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Processing of Porous Ceramics by 'Starch Consolidation'

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Abstract

A new consolidation method for forming porous ceramics was developed using starch as both consolidator/binder and pore former. Simple and complex-shaped components of porous alumina were shaped and demoulded in wet state. After drying, burn-out and sintering, materials with ultimate porosities between 23 and 70% were obtained. The overall pore structures were dominated by the large spherically shaped pores (10–80 μm) left by the starch particles. Furthermore, the average size of the small pores connecting the large pores, measured by Hg porosimetry, was controlled by the total solids loading and starch content in the originally prepared slips and varied between 0·5 and 9·5 μm. Chemically modified starch was found to give better dimensional control and regularity regarding average size of the connecting pores than native starch owing to more stable properties during water processing. This new forming technique can be used in the manufacture of various porous ceramics for thermal insulation applications, as filters/membranes and gas burners, or as bioceramics. Major advantages are the simplicity of the process, the possibilities of forming complex shapes using various mould materials and the low-cost processing equipment/materials needed. *© 1997 Elsevier Science Limited.*

1 Introduction

Porous ceramics have great potential in many applications in which chemical, thermal or mechanical stresses make metallic or polymeric materials unsuitable, as in thermally insulating applications, as filters, membranes and gas burners, or as bioceramics. The requirements for the ceramic matrix and the pore structure may vary depending on type of application. For effective thermal insulation it is favourable to have closed porosity whereas, on the other hand, filters and membranes require open porosity. In the bioceramics field it is desirable to use ceramic implants with certain porosity to promote integration with biological tissues.[1]

There exist various methods to obtain porous ceramics such as the *polymeric sponge* method, in which a ceramic slip is forced to penetrate a sponge.[2] After drying, the sponge is removed by a burn-out operation and the ceramic material is sintered, resulting in a material with open porosity. Another common technique is the *foaming* method in which a foaming agent is added to the ceramic suspension. By agitation a foam is built up which, after removal of the liquid phase, builds up a pore structure, essentially consisting of the closed pores that remain after sintering. Other techniques focus on the ceramic powder compounding (particle size distribution),[2,3] fugitive organic additives[4] and/or particle interactions in the powder suspension prior to the forming operation.[5] Each method has its advantages and potential uses. The control of the processing and, consequently, the ultimate material properties in terms of pore structure and component dimensions is a general problem, however.

Some of the techniques for the manufacture of porous ceramics are closely related to the forming technique, e.g. the use of the polymeric sponge method. Other methods can be used more freely when it comes to the forming technique, e.g. the use of organic additives as pore formers. Regardless of the technique used, the processing of the ceramic powder—with or without organic additives—must be properly controlled to obtain the desirable properties of the ultimate porous ceramic.

Powder-based forming of ceramics usually includes a step in which ceramic powders are dispersed in a liquid. To reach high solids loading of the suspension, electrostatic, steric or electrosteric stabilisation can be used to prevent the ceramic particles from flocculating.[5] Further steps in the processing of the slurry (slip) can involve spray-drying prior to dry pressing or wet forming by slip casting, injection moulding or tape casting.

There is also a new family of forming techniques in which ceramic slips are forced to consolidate in an inpermeable mould, for example by a polymerisation reaction (gel casting),[6] destabilisation (direct coagulation consolidation, DCC),[7] polycondensation reactions (hydrolysis assisted solidification, HAS)[8] or freezing (Quick Set®).[9,10] In these techniques, the particle structure of the slip is consolidated without powder compaction or removal of liquid. A potential advantage of these 'direct-consolidation' techniques is good material homogeneity which promotes control of the shrinkage during sintering and, hence, control of the ultimate dimensions of the components. However, each of the existing methods has disadvantages, such as the use of toxic initiators in water-based gel casting, expansion and ice crystals in water-based systems, or contraction when using organic solvents in freeze forming or low wet-body strength in DCC and HAS.

In this study, a new forming technique for the fabrication of porous ceramics was developed which belongs to the family of direct-consolidation methods. Porous alumina materials were manufactured using starch both as consolidator/binder and as a pore former. Components of various shapes and sizes were produced to evaluate the processing ability. After consolidation, burn-out of the organic material and sintering the ultimate materials were characterised with respect to their pore structure.

2 Starch Chemistry—Starch Consolidation

The new forming method for porous ceramics developed in this work is based on the fundamental property of starches—their gelling ability in water.[11]

For commercial uses starches are extracted from the seeds of cereal grains (corn, sorghum, wheat or rice), certain roots (potato, tapioca or cassava or arrowroot) and from the pith of the sago palm. Starches are used as components and/or processing aids in the manufacture of adhesives, textiles, paper, food, pharmaceuticals, and building materials. The important properties of starches, which make them so widely used, are their thickening, gelling, adhesive and film-forming abilities. These properties can be modified by chemical or physical treatments and/or enzyme treatments to obtain optimum characteristics for each specific application.

Starch grains are normally white, dense and water insoluble at room temperature. They vary in size between 2 and 170 μm. Most starches consist of mixtures of two polysaccharide types, a linear one, amylose, and a highly branched one, amylopectin. Amylose gives the starch its gelling property in aqueous suspensions. The glucose units that build up the polymeric chains in starch expose a large amount of hydroxyl groups and, therefore, give a strong hydrophilic character to starch granules (see Fig. 1).

