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Porosity and pore size control in starch consolidation casting of oxide ceramics—Achievements and problems

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Abstract

The possibilities and limits of porosity and pore size control via starch consolidation casting (SCC) are discussed from a principal point of view. The results for alumina ceramics indicate that porosity control between 25 and 50% is feasible, while lower and higher porosities are difficult to achieve by SCC. The main factor of pore size control is the selected starch type, although swelling should be taken into account for a more precise size control. Of the starch types investigated here, potato starch is the largest (resulting in pore sizes of 50 μm and higher) and corn starch is the smallest (14 μm), while wheat starch is intermediate (20 μm). A quantitative comparison of pore size results, however, is complicated by Wicksell's problem and (in the case of potato and wheat starch) the anisometric shape (median aspect ratios of 1.3 and 2.0 for prolate and oblate shape, respectively).

Keywords: Slip casting; Microstructure-final; Porosity; Al_2O_3; Starch consolidation casting

1. Introduction

Starch consolidation casting (SCC) is a promising near net-shaping method for the preparation of porous ceramics.[1–15] Starch is a frequently used pore-forming agent in ceramic technology, since due to its chemical composition (consisting essentially of C, H and O) it is easily burnt out during firing without residues in the final ceramic body. In addition to this traditional function of starch as a pore-forming agent the SCC process exploits the capability of starch to swell in hot water and thus to enable body-formation in situ, i.e. without dewatering across a semipermeable interface. It is precisely the phenomenon of starch swelling, however, that makes porosity control a difficult task. Furthermore, pore size control is complicated by the fact that starch is a natural biopolymer (and not a synthetic one), which exhibits a typically broad size distribution and for which the shape is more or less determined by the biological source and plant genotype.[13,16]

Previous work at the ICT Prague has been focussed on testing the viability of the SCC process to prepare alumina ceramics, zirconia ceramics and alumina–zirconia composite ceramics with potato and corn starch[7–10] and on modelling the swelling kinetics of potato starch.[11,12] Recently, a detailed study has been performed at the ICT Prague comparing the particle (granule) size distributions of five commercially available native starch types (potato, wheat, tapioca, corn, rice), as measured via microscopic image analysis and laser diffraction.[13] Up to now, however, only potato, corn and rice starch have appeared in the literature on SCC.[1–12] In this work we include new findings with wheat starch and compare them with recent results concerning potato and corn starch.[14] In particular, the state-of-the-art limits of porosity control and the possible influence of shape anisometry of potato and wheat starch on the results of pore size determinations via microscopic image analysis are discussed.

2. Experimental

Submicron alumina powder CT 3000 SG (Almatis GmbH, Germany) with a median particle size $D_{50} = 0.6$ μm was used in combination with three starch types, potato starch (Solamyl, Natura, Czech Republic) with $D_{50} = 49$ μm, wheat starch (Amylon, Czech Republic) with $D_{50} = 20$ μm and corn starch (Gustin, Dr. Oetker, Czech Republic) with $D_{50} = 14$ μm, cf.[13] Aqueous suspensions with 70–80 wt.% alumina were prepared in a standard way[7–10] and mixed with starch in amounts corresponding to 10 and 50 vol.% (related to the ceramic powder). After mixing they were poured into metal molds and heated to 80 °C for

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at least 1 h. After demolding and drying the bodies were fired at 1570 °C (heating rate 2 °C/min, dwell 2 h). Shrinkage was measured using a slide-caliper and calculated from the mold dimensions and the body dimensions after firing. Bulk density and open porosity were determined via the Archimedes method in water.

