grain fractions and $S_{V,0}$ is the specific surface of original (unpressed) fraction. S_V values calculated from the data of laser granulometer:

$$S_V = 6 \sum_{i=2}^{n} \frac{f(Q_i - Q_{i-1})}{\frac{x_i + x_{i-1}}{2}} \tag{4}$$

where n is the number of channels of analyser of laser granulometer, f is the shape factor, Q is the percent value of distribution function given by analyser and x is the upper size of the analyser channel. If the shape factor is constant Eq. (3) can be defined as:

$$GSS_p[\%] = \frac{\left(\sum_{i=2}^{n} \frac{Q_i - Q_{i-1}}{x_i + x_{i-1}} \right)_p}{\left(\sum_{i=2}^{n} \frac{Q_i - Q_{i-1}}{x_i + x_{i-1}} \right)_0} \tag{5}$$

where every variable on the right side is output value of the laser granulometer.

Five experimental fractions were pressed by different axial pressure. Based on Eq. (5), growth of specific surface was calculated and plotted against the forming pressure and the original average grain size in Fig. 2.

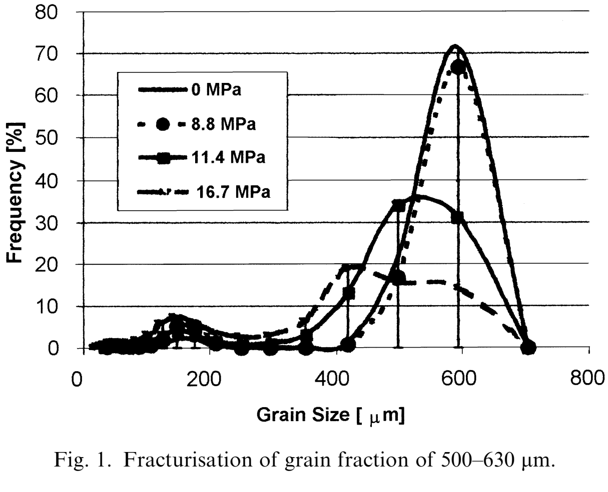

Fig. 1. Fracturisation of grain fraction of 500–630 μm.

Our aim was to have the same fracturisation level, i.e. the same *GSS*[%] value for each fraction. In order to determine this constant value the following experiment was carried out: Substrates were made from the grain fraction of 100–125 μm with 10%(m/m) binding material. The forming pressure was 10, 15, 20, 30 and 50 MPa, respectively. Fig. 3 shows pore size distribution of substrates obtained by a mercury porosimeter, the design and development of which was also part of our work [6].

Two characteristic peaks can be observed in Fig. 3. One belongs to forming pressure of 20 MPa and the other to 50 MPa. Bellow 20 MPa, the grains do not fit tight, above 20 MPa the characteristic pore size decreases because of considerable fracturisation of grains. Therefore, 20 MPa was considered as optimal forming pressure for the grain fraction of 100–125 μm, which belongs to 20% of *GSS*[%] value.

An optimal pressure–characteristic grain size function was established for the experimental range by calculating pressure belonging to 20% of *GSS*[%] value. Two other fractions (9–10 and 90–100 μm) were examined to obtain more exact result (Fig. 4). The approximate function of pressure against grain size is

$$p_{\mathrm{opt}} \approx 907\cdot\bar{d}_{\mathrm{grain}}^{-0.7327} \qquad (6)$$

where p_{opt} is the optimal forming pressure and d_{grain} is the characteristic grain size of the unpressed fraction.