The water insolubility of starch granules below about 50°C means that they can be handled and processed at room temperature without significant impact on the granule structure. However, when the starch suspension is heated to a temperature between 55 and 80°C (depending on type and concentration), the intermolecular bonds holding the granules together are weakened. During this process the granules undergo a rapid and irreversible swelling by water uptake which results in an increased granule size to many times the original size.[11]

Although the starch granule is insoluble in water below the gelling temperature there is limited water absorption when the granule is exposed to wetting or high humidity. This results in a slight swelling of the granule, which is reversible on drying. Under normal atmospheric conditions most commercial starches contain 10–17% moisture.

By mixing ceramic powders and starch in a water suspension, pouring it into a mould and heating it up to 60–80°C, the starch particle will swell by water uptake. This swelling removes water from the slip causing the ceramic particles to stick together and, consequently, consolidate into a solid body. As the starch granules or particles swell they will also act as a binder adding strength to the consolidated body which enables demoulding prior to drying. After burn-out of the starch and sintering of the ceramic matrix a material is obtained with a porosity corresponding to the original amount, shape and size of the starch particles including the allowed swelling during the consolidation.

Besides the favourable gelling properties of starches, they are environmentally friendly, easy to burn out and, not least important, they are very cheap.[4]

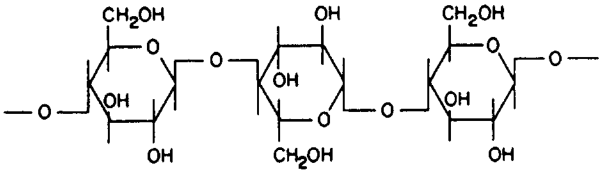

Fig. 1. Starch as a polymer consisting of condensed glucose units.

3 Materials

Ceramic and organic materials used in this work are listed in Table 1 together with some characteristics.

The starches used were of two types, one native potato starch, available in the supermarket for use in cooking, and one etherficated potato starch modified by hydroxy-propylation and cross linking. The latter one was used in two versions with different particle size distribution, TRECOMEX AET1, with the original potato starch average size of 55 μm (see Fig. 2), and MICROLYS, with a fractionised average size of 20 μm.

The native starch is expected to be more sensitive to chemical, thermal and physical treatment than the potato ethers. However, the latter give higher viscosity, although more stable, than the native starch owing to a certain swelling during the modification process. Furthermore, the gelling temperature is expected to decrease as a certain granule breakdown process is initiated already by the modification. The etherfication and early granule breakdown of the potato starch promote a stronger adhesion to ceramic particles such as inorganic pigments in paints.[11]

A polyacrylic acid, Dispex A40 (Allied Colloids Ltd, UK), a type commonly used in stabilising alumina slips, was used as dispersant. When using this dispersant the pH is kept in the range 9–9·5.

4 Experimental Procedures

4.1 Slip preparation

Alumina stock slips (800 cm^3) (including 0·05 wt% MgO based on solids) with 50 or 55 vol% solids loading were prepared by ball milling for 24 h using cylindrical grinding media of alumina with varied sizes (ϕ =20·5, 15·5 and 7·5 mm). The slips were stabilised using 0·40 wt% Dispex A40.

Samples of 100 cm^3 were taken from the stock slips and various quantities of the different starches (T = TRECOMEX, M = MICROLYS and N = Native) were added together with additional water. Based on a starch density of 1·43 g cm^{-3} and an alumina density of 3·98 g cm^{-3} the volume content of starch was calculated and varied between 17·3 and 66·2 vol% based on solids. The total solids loading was set to 52–54·2 vol% (low regime) or 57·1–59·1 vol% (high regime) with decreased solids loading when the amount of starch increased. After 2 h stirring for homogenisation and conditioning the slips were subjected to rheological measurements and forming experiments.

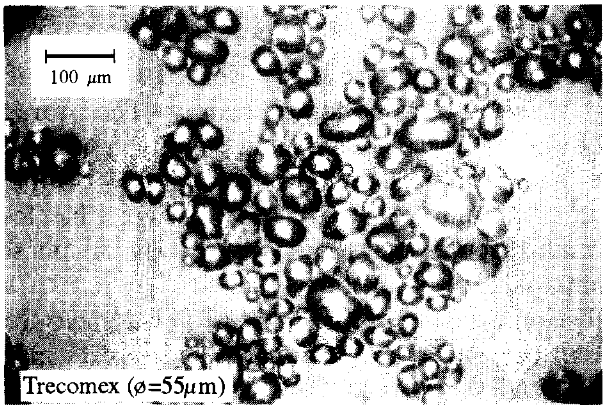

Fig. 2. Chemically modified potato starch (TRECOMEX) with an average particle size of 55 μm.

4.2 Rheological measurements

Steady shear measurements of the equilibrium viscosities at various shear rates were conducted with a control–stress rheometer (CSL 500, Carri-Med, UK) and a concentric cylinder measurement device with a 1 mm gap. The measurements were performed in the shear rate range of 1–500 s^{-1} at a constant temperature of 25°C. Before measurement all slips were exposed to a pre-shearing at about 500 s^{-1} for 1 min followed by a rest for 2 min.

