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LETTER

Porosity and pore space characteristics of starch-processed porous ceramics

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In the last few years starch has gained remarkable popularity as a pore-forming agent in ceramic technology [1–14], obviously due to the absence of hygiene and ecological concerns, easy handling and processing (including defect-free burnout), the easy commercial availability in arbitrary amounts, low cost and controlled quality, the rounded shape with well defined aspect ratio (usually close to unity, without large scatter) and the well-defined size distribution for each starch type [15]. Apart from its universal function as a pore-forming agent, starch can serve as a body-forming agent in a new shaping technique called starch consolidation casting (SCC), due to its ability to swell in water at elevated temperatures, thus enabling ceramic green bodies to be fabricated by slip-casting of suspensions with starch into non-porous molds (e.g. metal molds) [16–30].

In this paper we report on new results of a comparative study concerning the microstructure of porous alumina ceramics prepared from starch-containing ceramic suspensions by slip casting into plaster molds and from identical suspensions by starch consolidation casting (SCC) into metal molds. It is shown that a ceramic suspension prepared with 10 vol% starch results in a porous ceramic body with approx. 10% closed porosity (as expected) when the bodies are prepared by traditional slip-casting, whereas the same suspension results in a ceramic with more than 25% porosity (essentially open), when the bodies are prepared via SCC. For the former, the percolation threshold for the pore space to change from closed to partially open is approx. 18%, while the latter are clearly above the percolation threshold even for lower nominal starch contents, exhibiting a highly interconnected pore space in 3D. For the highest nominal starch contents approaching 50 vol%, the difference in the microstructures between the products of the two preparation techniques becomes negligible.

The suspensions were prepared by mixing submicron alumina powder (CT-3000SG, Almatis GmbH, Germany) and waxy corn starch (Amioca Powder TF, National Starch & Chemical, UK) in precisely defined amounts, adding 1 wt% of a commercial dispersant for alumina (Dolapix CE64, Zschimmer & Schwarz, Germany), and agitating for 2 h in a polyethylene bottle with alumina balls on a laboratory shaker (homogenization step). The alumina content, related to the water in the suspension, was 80 wt% (i.e. 50 vol%) in all cases, except for the suspensions with the highest concentration of starch (50 vol% related to alumina), where a lower alumina content (70 wt%, i.e. 36.8 vol% related to water) had to be used to achieve sufficient fluidity for casting. Nominal starch contents (i.e. the weighed-in amounts of starch) were chosen in a way to correspond to volumetric concentrations in the range between 5 vol% and 50 vol%, related to the alumina powder. The as-prepared suspensions were then cast into plaster molds and into metal molds with inner diameters 5 and 7 mm, respectively, and those in the metal molds were subsequently heated for 2 h to 80 °C (shaping or body formation step). The latter procedure enables the starch granules to absorb water from the suspension and to swell (whereas in the first case dewatering occurs via the semipermeable wall of the

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dry mold). After demolding and drying for 24 h in ambient atmosphere at room temperature and subsequently at 105 °C to constant weight all samples were fired at 1570 °C (heating rate 2 °C/min, 2 h dwell). Starch burnout takes place during the heating phase in the temperature range 300–600 °C (pore-formation step).

The as-fired samples were characterized by bulk density and open porosity (via the Archimedes method) and by linear shrinkage (measured using a slide caliper). The total porosity ϕ was calculated from the bulk density ρ via the formula

$$\phi = 1 - \frac{\rho}{\rho_0}, \tag{1}$$

where ρ_0 is the theoretical density of the pore-free solid material (for alumina 4.0 g/cm^3). Obviously, the closed porosity is the difference between total and open porosity, i.e.

$$\phi_{\text{closed}} = \phi - \phi_{\text{open}}. \tag{2}$$

Under the assumption of isotropy the volumetric shrinkage σ_V is related to the linear shrinkage σ_L via the expression

$$\sigma_V = 3\sigma_L - 3\sigma_L^2 + \sigma_L^3. \tag{3}$$

Tables 1 and 2 list the measured values of σ, ϕ, ϕ_{open} and σ_L (arithmetic mean values and standard deviations from 5 to 7 samples) for porous alumina ceramics prepared by traditional slip-casting (using starch as a pore-forming agent only) and by starch consolidation casting (using starch as a pore-forming and a body-forming agent), respectively. It is evident that in the latter case (cf. Table 2) the shrinkage is significantly lower for the bodies prepared from suspensions with 80 wt% alumina (approx. 14.3 %) than for those prepared from suspensions with 70 wt% alumina (approx. 21.1 %), whereas in the first case (cf. Table 1) no such dependence can be found (average shrinkage approx. 10.9%). The reason is clear: the plaster molds used in the first case are semipermeable and enable efficient dewatering of the suspensions, whereas the metal molds in the second case form a closed system, from which water cannot escape. Moreover, the lower shrinkage values when using plaster molds indicates a higher packing density of the alumina particles after shaping. Most important, however, in both cases the shrinkage is independent of the starch content, a finding that is in agreement with results in similar systems using other starch types [28–30] and which is a consequence of the fact that the shrinkage of large pores in a fine-grained matrix is dictated entirely by the matrix shrinkage [31].