Substrates were made from the five experimental fractions by optimal forming pressure adding binding material of 5%(m/m) to each fraction. The 5%(m/m) value fitted into our geometrical model and was determined by strength measurements. The aim was to make substrates at a minimum level of binding material with acceptable mechanical strength. At this low ratio of binding material, it is very important to homogenise the green powder carefully. For that purpose, a new method was developed to determine the length of homogenisation time: The green powder containing corundum grains and glassy binding material was examined by image analysis of Si-maps, via X-ray microanalysis as a function of homogenisation time. In the Si-maps, the geometrical distribution of Si conglomerates was analysed. Fig. 5 shows a Si-map of a green powder made of

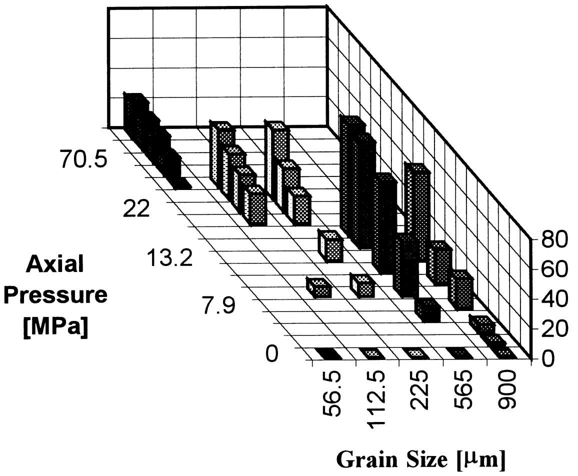

Fig. 2. Growth in specific surface caused by forming pressure.

Table 2
Statistical information gained by image analysis

Homogenisation time (min)	Mean	S.D.	Median	Q1	Q3
0.5	139	302	39	18	105
1	75	164	31	17	70
3	128	400	28	14	69
10	84	170	28	16	56
25	68	132	24	14	63
60	64	105	23	13	66

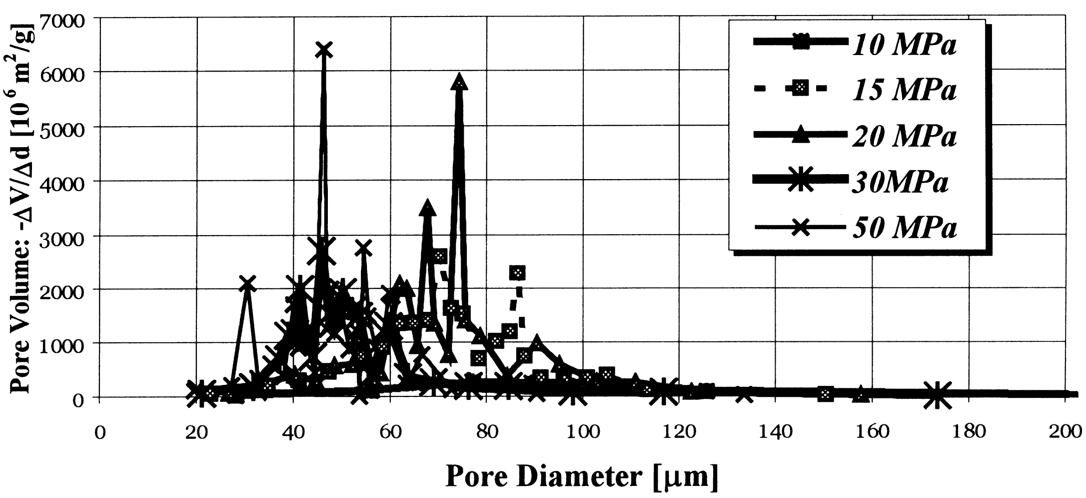

Fig. 3. Pore size distribution of substrates made by different forming pressures.

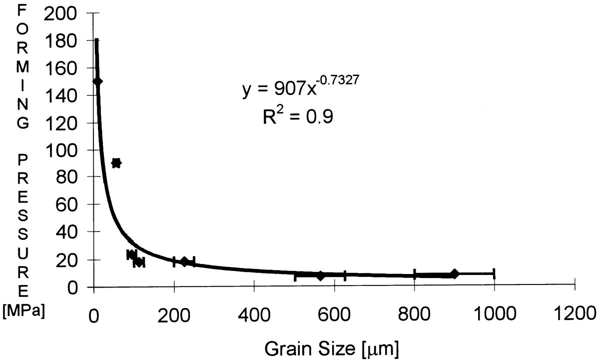

Fig. 4. Optimal forming pressures against original grain size.