To characterise the gelling behaviour when using the different types of starch (native and chemically modified), alumina slips with a total solids loading of 52 vol% and a starch content of 17·3 vol% based on solids, were subjected to sinusiodal oscillation at a constant frequency of 1 Hz and a stress, σ_0, of 2·5 Pa during increased temperature from about 35 to 60°C in a sequence of about 20 min. During this operation the responding strain, γ_0, of the material was measured. The strain amplitude is expected to decrease when consolidation occurs which causes an increase of the calculated storage modulus, G′, defined as,

Table 1. Data of the ceramic and organic materials used in this study

Material	*Producer*	*BET area (m^2 g^{-1})*	*Average particle size (μm)*	*Density (g cm^{-3})*
Alumina (A16 SG)	Alcoa Chemicals, USA	8·5[*]		3·98[§]
Magnesia (analytic grade)	Merck, Germany	25[*]	—	3.58[§]
Native potato starch	Ramazzotti Ltd., Portugal	—	55[†]	1·44[¶]
TRECOMEX AET 1	Lyckeby Stärkelsen AB, Sweden	—	55[‡]	1·43[¶]
MICROLYS	Lyckeby Stärkelsen AB, Sweden	—	20[‡]	—
Polyacrylic acid	Allied Colloids, UK	—	—	—

[*] Micromeritics FlowSorb II 2300, USA; [†] assumed; [‡] producer's data; [§] theoretical densities; [¶] helium multipycnometer, Model MVP-1, Quantachrome, USA.

$$G' = \sigma_0/\gamma_0 \cos\delta \qquad (1)$$

where δ represents the phase (loss) angle between the stress and responding strain.[12] The storage modulus, also called dynamic rigidity, represents the elastic (in phase) component of the complex shear modulus, $G^* = G' + iG''$, where the loss modulus represents the viscous (out of phase) component.

The temperature in the suspension was measured by an external thermocouple placed in the upper part of the slip sample. Pre-studies showed that the temperature difference between the bottom and the top of the sample did not exceed 1°C.

4.3 Forming

A wide range of shapes were formed by 'starch consolidation' using various plastic mould materials. For the materials evaluation small cylinders (ϕ =25 mm, h$\approx$15 mm) were formed. Various figures (10–30 mm thickness), bone shapes and pipes, were formed using latex rubber moulds. Flat plastic bags and balloons were used to form sheets (1–2 mm thick) between two metallic plates.

The slips were poured into the moulds which were heated in air (80°C, 1 h). To enhance the heat transfer the latex rubber moulds were placed in pre-heated water after being filled with slip. The moulds were covered to minimise evaporation of water before and during the solidification to prevent segregation phenomena and, hence, avoid uneven shrinkage and subsequent deformations during sintering. After consolidation the coverings were removed to enable a certain drying at the same temperature during an additional hour before demoulding. Some consolidated bodies were demoulded without initial drying. From the sheets formed, still in wet and plastic state, some contours were punched out using metallic tools.

Before further evaluations the shaped bodies were dried at 120°C for at least 24 h.

4.4 Burn-out and sintering

The organic additives were burned out at a slow temperature increase (1°C min^{-1}) up to 500°C, with holdings for 60 min at 200 and 300°C. During this operation air was pumped into the furnace to promote the burn-out. This process was either done in a separate cycle or integrated with a pre-sintering or sintering operation. Some samples with high starch content were subjected to a more sophisticated burn-out operation controlled by the weight-loss rate.[13,14] Pre-sintering was conducted at 1000°C for 1 h, without significant shrinkage, to enable density measurements when the starch had been removed. The sintering was conducted in a Super-Kanthal furnace at 1600°C for 2 h.

4.5 Material evaluations

4.5.1 Density and porosity measurements

The densities of consolidated bodies, after burn-out and pre-sintering as well as after sintering, were determined by the mercury immersion method. Before the measurements the bodies were dried at 120°C for 24 h and then kept in a desiccator during cooling to avoid moisture uptake.

The pore size distribution, characterising the interconnecting pores, i.e. the pores (necks) between the large ones left by the starch particles, in sintered materials was determined using a mercury porosimeter (PoreSizer 9320, Micromeritics, USA).

4.5.2 SEM studies

Studies of the microstructure, mainly concerning the overall pore structure formed by the starch particles, of sintered materials, were conducted in a SEM (S-4100, HITACHI, Japan). Pieces of the materials were impregnated with polymer resin and polished to evaluate the microstructure in the different materials.

5 Results and Discussion

5.1 Rheology

All alumina/starch slips showed various degree of shear-thinning behaviour with a decrease in viscosity as the shear rate increased. In general, the shear thinning decreased with an increased amount of starch, replacing alumina powder in the suspension, resulting in more or less newtonian behaviour with the largest amount of starch, particularly when using the native starch in the low solids-loading regime (see Fig. 3). Separate studies showed that pure starch suspensions (40 vol%) display newtonian behaviour. Figure 4 shows the viscosity of alumina suspensions at a shear rate of 100 s^{-1} with increased starch content in the slips prepared and clearly displays the differences between using native (N) starch and the chemically modified starch (T and M). At this shear rate the hydrodynamic forces dominate and the factors influencing the viscosity are essentially the solids loading, the particle morphology and the particle size distribution.[15] The modified starch generally gives a higher viscosity at a given solids loading, which can be related to the more open structure of the granules initiated by the modification process and, hence, a higher degree of water uptake at room temperature. When alumina is replaced by starch the viscosity decreases since the increased starch content is accompanied by a decrease in total volume fraction of solids. This is logical, not