Since the porosity due to the large pores remains essentially unchanged during sintering, the different shrinkage values in the case of SCC with different alumina contents (80 wt% vs. 70 wt%) must be the consequence of a different packing density of the alumina particles after the shaping step.

Taking the average value of 14.3 ± 0.4% for σ_L of the 80 wt% alumina suspension the corresponding volumetric shrinkage σ_V is 37.1 ± 0.6%, corresponding to an alumina packing fraction of 62.9%. Another estimate based on the measured final porosity (and using the respective linear shrinkage values as a bias) results in 64.8%. These values are close to the packing fraction of a random closest packing (rcp structure) of monodisperse spheres, which is approx. 64% [31]. In contrast, estimates of the alumina packing fraction after shaping are significantly lower (approaching 50%) for the 70 wt% alumina suspension in SCC and significantly higher (approaching 70%) in the case of traditional slip casting, as expected. The decreasing packing fraction with decreasing alumina content in the SCC suspensions correlates reasonably with the higher water content confined in the system when using the starch consolidation casting process, whereas in

Table 1 Bulk density, open porosity, closed porosity and linear shrinkage of porous alumina ceramics prepared by traditional slip casting with starch as a pore-forming agent

Nominal starch content [vol%]	Bulk density [g/cm^3]	Open porosity [%]	Total porosity [%]	Linear shrinkage [%]
5	3.72 ± 0.02	0.02 ± 0.02	7.1 ± 0.4	12.1 ± 3.3
10	3.52 ± 0.02	0.04 ± 0.02	12.1 ± 0.5	11.0 ± 2.1
15	3.34 ± 0.01	0.01 ± 0.01	16.6 ± 0.3	11.1 ± 1.9
17.5	3.23 ± 0.01	0.3 ± 0.3	19.2 ± 0.2	10.1 ± 1.6
18.5	3.21 ± 0.01	2.1 ± 0.5	19.7 ± 0.2	11.6 ± 1.9
20	3.21 ± 0.02	5.4 ± 0.6	19.9 ± 0.5	10.5 ± 2.7
22.5	3.06 ± 0.01	13.9 ± 0.8	23.5 ± 0.1	10.9 ± 2.1
27.5	2.90 ± 0.01	22.1 ± 0.4	27.5 ± 0.2	10.2 ± 2.0
30	2.75 ± 0.01	25.7 ± 0.3	31.3 ± 0.1	11.3 ± 1.6
50	2.02 ± 0.02	48.7 ± 0.4	49.5 ± 0.5	10.6 ± 1.6

Table 2 Bulk density, open porosity, closed porosity and linear shrinkage of porous alumina ceramics prepared by starch consolidation casting, using starch as a pore-forming and body-forming agent

Nominal starch content [vol%]	Bulk density [g/cm^3]	Open porosity [%]	Total porosity [%]	Linear shrinkage [%]
5	Not feasible			
10	2.90 ± 0.03	24.8 ± 0.8	27.7 ± 0.8	14.4 ± 0.5
20	2.74 ± 0.01	28.5 ± 0.5	31.4 ± 0.3	13.9 ± 0.1
25	2.72 ± 0.02	28.1 ± 0.1	31.9 ± 0.4	14.7 ± 0.2
30	2.60 ± 0.01	32.6 ± 0.2	35.1 ± 0.1	14.3 ± 0.3
50	2.09 ± 0.07	47.1 ± 1.7	47.7 ± 1.7	21.1 ± 1.1

traditional slip casting the packing density achieved is determined by the driving force, capillary suction, and is therefore largely independent of the alumina concentration.

Figure 1 compares the total porosity achieved by either process as a function of the nominal starch content. If the starch would not swell during the shaping step, the total porosity should correspond exactly to the nominal starch content (cf. the straight line with slope 1). This is approximately the case for the ceramics prepared by traditional slip-casting (where starch serves exclusively as a pore-forming agent, but not as a body-forming agent), (cf. Fig. 2). For ceramics prepared by starch consolidation casting, however, the total porosity is typically significantly higher than the nominal starch content, which is a clear indication of starch swelling (accompanied by a corresponding increase in the average pore size), (cf. Fig. 3). This finding is well known [28–30] and imposes a natural limit to the possibility of porosity control via starch consolidation casting: total porosities smaller than 20–25% are difficult to achieve.