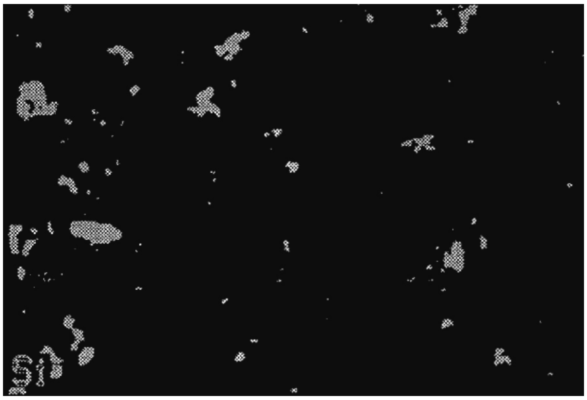

Fig. 5. Si-map of green powder.

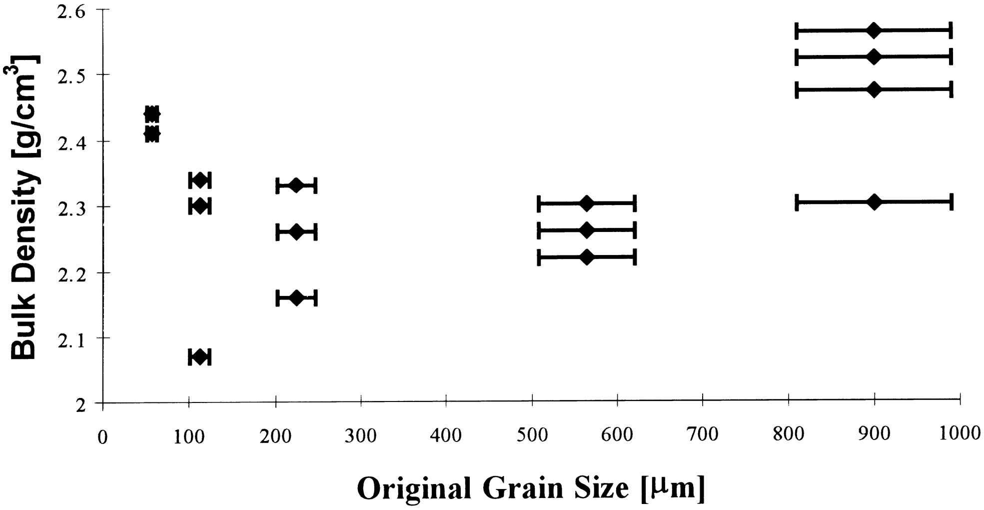

Fig. 6. Bulk density of substrates made with 5%(m/m) binding material.

corundum grains of diameter of 50–63 μm and of Si-containing binding material. A sample calculation can be seen in Table 2. It can be observed that between *25* and 60 min of homogenisation time, there is no significant improvement in homogeneity of the binding material. The experiment was carried out for the fraction of smallest characteristic grain diameter because this fraction needs the longest time to homogenise. Homogenisation time of 25 min was chosen for each fraction.

After sintering, bulk density of substrates containing binding material of 5%(m/m) was measured by hydrostatic method. Fig. 6 shows the result. There is no significant relationship between the density values and the grain size. Another proof of geometrical similarity is that the characteristic pore size ($\hat{d}_{\text{pore}}$) measured by porositmetry depends only on original grain size ($\hat{d}_{\text{grain}}$):

$$\hat{d}_{\text{pore}} \approx 0.54 \cdot d_{\text{grain}} \tag{7}$$

Eq. (7) is a linear regression function, where $R^2 > 0.99$.

3. Conclusion

Ceramic substrates were made from quasi homo-disperse corundum grain fractions with glassy binding material. Forming pressure was experimentally determined for each grain fraction so that calculated growth of specific surface of grains was set to 20%. In this way, geometrically similar substrates can be made with grain size range of 50–1000 μm applying the same amount of binding material. The optimal homogenisation time can be set based on statistical analysis of X-ray microanalysis compositional mapping.

Technological parameters were set experimentally and it was proved by regression model that pore size of substrates can be designed by the described method.

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