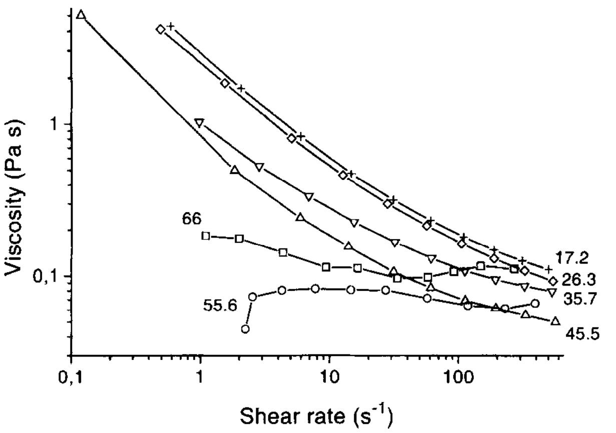

Fig. 3. Apparent viscosity versus shear rate for alumina/starch slips with various volume fractions of native potato starch in the low solids loading regime. With increased amount of starch the total solids loading decreased from 54·2 to 52·0 vol%.

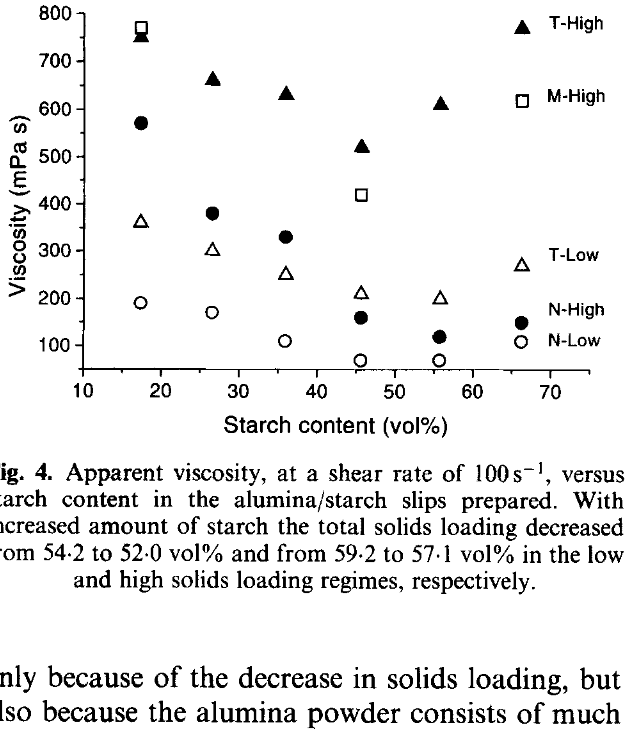

Fig. 4. Apparent viscosity, at a shear rate of $100\,s^{-1}$, versus starch content in the alumina/starch slips prepared. With increased amount of starch the total solids loading decreased from 54·2 to 52·0 vol% and from 59·2 to 57·1 vol% in the low and high solids loading regimes, respectively.

only because of the decrease in solids loading, but also because the alumina powder consists of much smaller particles (submicron) than the starch and, therefore, exposes a much larger surface area towards the liquid phase. However, when the starch content exceeds a certain fraction (in the range 45–55 vol%) of the total solids the viscosity starts to increase, in spite of the fact that the total volume fraction of solids further decrease. This effect can arise from the water uptake property of the starch which causes a decrease of free water with an increased amount of starch and/or as a result of being beyond the optimum particle packing. If water, absorbed by the starch, is excluded the effective volume concentration of solids in the slips will be higher than calculated. The change in particle size distribution as the starch content increases should also have an effect on the viscosity. It has been shown before that mixing different particle sizes gives lower viscosity than a monosized particle suspension as a more favourable particle packing is obtained.[16–18]

The slip viscosity seems to be controlled by the following mechanisms: the total solids loading, the total exposed surface area of the solids, possible existence of an optimum particle packing and the water uptake by the starch. The first two dominate at lower starch content. In this region the decrease of exposed surface area with the increased amount of starch results in a decreased viscosity. The other two mechanisms dominate at higher starch content. Consequently, in the region above a starch content of 55 vol% in the low solids-loading and above 45 vol% in the high solids-loading regime, the viscosity increases with an increased quantity of the modified starches. Similar behaviour was achieved with native starch. Based on present results, however, it is difficult to distinguish and separate the impact of the different mechanisms involved.

Overall, it is important to control the rheology to make certain that proper processing can be conducted. The viscosity of an alumina/starch slip should be low enough to permit adequate mould filling without entrapping air but, at the same time, high enough to avoid critical segregation phenomena at rest before consolidation takes place and significant shrinkage during consolidation and drying.