Concerning swelling behavior, potato starch exhibits the largest water absorption and swelling capacity (linear swelling by approximately a factor 4), while wheat and corn starch exhibit a significantly smaller swelling capacity (linear swelling by approximately a factor 2), cf.[14] The temperature range of swelling is broadest for potato starch and smallest for wheat starch, absolute swelling temperatures are lowest for potato starch (50–68 °C) and highest for corn starch (62–80 °C), cf.[13,16] From the rheological viewpoint starch swelling is accompanied by a viscosity increase, a transition to viscoelastic behavior and/or the formation of an elastic gel at temperatures between 60 and 80 °C.[13,17] This change in the rheological character of the starch suspension determines, together with the heating kinetics and the kinetics of swelling,[12] the body-formation kinetics. After approximately 1 h in a laboratory drier at 80 °C the system is heated to approximately 98% of the final temperature and the swelling step is usually finished. It was found that increasing the temperature to close to 100 °C did not significantly change neither the kinetics nor the final degree of swelling.[14] Potato starch granules can be considered as prolate spheroids, corn starch granules as isometric polyhedra with rounded corners and wheat starch as a bimodal system with a fine fraction of spherical particles and a coarse fraction of oblate spheroids.[13] In addition to their more anisometric shape, potato starch and wheat starch exhibit a broader size distribution (span 1.45–1.65) than corn starch (span 1.13), cf.[13]

The micrographs of polished sections of the porous alumina ceramics have been evaluated by quantitative image analysis, using a commercial software package (LUCIA G, version 4.81, Laboratory Imaging, Czech Republic). Detailed results of these measurements, including a discussion of the so-called Wicksell corpuscle problem (or random section problem), which is always relevant when size distributions obtained from 2D section planes are to represent true size distributions of 3D objects, will be reported in a forthcoming paper. In the present paper only the aspect ratio distribution is of concern, which has been obtained for the ceramics prepared with potato and wheat starch by manually circumscribing a sufficiently large number of pores (approximately 1700 for the ceramics prepared with potato starch and approximately 1600 for the ceramics prepared with wheat starch) with so-called five-point ellipses (i.e. ellipses approximating the pore shape and area, which have been constructed on the basis of five points marked on the pore boundary).

3. Results

3.1. Porosity control in starch consolidation casting

Experience has shown that porosity control in the SCC process is less trivial than it seems, because starch swelling interferes with the body-formation step. Fig. 1 shows that a nominal starch content of 10 vol.% (i.e. 10 vol.% starch weighed in with respect to alumina powder, assuming a starch density of 1.5 g/cm^3) results in a porosity more than twice this value (25.0 ± 1.3%), irrespective of the starch type used. With smaller starch contents it is difficult to achieve complete water absorption by the swelling starch, so that after opening the molds the bodies are too wet to be handled. With increasing starch content the final porosity corresponds more and more to the nominal starch content (52.8 ± 2.6% for a nominal starch content of 50 vol.%). For a nominal starch content ϕ_S between 10 and approximately 60 vol.% the total porosity ϕ can be roughly described via the empirical relation $\phi = 22.9 + 0.0725\phi_S^{1.54}$. This relation delivers a first general estimate of the final porosity which can be expected for a ceramic prepared with a certain selected amount of starch. Of course, whenever necessary the relation can be made more specific and precise, e.g. by determining the exact numerical values of the fit parameters for a certain starch type (this, however, makes sense only in connection with a statistical evaluation of the scatter of the porosity values and a highly precise He-pycnometric measurement of the starch density, taking into account ambient humidity).

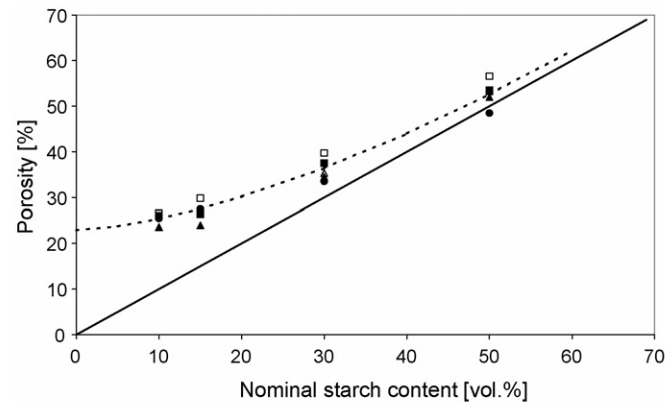

Fig. 1. Total porosity achieved in alumina ceramics vs. nominal starch content (potato starch—empty squares,[10] full squares,[14] corn starch—empty triangles,[10] full triangles,[14] wheat starch—full circles).[14].