Figure 4 compares the open porosity achieved by either process as a function of the nominal starch content. It is evident that the ceramics prepared by traditional slip-casting exhibit a percolation threshold at a nominal starch content of approx. 18 vol% (corresponding to a porosity of approx. 18%). Below this percolation threshold all pores are closed and above it the content of open pores increases with increasing porosity, until at approx. 50% almost all pores are open. The volume fraction of closed pores increases from moderate values for low porosities (e.g. 7.1 % for 5 vol% nominal starch content), exhibits a maximum (19%) at the percolation threshold and decreases again (to values of 5.6% and 0.8% at 30% and 50 vol%

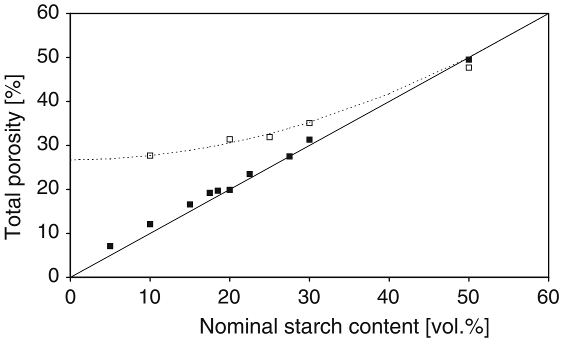

Fig. 1 Total porosity of as-fired ceramic bodies in dependence of the nominal starch content (traditional slip-casting: full symbols and straight line with slope 1; starch consolidation casting: empty symbols and dotted fit curve $\phi = 26.7 + 0.0109\phi_S^{1.96}$)

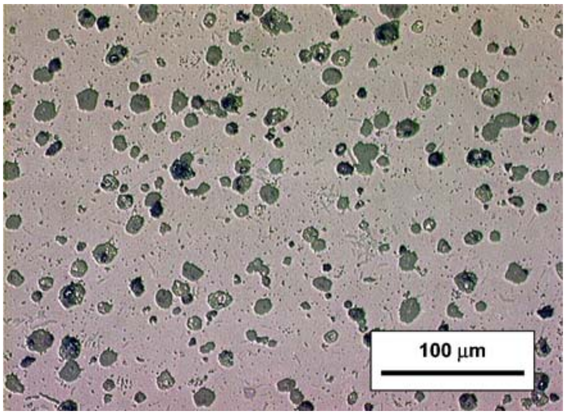

Fig. 2 Micrograph of porous alumina prepared by traditional slip casting with 10 vol% waxy corn starch as a pore-forming agent; the resulting total porosity is 12.1% (i.e. close to the expected value), open porosity close zero; pores are isolated

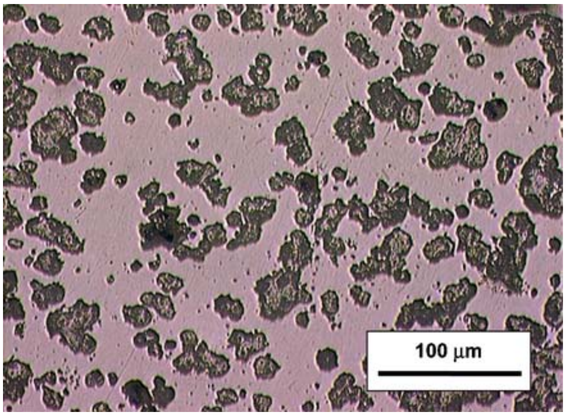

Fig. 3 Micrograph of porous alumina prepared by starch consolidation casting with 10 vol% waxy corn starch as a pore-forming and body-forming agent; the resulting total porosity is 27.7%, open porosity 24.8%; many pores exhibit overlap

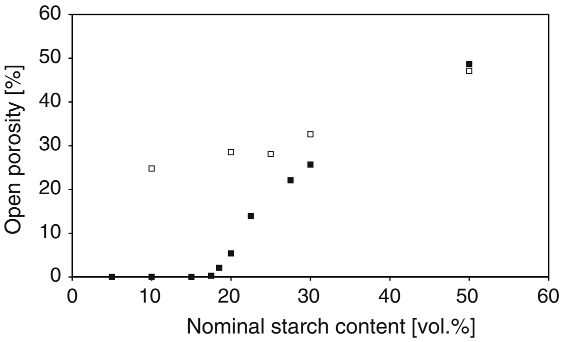

Fig. 4 Open porosity of as-fired ceramic bodies in dependence of the nominal starch content (traditional slip-casting: full symbols—note the percolation threshold at approx. 18%; starch consolidation casting: empty symbols)

nominal starch content, respectively). In contrast, ceramics prepared by starch consolidation casting exhibit significantly higher open porosities at low nominal starch contents and are characterized by the absence of a percolation threshold. Closed porosities are small and more or less independent of the nominal starch content (2.3 ± 1.1%). This indicates a highly 3D interconnected pore space (large pore bodies connected by small pore throats), even in the case of small nominal starch contents. At high nominal starch contents (50 vol%) the difference in the final products becomes negligible, presumably because in this case starch swelling is impeded by excluded volume effects.

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