Figure 5 shows how the storage modulus (dynamic rigidity) of two different alumina/starch slips vary with temperature. With this low content of starch (17·3 vol%) the storage modulus is on a similar level with both types of starch used. Besides, the increase in storage modulus (consolidation starts) occurs at a similar temperature (about 50°C). At this stage, when the starch granules swell, it can be assumed that the surrounding alumina particles (matrix) are compressed by the

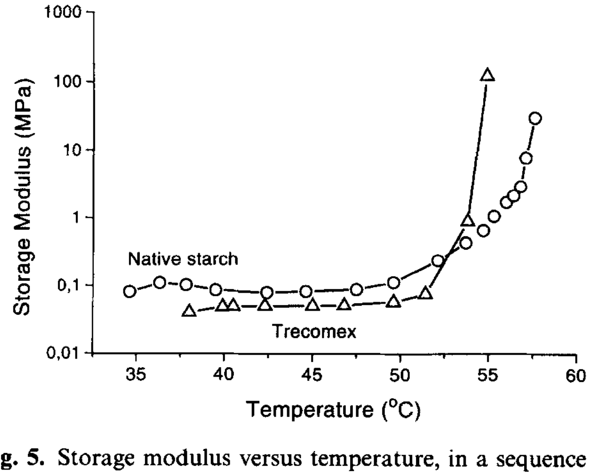

Fig. 5. Storage modulus versus temperature, in a sequence of 20 min, at a constant stress (2·5 Pa) and frequency (1 Hz) for alumina slips with 17·3 vol% native or chemically modified (TRECOMEX) starch.

draining of water, forcing the particles closer to each other and, eventually, causing a flocculation process, which may assist the consolidation of the entire particulate suspension into a rigid body. At the same time the opening up of the starch granules gives an adhesion to the ceramic matrix which further contributes to the rigidity of the consolidated body.

In Fig. 5 it can be seen that the increase of the storage modulus is more rapid and reaches a higher level at a lower temperature with TRECOMEX. Like the impact on the viscosity level this behaviour can be related to the effects of the chemical modification and faster water uptake supported by the more open starch-granule structure. This fast increase to a high storage modulus is favourable for the consolidation process as there is less risk of segregation phenomena before consolidation is completed and deformations of consolidated bodies when releasing them in wet state, owing to the higher rigidity.

5.2 Forming and demoulding

In spite of the more or less high-viscosity properties of the prepared slips they were reasonably easy to pour, which enabled proper mould filling even with complex shapes. A hardening of the slips at heat treatment was observed much earlier than the 1-h period used, which was also indicated by the rheological studies. After consolidation, with or without the initial drying, simple-shaped bodies were released without problems. However, demoulding of complex-shaped bodies, still in wet state, had to be done more carefully owing to risk of deformations. It must be noted that the complex-shaped bodies were cast in latex rubber moulds that must be turned inside out when demoulding, resulting in significant stresses on the bodies. If other concepts are used, divided moulds for example, this problem will be less severe and complex shapes can probably also be released in wet state without any problems.

Figure 6 shows the densities of consolidated bodies after drying. In comparison, predicted density, based on the content of alumina ($\rho = 3{\cdot}98$ g cm^{-3}) and starch ($\rho = 1{\cdot}43$ g cm^{-3}), versus starch content is plotted. The densities of samples containing the chemically modified starch (TRECOMEX) show very good agreement with predicted values, at least up to 45 vol% starch content in the low solids-loading regime, and even better in the high solids-loading regime. This indicates that there are no obvious dimensional changes during the consolidation/drying process. Only at a very high starch content, was a deviation from higher densities than the predicted obtained, suggesting some shrinkage during the process. The correlation between achieved and predicted density is less good with the native starch, especially in the low solids-loading regime. The deviation at high starch content and low total solids loading can be related to a low density of the alumina matrix in combination with a large quantity of shrinking starch granules during drying. A matrix with low density has a tendency to shrink during drying as there is, comparatively, much empty space between the alumina particles. Furthermore, if the matrix is weak the starch shrinking can cause a local breakdown when adhered alumina is removed leaving more open space.

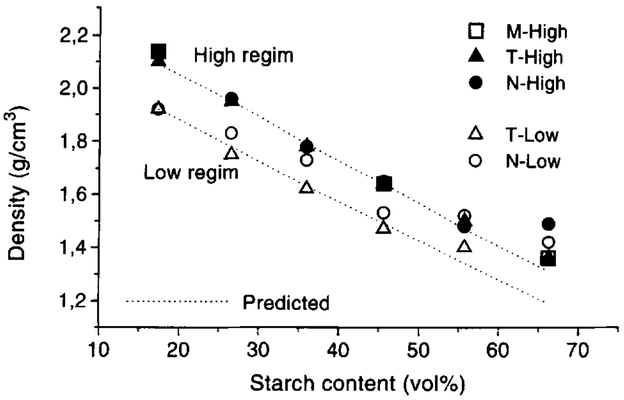

Fig. 6. Density after consolidation versus starch content in the alumina/starch slips prepared.

Overall, the results indicated less reliable behaviour with the native starch compared with the modified starch owing to the less stable properties in water processing. The densities obtained with the fractionised starch version (MIKROLYS) corresponded very well to the ones with TRECOMEX.

5.3 Burn-out and pre-sintering

In general, the 'starch-consolidated' bodies were burned out without serious problems even when the material thickness was in the range 30–40 mm. It was possible to integrate the burn-out and sintering processes which offers a more time/energy efficient process. Only with the highest starch content (66·2 vol%) did some cracking occur. The stresses generated by the burn-out process of large quantities of starch in combination with a ceramic matrix with low strength caused this problem. However, when using the rate-controlled burn-out route, in which the temperature increase is controlled and limited by a maximum weight loss per time unit, cracking was avoided. Figure 7 shows a burn-out process, in which the maximum weight loss was set to 0·23% (of the organic content) per minute and the maximum temperature increase to 1°C min^{-1}. The figure shows that under these conditions absorbed water is removed in the range 100–200°C, whereas the starch is removed in two