Higher porosities approaching 60% might be attainable, but at the cost of a higher shrinkage (apart from the problem of starch agglomeration), because the suspension viscosity increases considerably with increasing starch content so that the solids content would have to be reduced in order to guarantee sufficient flowability for casting and defect-free mold filling. The fact that no correlation has been found between shrinkage and starch content indicates the solids content in the suspension alone is responsible for shrinkage (linear shrinkage 16 ± 2% for alumina ceramics prepared by SCC).[10,14] Note that lower porosities, although not attainable via the SCC process, can readily be achieved by using starch as a mere pore-forming agent, e.g. in traditional slip casting with plaster molds.

3.2. Pore size control in starch consolidation casting

Since the starch-pores are more than one order of magnitude larger than the interstitial voids between the alumina particles, they will not shrink significantly during sintering. Figs. 2–4 show

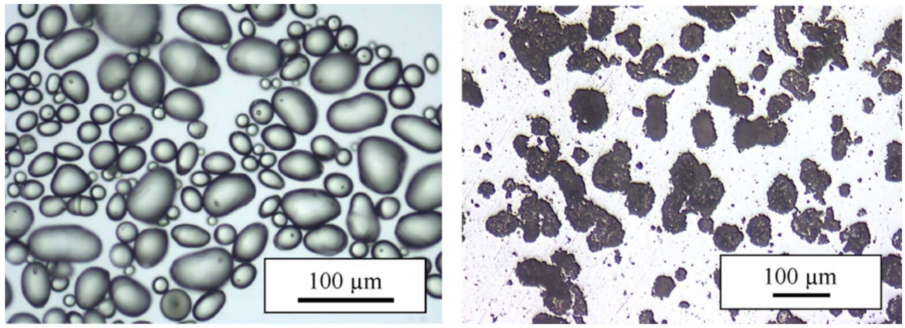

Fig. 2. Potato starch (left) and alumina ceramics prepared with potato starch (right).

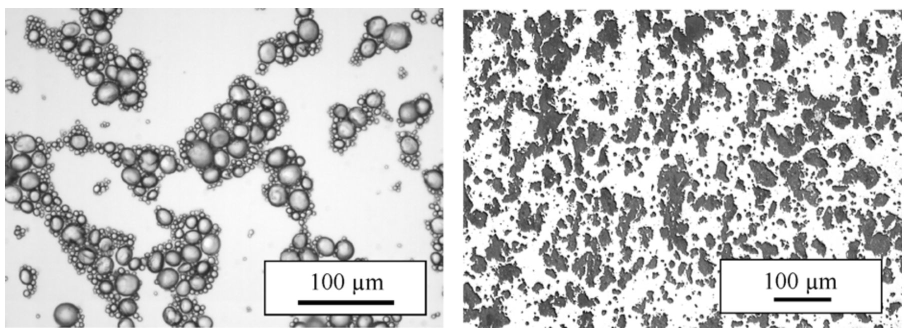

Fig. 3. Wheat starch (left) and alumina ceramics prepared with wheat starch (right).

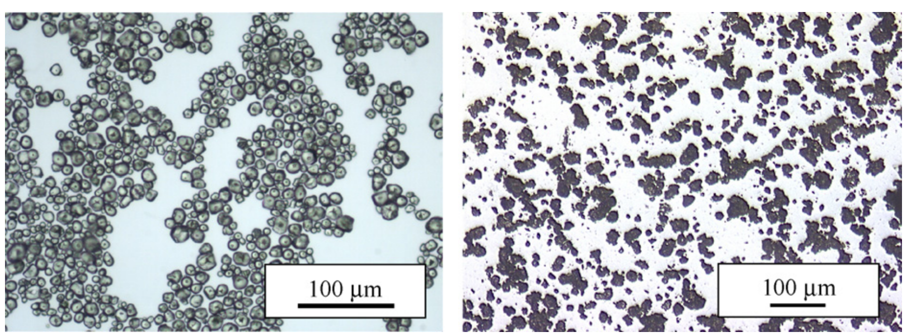

Fig. 4. Corn starch (left) and alumina ceramics prepared with corn starch (right).

potato, wheat and corn starch, respectively, and the corresponding microstructures of porous alumina ceramics prepared from them.

