LETTER

# Porous alumina ceramics produced with lycopodium spores as pore-forming agents

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Many applications of porous ceramics require a precise control of porosity, as well as pore size, pore shape and pore space topology. Among the various pore-forming agents (PFA) used in ceramic technology, those of biological origin are especially popular for fabricating porous ceramics, due to the fact that their burnout is usually harmless from the ecological and hygiene point of view, while their content of ash-producing inorganic salts is mostly low enough to be neglected with respect to the ceramic composition. Examples are wood flour (saw dust), crushed nut shells [1–3] and poppy seed [4] for pore sizes of several hundreds of micrometers and, on the other hand, starch for pore sizes below 100 μm [5–25]. Commercially available starch types cover the size range from approx. 5 μm for rice starch to approx. 50 μm for potato starch (median diameter) [5–25]. Unfortunately, closer inspection reveals that between corn and tapioca starch, which both have a median size of approx. 12–15 μm, there is a size gap which can currently only be satisfied by wheat starch (median size approx. 21 μm) [14]. Wheat starch, however, is known to be strongly bimodal, with the large size fraction being highly anisometric (oblate shape), which of course cannot be tolerated for all applications. As a consequence, there is currently no biogenic pore-forming agent available that would fill this gap and thus enable e.g. ceramic filters to better compete on the market with their polymeric counterparts for water treatment, which are commonly commercially available with logarithmic pore

size grades, e.g. 1, 2, 5, 10, 20, 50 μm. In this paper, therefore, we have tested the use of lycopodium spores as a new PFA for the preparation of porous alumina ceramics. As shown in this paper, lycopodium spores can be easily mixed with ceramic suspensions, exhibit satisfactory rheological behavior (up to a certain concentration), as well as defect-free burnout and lead to a uniform microstructure with isometric pores of a size of slightly below 30 μm and a percolation threshold of slightly above 10%. We would like to emphasize, that the filtration performance mentioned above is not primarily determined by the size of the pore-forming agent, but by the interconnections between the pores in the sintered ceramic (which extends essentially to the submicron range). Thus the materials in this paper will exhibit fine particle retention [26], which makes them possible candidates for particulate filters.

Lycopodium powder (for this work supplied by H. Klenk, Schwebheim, Germany) consists of isometrically shaped spores of certain club mosses (ground pines), especially *Lycopodium clavatum* L. [27–29], cf. Fig. 1. The particle size distribution was determined via laser diffraction (Analysette 22 NanoTec, Fritsch, Idar-Oberstein, Germany) using the Fraunhofer approximation and via microscopic image analysis (Jenapol, Zeiss, Jena, Germany and Lucia G 4.81, Laboratory Imaging, Prague, Czech Republic) by manual sampling of 1,000 spores. The median diameter is 30.6 μm according to laser diffraction and 33.1 μm according to image analysis (after transforming the number-weighted distribution to a volume-weighted one), cf. Fig. 2. Obviously, the reason for the slight difference is the certain amount (<7 vol.%) of spore fragments and dust with a size below 20 μm, which has been neglected in the image analysis. The size distribution of the spores proper is very narrow, indicating that the natural

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Fig. 1 Optical micrograph of lycopodium spores

growth conditions lead to rather monodisperse systems in this case. This is of course an advantage with respect to the pore size controllability in porous ceramics.

Figure 3 shows the thermogravimetric and differential thermal analysis curves of lycopodium powder measured with a heating rate of 10 °C/min (Setsys Evolution 1750, Setaram, France). It is evident that lycopodium powder burns out in an exothermic reaction in the temperature range between 200 and 530 °C. This temperature range is broader than that for starch (270–540 °C) and therefore it is expected that no special firing schedule is required when high-temperature processing is done with a heating rate of 2 °C/min, say.

In this work, alumina ceramics were prepared from submicron alumina powder (CT 3000 SG, Almatis, Ludwigshafen, Germany) by slip casting aqueous suspensions, deflocculated by a polyelectrolyte (0.5% of Dolapix CE 64, Zschimmer & Schwarz, Lahnstein, Germany), into plaster molds. After demolding and drying the resulting green bodies (cylindrical rods, diameter approx. 5 mm, length approx. 50 mm) were fired at 1570 °C (heating rate 2 °C/min, hold 2 h). For lycopodium contents of up to 15 vol.%
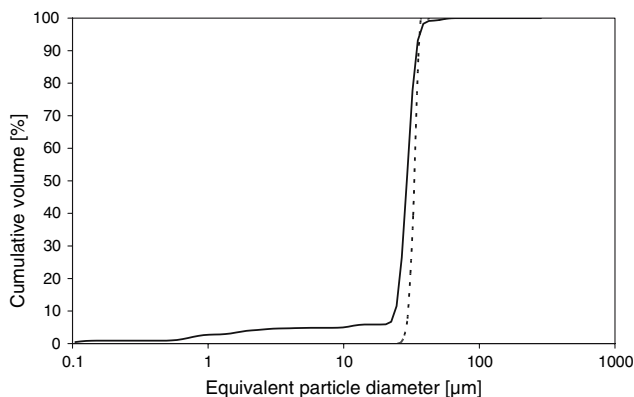