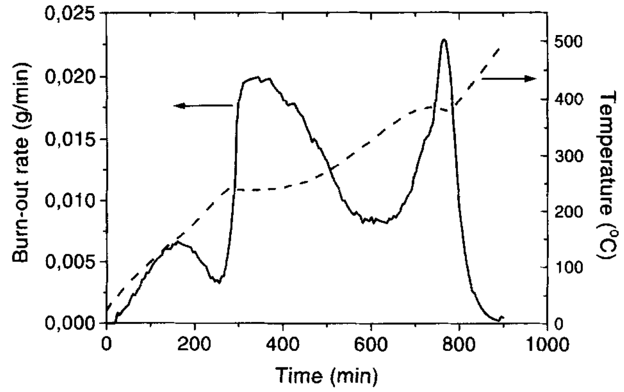

Fig. 7. Burn-out rate and temperature versus time in a rate-control burn-out operation for an alumina sample containing 66·2 vol% (based on solids) MICROLYS.

sequences at 240 and 380°C, respectively. The two different polymer types in starch, the linear and the branched, obviously have different decomposition behaviour, however, this is not further investigated in this study. Note that the temperature even decreases in the polymer removal sequences to limit the burn-out rate. With this technique the burn-out can be optimised, both regarding time efficiency and avoidance of cracks.

Figure 8 shows the densities of burned-out and pre-sintered bodies based on the chemically modified starches (M and T). Depending on the total solids loading and composition of the original slips the density varies between 20 and 50% of full density based on $\rho(Al_2O_3) = 3{\cdot}98\,g\,cm^{-3}$. Predicted density in Fig. 8 is based on there being no dimensional changes during the process and only the alumina matrix left. In general, the density increased with decreased starch content and total solids loading, but a slight deviation from the predicted densities can be seen, which increases with increased amount of starch added. In contrast to the consolidated densities shown in Fig. 6, the pre-sintered densities are slightly above the predicted. There is obviously some shrinkage during the burn-out and/or pre-sintering step, not detectable with manual measurements. Still, there is good correlation between the different samples and, at least with lower starch content, there is good agreement with the predicted density, which indicates that dimensional tolerances can be controlled.

The densities obtained with the native starch (not included in Fig. 8) showed less good correlation to those predicted, particularly at larger amounts of starch. This, again, can be referred to the more unstable properties which may lead to a higher degree of breakdown of the starch granules during the water processing, resulting in more irregular shrinkage of the alumina matrix. The degree of breakdown can vary from sample to sample depending on the amount of water available in the different compositions as well as minor variations in processing time.

5.4 Sintering

With the exception of samples with large amounts of native starch the sintering was performed without significant deformations which indicated good homogeneity of the materials. Figure 9 shows a collection of various formed and sintered components, which illustrates the possible variations in shape and size when using this new technique.

The relative densities of sintered samples obtained using the modified starches (T and M), displayed in Fig. 10, were in the range 30–77% of the theoretical which means a porosity of 23–70%. Here, predicted density is based on the assumption of full densification of the alumina matrix and that the porosity left corresponds to the volume fraction of originally added starch. Similar relations between the different materials as seen in the pre-sintered state were preserved after sintering. However, a larger deviation from the predicted density was obtained, now in the other direction, with lower densities than predicted. This can be

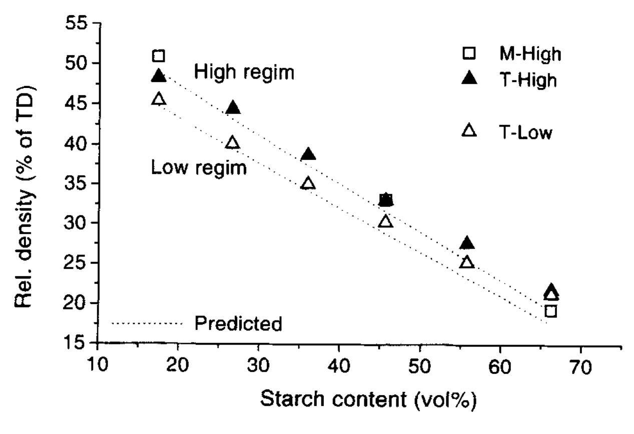

Fig. 8. Relative density of consolidated bodies after burn-out and pre-sintering (1000°C) versus content of the chemically modified starches (TRECOMEX, MICROLYS).

Fig. 9. Collection of sintered components for porous alumina manufactured by 'starch consolidation'; 45 and 60 mm height of the owl and thumb, respectively.

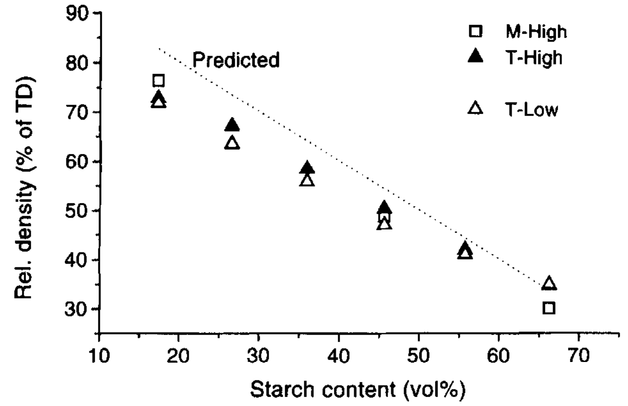

Fig. 10. Relative density of sintered alumina versus content of the chemically modified starches (TRECOMEX, MICROLYS) in the originally prepared slips.

explained by an incomplete densification of the alumina matrix during sintering. The linear shrinkage was in the range 12–14% and, for the materials with TRECOMEX, the shrinkage increased with increased starch content. The less densely packed alumina matrix at consolidation will not only give rise to larger shrinkage at drying after consolidation (see Fig. 6), but also, at sintering.