It is evident that the pore size corresponds approximately to the size of the starch granules. However, although this finding is in accordance with that of other authors,[1–6] it is very difficult to quantify this statement for two reasons: first, in the case of anisometric particles it may not be possible or reasonable to transform the size distribution measured via microscopic image analysis from polished sections to a volume-weighted distribution. Second, even if correctly transformed to a volume-weighted size distribution,[18] such a distribution is always shifted to smaller sizes because of Wicksell's corpuscle problem (sphere intersection problem).[19] In order to solve the latter at least approximately, non-trivial statistical calculations must be invoked (at least a so-called Saltykov transformation).[19] Fig. 5 shows the cumulative aspect ratio distribution of 2D sections of pores due to corn, potato and wheat starch, respectively. Potato starch is

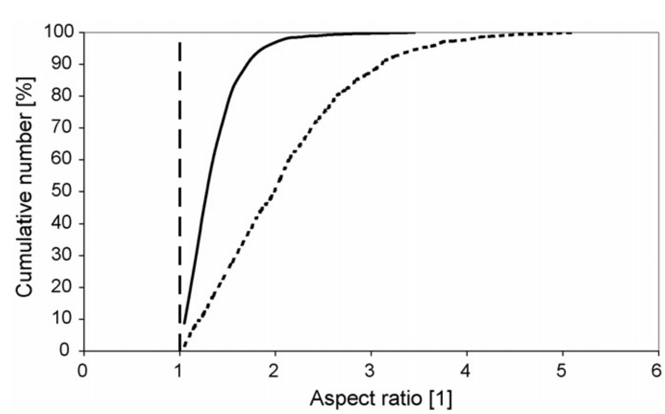

Fig. 5. Aspect ratio distribution of 2D sections of pores due to potato starch (full line, center) and wheat starch (dotted line, right), determined from polished sections; isometric pores (e.g. due to corn starch) are close to the vertical dashed line on the left.

prolate and the corresponding pores exhibit a narrow distribution with a median aspect ratio of 1.3, in good agreement with the average aspect ratio of 1.3–1.4 determined for potato starch in.[13] The coarse fractions of wheat starch are oblate and the corresponding pores exhibit a relatively broad distribution with a median aspect ratio of 2.0, a quantity which is not accessible via microscopic image analysis of wheat starch particles on an object slide. Note, however, that 2D sections usually indicate aspect ratios lower than the real ones, and special orientations are needed to reveal the maximum aspect ratios in a system. The vertical line, corresponding to pores with a unit aspect ratio, has been included as a guide to the eye. It approximates the isometric shape of the corn starch granules.

4. Conclusions, summary and outlook

The possibilities and limits of porosity control and pore size control via starch consolidation casting (SCC) have been discussed from a principal point of view. The results for alumina ceramics indicate that porosity control between 25 and 50% is feasible, while lower and higher porosities are difficult to achieve. Of course, lower porosities can readily be attained by using starch as a mere pore-forming agent, e.g. in traditional slip casting with plaster molds. The main factor of pore size control is clearly the selected starch type, although swelling must be taken into account when precise size control is to be achieved in the SCC process. Of the starch types investigated here, potato starch is the largest (resulting in pore sizes of 50 μm and higher) and corn starch is the smallest (14 μm), while wheat starch is intermediate (20 μm). Rice starch, the smallest of the commonly available starch types (5 μm) will be the subject of future research. A quantitative comparison of pore size results, however, is complicated by Wicksell's problem and (in the case of potato and wheat starch) the anisometric shape (median aspect ratios of 1.3 and 2.0 for prolate and oblate shape, respectively).

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