Fig. 2 Particle size distribution of the lycopodium powder (*full line* laser diffraction, *dotted line* microscopic image analysis)
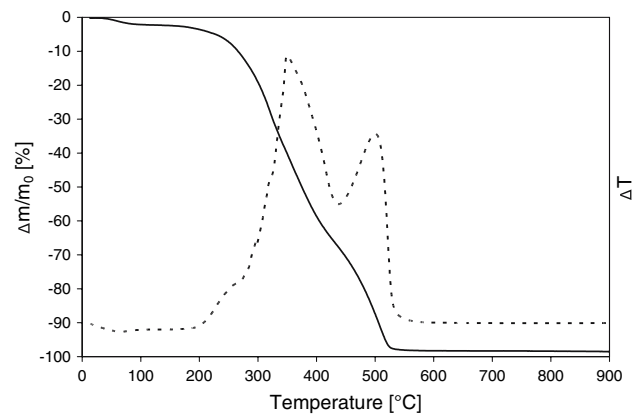


Fig. 3 Thermal analysis of lycopodium powder, indicating burnout behavior (*full line* thermogravimetry—left ordinate in relative mass loss, *dotted line* differential thermal analysis—right ordinate in arbitrary temperature units)

(with respect to alumina) suspensions with an alumina content of 80 wt.% (i.e. 50 vol.%) exhibited a sufficiently low viscosity to enable casting (<200 mPas at a shear rate of 100 $s^{-1}$ and <100 mPas at 1,000 $s^{-1}$, as determined from flow curves at room temperature using rotational viscometry—RV1, ThermoHaake, Karlsruhe, Germany). In order to achieve higher lycopodium contents while retaining similarly low apparent viscosities, the alumina content had to be reduced, cf. Table 1. The density of lycopodium (which is a necessary input information for the calculation of the volume percentage of PFA) is 1.2 $g/cm^3$ (determined by neutral floating in a sugar solution), cf. also [29]. The Archimedes method (double weighing in water) was used to determine the bulk density, open porosity and total porosity (based on the theoretical density of alumina, which is 4.0 $g/cm^3$) of the as-fired porous alumina ceramics. Total shrinkage was measured using a slide caliper. Table 1 lists the average values (arithmetic mean) and the standard deviation of 5–10 samples. Figure 4 shows the values of bulk density and porosity. It is evident that for a lycopodium content of 10 vol.% open porosity is not detectable, while for higher lycopodium contents the percolation threshold is exceeded and up to approx. 30% total porosity the closed porosity remains at a constant level of 10–12%. Moreover, the total porosity can be well controlled up to 30 vol.%, whereas the porosity of samples prepared with a lycopodium content of 40 vol.% is significantly higher than expected.

Figure 5a–d show micrographs of polished sections after cutting and grinding with 1 μm diamond paste. It is evident that for lycopodium contents from 10–30 vol.% the microstructure is uniform and the pores are randomly distributed, while for 40 vol.% lycopodium there is a steep porosity gradient from the sample surface to the interior. Due to this porosity gradient (dense shell—porous core) cracks appear

**Table 1** Microstructural characteristics of as-fired alumina ceramics prepared with lycopodium as a PFA: initial concentrations of suspensions (alumina content in wt.% related to water), lycopodium content (in vol.% related to alumina), bulk density (in g/cm$^3$), open porosity (in %), total porosity (in %) and linear shrinkage after firing (in %)