As before, deviations and irregularities of the final density and shrinkage behaviour when using the native starch were shown. The density, for example, was more or less constant in the range 45–66 vol% of the native starch content. Furthermore, these samples were significantly deformed during sintering. The results clearly showed that the native starch had less favourable processing properties compared with the chemically modified starches, which gave much more regularity and predictability of shrinkage and ultimate density.

5.4.1 Microstructure

The evaluation of the sintered microstructures, in terms of porosity, of the sintered alumina materials obtained in this work, was done by two complementary techniques: Hg porosimetry and SEM investigations. Hg porosimetry was used to measure the smaller pores, corresponding to the connecting contacts areas or necks between much larger spherically shaped pores created by the original starch particles. On the other hand, the SEM investigations visually displayed the overall pore structure dominated by the large pores left by the starch particles. The use and purpose of determining the size of the connecting pores and/or emphasising the dominating large spherical pores depend on the material's intended use. For use as filters in separation processes the smaller connecting pores will be essential, whereas the large pores will be the determining factor for the capacity in thermally insulating applications.

Figure 11 shows the pore size distribution, obtained by Hg porosimetry, of some of the sintered materials obtained using the modified starch TRECOMEX, and it displays how the pore volume and the pore size increased with increased amounts of starch added. Figure 12 shows how the average pore sizes were clearly influenced by the original slip composition. With the chemically modified starches (M and T) there is a significant and expected increase in the pore size with decreasing solids loading and increasing starch content. The use of the fractionised starch (M) tended to give a smaller average pore size, simply because of the smaller starch particles. The native starch gave more irregularities regarding the pore size which, again, confirmed the unpredictable processing properties when using this type of starch. When increasing the amount of starch the number and degree of contacts between the starch particle also increase, which results in a larger average pore size.

Figure 13 shows SEM images with overall views of the microstructure of two sintered alumina

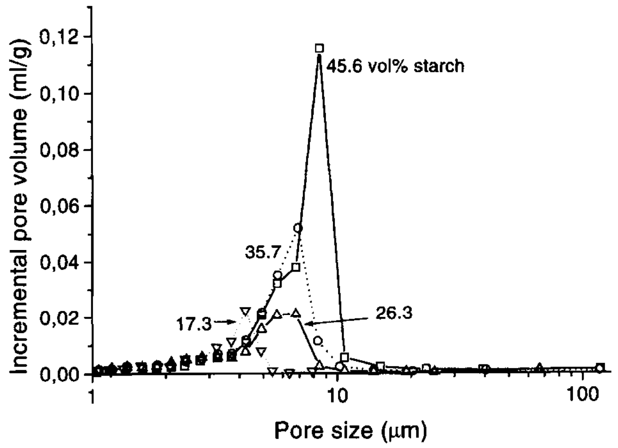

Fig. 11. Pore size distributions in sintered alumina samples, obtained using various amounts of the chemically modified starch TRECOMEX in the low solids loading regime.

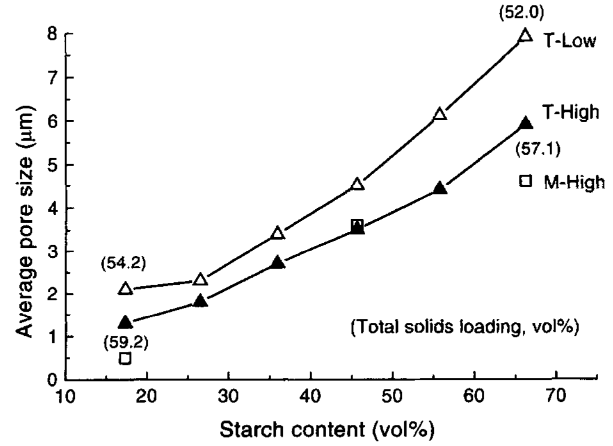

Fig. 12. Average pore size of sintered alumina versus content of the chemically modified starches (TRECOMEX, MICROLYS) in the originally prepared slips.