| Alumina content (wt.%) | Lycopodium content (vol.%) | Bulk density (g/cm$^3$) | Open porosity (%) | Total porosity (%) | Linear shrinkage (%) |
|---|---|---|---|---|---|
| 80 | 10 | 3.56 ± 0.01 | 0 | 10.9 ± 0.2 | 8.7 ± 0.1 |
| 80 | 15 | 3.34 ± 0.03 | 4.3 ± 0.8 | 16.5 ± 0.7 | 8.7 ± 0.1 |
| 78 | 20 | 3.21 ± 0.02 | 6.9 ± 0.4 | 19.7 ± 0.4 | 9.4 ± 0.1 |
| 75 | 30 | 2.86 ± 0.03 | 19.3 ± 0.9 | 28.7 ± 0.7 | 11.0 ± 0.1 |
| 70 | 35 | 2.53 ± 0.03 | 31.1 ± 1.6 | 36.9 ± 0.8 | 11.4 ± 0.1 |
| 68 | 40 | 2.17 ± 0.05 | 43.7 ± 1.1 | 45.6 ± 1.2 | (not meas.) |
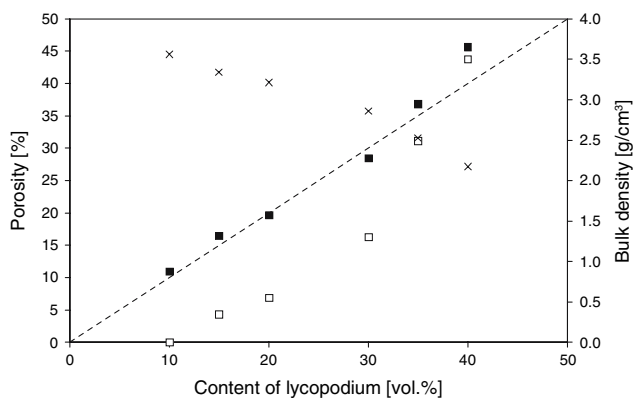


**Fig. 4** Bulk density (*crosses*) and porosity (*open squares*—open porosity, *full squares*—total porosity) of porous alumina ceramics prepared with lycopodium powder as a pore-forming agent

inside these samples, which contribute to the high total porosity value and the high degree of open porosity.

From Table 1 it is also evident that the shrinkage (in the range 9–11%) shows a distinct dependence on the alumina concentration in the suspension, but is largely independent of the PFA content. The absolute values are typical for slip-cast ceramics and the qualitative trend is in agreement with previous experience with other types of PFA, particularly starch [15].

In addition to the samples prepared with lycopodium as the only PFA, tests have been made with a combination of lycopodium together with other PFA of smaller and larger size, respectively: corn starch (median size 14 μm) and potato starch (median size 49 μm), cf. [14]. The composition and microstructural characteristics of these samples are given in Table 2. It is evident, that the bulk density and total porosity of both types of samples (which have a total PFA content of 30 vol.%) correspond very closely to the values for samples prepared with lycopodium alone (30 vol.%). There are, however, differences in the open porosity, which is significantly lower for the samples prepared with potato starch in combination with lycopodium (11% compared to 19%). Although the reason for this phenomenon is not definitely clear, it can be surmised that

the large potato starch granules tend to be surrounded by a thin layer of ceramic suspension (free of PFA), similar to the observed effect of PFA depletion in the suspension close to the mold wall at high PFA concentration (cf. Fig. 5d). Therefore, after firing, the resulting large pores resulting from potato starch will represent isolated void volumes surrounded by a thin shell of dense alumina and thus are not connected to the percolating pore space network, which is essentially formed by the touching pores resulting from lycopodium burnout. The shrinkage values listed in Table 2 are in good agreement with the shrinkage values measured for ceramics prepared with lycopodium alone from suspensions with corresponding alumina concentration, i.e. approx. 11%.

Figure 6 shows the size distribution of the equivalent pore diameters measured by mercury intrusion (AutoPore IV 9500, Micromeritics, USA). It is evident, that the pore size measured does not correspond to the size of the pore bodies (which are clearly spherical and exhibit diameters corresponding to those of the PFA, corrected by shrinkage, i.e. 27.5–29.8 μm), but represent essentially the size of the interconnections between pores (pore throats with a size from below 1 μm to approx. 10 μm), resulting from the contact points of touching lycopodium spores, in accordance with the usual interpretation of mercury porosimetry results in terms of equivalent cylinder diameters (evaluated via the Washburn equation). The pore throat size exhibits a trend from very small values (approx. 0.4 μm) for small PFA concentrations to significantly higher values (several μm) for higher PFA concentrations, and the cumulative volume of large-diameter throats (approx. 10 μm) plays a more significant role in the systems with higher PFA content, as expected. Also, for the PFA combinations lycopodium/corn starch and lycopodium/potato starch the mercury porosimetry results seem to corroborate the above hypotheses: the cumulative volume of large-diameter (10 μm) pore throats in the ceramic body plays only a minor role in the pore size distribution when the PFA system consists of lycopodium and potato starch, while it is more than twice as large when lycopodium alone is used as a PFA.