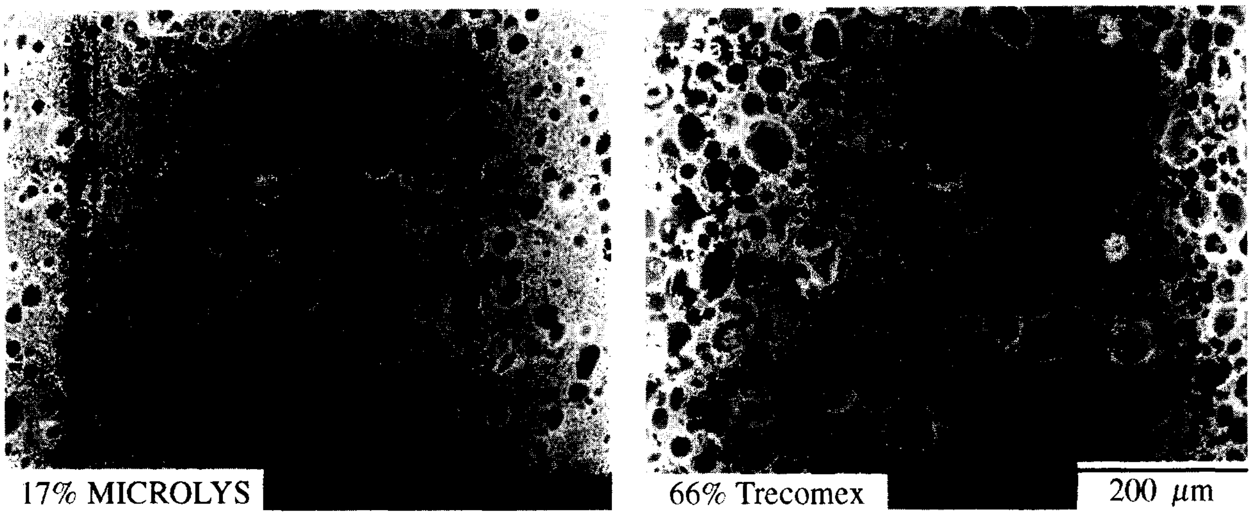

Fig. 13. SEM images of a sintered alumina, obtained using 17·3 or 66·2 vol% starch (TRECOMEX).

materials, one with a low content (17·3 vol%) and the other one with high content (66·2 vol%) of chemically modified starch (T) in the original slip compositions. The large, spherically shaped pores correspond well to the shape and size of the original starch particles. The possibility of the starch particles swelling is obviously restricted by the limited space available owing to the high solids loadings used. This also means that the consolidation will proceed rapidly when the temperature is reached and the water uptake occurs. However, in Fig. 14, showing a SEM image of another formed and sintered material, shells, separated from the rest of the alumina matrix, can be seen at the outer part of the large pores left by the starch particles. This indicates that there is some contraction of the starch particles during drying after the swelling. A shell of alumina particles, adhering to each starch particle, in the surrounding matrix is released from the rest of the matrix and follows the shrinking starch particles during drying. Hence, a space between the formed shell of alumina and the main alumina matrix is left after sintering. This phenomenon is not expected to give any serious effects on the mechanical strength of the ultimate materials. As mentioned before the measured pore size corresponds to the degree of contact between the starch granules but also to the degree of densification in the alumina matrix. The SEM images above confirm that the alumina matrix is not fully densified and, therefore, the observed deviation from the theoretical densities occurs. Because of the incomplete densification of the alumina matrix the porosity is higher than the amount of added starch when lower starch content is used (see Fig. 10). However, the opposite occurs at larger starch additions, i.e. all of the added starch does not result in porosity. This can be an effect of some minor breakdown of the starch granules during consolidation, resulting in smaller, unstable pores that are excluded during sintering. This can also be the case with pores left by an existing fraction of small starch granules.

6 Summary—Conclusions

The new forming technique for the manufacture of porous ceramics developed in this study has been shown to work very successfully. Also, components with very complex shapes were formed and sintered in a simple way without critical deformations. The favourable properties of starch in terms of dispersibility in water, gelling ability, burn-out properties and low cost make this method one of the most promising shaping techniques when porous ceramics are to be produced.

It was clearly shown that the chemically modified starches have more favourable properties than the native starch, which also gives better control of the processing and the ultimate material properties.

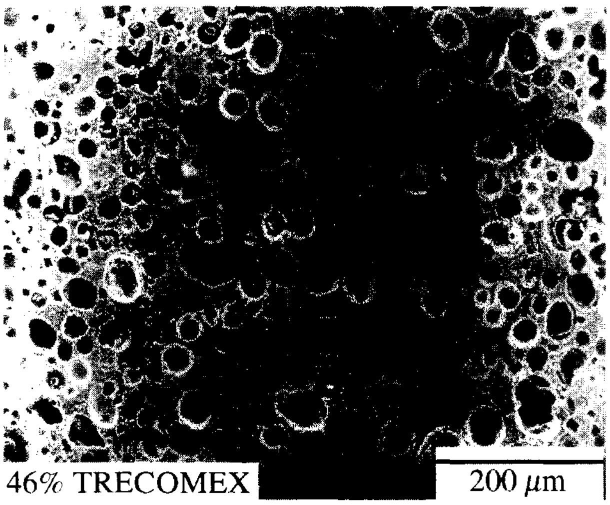

Fig. 14. SEM image of sintered alumina, obtained using 45·6 vol% starch (TRECOMEX).

The overall porosity and the size distribution of the connecting pore necks in the material can be controlled by the original slip composition regarding the total solids loading and the starch content. Furthermore, the abscence of significant dimensional changes during consolidation and drying gives better conditions for accurate control of the ultimate dimensions after sintering.

The 'starch-consolidation' technique can be used in the manufacture of various porous ceramics, such as for thermal insulation, as membrane/filters and gas burners, or as bioceramics. Besides, components, in which high mechanical properties are of minor importance and in which a limited degree of porosity is accepted, can be manufactured. Regarding the possible range of ceramic materials to be fabricated by this technique the only restriction is the requirement for water-based processing. Potentially, there exist many possibilities of further developing this technique. To meet specific requirements regarding the pore structure, modifications can be done by adding other organic materials. To simplify the forming and further increase the control of component dimensions, binder (Latex, PVA, PEG etc) can be added to enhance the green machining properties. Some of these developments are in progress and will be presented in later publications.

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