**Fig. 5** Optical micrographs of polished sections of porous alumina ceramics prepared with lycopodium contents of 10% (**a**), 20% (**b**), 30% (**c**) and 40% (**d**)
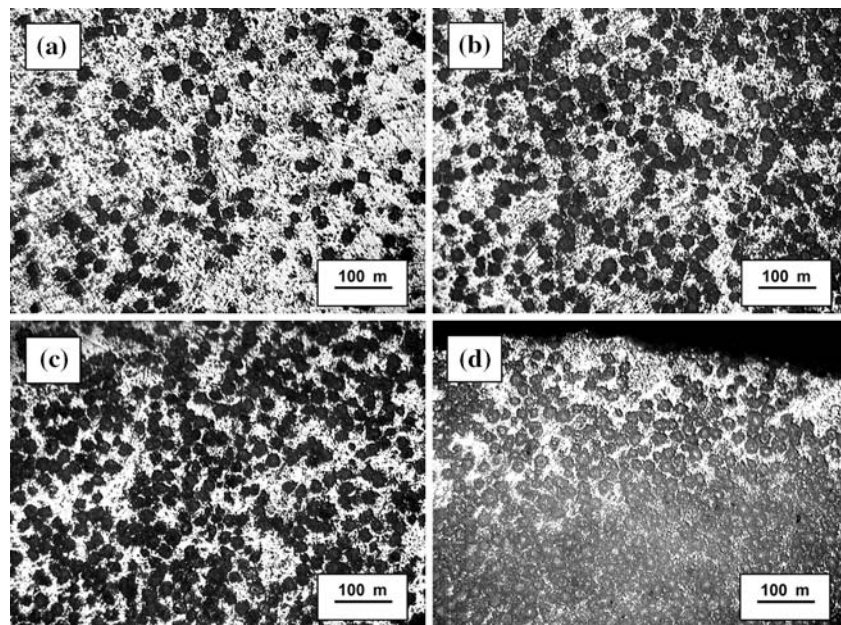


**Table 2** Microstructural characteristics of as-fired alumina ceramics prepared with lycopodium (density 1.2 g/cm$^3$) and starch (density 1.5 g/cm$^3$) as PFA: starch type (C—corn starch, P—potato starch), nominal lycopodium content and nominal starch content (both in vol.% related to alumina), bulk density (in g/cm$^3$), open porosity (in %), total porosity (in %) and linear shrinkage after firing (in %); alumina content 75 wt.% (related to water), total PFA content 30 vol.%

| Starch type | Nominal lycopod. content (vol.%) | Nominal starch content (vol.%) | Bulk density (g/cm$^3$) | Open porosity (%) | Total porosity (%) | Linear shrinkage (%) |
| --- | --- | --- | --- | --- | --- | --- |
| C | 22 | 8 | 2.85 ± 0.02 | 18.7 ± 1.3 | 28.7 ± 0.6 | 11.8 ± 0.2 |
| P | 22 | 8 | 2.79 ± 0.01 | 11.4 ± 0.3 | 30.3 ± 0.3 | 10.9 ± 0.1 |
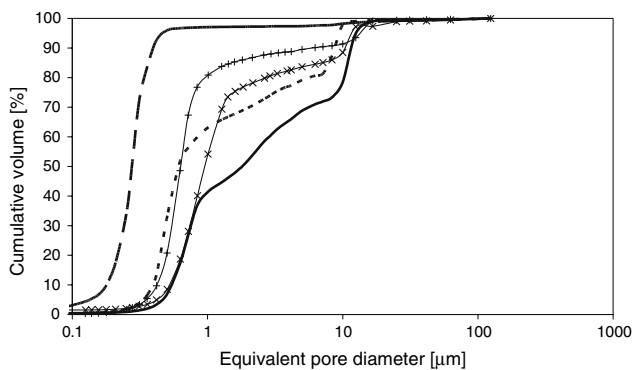


**Fig. 6** Size distribution of equivalent pore diameters determined by mercury intrusion porosimetry (*bold dashed*—20%, *bold dotted*—30%, *bold solid*—35% lycopodium, *thin with plusses*—22% lycopodium and 8% potato starch, *thin with crosses*—22% lycopodium and 8% corn starch)

In concluding, it can be said that the monodispersity of lycopodium powder systems (narrow particle size distribution) makes them promising candidates for pore-forming agents usable to efficiently control pore size in porous ceramics. Thermal analysis indicates that the burnout behavior of lycopodium spores is similar to starch, and in this work it has been confirmed that it does not pose any problems in high-temperature processing. Of course, the rheology has to be carefully controlled when slip casting is used for shaping of the green bodies. This requires lowering the alumina concentration in the suspension (of course at the cost of higher shrinkage) according to the desired content of pore-forming agent and currently limits the lycopodium content to values below 40 vol.%. At this concentration, although the fluidity of the system is sufficiently high when the alumina content is lowered to 68 wt.%, the resulting ceramic bodies exhibit significant porosity gradients, with a higher lycopodium concentration (higher porosity) in the center and an almost lycopodium-free (i.e. dense after firing) surface layer. It may be expected, however, that these problems can be solved by optimizing the dispersion of lycopodium at higher lycopodium concentrations via a control of the mutual interaction forces e.g., using appropriate deflocculants, so that porous ceramics with up to 50% porosity with uniform microstructure consisting of approx. 30 μm pores seem to be a realistic target for the near future. Therefore lycopodium is a promising candidate to fill the gap in PFA sizes

(and the ensuing pore sizes) set by the commercially available starch types [14]. As a by-result of this work, it has been shown that mixing lycopodium spores with other pore-forming agents (e.g. starch) might be a viable route to control the ratio of open and closed porosity, while retaining the same level of total porosity.

## References

1. Rice RW (1998) Porosity of ceramics. Marcel Dekker, New York, p 10
2. Rice RW (2003) Ceramic fabrication technology. Marcel Dekker, New York, p 283
3. Woyansky JS, Scott CE, Minnear WP (1992) Am Ceram Soc Bull 71:1674
4. Gregorová E, Pabst W (in press) Ceram Int. doi:10.1016/j.ceramint.2006.05.019
5. Corbin SF, Apte PS (1999) J Am Ceram Soc 82:1693
6. Davis J, Kristoffersson A, Carlström E, Clegg W (2000) J Am Ceram Soc 83:2369
7. Galassi C, Roncari E, Capiani C, Fabbri G, Piancastelli A, Peselli M, Silvano F (2002) Ferroelectrics 268:47
8. Kim JG, Cho WS, Sim JH (2002) J Mater Sci Mater Electron 13:497
9. Kim JG, Kwon YJ, Oh JH, Cho WS, Whang CM, Yoo YC (2004) Mater Chem Phys 83:217
10. Mattern A, Huchler B, Staudenecker D, Oberacker R, Nagel A, Hoffmann MJ (2004) J Eur Ceram Soc 24:3399
11. Diaz A, Hampshire S (2004) J Eur Ceram Soc 24:413
12. Reynaud C, Thévenot F, Chartier T, Besson JL (2005) J Eur Ceram Soc 25:589
13. Barea R, Osendi MI, Ferreira JMF, Miranzo P (2005) Acta Mater 53:3313
14. Gregorová E, Pabst W, Bohačenko I (2006) J Eur Ceram Soc 26:1301
15. Gregorová E, Živcová Z, Pabst W (2006) J Mater Sci 41:6119
16. Lyckfeldt O, Ferreira JMF (1998) J Eur Ceram Soc 18:131
17. Alves HM, Tari G, Fonseca AT, Ferreira JMF (1998) Mater Res Bull 33:1439
18. Lyckfeldt O (1999) Br Ceram Proc 60:219
19. Lemos AF, Ferreira JMF (2000) Mater Sci Eng C 11:35
20. Pabst W, Gregorová E, Havrda J, Týnová E (2001) In: Heinrich JG, Aldinger F (eds) Ceramic materials and components for engines. Wiley-VCH, Weinheim, p 587
21. Bowden ME, Rippey MS (2002) Key Eng Mater 206–213:1957
22. Týnová E, Pabst W, Gregorová E, Havrda J (2002) Key Eng Mater 206–213:1969
23. Pabst W, Týnová E, Mikač J, Gregorová E, Havrda J (2002) J Mater Sci Lett 21:1101
24. Týnová E, Pabst W, Mikač J (2003) Macromol Symp 203:295
25. Gregorová E, Pabst W (2007) J Eur Ceram Soc 27:669
26. Adler J (2005) Int J Appl Ceram Technol 2:429
27. Wilder GJ (1970) Am J Bot 57:1093
28. Chu MCY (1974) Am J Bot 61:681
29. Wanner SC, Pusch M (2000) J North Am Benthol Soc 19:648